6-2016

Development and Evaluation of Matrix Material Formulations for Potential Integration into Immunodiagnostic Biosensors

Payam Aminayi
Western Michigan University

DEVELOPMENT AND EVALUATION OF MATRIX MATERIAL FORMULATIONS FOR POTENTIAL INTEGRATION INTO IMMUNODIAGNOSTIC BIOSENSORS

by

Payam Aminayi

A dissertation submitted to the Graduate College
in partial fulfillment of the requirement
for the degree of Doctor in Philosophy
Chemical and Paper Engineering
Western Michigan University
June 2016

Doctoral Committee:

Brian Young, Ph.D., Chair
Massood Zandi Atashbar, Ph.D.
Margaret Joyce, Ph.D.
James Springstead, Ph.D.

DEVELOPMENT AND EVALUATION OF MATRIX MATERIAL FORMULATIONS FOR POTENTIAL INTEGRATION INTO IMMUNODIAGNOSTIC BIOSENSORS

Payam Aminayi, Ph.D.

Western Michigan University, 2016

This study supports the development, characterization and optimization of biosensor material formulations for immunodiagnostic applications based on experimental findings and hypotheses by Wang and Wu [1, 2], and using a test-plate apparatus and thin-film design developed by Young [3].

Certain biosensors working on the basis of conductance/impedance changes have demonstrated their potential to detect various bacteria, enzymes, and biomolecules due to their enhanced electrical properties with incorporated single-walled carbon nanotubes (SWNT). From the work conducted in our laboratory, we are attempting to determine and develop a matrix formulation containing highly dispersed SWNT, antibody and other components that elicit a significantly larger change in matrix conductivity with antigen binding than would occur from only electrochemical impedance effects.

One of the most challenging aspects of using SWNT in biosensors is uniformly dispersing them within the sensing component. The dispersion of the SWNTs in an aqueous solution is particularly challenging. In aqueous solutions, cylindrical SWNTs tend to form aggregates/bundles, appearing as a micro-meshwork or a network of ropes. The resulting semi-solid solutions therefore do not often show the anticipated electrical properties after solution deposition and drying.

Studies included in this dissertation focus on obtaining uniform SWNT dispersions (using a well characterized commercially available conductive SWNT) with either poly(sodium 4-styrenesulfonate) (PSS) or carboxymethylcellulose (CMC), two dispersing agents, and other components in aqueous solutions using various sonication protocols. The high/low values used for the statistical design ranges chosen were based on preliminary work that showed roughly where SWNT dispersion was visually incomplete or dried coated matrix film resistances exceeded the limits of the test equipment used. Once characterized, SWNT dispersions were selected based on resistance level, processing attributes and film characteristics and used in a second phase of the research by combining with antibody (for future use as a capture molecule in biosensing) and glycerin (added as a wetting and perhaps antibody stabilizing agent). These SWNT dispersions together with varying levels of antibody and glycerin using a statistical design protocol were deposited within test sensor channels, dried into a semi-solid/fluid film, and resistance-tested as before.

Formulated solutions were characterized using dynamic light scattering. Dried, semi-solid/fluid composite "matrix" films deposited on test plate templates were characterized using 3D optical microscopy. Visualizing the structural aspects of the matrix film allows for a better understanding of physical factors that may affect the resistivity of the matrices, perhaps allowing for better predictability of resistance with parameter changes. Film characterization with scanning electron microscopy was also attempted, but with very limited success perhaps due to the presence of glycerin within the sample.

Printing technologies consisting of screen printing and material plotting were used to create various elements of the test plate used in these studies. From the results obtained in this study, it

was found that run 15 matrix solution (SWNT:CMC=2, sonication amplitude=40%, sonication duration=24 hr) resulted in dried matrix films with the lowest resistance ($1.23\times10^{-02}\Omega$.cm) and possessed an average particle size of ~115 nm. In contrast, the largest particle size (where 81% of the particles have an average particle size of ~5000 nm), for the set of formulation experiments in which CMC was used, was observed in Run 3 (SWNT:CMC=0.5, Sonication amplitude=20%, and sonication duration= 2 hr) in which the highest dried film resistivity was obtained. From this it was concluded that a lower SWNT:CMC ratio (lower conductive:insulating components) is contributing to larger SWNT particle size that together are contributing to higher film resistivity. The sonication factor was also found to play an important role in the dispersion and conductivity of SWNTs. The analysis of variance of the particle sizes obtained in the PSS-dispersed matrix solutions shows that the sonication amplitude and its interaction with the concentration of PSS are the only significant parameters among all that parameters were studied (α=0.05).

Profilometry of Run 3 (CMC-dispersed coating) at 100% (no dilution) showed an average roughness of 0.274 µm while profilometry of Run 15 at 100% (no dilution) showed an average roughness of 0.067 µm. The same trend was noted for matrix coatings at higher dilutions (70% and 40%). Therefore, increased particle size of the matrix formulations had a strong correlation with increased roughness, and increased resistance of the CMC-dispersed coatings. The thickness of the dried matrix films was found to decrease with the dilution of the matrix solution as would be expected due to reduced solids content. Calculated thickness values based on mass balance results for each prepared solution were compared with thickness measurements by the 3D optical microscope. The calculated values were found to be very close to the experimentally measured thickness measurements.

ACKNOWLEDGEMENTS

Much of this work was carried out using equipment and facilities available at the Center for the Advancement of Printed Electronics (CAPE), Western Michigan University. Support provided by faculty and staff associated with this facility is greatly appreciated. This work was also supported by funding from the 2012 Faculty Research and Creative Activities Award (FRACAA), Western Michigan University, and funding from the Western Michigan University Research Foundation 2013 Technology Development Fund, Kalamazoo, MI. I would also like to acknowledge, Dr. Young, without whom this dissertation would not have been possible.

Payam Aminayi

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

IMMUNODIAGNOSTIC BIOSENSORS BACKGROUND REVIEW

1.1 Abstract

This study supports the development, characterization and optimization of biosensor material formulations for immunodiagnostic applications based on experimental findings and hypotheses by Wang and Wu [2, 3], and using a test-plate apparatus and thin-film design developed by Young [1].

Certain biosensors working on the basis of conductance/impedance changes have demonstrated their potential to detect various bacteria, enzymes, and biomolecules due to their enhanced electrical properties with incorporated single-walled carbon nanotubes (SWNT). From the work conducted in our laboratory, we are attempting to determine and develop a matrix formulation containing highly dispersed SWNT, antibody and other components that elicit a significantly larger change in matrix conductivity with antigen binding than would occur from only electrochemical impedance effects.

One of the most challenging aspects of using SWNT in biosensors is uniformly dispersing them within the sensing component. The dispersion of the SWNTs in an aqueous solution is particularly challenging. In aqueous solutions, cylindrical SWNTs tend to form aggregates/bundles, appearing as a micro-meshwork or a network of ropes. The

resulting semi-solid solutions therefore do not often show the anticipated electrical properties after solution deposition and drying.

Studies included in this dissertation focus on obtaining uniform SWNT dispersions (using a well characterized commercially available conductive SWNT) with either poly(sodium 4-styrenesulfonate) (PSS) or carboxymethylcellulose (CMC), two dispersing agents, and other components in aqueous solutions using various sonication protocols. The high/low values used for the statistical design ranges chosen were based on preliminary work that showed roughly where SWNT dispersion was visually incomplete or dried coated matrix film resistances exceeded the limits of the test equipment used. Once characterized, SWNT dispersions were selected based on resistance level, processing attributes and film characteristics and used in a second phase of the research by combining with antibody (for future use as a capture molecule in biosensing) and glycerin (added as a wetting and perhaps antibody stabilizing agent). These SWNT dispersions together with varying levels of antibody and glycerin using a statistical design protocol were deposited within test sensor channels, dried into a semi-solid/fluid film, and resistance-tested as before.

Formulated solutions were characterized using dynamic light scattering. Dried, semi-solid/fluid composite "matrix" films deposited on test plate templates were characterized using 3D optical microscopy. Visualizing the structural aspects of the matrix film allows for a better understanding of physical factors that may affect the resistivity of the matrices, perhaps allowing for better predictability of resistance with parameter changes. Film characterization with scanning electron microscopy was also attempted, but with very limited success perhaps due to the presence of glycerin within the sample.

Printing technologies consisting of screen printing and material plotting were used to create various elements of the test plate used in these studies. From the results obtained in this study, it was found that run 15 matrix solution (SWNT:CMC=2, sonication amplitude=40%, sonication duration=24 hr) resulted in dried matrix films with the lowest resistance ($1.23\times10^{-02}\Omega$.cm) and possessed an average particle size of ~115 nm. In contrast, the largest particle size (where 81% of the particles have an average particle size of ~5000 nm), for the set of formulation experiments in which CMC was used, was observed in Run 3 (SWNT:CMC=0.5, Sonication amplitude=20%, and sonication duration= 2 hr) in which the highest dried film resistivity was obtained. From this it was concluded that a lower SWNT:CMC ratio (lower conductive:insulating components) is contributing to larger SWNT particle size that together are contributing to higher film resistivity. The sonication factor was also found to play an important role in the dispersion and conductivity of SWNTs. The analysis of variance of the particle sizes obtained in the PSS-dispersed matrix solutions shows that the sonication amplitude and its interaction with the concentration of PSS are the only significant parameters among all that parameters were studied (α=0.05).

Profilometry of Run 3 (CMC-dispersed coating) at 100% (no dilution) showed an average roughness of 0.274 µm while profilometry of Run 15 at 100% (no dilution) showed an average roughness of 0.067 µm. The same trend was noted for matrix coatings at higher dilutions (70% and 40%). Therefore, increased particle size of the matrix formulations had a strong correlation with increased roughness, and increased resistance of the CMC-dispersed coatings. The thickness of the dried matrix films was found to decrease with the dilution of the matrix solution as would be expected due to reduced solids content. Calculated thickness values based on mass balance results for each prepared solution were

compared with thickness measurements by the 3D optical microscope. The calculated values were found to be very close to the experimentally measured thickness measurements.

Based on the experimentally-determined higher quality and superior workability of the formulations and resulting dried matrix films, it was concluded that CMC rather than PSS was more consistent and should be used as the dispersant in the matrix formulations developed in the 2nd phase (chapter 3) of this dissertation where the addition of antibody and glycerol to the matrix was studied. Matrix formulation protocols from Run 14 (SWNT:CMC= 0.5, Sonication amp (%)=40, Sonication durations (h)=2), Run 17 (SWNT:CMC= 1.25, Sonication amp (%)=30, Sonication durations (h)=13), and Run 12 (SWNT:CMC= 2, Sonication amp (%)=40, Sonication durations (h)=2) were selected and labeled as CMC-14, CMC-17, and CMC-12, respectively. The uniformity of the coatings prepared from CMC-12 matrix solutions were found to be the highest among the different matrix solutions tested and the superior uniformity resulted in lower resistance.

Among the three different ratio variations of SWNT:Glycerol studied with CMC-12, the highest 1:1 ratio of the three ratios tested was found to lead to the lowest electrical resistance. These levels of antibody and glycerol together with a base matrix formulation using the CMC dispersant at the ratio of SWNT:CMC=2 and the sonication amplitude of 40% for 2 hours was found to give the best properties. It is hoped that information from this research will be helpful in the design of immunodiagnostic biosensors relying on antibody-SWNT design elements.

1.2 Introduction

The concept of biomolecular interactions detection using a fast and versatile biosensor has gained attention in the last two decades. By definition, a device intended to detect or quantify a bio-molecule such as a cell or a particular protein is called a biosensor [4]. Biosensors can be classified into two major categories: enzyme and affinity biosensors (Figure 1). The main difference lies in the signal nature: enzyme sensors require kinetic methods of analysis in which the maximum signal intensity occurs in the first few minutes, corresponding to the substrate conversion. In contrast, affinity biosensors work on the basis of reversible biochemical interactions such as antigen–antibody or DNA–protein in which the maximum response corresponds to the equilibrium state. More complicated biochemical components lead to more variable responses, and thus it is difficult to use the term ‘‘equilibrium’’ for biological cells or receptors [5].

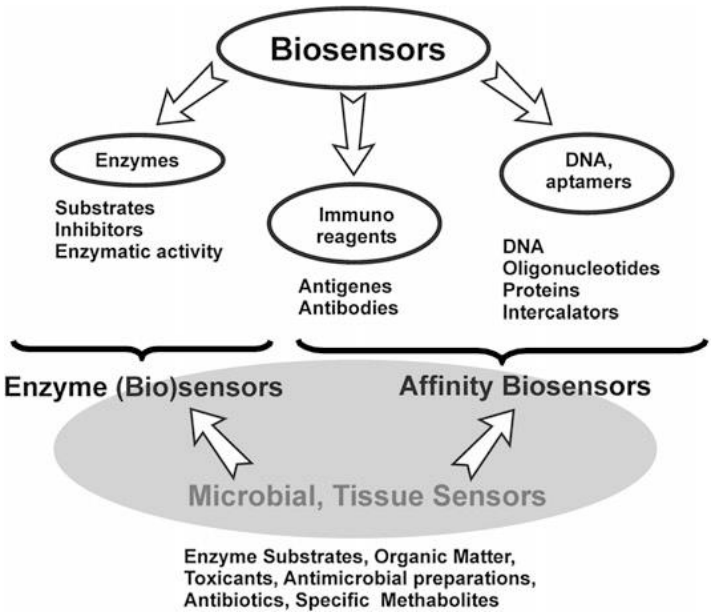


Figure 1. Biochemical components used in the biosensor design and specific analyte determined (Courtesy of [5])

The principal of most biosensors is based on affinity in which a functionalized and immobilized capture electrode binds the target biomolecule or analyte, selectively. This results in a change at a localized surface [6]. This change can be quantified or detected using numerous methods. One of the methods is to detect a change in impedance, voltage, or current which forms the basis of "electrical biosensors"[7] and this study. Therefore, this study excludes the different methods which employ: optical [8-12], piezoelectric [13, 14], mechanical [15, 16], and impedimetric techniques [17-20] for the detection mechanism and biosensor fabrication. Biosensors can also be classified in terms of their signal generation principles as presented in Figure 2.

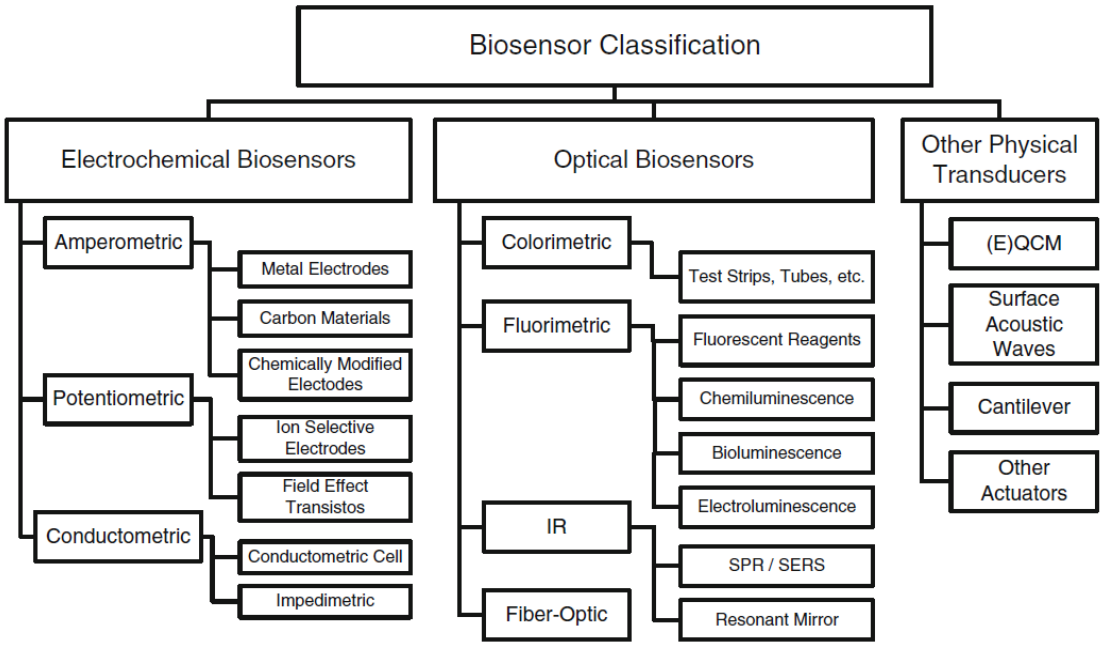


Figure 2. Classification of the biosensors in accordance with the transducer/signal transduction principles (Courtesy of [5])

Out of the mentioned types of biosensors, the optical approach is believed to be the most accurate. However, the disadvantages of this type of biosensor are its bulkiness and high cost. Also, the optical alignment impediments have limited its functionality as a versatile, portable, and easy-to-use device. On the other hand, biosensors based on the electrochemical method have the advantages of low fabrication cost and low power consumption, which make them suitable for miniaturization. Therefore, an electrochemical biosensor is more suitable for applications where small size and cost are crucial, such as in remote areas where portable diagnostics devices are especially desirable [4]. Table 1 shows a concise list of electrochemical biosensors for cancer analysis.

Table 1- Examples of biosensors for cancer biomarkers analysis (Courtesy of [21])

Cancer marker detected	Biosensor principle	Assay principle	Limit of detection

Table 1 - continued

AFP	Electrochemical	Protein array with 36 platinum electrodes.	–
		Prussian blue with screen-printed amperometric sensor.	(range 5–500 ng ml−1)
AFP and CEA	Electrochemical	Dual-electrode with amperometric detection.	1 ng ml−1
CA15-3	Electrochemical	Antibody functionalized sol–gel film with potentiometric detection.	5 U ml−1
CA125	Electrochemical	Capillary electrophoretic.	–
		Titania sol–gel on glassy carbon electrode with direct electrochemical detection of HRP.	1.29 U ml−1 (range 2–14 U ml−1)
CA19-9	Electrochemical	Titania sol–gel on carbon electrode as an amperometric immunosensor.	–
CEA	Electrochemical	Faradic impedance spectroscopy using gold nanoparticle modified glassy carbon electrode.	–
		Immobilized thionine as a mediator between the electrode and HRP-labelled antibody.	(range 0.6–17 ng ml−1<comma> 17–200 ng ml−1)
		Direct electrochemical detection of HRP in an immunosensor.	0.4 ng ml−1 (range 0.5–3.0 ng ml−1<comma> 3.0–120 ng ml−1)
	Optical	Chemiluminescence immunosensor.	–
Ferritin	Mass sensitive	Antibody immobilised on gold chip of a quartz crystal microbalance.	(range 0.1–100 ng ml−1)
	Optical	SPR based immunosensor.	–
hCG	Mass sensitive	A multi-channel piezoelectric quartz micro-array immunosensor.	–

	Optical	Fluorescence immunosensor.	(range 25–1500 U ml−1)
PSA	Electrochemical	Gold coated microporous membrane.	–
		Amperometric disposable electrode.	0.25 ng l−1
		Capacitive immunosensor using lateral flow and impedance detection.	–
	Mass sensitive	Antibody immobilized on gold chip of a quartz crystal microbalance.	–
		Microcantilever immunosensor.	–
		Microcantilever immunosensor.	(range 0.2–60 μg ml−1)
	Optical	SPR with colloidal gold nanoparticles.	0.15 ng ml−1

Electrical biosensors can be categorized by how the electrical measurement is made. These measurements include voltammetric, amperometric/coulometric, and impedance sensors. Impedance biosensors can be further subdivided to non-faradaic and faradaic [22]. A non-faradaic biosensor, also called a capacitive biosensor, works on the basis of change in the capacitance or non-faradaic current as a function of bio-molecular interactions. Factors that affect capacitance properties include changes in the dielectric constant, charge distribution, dimension, and shape which occur as bio-molecular interactions take place. However, the integrity of the conductive layer and the bio-recognition layer is vital for the device functionality, since any defect or pin-hole can cause a short circuit, resulting in device malfunction [23]. In contrast to a capacitance biosensor, a biosensor which works based on the faradaic current method measures the variation in the faradaic current which results from the oxidation/reduction reaction. This variation in the faradaic current is a product of steric hindrance and electrostatic repulsion [4, 24, 25]. Steric hindrance has a direct relationship with the interaction between the biological

element, the substrate and analyte, and as a result, is translated into a change in the faradaic current and impedance. In one approach, known as electrochemical impedance spectroscopy (EIS), an impedance biosensor quantifies the electrical impedance of an interface in AC steady state with constant DC bias conditions. For this purpose, usually, a sinusoidal voltage at a certain frequency is imposed, and the resulting current is measured; this experiment is repeated for a wide range of frequencies. The impedance can then be calculated as the current:voltage ratio [26]. Additionally, an increase in the number of free charges on the bio-molecule will result in an electrostatic repulsion between the bio-molecule and the redox-active species. Consequently, a change in the faradaic current will occur. Therefore, a faradaic biosensor has the ability to virtually detect molecules with any size, including large bio-entities such as cells [27] and small bio-molecules such as DNA [28, 29]. A faradaic biosensor can also measure the concentration of the analyte based on the changes in impedance. In this type of biosensor, a high frequency AC voltage is applied to films consisting of biochemical reagents and auxiliary components, such as immobilization supports, mediators, etc., and the charge transfer resistance and capacitance of the surface layer is monitored. Such measurements are generally performed in the presence of a redox buffer. Therefore a very sensitive biosensor can be developed which measures biomolecular interactions on the electrode interface and the surface layer. The drawback of such biosensors is the weak reproducibility of the results. However, unique information which in some cases cannot be obtained by other electrochemical techniques can be achieved by this method.

With impedance-based biosensors, the attachment of the biomolecule to the substrate material is often achieved by using a linker compound such as thiol or silane to

immobilize and chemically crosslink the biomolecule to the substrate [30, 31]. Other methods have also been used to trap the biomolecules physically on the substrate [32]. In either case, the impedance needs to be within the detectable range of the impedance analyzer to be able to detect the changes resulting from protein interactions. For instance, if the impedance of an immobilization layer is 1.07 MΩ in the system, and the applied voltage is 5 mV, then the resulting current (4.67 nA) will not be distinguishable from the noise in an electrical circuit. Because binding events lead to very low impedance changes, impedance-based biosensors have significant limitations.

Even though traditional methods, such as enzyme-linked immunosorbent assay (ELISA), high-performance liquid chromatography (HPLC), mass spectrometry (MS), and magnetic resonance screening are well established and sensitive for biomolecule detection, they have disadvantages. The ELISA method, for example, is time-consuming and the required reagents are expensive. All of these instruments require trained personnel to operate the tests, a serious disadvantage for use in remote areas. In addition to these impediments, none of the mentioned methods are portable, and they require a full laboratory setup. Therefore there is a pressing need for a portable, disposable, inexpensive, and sensitive device which is capable of detecting and quantifying the target biomolecules.

In a study by Wang et al., a portable and sensitive biosensor was developed by mixing an antibody specific to the microcystin-LR (MC-LR), a poisonous compound found in water, with SWNTs and dip-coating the resulting mixture on paper strips (5cm×0.5cm) and freeze-drying the papers [2]. The prepared paper strips were capable of detecting 0.6 nmol/L to 40 nmol/L of MC-LR in the water by merely measuring the change in conductivity of the paper in solutions containing MC-LR at various concentrations. The

detection limit of this approach is comparable to that of the traditional ELISA method of MC-LR detection. The SWNT/Ab ratio used in this study was about 5000:1. The sensing mechanism was hypothesized to be a change in the gaps between carbon nanotubes upon formation of Ab-antigen complex. Since Carbon nanotubes are highly conductive, such change can affect the electron transport, and consequently provide a platform for detecting the presence of the antigen in the system. Similarly, Wu et al. [3] employed a similar method to dip coat SWNTs/antibody mixture onto paper to prepare highly sensitive impedance-based sensors used for the detection neomycin in milk samples.

The work in this dissertation is directed toward designing a conductive antibody-containing material (comprised of SWNT, antibody and other constituents), that, as a semi-solid film micro-structurally flexes upon binding antigen, and imparts a binding-extent-dependent resistivity change that can be measured that is much greater than from purely faradaic impedance. If developed, it is hoped that such a material could be incorporated into a rapid, portable, and inexpensive device for the detection of toxins and chemicals with a level of sensitivity and selectivity on par with immunoassay techniques such as ELISA.

The experiments presented in this dissertation focus on evaluating/analyzing the material properties of matrices by changing the composition of the material components together with surface analysis of the resulting matrix film. The longer term aim resulting from this thesis work is to produce a conductive antibody-containing matrix that microstructurally changes/flexes with specific antibody-antigen binding, causing significant resistivity changes in the material. Thus the prepared matrices in this study may

be eventually tested to attempt to detect antigen binding via electrical resistance measurements, beyond the scope of the work presented in this thesis.

1.3 Theory

The hypothesis behind this work is that under certain conditions, an antibody/SWNT matrix responds to antigen binding by changing the SWNT-to-SWNT contact distance (by expansion or swelling), resulting in a change in resistance of the matrix.

Our long-term goal in this work is to attempt to develop a thin film matrix formulation that elicits a resistance change to an applied microamp current based on the structural changes that occur during the interaction of antibodies and SWNT in the matrix system when exposed to antigen-containing solutions and as antibody-antigen binding occurs.

This conformational change can continue with time as applied antigen continues to bind to the matrix's antibodies. Therefore the current response will continue to change over time until equilibrium (constant resistance) is reached. At this stage, the current response will reach a plateau [6]. Figure 3 shows a conceptual, enlarged schematic of SWNT conformational change before and after antibody-antigen binding interactions [1]. Note SWNT-to-SWNT contacts are changed with binding, (see circled areas before and after antigen binding). Figure 3 only shows several layers of SWNT. In reality, the SWNT and antibody will coexist in many layers, preferably with interstitial spaces large enough to allow antigen to move into the interior of the SWNT:Antibody matrix to allow for a more uniform matrix resistivity change when binding antigen.

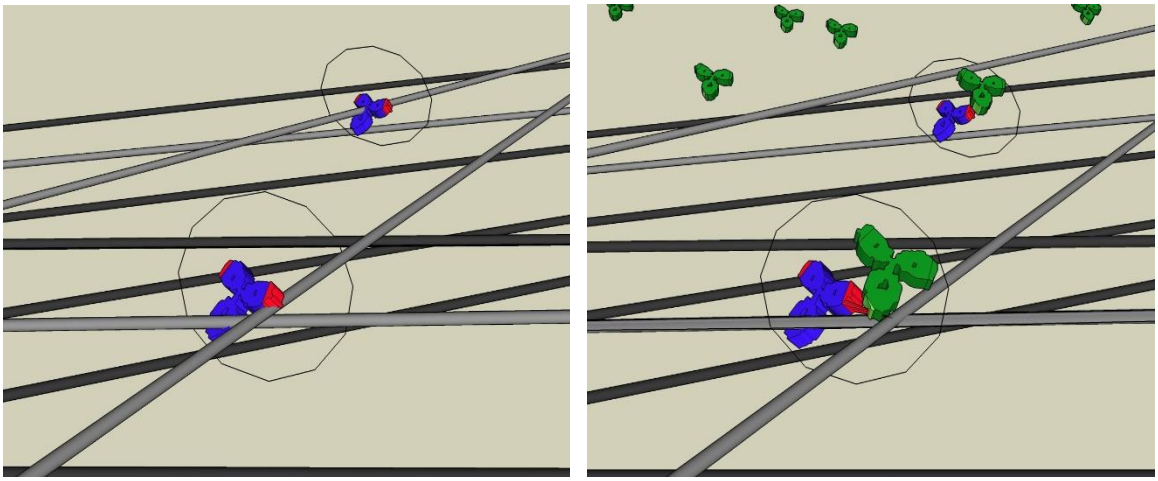


Figure 3. Enlarged schematic of SWNT conformational change before (left) and after (right) antibody-antigen interactions [1]. Blue is matrix bound antibody, green is antigen bound to antibody (antigen depicted here is a different antibody).

In 2009, paper test strips impregnated with an antibody:nanotube dispersion were successfully used in a standard three electrode chemical cell, with the test strip as one of the electrodes, to correlate chemical potential change of the strip with concentration of a specific toxin (antigen) in water [2]. It was hypothesized that as antigen bound to the antibody, the conductive nanotubes were pushed apart from each other reducing the conductivity of the paper strip. The most significant challenge and time spent to complete the work was in fabricating the paper test strips by dipping them in a nanotube/poly(sodium 4-stryrene-sulfonate) dispersion containing antibody (specific for binding microystin-LR) followed by drying. This dipping/drying process was repeated 13 times to achieve an appropriate conductivity for the paper test strip. Although cumbersome to produce the filter paper construct, work by the authors established this as a potentially useful method for environmental testing of harmful chemicals (those chemicals that are antigenic and to which specific antibodies can be created and used in the biosensor design).

The mechanism of resistance change is hypothesized to be due to the physical micro-expansion that occurs due to mechanical forces driving conductive elements, the polymer/antibody-coated nanotubes, further apart upon binding the target molecule. Figure 3 (left) shows a graphical depiction of a thin layer of nanotubes with antibody adsorbed on the nanotube, and intercalated between different nanotubes at many junctions. The hypothesis is that when antibody that is intercalated between two different nanotubes binds antigen, the binding event perturbs or forces the two nanotubes further apart (Figure 3 (right)), thus lowering their electrical charge transfer capability from one nanotube to the next, and thus increasing the resistance of the matrix. Therefore, obtaining a uniform SWNT dispersion for use as a thin film is critical for producing the biosensors in this study and hence is a major focus of this dissertation. Uniform dispersion within an optimized formulation of dispersant agents and surfactants is a key aim.

1.3.1 Thesis statement

The objective of this thesis is to characterize and attain stable and uniform aqueous SWNT dispersions using sonication/centrifugation/filtration techniques (1) that when combined with antibody and wetting and surfactant elements is used to produce thin, dispersed semi-solid "matrix" films (2) for characterization and modeling (3). The properties being sought should be suitable for incorporation into a test plate for evaluation of and testing (4) to show microstructural changes due to antigen-antibody binding that can be detected as matrix film resistance changes.

1.3.2 SWNTs in biosensor's matrix formulations

Carbon nanotubes (CNTs), discovered in 1991 [33], are considered to be a new form of carbon material with unique electrical, mechanical, and chemical properties. CNTs

have gained attention because of their potential applications such as additives for high-strength polymer composites, electrode materials for high-capacity batteries, efficient field-emitters as electron sources, and functional components for nanoscale electronic devices [34]. SWNTs have been extensively studied over the past few years [35-38]. In the most commonly used form, atoms of carbon form planar layers of carbon that are rolled to form tubes [39, 40]. Each layer is made up of rings containing six carbon atoms. The rings are linked to each other in a hexagonal structure. Each atom has three sigma bonds with an angle of 120° in between and connects to three neighboring rings. The fourth electron of each atom becomes part of an extensive p bond structure. SWNTs conduct electricity because of the electrons in the p bond structure can move around throughout the graphite structure [41]. Notably, the critical challenge related to achieving the superior electrical properties for application in biosensors lie in uniformly dispersing the nanotubes. Figure 4 shows an example of SWNT aggregate morphology in the dried state.

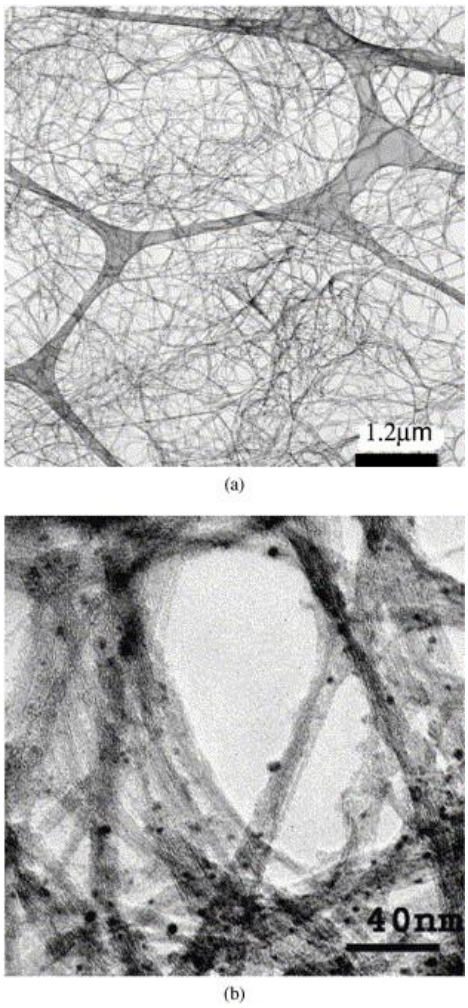


Figure 4. TEM image of the as-received HiPCO SWNT dispersion sample under (a) low magnification and (b) higher magnification. (Courtesy of [40])

Because of the strong van der Waals interaction between the nanotubes, avoiding or controlling the SWNT agglomeration is difficult. It is critical to attain good dispersion to benefit from the electrical properties of the SWNTs in a network structure suitable for the biosensors. Because of the high aspect ratio of the nanotubes (the spaghetti/rope like structure), uniform nanotube dispersion is a particularly challenging problem. In addition to the long aspect ratios, lack of rigidity in nanotubes makes entanglement with complex morphology inevitable. This entanglement is extensive enough to make large and dense nanotube agglomerates in the liquid suspension visible even to the naked eye. TEM and

AFM images confirm the complex network structures of the entangled and intertwined nanotubes. The structure of the nanotube networks is strongly affected by the tube dimensions and colloidal conditions. Since SWNTS are insoluble in water and common solvents, sonication with the presence of surfactants or polymers is required for SWNT dispersion in aqueous solutions. Other methods have also been employed for the dispersion of SWNTs such as treating with condensed acid under sonication (Figure 5). Acid treatment results in the functionalization of the SWNT's surfaces which renders them hydrophilic at their interfacial ends. Further chemical modification is also made possible using this approach [40].

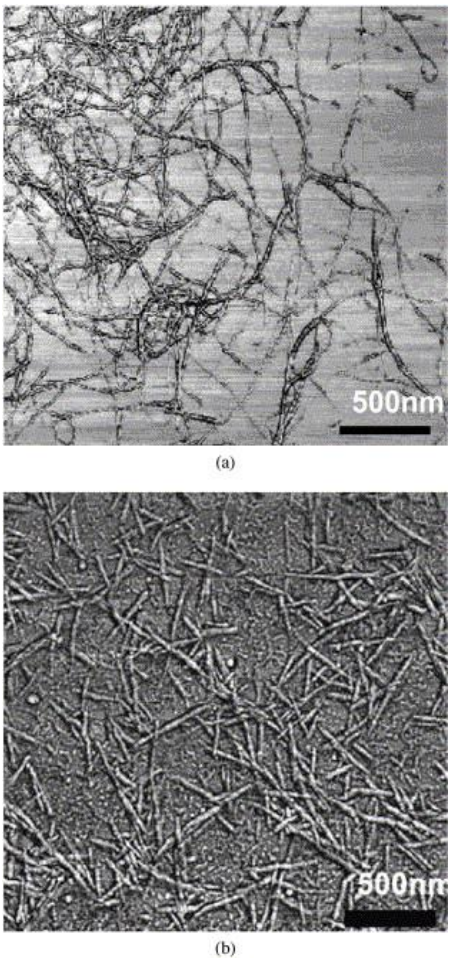


Figure 5. 2.5×2.5 µm AFM tapping mode scan of (a) as-received and (b) acid-treated HiPCO SWNT (Courtesy of [40])

Characterization of the nanotube network structure in suspension is also a very challenging problem. Despite the advantages of the electron microscope and scanning probe instruments in observing the nanotubes directly (in small length scales as low as a few nanometers), there are drawbacks for using such techniques for the characterization of the nanotube network structure. The mentioned techniques require samples to be analyzed in a dried state. Therefore, they cannot be used to investigate the network structure in suspension. Additionally, these techniques require strong vacuuming which may affect the network structure, and, as a consequence, affect the statistical analysis of the dispersion.

Therefore, there is a need for non-invasive probing methods that are capable of being applied on liquid suspensions. Electromagnetic scattering has been used to study the particle dispersion. However, because of the limitation in the wavelengths that the instrument can use, the length scales of the particles analyzed are limited. Small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) are two methods which have been used for the study of nanotube dispersions [42, 43]. These methods benefit from a small probing range varying from Angstroms to few hundred nanometers and require the samples to be suspended in high-density fluids. The drawbacks of such instrumentation are its high cost and restricted availability. The range of static light scattering detection is limited to ~50 nm to several microns, which is not suitable for the length scale of single-walled nanotube agglomerates with the size of only a few nanometers [40]. Evidently, further studies are considered necessary to establish light scattering as a reliable methodology for nanotube dispersion. The number of reports on the morphology of the SWNT is very limited, and, therefore, a need for a method to study the SWNT in suspension obviously exists. Figure 6 shows the branched rope morphology of the SWNT in the solution, and Figure 7 shows very long and uniform nanotubes that are successfully dispersed in the solution.

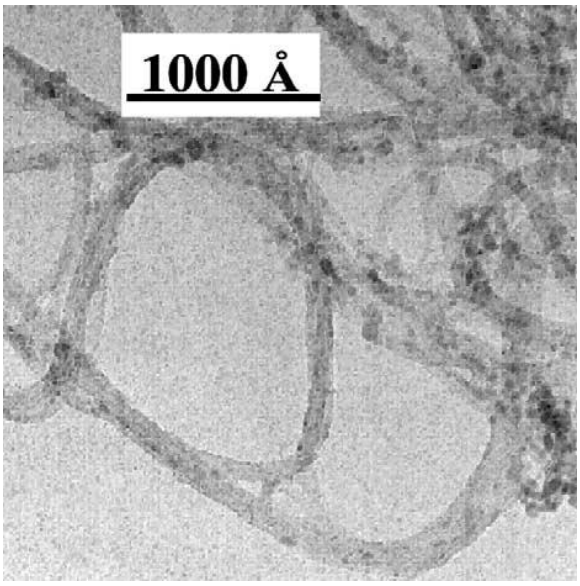


Figure 6. Transmission electron micrograph of a dried suspension showing the branched rope morphology. (Courtesy of [42])

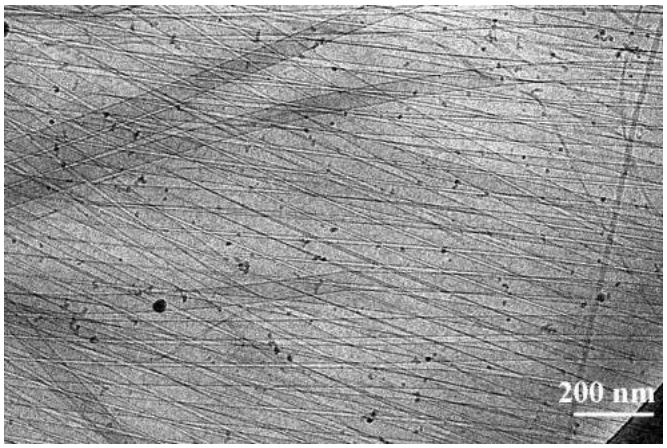


Figure 7. Low-magnification cryo-TEM image of a 0.1% SLC vitrified aqueous dispersion. Very long and uniform tubules form the suspension. (Courtesy of [43])

Variations of carbon nanomaterials such as carbon nanotubes [44, 45], carbon nanofiber [46, 47], and carbon nanoparticles [48] have been used in biosensors for accurate detection of genotoxic analytes, proteins, and cells. However, due to superior chemical and electrical properties and outstanding mechanical strength, carbon nanotubes (CNTs) have specifically gained special attention [49, 50]. The CNTs can be dispersed in a variety of

surfactants, and polymers such as the nafion, poly(3-hexylthiophene), poly(sodium 4-styrenesulfonate) (PSS), chitosan and carboxymethylcellulose (CMC) [2] which give it the functionality suitable for biosensor device manufacturing [50].

1.3.3 Methods of SWCNT dispersion

There is ongoing research on single-walled carbon nanotubes (SWNTs or SWCNTs) due to their nano-scale sizes and remarkable electronic, mechanical and thermal properties [51, 52]. These properties have made SWNTs suitable for next generation electronics such as transparent electrodes, solar energy applications, supercapacitors in transistors, and batteries [53-58]. However, SWNTs tend to form bundle or aggregates in aqueous solvents [59] which inhibits the successful implementation of intended promising applications and adversely affect the functional performance properties. As the focus of this dissertation is to produce conductive thin SWCNT films, the formation of SWCNT aggregation can impede conductivity, and therefore, impede the overall performance [60].

A number of methods exist to promote the dispersion of SWNTs in aqueous solutions which can be divided into two main categories: 1- covalent (chemical) [61-63], and 2- non-covalent (physical) surface modifications [64, 65]. Chemical modifications includes nitric acid and ozone treatments [61-63, 66] in which hydrophilic functional groups are covalently bonded to SWNTs [67]. In contrast, physical treatment is accomplished by employing a surfactant which induces non-covalent adsorption of macromolecules to the SWNTs (Figure 8). The mechanism of physical modification is disruption of Van der Waals forces under sonication-induced shears [68]. It is also important to note that exposing SWNT mixtures to high shear for extended duration can play an important role in the agglomeration of SWNTs [60]. Therefore, the sonication

amplitude and the duration of the sonication should be considered when physical modification of SWNTs is being studied.

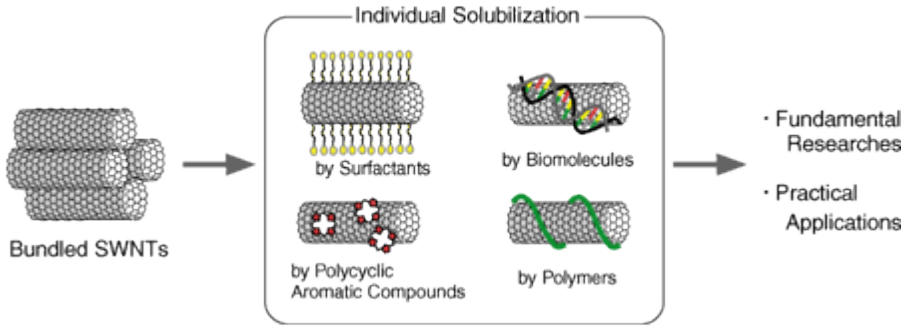


Figure 8. Individual solubilization of single-walled carbon nanotubes (SWNTs) in water (Courtesy of [64])

Chemical functionalization of SWNTs using covalently bonded amine (NH_2), carboxyl (COOH), or polyethylene glycol (PEG) functional groups enhances the ability to disperse SWNTs, but changes many of the intrinsic properties of nanotubes for biological applications [69-72]. As an example, chemical functionalization leads to surface defects which will result in a change in the surface reactivity, such as the rate at which these sites can scavenge electrons [73, 74]. Furthermore, it is believed that under UV-light exposure, chemically functionalized CNTs may lose some of their more polar (e.g., carboxyl) functional groups. Thus, non-covalent association with natural organic matter (NOM) may ultimately be responsible for CNTs dispersion in aqueous solutions [75, 76].

Physical treatment has been shown to preserve the SWNTs' fundamental properties [77, 78] due to the fact that the dispersion can be achieved through the non-covalent association with dispersants (e.g., surfactants, biomolecules, and polymers) with the CNTs. Studies show that the weak CNT-dispersant interactions have a negligible effect on the conjugated carbon arrays [79-81]. Consequently, a number of surfactants (such as Tween

and SDS) and biomolecules (such as bovine serum albumin) have been employed to disperse CNTs for biological purposes [82, 83]. It is expected that nonfunctionalized CNTs in aqueous solutions will interact with NOM, which results in an increase in their colloidal stability and bioavailability [84-86]. However, it is important to note that many conventional surfactants used to disperse SWNTs are not suitable for biological applications as they can be highly toxic [87, 88]. Therefore, biocompatible dispersants should be selected for biological applications [89]. Carboxymethyl cellulose (CMC) and Poly(sodium 4-styrenesulfonate) (PSS) are characterized by their inherent biocompatibility, low toxicity, disposability, and affordability [90, 91]. However, despite the advantages, there are only a few reports available with regards to the application of these dispersants for the dispersion of SWNTs. Therefore in this thesis study, CMC and PSS were used and compared for potential integration into immunoassay biosensors.

The downside of using physical SWNT modification is having to deal with an insulating layer of surfactant/polymer which significantly increases the resistance of thin films made of SWNTs [92, 93]. Therefore the amount of the dispersant added for the dispersion of SWNTs plays an important role in the functionality of the thin film of SWNTs for a sensing device. There is lack of a systematic approach in the literature to identify optimized conditions in which maximum connectivity of SWNTs is obtained with a completely dispersed SWNT suspension when dried in thin films. In this dissertation, experiments have been designed as a reliable method for achieving uniform, stable and highly dispersed SWNTs by employing physical modification suitable for biological applications. This study may be the first to employ a statistical approach to study, compare, model, and optimize the most suitable conditions for SWNTs dispersion.

1.3.4 Modeling SWNT dispersion

Dispersion of SWNT in an aqueous solution has proven difficult, and the resulting matrix solutions often do not show the anticipated electrical properties. This study seeks to find the statistical relationship between the mass unbundled SWNTs in the solution, the weight ratio of dispersant to SWNT, and the resistance of the matrix film after drying. Dynamic light scattering method was employed to assess the morphology of the SWNTs dispersed in aqueous solutions (shorter and thinner SWNT bundles resulting in greater or lesser conductivity). When SWNT is dispersed in aqueous solutions using chemical processing (acid or dimethylforamide (DMF) immersion) as dispersive aids, micromeshing, or networking of ropes, which are the indicative of nanotube aggregates, are observed [94, 95]. These fractal-like aggregate morphologies can be distinguished by the relationship between the scattering wave vector and the scattered light intensity according to:

$$I(q) \sim q^{-D_f}$$

where I(q) represents the scattered light intensity and D_f represents the fractal dimension of the SWNT network. By plotting the log[I(q)] versus log(q), the fractal-like morphology at the length scale of q^{-1} can be identify by determining the absolute value of the slope of the straight-line [40]. This value corresponds to the fractal dimension of the SWNT network. Higher the fractal dimension indicates the compact morphological structure of the aggregate. As a rule of thumb, D_f varies between 2.6 and 1.2, representing a very compact to a very loose, stringy agglomerate structure, respectively.

SWNTs have been dispersed with polyvinyl pyrrolidone (PVP), PVP copolymers, polystyrene sulfonate ($PSSO_3$), $PSSO_3$ copolymers, polyvinyl sulfate, dextran, dextran sulfate, and bovine serum albumin [96]. Anionic surfactants such as sodium dodecyl sulfate (NaDS) have also been used for the nanotube dispersion [97]. In this study carboxy methyl cellulose (CMC) and poly(styrene sulfonate) (PSS) is used for the SWNT dispersion due to their compatibility with the biomolecules. The mechanism of the dispersion using these polyelectrolytes is known to be the adhesion of these long chain polymeric dispersants to the oppositely charged surfaces of nanotubes. Figure 9 shows the hypothesized simulated mechanism of dispersion using PSS and CMC.

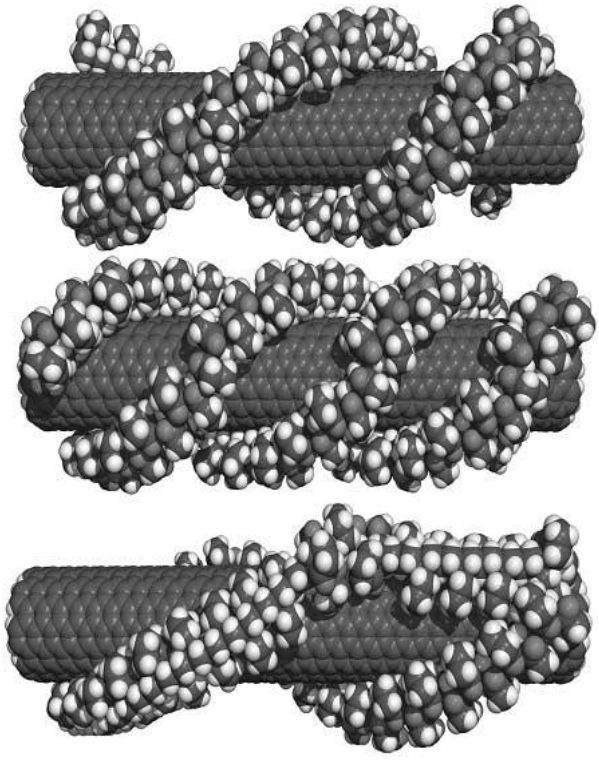


Figure 9. Some possible/hypothesized wrapping arrangements of PSS on a SWNT. A double helix (top) and a triple helix (middle). Backbone bond rotations can induce switch-backs, allowing multiple parallel wrapping strands to come from the same polymer chain (bottom). (Courtesy of [96])

Molecular dynamics (MD) simulation is a useful tool to investigate the effect of dispersant concentration on the SWNT dispersion in aqueous solutions and the interactions between the SWNTs and the dispersants. It is believed that the conjugated structure in the dispersant forms multi-layers on the surface of SWNT, while the dispersants which do not have conjugation will form semi-micelles on the surface [98]. Moreover, the concentration of the dispersant will affect the dispersant layers around the headgroups. Figure 10 shows an example of different dispersants over the SWNTs surfaces.

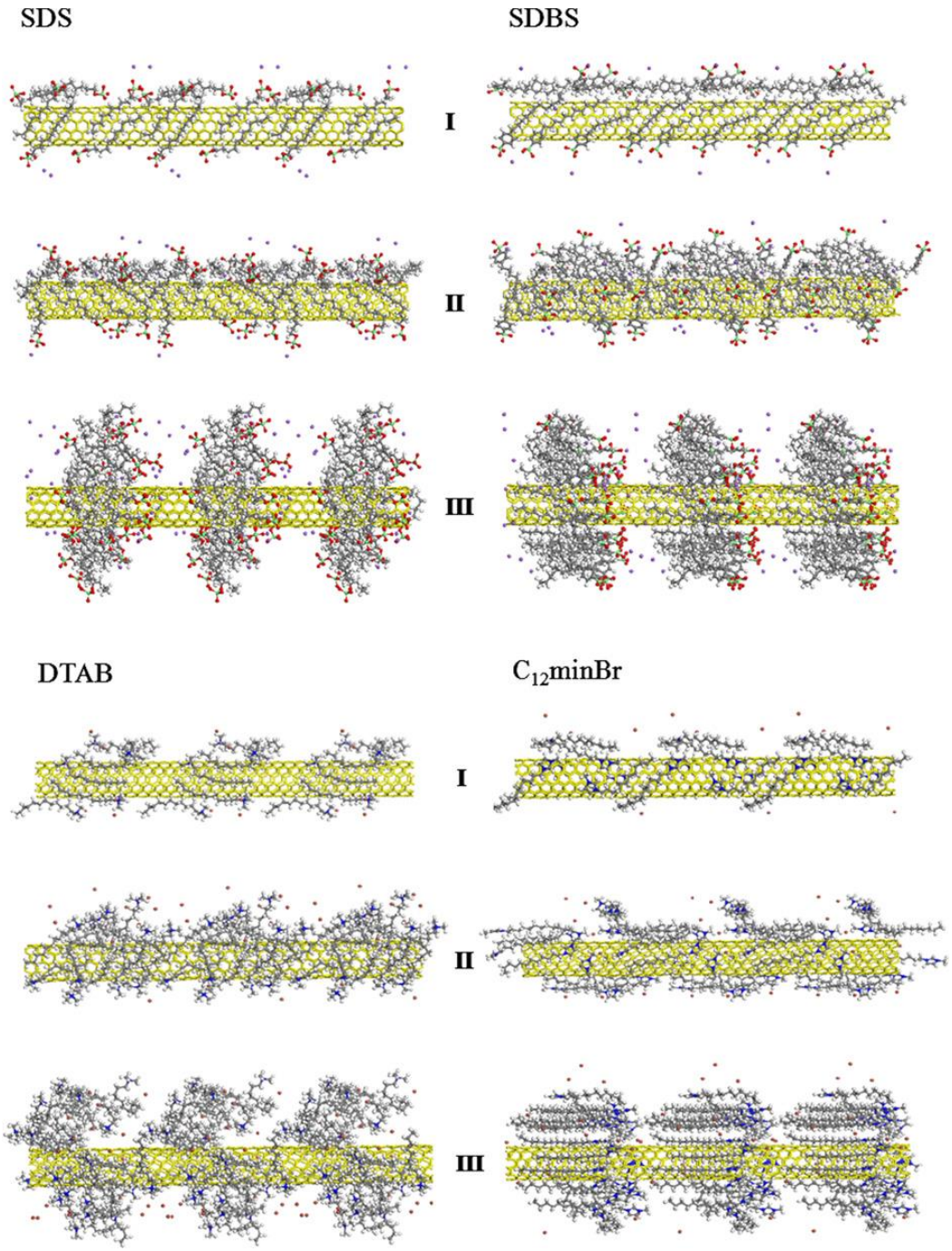


Figure 10. Snapshots of surfactant/SWNT configurations in systems I, II and III. Atoms C, H, O, N and S are in grey, white, red, blue and green. Counterions are small points in figures. For clarity, water molecules are invisible and SWNT is marked in yellow. (Courtesy of [98])

In literature, one can find computer simulation studies to obtain information about the adsorption, interaction, and morphology of the dispersant over the SWNTs surface. While SWNTs dispersion in aqueous solutions can be evaluated via experimental

investigations, obtaining the microscopic information due to adsorption and the interaction process is difficult through experimental analysis. Thus, computer simulation can be employed to investigate how dispersants wrap the SWNTs in the solution [98]. Molecular dynamics (MD) simulation is capable of simulating the wrapping of surfactants [98-100], polymers [101-103] and biological macromolecules [104-106] around the nanotubes. Simulations in literature have been carried out in a simulation program (Material Studio) at a fixed temperature (298 K) with the relaxation time of 0.2 ps. A structure optimization has been performed using a Smart Minimizer method. Target systems have been conducted for 10 ns with a time step of 1 fs at a constant volume and temperature (NVT) canonical ensemble. Partial charge of each one of the atoms of the dispersant has been calculated using a Charge Method in the simulation software (i.e Material Studio).

Total potential energy of the system was calculated using the following equation [98, 107]:

$$E_{total} = E_{bonds} + E_{angles} + E_{dihedrals} + E_{cross} + E_{non-bond}$$

The non-bond interaction will also be calculated using:

$$E_{non-bond} = \sum_{ij} \varepsilon_{ij} \left[2\left(\frac{r_{ij}^0}{r_{ij}}\right)^9 - 3\left(\frac{r_{ij}^0}{r_{ij}}\right)^6 \right] + \sum_{ij} \frac{q_i q_j}{r_{ij}}$$

where ε_{ij}, r_{ij}^0, r_{ij} q_i, and $q_j$are energy parameter, dimension parameter, distance between particles i and j, and the charges of i and j, respectively. Therefore, the feasibility of MD simulation in SWNT systems studies has been established and can be employed in conjunction with empirical experiments.

1.3.5 Preservation of bioactive elements within biosensors

A variety of biochemical components has been used for application in biosensors such as enzymes, antibodies, proteins/peptide receptors, nucleic acids, etc. The biochemical element should be immobilized on the surface of a signal transducer to improve performance and stability. Stability of the antibody/proteins in a sensing device toward oxidants, organic solvents, digesting enzymes, etc. plays a crucial role in the point-of care biosensors. Since, in this dissertation, the incorporation of an antibody within the sensing device is envisaged, it is also critical to preserve the functionality of the antibody in extreme application/storage conditions.

The native conformation of proteins is maintained by a balance of stabilizing and destabilizing forces leading to a stable conformation. Moreover, intermolecular forces comprised of van der Waals interactions and hydrogen bonding stabilizing the structure of the molecule. These forces are sensitive to the temperature: by increase in the temperature these interactions weaken, leading to a change in the protein conformation from the native to a denatured state [109]. Therefore, considering the protein–solvents interactions is crucial for storage of antibodies. It accepted that numerous organisms are able to survive extreme temperatures or dehydration by producing some sugars or polyalcohols in both their intra- and intercellular fluids [110]. This process, called biopreservation, produces compounds like glycerol and trehalose that are now widely used in pharmaceutical industry [111]. Such stabilizers are added to the antibody containing matrix to reduce the degradation phenomena during processing and storage [112]. However, the mechanism by which protein is stabilized using these substances is not completely understood [109, 113-115].

Two main hypotheses exist that explain the role of stabilizers in stabilizing proteins during drying and storage. 1- “glass dynamics hypothesis” and 2- “water substitute hypothesis”. In the “glass dynamics hypothesis” a stabilizer forms a rigid, inert matrix which engulfs the molecularly dispersed protein. Therefore protein molecules are trapped and separated in the glass matrix of the stabilizer which limits their mobility and bimolecular interactions. The rigid matrix formed by the stabilizer also prohibit or hinder the unfolding and other degradations, such as chemical degradation, which require mobility. Therefore, stabilization is virtually achieved through a kinetic mechanism [116, 117]. The “water substitute hypothesis” states that the formation of hydrogen bonds between stabilizers and specific sites on the surface of the proteins is responsible for providing the thermodynamic stabilization functionality of water that is lost during drying. Therefore, the denaturation of protein, such as unfolding, is hindered thermodynamically during the drying process (for example, hydrogen bonding increases the free energy of unfolding), and increase the shelf life as the result of native structure preservation [118-120].

Regardless of mechanism, bioprotection during drying is needed to preserve the functionality of antibody via preserving the native structure of protein in the dried state [114]. The superiority of bioprotection offered by glycerol to naturally occurring biological systems has been investigated and confirmed [121]. Therefore, in this study, glycerol is used to preserve the functionality of antibody and increase the shelf life of the potential sensors. Various ratios of SWNT to glycerol were studied to investigate the effect of glycerol on the electrical resistance characteristics of the matrix coatings. Different SWNT

to antibody ratio was also examined to explore the effect of antibody on the electrical resistance characteristics.

1.3.6 Test plate and test system

A laboratory test plate has been designed for the coating and "drying" of SWNT matrix films and the measuring of their resistance [1]. The plate design allows for 5 matrix channels to be tested at a time on one test plate. Figure 11, Figure 12, and Figure 13 represent this plate configuration. One formulation or multiple formulations can be tested on one plate. The A and C labels in the figures represent triplicate channels of one formulation and duplicate channels of a second formulation. The test plate design is shown from a top-angled viewing perspective in Figure 11. A side view looking parallel with the matrix channels on the plate showing the inside schematic of the deposited layers is shown in Figure 12 and Figure 13.

The single use 5-channel single-use plates are constructed by (see Figure 11):

1) Applying and drying conductive carbon-coated conductive silver ink electrical contacts to IPA-cleaned PET (4 separate small unfilled squares on each side of the plate). (The silver and carbon layers are screen printed, with oven dying at 100°C for 10 minutes between layers). The addition of the conductive carbon layer prevents silver electrolysis and migration from potentially interfering with the response of the device. (the carbon contact is exposed to the interior of each end of each channel and directly contacted by the matrix).

2) Applying and drying non-wetting polymer as unfilled rectangular boxes overlapping each electrical contact at the sides of the glass plate to create a total of 5 channels. This is applied using a Sonoplotter microplotter. PET templates fabricated with steps 1-4 below completed were produced in mass and stored.

3) UV-O_3 treating PET templates

4) Laminating PET film to the ~2"x3" glass base slide.

5) Adding matrix solution to each channel (matrix is contained due to the non-wetting polymer barrier) and then “air drying” the matrix and room temperature to obtain a semi-solid film matrix.

Once dry, positive and negative alligator clips are attached to each channel from a Keithley 2700/7700 Data Acquisition System (20 channel multiplexing capability) for measuring resistance of each channel as a function of time. Once the matrix solution is added to the test plate, the resistance can be measured after drying. The matrix typically dries to a semi-solid thin film within 6 hours following coating at room conditions.

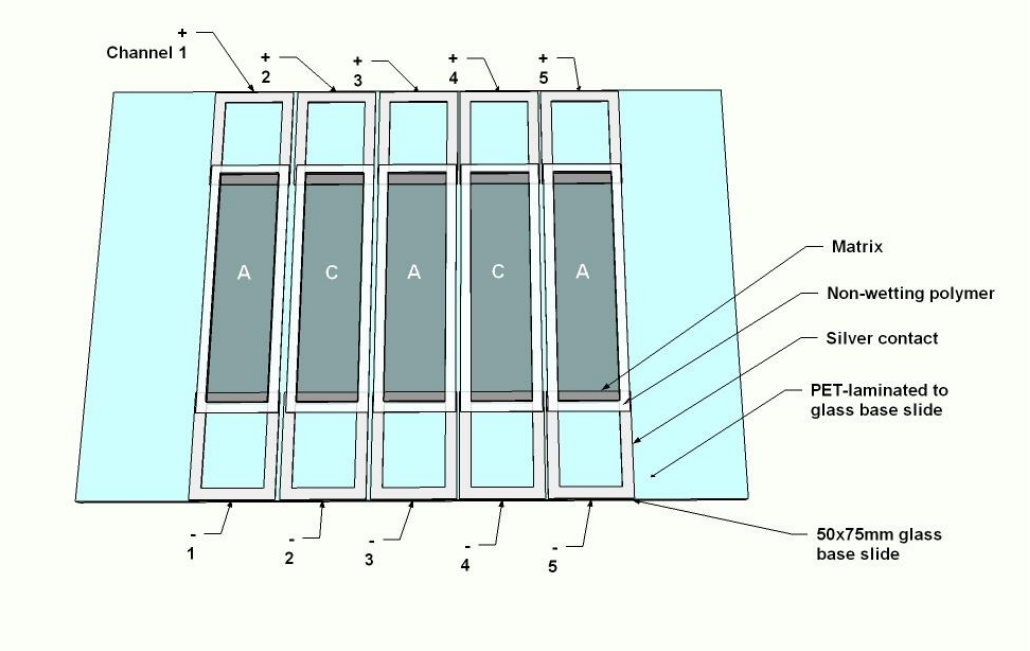


Figure 11. Schematic of five-channel test plate for testing matrix formulations. Once connected to the data acquisition system, the resistance of each matrix channel can be measured at different time intervals.

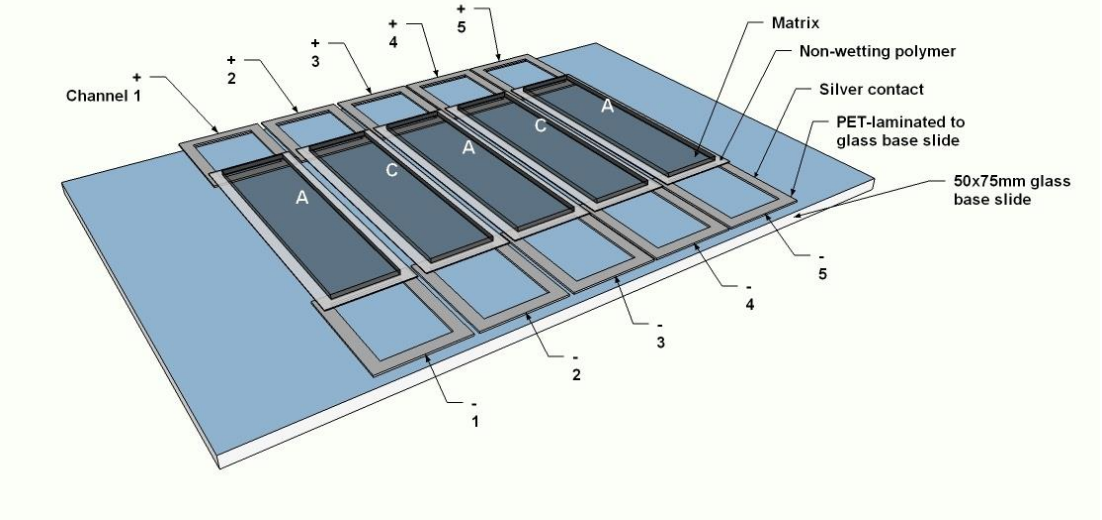


Figure 12. Angle view of a five-channel test plate.

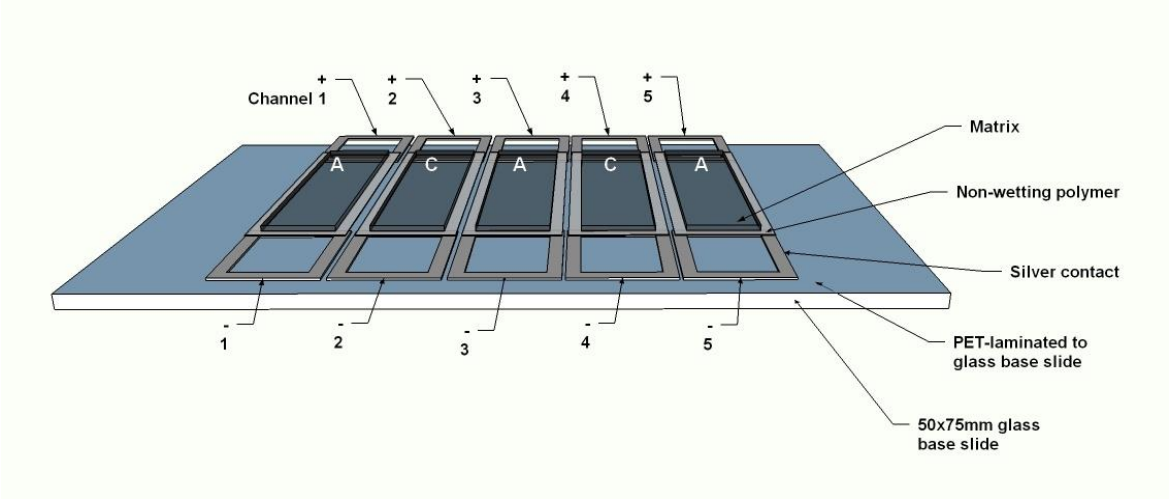


Figure 13. Side view of a five-channel test plate.

1.3.7 Printed sensor components

One of the critical aspects of biosensor fabrication is designing and patterning conductive, insulating, and functional materials in a way that serves for the ultimate biosensor functionality. Different approaches have been employed to deposit these functional materials on substrates including lithography [122], chemical vapor deposition (CVD) [123], and spin coating [124]. However, these approaches are complicated, time consuming, and expensive. The direct patterning method is a technique that overcomes the drawbacks of the other techniques, consumes less material, and can be run at lower manufacturing temperatures [125, 126]. Masking the substrate (necessary in lithography) is not required, further making direct patterning an economical method.

The development of printed electronics on flexible substrates, referred to as "direct printing," has been the focus of attention in recent years. New electronic ink formulations will allow these printing processes to be cost-effective as compared with the conventional methods of electronics fabrication [127]. The benefits of the direct printing process are high material usage efficiency, elimination of expensive processing steps such as photo-

lithography, etching, and, vacuum deposition, and the ability to rapidly change circuit designs in production lines [127]. Thin and flexible substrate materials may be used, increasing their potential application in areas such as biometric device electronics. Various functional materials can be deposited accurately (printing resolution, ±5 μm) and precisely (1–100 picoliter) where small feature patterning is desired [128].

Numerous printing methods exist such as flexography, gravure, screen printing, and inkjet printing. Out of the mentioned methods, screen printing and inkjet printing methods have gained attention for printed electronics in the past decade. Inkjet printing (Figure 14) is a relatively new technology for the fabrication of microelectronic devices. Inkjet printers use piezoelectric motion to deposit droplets of liquid materials (referred to as inks) onto the substrate [129]. Figure 15 shows a representation of droplets deposited using an inkjet printer.

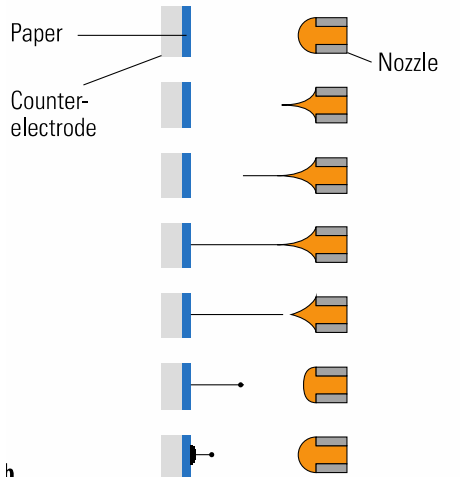


Figure 14. DOD droplet generator. (Courtesy of [130])

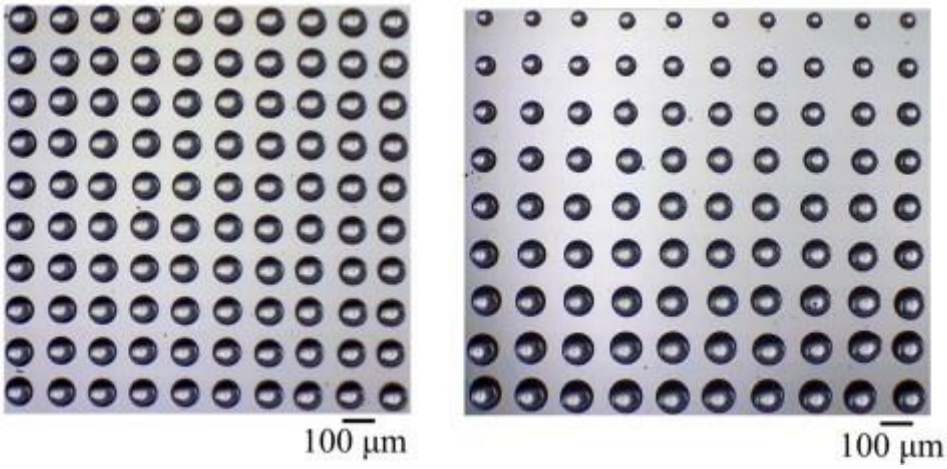


Figure 15. Droplets deposited by DOD droplet generator. (Courtesy of [131])

The screen printing method is also a very simple printing method which can deposit large area patterns with very high precision. The screen printing method has been also widely used for the fabrication of different types of electronic devices such as solar cells [132] and surface enhanced Raman spectroscopy (SERS) based sensors [133, 134]. Figure 16 shows a schematic of a screen printing process.

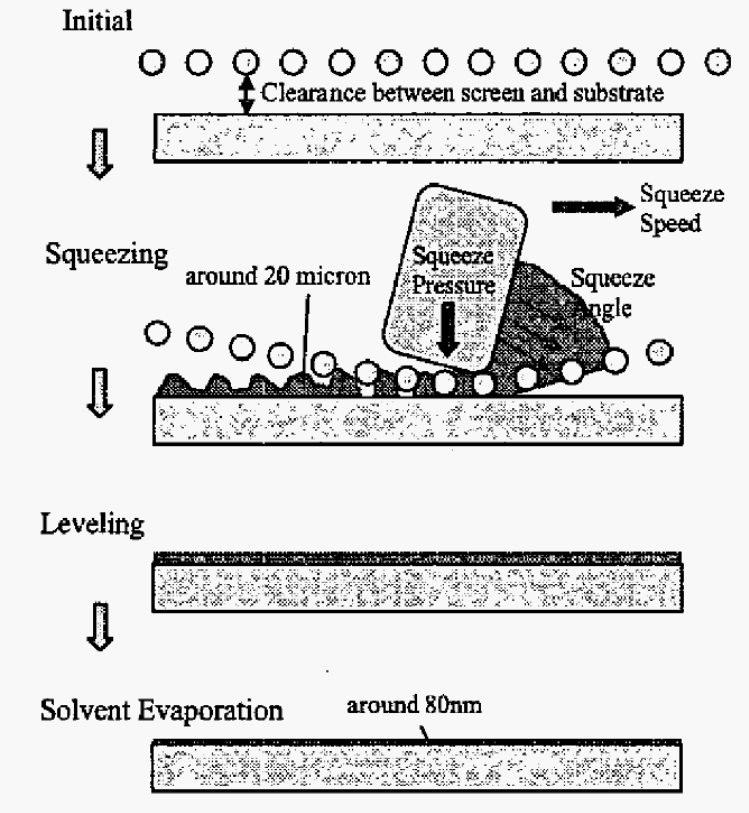


Figure 16. Schematic of screen print deposition. (Courtesy of [132])

In this study, a couple of printing methods were employed and for the depositing sensor materials onto surfaces for testing.

1.3.7.1 Microplotter printing

Microplotters are similar in nature to the inkjet printers. However there is a significant difference between the dispensing mechanism of the Microplotter systems and the existing inkjet technology. In the Microplotter systems (Figure 17), the dispenser acts like a pen plotter, unlike the inkjet printers which eject droplets over a distance to a surface. The Microplotter directly dispenses the liquids as continuous features over the surface. The dispenser employs an ultrasonic pumping action to force the liquid out from the nozzle and

form a meniscus on the surface, from where the surface tension force takes action and dispenses the liquid where programmed.

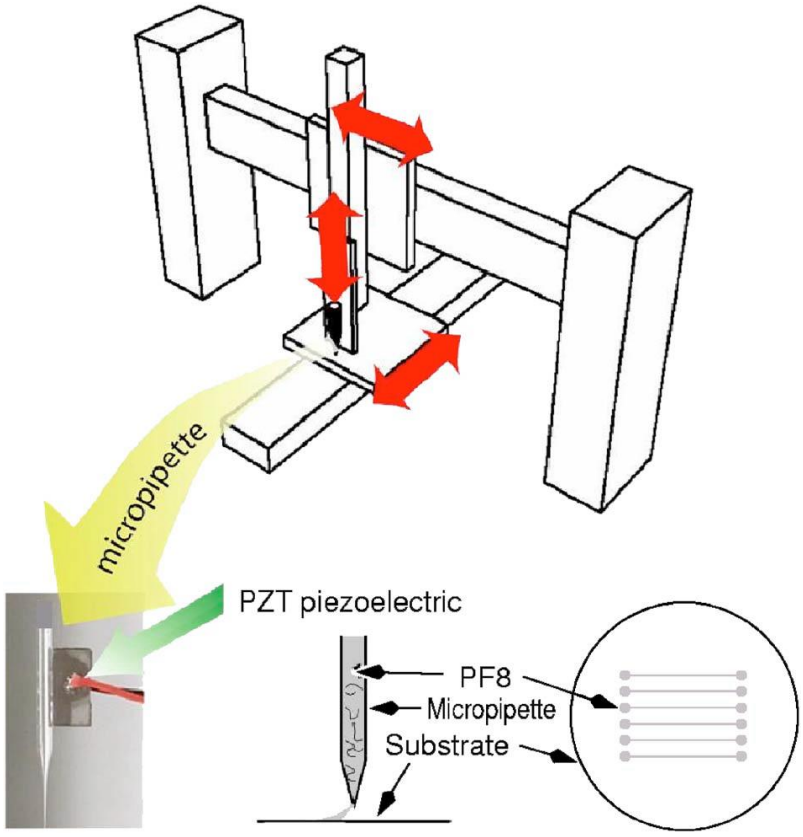


Figure 17. Top: schematic layout of the XYZ microplotter system that provides micron positional precision. Bottom: a photograph of the micropipette/piezoelectric crystal assembly and a typical test pattern of 1 cm long lines on the sapphire substrate (Courtesy of [135])

One of the most important characteristics of Microplotters which distinguish them from the inkjet printers is the ability to work with a much wider variety of solutions. Solutions with viscosities as high as up to 450 centipoise can be dispensed which would be impossible to print with inkjet printers. Microplotters also have the advantage of printing solutions that would normally present clogging problems to inkjet printers, like suspensions with high solid particle content such as carbon nanotube solutions. This advantage enables the Microplotters to print a variety of inks with minimum tuning as opposed to the modifications and refinement required for an inkjet printer. Another

important advantage of Microplotters is the capability to print continuous features such as lines. The objects deposited by Microplotters possess smooth edges, in contrast to objects printed by overlapping inkjet droplets. Various features with line widths as narrow as 1 micron and as wide as ~2 mm can be deposited in this method [136]. Although a microplotter was used to deposit anti-wetting polymer in this study, numerous disadvantages such as slow speed and inability to deposit certain solutions or dispersions due to clogging limits the application of this method. In this study, a GIX Microplotter II microplotter was employed to print the non-wetting features in the test template design which will be discussed later.

1.3.7.2 Screen printing

The screen printing method is an ancient technique which was introduced thousands of years ago for applications in art, textiles, and advertising. Screen printers use a woven mesh with the desired pattern and a roller or squeegee which moves across the woven screen and forces the ink past the mesh deposit over the surface of the target substrate (see Figure 19 and Figure 18). The screen mesh design (Figure 18) defines the different parts of the electrode of the biosensors. After the ink deposition, a thermal treatment is required to set the electrodes.

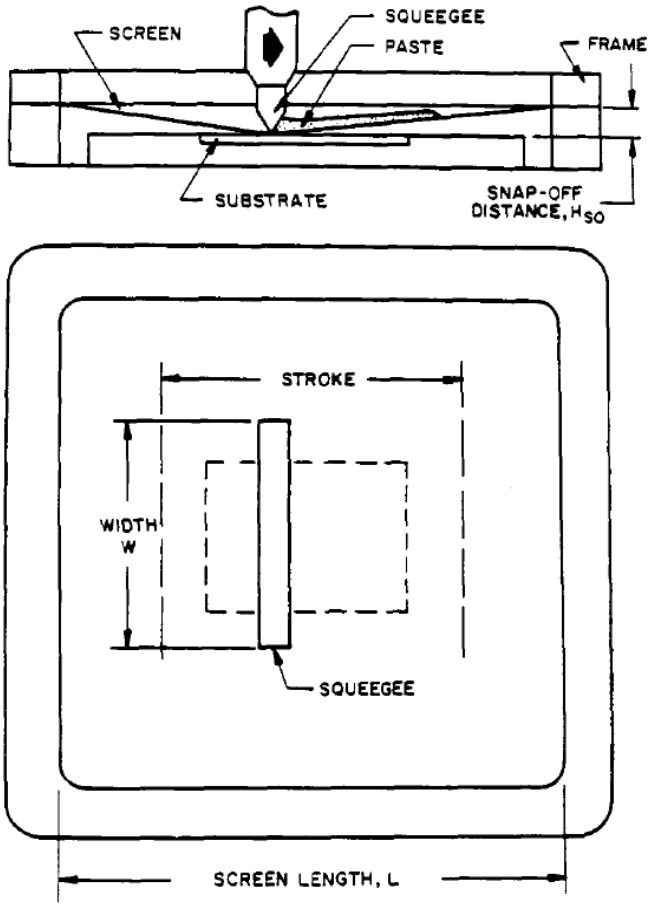


Figure 18. Schematic of the screen print machine. (Courtesy of [137])

Two of the most common inks/pastes for developing devices using screen print technology are silver and carbon. Silver inks are very conductive and therefore work as the electrodes, whereas the carbon inks (less conductive) are printed over the silver inks to prevent the silver electrons from migration. Carbon inks have inert chemical characteristics and are relatively inexpensive. Gold inks are also available, however because of the high cost of such inks their application has been limited to electronics where a very high conductivity is needed, such as in enzymatic, immuno-, or genosensors [138-141].

The limitation of screen printing technology is the incompatibility with non-planar substrates. Therefore, special attention must be focused on surface treatments if a non-planar substrate is used.

The development of a flow pattern in a screen printing process is presented in Figure 19. The advancements in functional electronic inks are making conventional printing methods useful for manufacturing electronic devices. Figure 20 shows examples of how diversified and creative screen printed sensors can be. Highly sophisticated printers are now capable of miniaturizing and developing electronic devices such as highly sensitive and selective electrochemical sensors. Miniaturized sensors are very useful where the sample volume being tested is limited. Highly sensitive electrochemical sensors are capable of detecting the target compound in sample volumes as low as a few microliters. This capability allows sensors to be miniaturized while increasing the number of possible target compounds. The screen printing method is one of the powerful methods which make the fabrication of microelectrodes possible and has been the focus of attention for numerous studies in the field of sensing technology [142, 143]. The accuracy and sensitivity of the fabricated sensors using printing methods have shown to be competitive with that of the conventional microelectromechanical systems (MEMS) sensors.

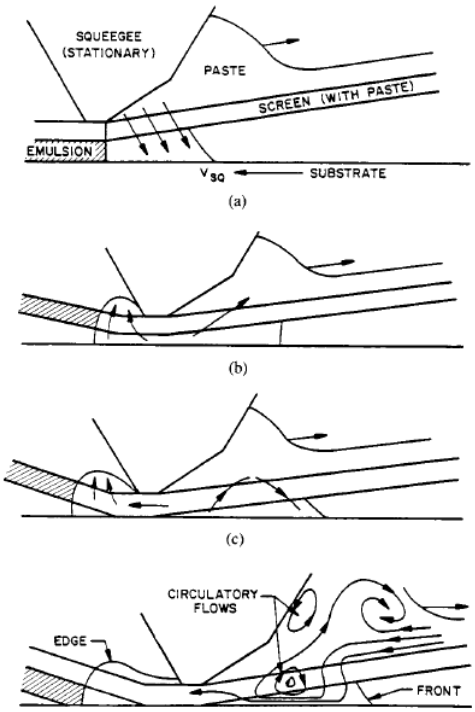


Figure 19. Development of flow pattern in a screen printing process viewed in reference frame of the squeegee. (a) Squeegee at the edge of emulsion. (b) Squeegee begins to deflect the screen. (c) Screen touches the substrate (when printing wide patterns). (d) Developed flow pattern. (Courtesy of [137])

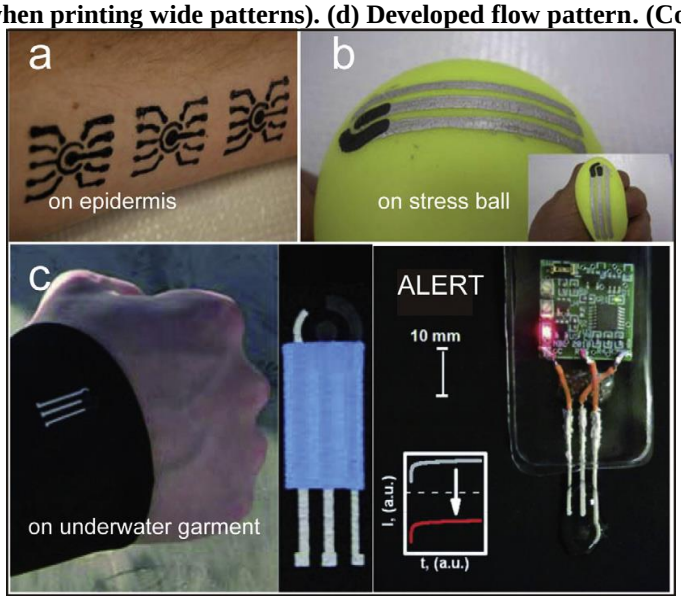


Figure 20. Photos of (a) three eight-electrode carbon ink-based arrays stamped on the epidermis and (b) three-electrode contingent on a stress ball. (c) Photo of SPE on an underwater garment (left) and a red indicative LED (right) when pollutant content in seawater exceeds a certain level. (Courtesy of [144])

Screen printing technology has also been successfully used for the fabrication of point-of-care biosensors for environmental analyses. Screen-printed electrodes (SPEs)

have been commonly developed using screen printing technology [144]. It is believed that SPEs are the most appropriate electrochemical sensors for point-of-care for electrochemical biosensors because of their linear output, low power consumption, and rapid response with high sensitivity [145, 146]. Screen-printing machines are easy to use and fast for research scales. Since the above mentioned impediments of the inkjet printing inks do not exist for the screen printers, they are also convenient to use. As a consequence, SPEs can be used in the fabrication of biosensors requiring a low detection limit.

In this study dissertation, screen printing and microplotting were employed in the fabrication of the test system/sensors in this dissertation as inkjet printing was found to have significant limitations with the materials used. Preliminary work using inkjet for a different test system was conducted and difficulty in printing SWNT-containing materials reliably required designing an entirely new laboratory biosensor test system and approach.

SINGLE-WALLED CARBON NANOTUBES DISPERSION AND ITS EFFECT ON THE ELECTRONIC TRANSPORT PROPERTIES

2.1 Objective

Obtaining a uniformly dispersed SWNT within an aqueous system is a challenge for biosensor coating. Moreover, after solution deposition and drying, the resulting semi-solid materials often do not show the anticipated electrical properties. In this section, obtaining uniform SWNT dispersions in aqueous solution using various sonication protocols along with poly(sodium 4-styrenesulfonate) (PSS) and carboxymethylcellulose (CMC), two dispersing agents, and other additives comprised of phosphate buffer and sodium azide is studied. An experiment using designed using Response Surface Methodology (RSM) in order to analyze, model and predict the resistance of dried thin films of matrix solution produced under various conditions. Dispersed SWNT and aggregated/bundled SWNT present after various sonication protocols were separated by centrifugation and microfiltration, and percent dispersed was determined by weight difference of dried samples. This information was augmented with particle size distribution data using the dynamic light scattering technique. In addition, SEM was attempted and 3D optical microscopy was performed on the dried matrix films to investigate the morphology and draw correlations and trends in dispersion conditions.

Once characterized, selected SWNT dispersions were combined with antibody and other constituents (such as wetting agent glycerin) and deposited within test sensor

channels, dried into a semi-solid/fluid film, and resistance tested using a constant microamp current (see Section 3.2.1.2).

2.2 Methodology

2.2.1 Template production procedure

The schematic picture of a fabricated laboratory test biosensor plate is depicted in Figure 21, Figure 22 and Figure 23. The testing template was fabricated as follows (slightly modified from [1]): Conductive Ag silver ink (Electrodag 7019 from Henkel) was deposited as a 175 μm thick electrode on DuPont Teijin Films™ (Melinex® ST505) polyester films using Western Michigan University's (WMU) MSP-485 screen printer (from Affiliated Manufacturers Inc.). The resulting Ag electrode prints were cured for 10 min at 107°C in a VWR 1320 oven. Carbon ink (Electrodag 440B) was screen-printed on the silver layer as an over-layer to protect the silver layer from electron migration. The patterns on the screen used for this layer were deliberately slightly larger than that of the silver pattern to make sure that the carbon layer completely covered the silver. The carbon layer print was then cured for 10 min at 107°C. A SonoPlot® GIX Microplotter II was used to fabricate the matrix containment channels as pictured in Figure 21. 3M™ Novec™ 2702 Electronic Grade Coating fluorochemical acrylic polymer carried in a hydrofluoroether solvent as a non-wetting polymer was used for printing the containment well. This polymer has been characterized as a low viscosity and low surface tension solution and comes in clear aqueous solution. The deposited channels were then cure at 100 °C for 1 hr for maximum attachment.

In order to confirm that a matrix solution’s surface tension was appropriate for wetting the PET, a dynamic contact angle analyzer FTA200 from First Ten Angstroms

Inc., equipped with image analysis software, was used to investigate the surface energy of the PET substrate using the sessile drop method. PET was subjected to various UV-O_3 treatment times (UV-O3-CLEANER Model 144AX) and the optimum amount of time for UV-O_3 treatment (5 min) was selected. The PET sheets were then UV-O_3 treated for 5 minutes and attached to 75×50 mm microscope slides. 0.15 ml of matrix solution (Figure 21) was deposited in the channels (Figure 21) using a pipette and allowed to dry. Each channel was then resistance tested (Figure 23).

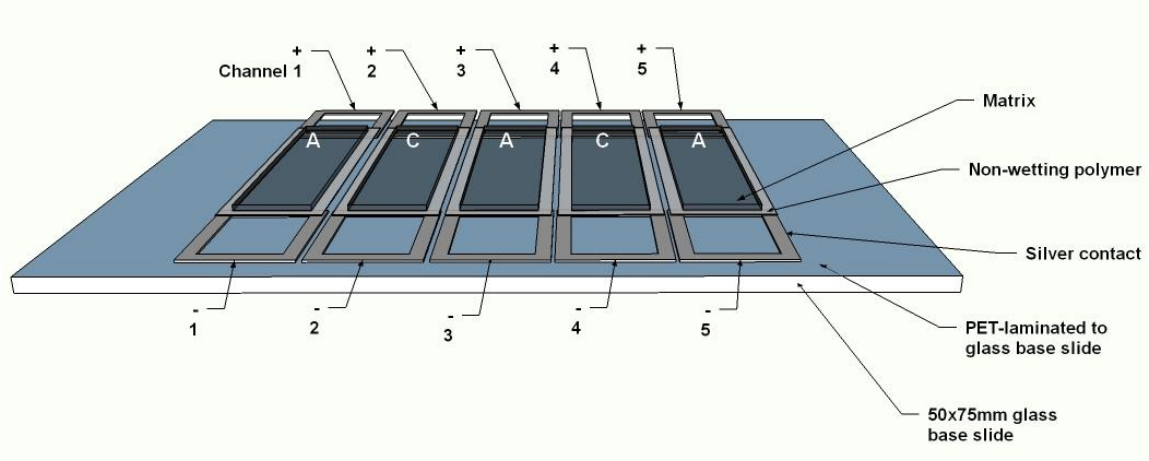


Figure 21. Side view of a five-channel test plate (adapted from [1]). The test template is UV-O_3 treated to improve the wetting of the deposited solutions.

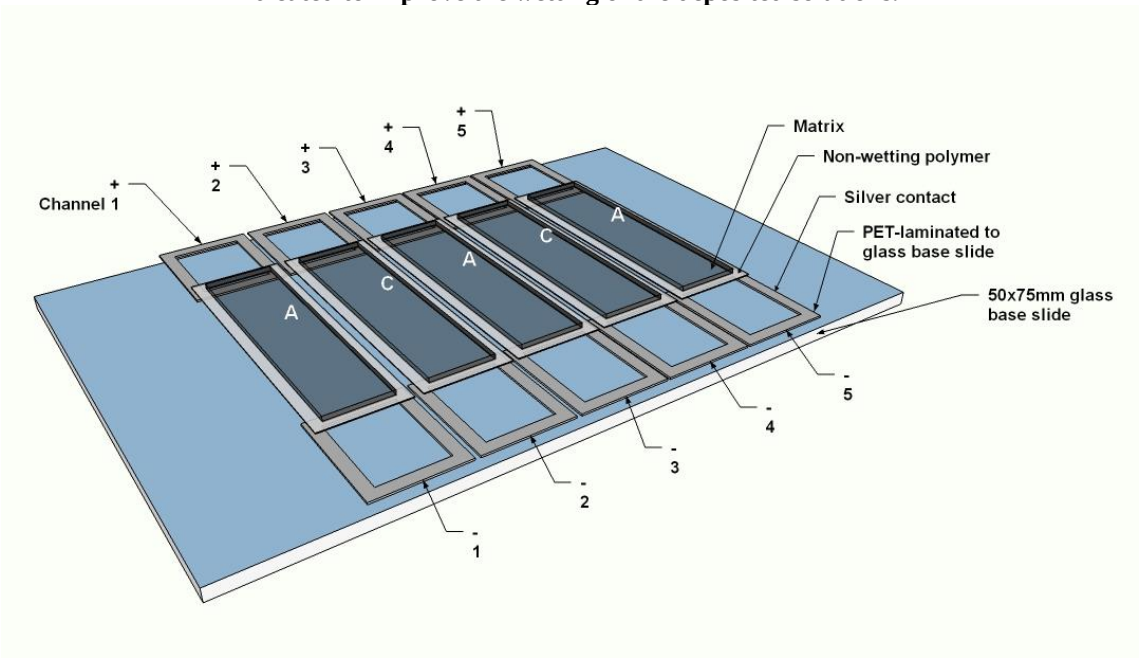


Figure 22. Schematic of five-channel test plate (adapted from [1]) for testing matrix formulations. Once connected to data acquisition system, the resistance of each matrix channel was measured.

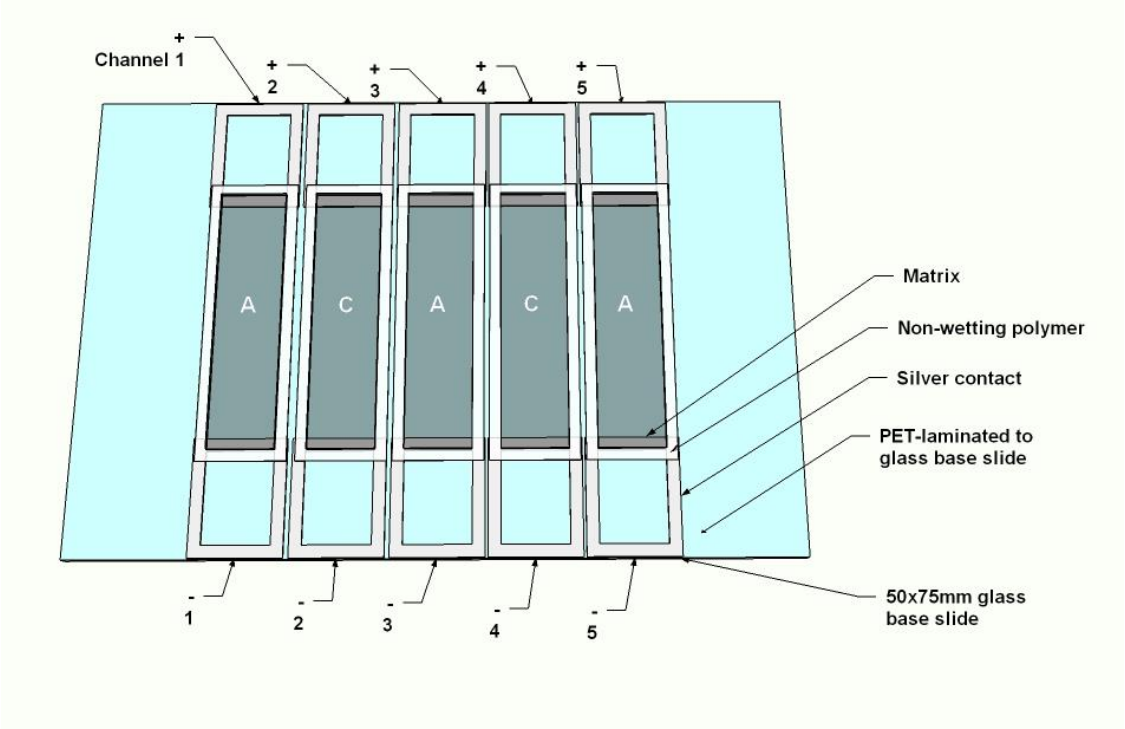


Figure 23. Top view of the various layers that are affixed to the glass base slide of a test plate (adapted from [1]).

2.2.2 Matrix Formulation

2.2.2.1 Single-walled nano-tube (SWNT) dispersion

SWNTs were dispersed with different concentrations of PSS and CMC. The formulations include SWNT and additives (phosphate buffer pH 8, and azide (at fixed concentrations of 0.07% and 0.003%, respectively)) in water. These additives are necessary to preserve the protein functionality in the future studies, which will be discussed later in this dissertation. The following parameters are investigated in this study at a constant SWNT concentration of 0.21%.

1) 3 SWNT to PSS or CMC weight ratios (0.5:1, 1.25:1, 2:1)
2) 3 Sonication amplitudes (20%, 30%, 40%)
3) 3 time durations (2, 13, 24 hrs)

4) Centrifuge at 1000 G for 1 minutes, followed by filtration through 10 µm filter (Versapor 25 mm syringe filters).

The sensor and formulation materials used in this study are presented in Table 2.

Table 2- The key materials for investigating the resistance response of different matrix formulations.

Materials	Source
Single Wall Nanotube (SWNT):	SWeNT SG 76 (High Conductivity, 1,000 aspect ratio to tube diameter 0.92+/-0.27nm), Specific Surface Area 800, Raman G/D Ratio >16, Bulk Density (Tapped) 0.1 g/cm^3 , has both metal and semiconductor chirality
Nanotube dispersant:	Carboxymethylcellulose (CMC) (MW 90,000) Poly(sodium 4-styrenesulfonate) (PSS) (MW 70,000)
Silver Ink:	Henkel Electrodag 479SS
Conductive Carbon Ink:	Henkel Electrodag 965SS
Flouropolymer:	3M™ Novec™ 2702 Electronic Grade Coating
PET Film:	Polyethylene terephthalate, Dupont Teijin Films Melinex® ST505

The sonicator used was a 130 Watt Ultrasonic Processor (Sonics & Materials, Inc.) employing a standard titanium alloy probe with tip diameter of 1⁄8" (3 mm) and length of 57⁄16" (138 mm). Each 5ml matrix solution was sonicated in a 15 ml polypropylene vial (VWR® centrifuge tubes with flat caps Cat. No. 89004-368) with the sonicator tip extended down to the vial's 2ml graduation line. The obtained suspended filtrate particles size distribution was evaluated by dynamic light scattering method (Particle Size Analyzer, Nicomp 370 and Accusizer 770) immediately after the sample preparation.

2.2.2.2 Matrix formulation materials (with SWNT, PSS or CMC)

The base composite matrix material consists of conductive nanotube, polymer, phosphate buffer, and sodium azide. The mixture is referred to as the "matrix" formulation. This matrix is coated onto a polyethylene terephthalate (PET) (DuPont Teijin Films™ Melinex® ST505) film test channels at different component ratios and film thicknesses. The purpose of this part of the study is to evaluate the coating uniformity properties and resistance of coated matrix formulations (with SWNT and PSS or CMC). A 3D optical microscope (White light interferometer ContourGT-I) was used as a profilometer to visualize surface topography, and to provide a complete 3D surface profilometric image. The morphology of the dried matrix coating was also assessed by SEM for select formulations. The purpose of the above experiments is to find matrix film formulations that have a low dried resistance (less than 2000 ohms) and to correlate resistance with film properties. Several promising matrix formulations produced from stable SWNT dispersions in this experiment were selected, and aliquots of the SWNT dispersion were mixed with solutions of antibody, and glycerol and reported in the next chapter (section 3.3).

Dispersed nanotubes in solution (0.15 ml) was deposited on test channels (see Figure 21 and Figure 22 and Figure 23) and let dry in a desiccant chamber. The test channel on which the matrix material is coated is 2.5 cm long. Three different matrix film thicknesses based on the theoretically calculated densities of the varying components in the formulations for the remaining solids (SWNT and PSS or CMC) was achieved by preparing diluted aliquots of the dispersions (as noted in section 2.2.2.1 at 100% (no

dilution with water), 70% (addition of 30% purified water), and 40 % (addition of 60% purified water) before coating.

The research test template uses a 2-wire constant current resistance measurement with a Keithley 2700/7700 multichannel data acquisition system to record matrix resistance. All matrix-coated plates were tested following drying in a desiccant chamber to reduce moisture. Test matrix resistance was assessed immediately after complete drying in the desiccant chamber.

2.2.3 RSM

Response surface methodology (RSM) is an empirical statistical approach in which quantitative data is obtained from appropriately designed experiments in order to identify the best regression model and operating conditions [147, 148]. This technique employs a factorial design in order to construct mathematical models which describe the effects of several factors on the response. This statistical approach is a suitable technique for multi-factor experiments and has the advantage of identifying the most favorable conditions of the processes by determining the common relationship between various factors. Central composite design (CCD), which is a popular response surface method for the experimental design, was employed to optimize the dispersion conditions [149]. The objective of employing CCD is to optimize the effects of the variables to get the best response. This design has the following components: 1- full or fractional factorial points, 2- an additional design (a star design) at a distance of α ($\alpha=2^{(k-p)/4}$) calculated from the center, and 3- central points. The total number of experiments can be calculated by $N=k^2+2k+c_p$ in which k is the factor number, and c_p is the number of replications of the experiment at the central point

[150]. For statistical calculations, the actual variables can be converted to coded variables using the relation below:

$$X_i=\frac{x_i-x_0}{\partial x} \quad (1)$$

where X_i is a coded value of the variable, x_i is the actual value of the variable, x_0 is the actual value of X_i at the center point, and ∂x is the step change of the variable.

In this experiment, the design was composed of three factors (SWNT:CMC ratio, Sonication amplitude (%), and Sonication durations (hr)), each with two levels (low, high), and a total of 20 runs were carried out to optimize the chosen variables. For the purpose of statistical computations, the three independent variables were denoted as x_1, x_2, and x_3, respectively. The range of the values used for the levels of each factor investigated in the experiments was selected based on the preliminary experiments and are listed in Table 3. The quadratic equation can be used for this methodology to fit the response variables:

$$Y = \beta_0 + \sum_{i=1}^{k} k\, \beta_i x_i + \sum_{i=1}^{k} \beta_{ii}\, x_i^2 + \sum_{i}^{i<j} \sum_{j} \beta_{ij} x_i\, x_j \quad (2)$$

where Y, k, β_0, β_i, β_{ii}, and β_{ij} are the predicted response variable, number of variables, a constant term, coefficients of the linear parameters, coefficients of the quadratic parameters, and coefficients of the interaction parameters, respectively. The coefficient of determination (R^2) can be estimated to test the certainty of the above polynomial model [151]. In this dissertation, RSM was employed as a useful method to investigate the effect of SWNT:CMC ratio, Sonication amplitude (%), and Sonication durations (hr) on the resistance and particle size of the prepared matrix solutions.

Table 3- Factors and levels used in this experimental design (DOE)

Factor	Low level (-1)	High level (+1)
SWNT:CMC (X_1)	0.5	2
Sonication amp (%) (X_2)	20	40
Sonication durations (h) (X_3)	2	24

Different mixtures using SWNT:PSS/CMC ratios were prepared as shown in Table 4 through Table 9 and sonicated for durations varying from 0.9 hr to 25.1 hr (see Table 4 through Table 9). The amplitude of the sonicator was selected according to the design of experiment (up to 40% as presented in Table 4 through Table 9). The particle size analysis was performed immediately following the matrix solution preparation. The matrix preparation parameters were set according to the response surface methodology (RSM) experimental design, with the parameters tabulated in Table 4 through Table 9. Dilutions of the prepared solution (100%, 70%, and 40%) were prepared as explained earlier and 0.15 ml of the resulting solutions was deposited into the designated channels in duplicates. The prepared templates were then dried in a desiccant chamber for 24 hr. Subsequently, the surface profile of the select dried matrix was obtained and analyzed. The predicted resistance values using the statistical model (discussed in section 2.2.3) were also estimated and tabulated in Table 4 through Table 9. The predicted resistance values of the outlier data points are also reported and will be discussed in detail in the results section.

Table 4- The design of experiment based on RSM showing the factor levels and their responses. The three independent variables were denoted as x_1, x_2, and x_3, which represent SWNT:CMC, Sonication amplitude (%), and Sonication durations (h), respectively for the CMC matrix solution at 100% (no dilution)

Runs	X_1 *(SWNT:CMC)*	X_2 *(Sonication amp (%))*	X_3 *(Sonication duration (h))*	*Resistance (ohm)*	*Predicted Resistance ohm(eq. 5)*	*particle size (nm)*
1	1.250	30	13.0	134	164	110
2	1.250	30	13.0	149	164	110
3	0.500	20	2.0	3868395	*157**	4131
4	2.075	30	13.0	555	492	2230
5	1.250	30	13.0	130	164	66
6	0.500	20	24.0	24231	*157*	112
7	1.250	30	25.1	199	465	270
8	2.000	20	24.0	58878	*1211**	193
9	0.500	40	24.0	1317	1212	932
10	1.250	19	13.0	149	164	313
11	2.000	20	2.0	10914	*1211**	675
12	2.000	40	2.0	148	157	554
13	1.250	30	13.0	166	164	235
14	0.500	40	2.0	1069	1212	2731
15	2.000	40	24.0	128	157	115
16	1.250	30	13.0	165	164	348
17	1.250	30	13.0	147	164	247
18	0.425	30	13.0	6256	*493**	213
19	1.250	30	0.9	794	465	409
20	1.250	41	13.0	225	164	180

*Fitted values in italic denotes an extremely unusual point relative to predictor levels used to fit the model

Table 5- The design of experiment based on RSM showing the factor levels and their responses. The three independent variables were denoted as x_1, x_2, and x_3, which represent SWNT:CMC, Sonication amplitude (%), and Sonication durations (h), respectively for the CMC matrix solution diluted to 70% (70%)

Runs	X_1 *(SWNT:CMC)*	X_2 *(Sonication amp (%))*	X_3 *(Sonication durations (h))*	*Resistance (ohm)*	*Predicted Resistance ohm(eq. 6)*	*particle size (nm)*
1	1.250	30	13.0	190	235	110
2	1.250	30	13.0	214	235	110
3	0.500	20	2.0	2812535	*238*	4131
4	2.075	30	13.0	866	744	2230
5	1.250	30	13.0	174	235	66
6	0.500	20	24.0	28272	*238*	112
7	1.250	30	25.1	254	608	270

Table 5 - continued

8	2.000	20	24.0	71517	*1690**	193
9	0.500	40	24.0	1812	1692	932
10	1.250	19	13.0	210	235	313
11	2.000	20	2.0	15109	*1690**	675
12	2.000	40	2.0	202	238	554
13	1.250	30	13.0	244	235	235
14	0.500	40	2.0	1498	1692	2731
15	2.000	40	24.0	200	238	115
16	1.250	30	13.0	223	235	348
17	1.250	30	13.0	195	235	247
18	0.425	30	13.0	8141	*745**	213
19	1.250	30	0.9	1085	608	409
20	1.250	41	13.0	331	235	180

*Fitted values in italic denotes an extremely unusual point relative to predictor levels used to fit the model

Table 6- The design of experiment based on RSM showing the factor levels and their responses. The three independent variables were denoted as x_1, x_2, and x_3, which represent SWNT:CMC, Sonication amplitude (%), and Sonication durations (h), respectively for the CMC matrix solution diluted to 40% (40%)

Runs	***X_1 (SWNT:CMC)***	***X_2 (Sonication amp (%))***	***X_3 (Sonication durations (h))***	***Resistance (ohm)***	***Predicted Resistance ohm(eq. 7)***	***particle size (nm)***
1	1.250	30	13.0	362	448	110
2	1.250	30	13.0	410	448	110
3	0.500	20	2.0	4405986	*469**	4131
4	2.075	30	13.0	1420	1150	2230
5	1.250	30	13.0	333	448	66
6	0.500	20	24.0	36426	*469**	112
7	1.250	30	25.1	463	1028	270
8	2.000	20	24.0	122910	*2547**	193
9	0.500	40	24.0	2838	2548	932
10	1.250	19	13.0	342	448	313
11	2.000	20	2.0	20437	*2547**	675
12	2.000	40	2.0	372	468	554
13	1.250	30	13.0	481	448	235
14	0.500	40	2.0	2095	2548	2731
15	2.000	40	24.0	401	468	115
16	1.250	30	13.0	423	448	348
17	1.250	30	13.0	423	448	247
18	0.425	30	13.0	10685	*1152**	213
19	1.250	30	0.9	1862	1028	409

Table 6 - continued

20	1.250	41	13.0	595	448	180

*Fitted values in italic denotes an extremely unusual point relative to predictor levels used to fit the model

Table 7- The design of experiment based on RSM showing the factor levels and their responses. The three independent variables were denoted as x_1, x_2, and x_3, which represent SWNT:PSS, Sonication amplitude (%), and Sonication durations (h), respectively for the PSS matrix solution at 100% (no dilution)

Runs	***X_1 (SWNT:PSS)***	***X_2 (Sonication amp (%))***	***X_3 (Sonication durations (h))***	***Resistance (ohm)***	***Predicted Resistance ohm(eq. 8)***	***particle size (nm)***
1	1.250	30	13.0	459	643	206
2	1.250	30	13.0	749	643	107
3	0.500	20	2.0	6,453,796	*1232**	152
4	2.075	30	13.0	304	515	15
5	1.250	30	13.0	393	643	18
6	0.500	20	24.0	16,316,438	*1232**	133
7	1.250	30	25.1	163	643	155
8	2.000	20	24.0	701,788	*550*	53
9	0.500	40	24.0	277	286	110
10	1.250	19	13.0	2,174,028	*916**	169
11	2.000	20	2.0	332,381	*550*	211
12	2.000	40	2.0	220	503	914
13	1.250	30	13.0	1,211	643	915
14	0.500	40	2.0	431	286	292
15	2.000	40	24.0	921	503	2880
16	1.250	30	13.0	365	643	122
17	1.250	30	13.0	1,557	643	127
18	0.425	30	13.0	560	770	110
19	1.250	30	0.9	17,817	*643**	161
20	1.250	41	13.0	125	370	110

*Fitted values in italic denotes an extremely unusual point relative to predictor levels used to fit the model

Table 8- The design of experiment based on RSM showing the factor levels and their responses. The three independent variables were denoted as x1, x2, and x3, which represent SWNT:PSS, Sonication amplitude (%), and Sonication durations (h), respectively for the PSS matrix solution diluted to 70%

Runs	***X_1 (SWNT:PSS)***	***X_2 (Sonication amp (%))***	***X_3 (Sonication durations (h))***	***Resistance (ohm)***	***Predicted Resistance ohm(eq. 9)***	***particle size (nm)***
1	1.250	30	13.0	650	922	206
2	1.250	30	13.0	1,299	922	107
3	0.500	20	2.0	6,855,038	*1932**	152

Table 8 - continued

4	2.075	30	13.0	390	707	15
5	1.250	30	13.0	544	922	18
6	0.500	20	24.0	16,505,225	*1932**	133
7	1.250	30	25.1	241	922	155
8	2.000	20	24.0	1,141,095	*202*	53
9	0.500	40	24.0	366	301	110
10	1.250	19	13.0	4,977,047	*1081**	169
11	2.000	20	2.0	509,977	*202**	211
12	2.000	40	2.0	1,339	1252	914
13	1.250	30	13.0	1,698	922	915
14	0.500	40	2.0	555	301	292
15	2.000	40	24.0	1,484	1252	2880
16	1.250	30	13.0	502	922	122
17	1.250	30	13.0	2,094	922	127
18	0.425	30	13.0	819	1136	110
19	1.250	30	0.9	21,716	*922**	161
20	1.250	41	13.0	183	762	110

*Fitted values in italic denotes an extremely unusual point relative to predictor levels used to fit the model

Table 9- The design of experiment based on RSM showing the factor levels and their responses. The three independent variables were denoted as x_1, x_2, and x_3, which represent SWNT:PSS, Sonication amplitude (%), and Sonication durations (h), respectively for the PSS matrix solution diluted to 40% (40%)

Runs	***X_1 (SWNT:PSS)***	***X_2 (Sonication amp (%))***	***X_3 (Sonication durations (h))***	***Resistance (ohm)***	***Predicted Resistance ohm(eq. 10)***	***particle size (nm)***
1	1.250	30	13.0	1,464	2078	206
2	1.250	30	13.0	2,176	2078	107
3	0.500	20	2.0	14,250,756	*4465**	152
4	2.075	30	13.0	770	1532	15
5	1.250	30	13.0	1,202	2078	18
6	0.500	20	24.0	25,362,920	*4465*	133
7	1.250	30	25.1	575	2078	155
8	2.000	20	24.0	7,231,889	*1002**	53
9	0.500	40	24.0	801	685	110
10	1.250	19	13.0	12,746,253	*2799**	169
11	2.000	20	2.0	1,099,619	*1002**	211
12	2.000	40	2.0	2,529	2162	914
13	1.250	30	13.0	4,164	2078	915
14	0.500	40	2.0	1,100	685	292
15	2.000	40	24.0	2,326	2162	2880

Table 9 - continued

16	1.250	30	13.0	1,099	2078	122
17	1.250	30	13.0	5,297	2078	127
18	0.425	30	13.0	1,863	2625	110
19	1.250	30	0.9	52,246	*2078**	161
20	1.250	41	13.0	391	1358	110

*Fitted values in italic denotes an extremely unusual point relative to predictor levels used to fit the model

2.2.4 Particle size analysis

Dynamic light scattering system, Nicomp, was used to measure the particle size of the prepared formulations after the filtration. For this study, the angle of detection was selected to be 90° which is recommended by the manufacturer. The purpose of using a particle size analyzer was to monitor agglomeration or entanglement caused by long nanotubes. As discussed earlier, the effect of SWNT:CMC/PSS ratio, sonication amplitude, and sonication duration on the particle size was investigated. Volume-based PSD is most sensitive to the appearance of large particle size. Therefore, in this study, volume-based size distribution was reported and analyzed.

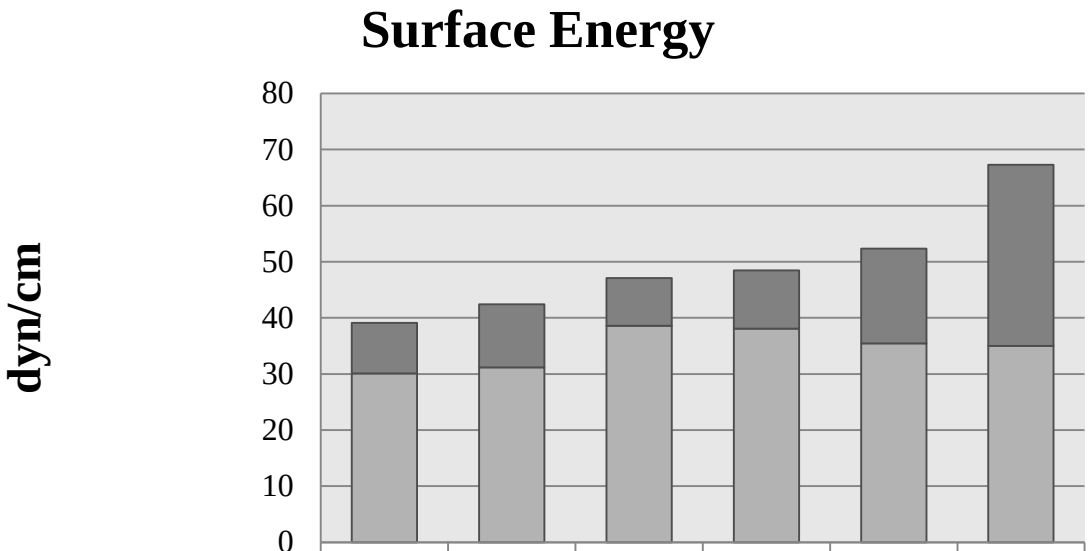
2.3 Results and Discussion

2.3.1 Substrate modification

In order to confirm that a matrix solution surface tension was appropriate for wetting the PET, the surface energy of the PET was measured using a First Ten Angstrom, FTA200, contact angle instrument. The surface tension of the solutions was around 72 dynes/cm because the solutions were mostly constituted of water. As a rule of thumb, the surface energy of a substrate needs to be higher than (or similar to) the surface energy of the solution, a larger difference will improve the wetting [152].

Figure 24 shows the effect of a 1 through 5 minute UV−O_3 treatment on the surface energy of the IPA-cleaned PET. With the 5 minute UV-O_3 treatment, the surface energy

increased by ~25 dynes/cm for the PET by making the surfaces significantly more polar and more similar to the surface tension of the matrix solutions to allow some wetting. This showed that UV-O_3 treatment improved surface wetting. Five minutes of UVO exposure was used to treat all PET templates prior to coating matrix.



	PET Before UVO Treatment	PET After 1' UVO Treatment	PET After 2' UVO Treatment	PET After 3' UVO Treatment	PET After 4' UVO Treatment	PET After 5' UVO Treatment
Polar	9	11.23	8.478	10.39	16.88	32.33
Dispersive	30.1	31.17	38.59	38.07	35.46	34.97
Total Surface Energy	39.1	42.4	47.07	48.46	52.34	67.3

Figure 24. Bar graph showing the effect of UV−O_3 treatment for up to 5 minutes on the surface energy of cleaned PET. The sum of the polar and dispersive components is equal to the total surface energy of the substrate.

2.3.2 Resistance response analysis of variance

The dimensions of the test templates are identical for all of the experiments and therefore the resistance of a coated and dried matrix will be indicative of the physical/electrical properties of a particular matrix formulation once its final thickness is taken into account. Table 10 and Table 11 show the summary of the resistance test results

sorted by dilution percentage (100% (no dilution), 70%, and 40%), SWNT:CMC/PSS ratio (2 to 0.5), Sonication amplitude (40% to 20%), and sonication duration (24 to 2 hr). They are also color coded according to resistance (green (low) to red (high)).

Table 10. Summary of resistance test results for CMC matrix, color coded by resistance (green (low), red (high))

Runs	*X_1 (SWNT:CMC)*	*X_2 (Sonication amp (%))*	*X_3 (Sonication durations (h))*	*diluted to*	*particle size (nm)*	*Resistance (ohm)*	*Predicted Resistance (ohm)*	*Calculated coatings thickness (µm)*	*Measured coatings thickness (µm)*	*Coating resistivity (ohm.cm)*
15	2	40	24	100%	115	128	157	3.84	3.86	0.0123
5	1.25	30	13	100%	66	130	164	4.04	-	0.0131
1	1.25	30	13	100%	110	134	164	4.23	-	0.0141
17	1.25	30	13	100%	247	147	164	4.19	-	0.0154
12	2	40	2	100%	554	148	157	3.56	-	0.0131
2	1.25	30	13	100%	110	149	164	4.13	-	0.0153
10	1.25	19	13	100%	313	149	164	3.95	-	0.0147
16	1.25	30	13	100%	348	165	164	4.13	-	0.0170
13	1.25	30	13	100%	235	166	164	4.26	-	0.0177
7	1.25	30	25.1	100%	270	199	465	4.26	-	0.0212
20	1.25	41	13	100%	180	225	164	4.15	-	0.0234
4	2.075	30	13	100%	2230	555	492	2.26	-	0.0313
19	1.25	30	0.9	100%	409	794	465	0.85	-	0.0169
14	0.5	40	2	100%	2731	1069	1212	4.60	-	0.1230
9	0.5	40	24	100%	932	1317	1212	4.81	-	0.1580
18	0.425	30	13	100%	213	6256	*493**	4.78	-	0.7470
11	2	20	2	100%	675	10914	*1211**	2.55	-	0.697
6	0.5	20	24	100%	112	24231	*157**	4.27	-	2.580
8	2	20	24	100%	193	58878	*1211**	2.53	-	3.730
3	0.5	20	2	100%	4131	3868395	*157**	3.70	3.81	357.00
5	1.25	30	13	70%	66	174	235	2.83	-	0.0123
1	1.25	30	13	70%	110	190	235	2.96	-	0.0140

Table 10 - continued

17	1.25	30	13	70%	247	195	235	2.93	-	0.0143
15	2	40	24	70%	115	200	238	2.69	2.81	0.0134
12	2	40	2	70%	554	202	238	2.49	-	0.0126
10	1.25	19	13	70%	313	210	235	2.76	-	0.0145
2	1.25	30	13	70%	110	214	235	2.89	-	0.0155
16	1.25	30	13	70%	348	223	235	2.89	-	0.0161
13	1.25	30	13	70%	235	244	235	2.98	-	0.0182
7	1.25	30	25.1	70%	270	254	608	2.98	-	0.0189
20	1.25	41	13	70%	180	331	235	2.91	-	0.0241
4	2.075	30	13	70%	2230	866	744	1.58	-	0.0342
19	1.25	30	0.9	70%	409	1085	608	0.6	-	0.0161
14	0.5	40	2	70%	2731	1498	1692	3.22	-	0.1210
9	0.5	40	24	70%	932	1812	1692	3.36	-	0.1520
18	0.425	30	13	70%	213	8141	*745**	3.34	-	0.6810
11	2	20	2	70%	675	15109	*1690**	1.79	-	0.6750
6	0.5	20	24	70%	112	28272	*238**	2.99	-	2.1100
8	2	20	24	70%	193	71517	*1690**	1.77	-	3.1700
3	0.5	20	2	70%	4131	2812535	*238**	2.59	2.42	285.00
5	1.25	30	13	40%	66	333	448	1.62	-	0.0135
10	1.25	19	13	40%	313	342	448	1.58	-	0.0135
1	1.25	30	13	40%	110	362	448	1.69	-	0.0153
12	2	40	2	40%	554	372	468	1.42	-	0.0132
15	2	40	24	40%	115	401	468	1.54	1.63	0.0154
2	1.25	30	13	40%	110	410	448	1.65	-	0.0169
16	1.25	30	13	40%	348	423	448	1.65	-	0.0175
17	1.25	30	13	40%	247	423	448	1.68	-	0.0177
7	1.25	30	25.1	40%	270	463	1028	1.7	-	0.0197

Table 10 - continued

13	1.25	30	13	40%	235	481	448	1.7	-	0.0205
20	1.25	41	13	40%	180	595	448	1.66	-	0.0247
4	2.075	30	13	40%	2230	1420	1150	0.9	-	0.032
19	1.25	30	0.9	40%	409	1862	1028	0.34	-	0.0158
14	0.5	40	2	40%	2731	2095	2548	1.84	-	0.0963
9	0.5	40	24	40%	932	2838	2548	1.92	-	0.1360
18	0.425	30	13	40%	213	10685*	*1152*	1.91	-	0.5110
11	2	20	2	40%	675	20437*	*2547*	1.02	-	0.5220
6	0.5	20	24	40%	112	36426*	*469*	1.71	-	1.550
8	2	20	24	40%	193	122910*	*2547*	1.01	-	3.110
3	0.5	20	2	40%	4131	4405986*	*469*	1.48	1.18	104.00

*Fitted values in italic denotes an extremely unusual point relative to predictor levels used to fit the model

Table 11- Summary of resistance test results for PSS matrix, color coded by resistance (green (low), red (high))

Runs	*X_1 (SWNT:PSS)*	*X_2 (Sonication amp (%))*	*X_3 (Sonication durations (h))*	*diluted to*	*particle size (nm)*	*Resistance (ohm)*	*Predicted Resistance (ohm)*	*Calculated coatings thickness (µm)*	*Measured coatings thickness (µm)*	*Coating resistivity (ohm.cm)*
20	1.25	41	13	100%	110	125	370	6.23	5.66	0.0194
7	1.25	30	25.1	100%	155	163	643	5.04	-	0.0206
12	2	40	2	100%	914	220	503	0.47	-	0.0026
9	0.5	40	24	100%	110	277	286	8.11	-	0.0561
4	2.075	30	13	100%	15	304	515	3.82	-	0.0291
16	1.25	30	13	100%	122	365	643	4.87	-	0.0444
5	1.25	30	13	100%	18	393	643	4.29	-	0.0422
14	0.5	40	2	100%	292	431	286	8.30	-	0.0894
1	1.25	30	13	100%	206	459	643	4.78	-	0.0549
18	0.425	30	13	100%	110	560	770	8.51	-	0.1190

Table 11 - continued

2	1.25	30	13	100%	107	749	643	4.23	-	0.0793
15	2	40	24	100%	2880	921	503	3.19	-	0.0735
13	1.25	30	13	100%	915	1211	643	4.61	-	0.1400
17	1.25	30	13	100%	127	1557	643	4.00	-	0.1560
19	1.25	30	0.9	100%	161	17817	*643**	0.66	-	0.2950
11	2	20	2	100%	211	332381	*550**	3.57	-	29.700
8	2	20	24	100%	53	701788	*550**	3.44	-	60.400
10	1.25	19	13	100%	169	2174028	*916**	3.71	-	202.00
3	0.5	20	2	100%	152	6453796	*1232**	6.27	-	1010.00
6	0.5	20	24	100%	133	16316438	*1232**	6.57	6.15	2680.00
20	1.25	41	13	70%	110	183	762	4.36	4.23	0.0199
7	1.25	30	25.1	70%	155	241	922	3.53	-	0.0212
9	0.5	40	24	70%	110	366	301	5.68	-	0.0519
4	2.075	30	13	70%	15	390	707	2.67	-	0.0261
16	1.25	30	13	70%	122	502	922	3.41	-	0.0428
5	1.25	30	13	70%	18	544	922	3.00	-	0.0409
14	0.5	40	2	70%	292	555	301	5.81	-	0.0807
1	1.25	30	13	70%	206	650	922	3.35	-	0.0544
18	0.425	30	13	70%	110	819	1136	5.96	-	0.1220
2	1.25	30	13	70%	107	1299	922	2.96	-	0.0962
12	2	40	2	70%	914	1339	1252	0.33	-	0.0109
15	2	40	24	70%	2880	1484	1252	2.23	-	0.0829
13	1.25	30	13	70%	915	1698	922	3.23	-	0.1370
17	1.25	30	13	70%	127	2094	922	2.80	-	0.1470
19	1.25	30	0.9	70%	161	21716	*922**	0.46	-	0.2520
11	2	20	2	70%	211	509977	*202**	2.50	-	31.900
8	2	20	24	70%	53	1141095	*202**	2.41	-	68.800

Table 11 - continued

10	1.25	19	13	70%	169	4977047	*1081**	2.60	-	323.00
3	0.5	20	2	70%	152	6855038	*1932**	4.39	-	753.00
6	0.5	20	24	70%	133	16505225	*1932**	4.60	4.29	1900.00
20	1.25	41	13	40%	110	391	1358	2.49	2.54	0.0244
7	1.25	30	25.1	40%	155	575	2078	2.02	-	0.0290
4	2.075	30	13	40%	15	770	1532	1.53	-	0.0294
9	0.5	40	24	40%	110	801	685	3.24	-	0.0650
16	1.25	30	13	40%	122	1099	2078	1.95	-	0.0535
14	0.5	40	2	40%	292	1100	685	3.32	-	0.0913
5	1.25	30	13	40%	18	1202	2078	1.72	-	0.0516
1	1.25	30	13	40%	206	1464	2078	1.91	-	0.0700
18	0.425	30	13	40%	110	1863	2625	3.41	-	0.1590
2	1.25	30	13	40%	107	2176	2078	1.69	-	0.0921
15	2	40	24	40%	2880	2326	2162	1.28	-	0.0742
12	2	40	2	40%	914	2529	2162	0.19	-	0.0118
13	1.25	30	13	40%	915	4164	2078	1.84	-	0.1920
17	1.25	30	13	40%	127	5297	2078	1.60	-	0.2120
19	1.25	30	0.9	40%	161	52246	*2078**	0.27	-	0.3470
11	2	20	2	40%	211	1099619	*1002**	1.43	-	39.300
8	2	20	24	40%	53	7231889	*1002**	1.38	-	249.00
10	1.25	19	13	40%	169	12746253	*2799**	1.48	-	473.00
3	0.5	20	2	40%	152	14250756	*4465**	2.51	-	894.00
6	0.5	20	24	40%	133	25362920	*4465**	2.63	2.46	1670.00

*Fitted values in italic denotes an extremely unusual point relative to predictor levels used to fit the model

For CMC as the dispersant, the minimum resistance (average of 2 duplicates) of 128 Ω was observed in Run 14 (see Table 4). In this run, CMC was used at 100% (no dilution). The SWNT:CMC ratio (2), sonication amplitude (40%), and sonication duration (24 hr), were all maximal for their parameter for the study. The maximum resistance of 3.9MΩ was observed when matrix was used at no dilution was noted in Run 3 (see Table 4) This corresponded to the minimum values of each parameters at: SWNT:CMC ratio of 0.5, sonication amplitude of 20%, and sonication duration of 2 hr. Thus for CMC, resistance decreases with more sonication processing (higher amplitude, longer processing) and higher SWNT concentration and ratios of SWNT (conductive):CMC (low/non-conductive), as one might logically hypothesize. The relationship is a bit more complex in that the response is the culmination of the interplay between all three parameters.

For PSS as the dispersant, the minimum resistance of 125 Ω was noted in Run 20 (see Table 7).This corresponds to the maximum for sonication amplitude (41%), but only intermediate values of the other parameters, SWNT:PSS ratio of 1.25, and sonication duration of 13 hr, unlike what was observed for CMC. The maximum resistance of 25 KΩ was used observed at 60% dilution was noted in Run 6 (see Table 9). This corresponds to the minimum values SWNT:PSS ratio of 0.5 and sonication amplitude of 20%, but maximum value of sonication duration of 24 hours, again unlike CMC. For PSS, the maximum and minimum resistance process conditions do not occur as one might deduce from logic.

The analysis of variance, presented in Table 12 through Table 17, shows that the resistance of the matrix solutions containing CMC as the dispersant are significantly dependent on the SWNT:CMC ratio, sonication amplitude, and sonication duration as well

as the interaction terms. Considering the t-statistics for each model term and the provisions of the RSM, the following models can be used to fit the resistance responses where x_1, x_2, and x_3, which represent *coded values of* SWNT:PSS, Sonication amplitude (%), and Sonication durations (h), respectively :

CMC at 100% (no dilution):

$$\text{Resistance (ohm)} = 164.1 + 271.3\ X_1*X_1 + 249.0\ X_3*X_3 - 527.7\ X_1*X_2 \quad (5)$$

CMC diluted to 70%

$$\text{Resistance (ohm)} = 234.7 + 421\ X_1*X_1 + 309\ X_3*X_3 - 727\ X_1*X_2 \quad (6)$$

CMC at 40%

$$\text{Resistance (ohm)} = 448 + 581\ X_1*X_1 + 480\ X_3*X_3 - 1040\ X_1*X_2 \quad (7)$$

PSS at 100% (no dilution)

$$\text{Resistance (ohm)} = 2704 - 1053\ X_1 - 62.3\ X_2 + 30.0\ X_1*X_2 \quad (8)$$

PSS diluted to 70%

$$\text{Resistance (ohm)} = 5033 - 2941\ X_1 - 126.2\ X_2 + 89.4\ X_1*X_2 \quad (9)$$

PSS diluted to 40%

$$\text{Resistance (ohm)} = 11047 - 5602\ X_1 - 271\ X_2 + 165\ X_1*X_2 \quad (10)$$

Table 12- Analysis of variance for the resistance and particle size of the samples obtained under various preparation conditions for the CMC matrix solution at 100% (no dilution)

	Resistance (ohm)			Particle size (nm)	
Source	DF†	F-Value†	P-Value†	F-Value	P-Value
Model	9	3.6	0.029	2.24	0.112
Linear	3	4.28	0.035	2.9	0.088
SWNT:CMC	1	4.21	0.067	2.29	0.161
Sonication amp (%)	1	4.5	0.06	0.11	0.744
Sonication durations	1	4.13	0.069	6.3	0.031
Square	3	1.01	0.428	2.14	0.159
SWNT:CMC*SWNT:CMC	1	0.37	0.555	3.78	0.08

Table 12 - continued

Sonication amp (%)*Sonication amp (%)	1	0.36	0.56	0.01	0.935
Sonication durations*Sonication durations	1	0.36	0.56	0.07	0.799
2-Way Interaction	3	5.5	0.017	1.68	0.233
SWNT:CMC*Sonication amp (%)	1	5.45	0.042	0.02	0.878
SWNT:CMC*Sonication durations	1	5.66	0.039	4.14	0.069
Sonication amp (%)*Sonication durations	1	5.38	0.043	0.89	0.369

†DF: degree of freedom; F-value: the ratio of the variance between groups to the variance within groups; P-value: probability value

Table 13- Analysis of variance for the resistance and particle size of the samples obtained under various preparation conditions for the CMC matrix solution diluted to 70%

		Resistance (ohm)		Particle size (nm)	
Source	DF	F-Value	P-Value	F-Value	P-Value
Model	9	3.59	0.029	2.24	0.112
Linear	3	4.28	0.035	2.9	0.088
SWNT:CMC	1	4.2	0.068	2.29	0.161
Sonication amp (%)	1	4.51	0.06	0.11	0.744
Sonication durations	1	4.13	0.07	6.3	0.031
Square	3	1.01	0.426	2.14	0.159
SWNT:CMC*SWNT:CMC	1	0.38	0.553	3.78	0.08
Sonication amp (%)*Sonication amp (%)	1	0.36	0.56	0.01	0.935
Sonication durations*Sonication durations	1	0.36	0.559	0.07	0.799
2-Way Interaction	3	5.49	0.017	1.68	0.233
SWNT:CMC*Sonication amp (%)	1	5.43	0.042	0.02	0.878
SWNT:CMC*Sonication durations	1	5.66	0.039	4.14	0.069
Sonication amp (%)*Sonication durations	1	5.38	0.043	0.89	0.369

Table 14- Analysis of variance for the resistance and particle size of the samples obtained under various preparation conditions for the CMC matrix solution diluted to 40%

		Resistance (ohm)		Particle size (nm)	
Source	DF	F-Value	P-Value	F-Value	P-Value
Model	9	3.5	0.032	2.24	0.112
Linear	3	4.17	0.037	2.9	0.088
SWNT:CMC	1	3.94	0.075	2.29	0.161
Sonication amp (%)	1	4.76	0.054	0.11	0.744
Sonication durations	1	3.81	0.079	6.3	0.031
Square	3	1.07	0.404	2.14	0.159
SWNT:CMC*SWNT:CMC	1	0.41	0.538	3.78	0.08
Sonication amp (%)*Sonication amp (%)	1	0.38	0.552	0.01	0.935

Table 14 - continued

Sonication durations*Sonication durations	1	0.38	0.55	0.07	0.799
2-Way Interaction	3	5.26	0.02	1.68	0.233
SWNT:CMC*Sonication amp (%)	1	5.07	0.048	0.02	0.878
SWNT:CMC*Sonication durations	1	5.75	0.037	4.14	0.069
Sonication amp (%)*Sonication durations	1	4.97	0.05	0.89	0.369

Table 15- Analysis of variance for the resistance and particle size of the samples obtained under various preparation conditions for the PSS matrix solution at 100% (no dilution)

		Resistance (ohm)		**Particle size (nm)**	
Source	DF	F-Value	P-Value	F-Value	P-Value
Model	9	7.01	0.003	2.55	0.081
Linear	3	10.57	0.002	3.47	0.059
SWNT:PSS	1	11.86	0.006	4.26	0.066
Sonication amp (%)	1	17.22	0.002	5.12	0.047
Sonication durations	1	2.62	0.137	1.02	0.336
Square	3	3.19	0.071	0.79	0.526
SWNT:PSS*SWNT:PSS	1	0.56	0.471	0.12	0.741
Sonication amp (%)*Sonication amp (%)	1	2.73	0.13	0.35	0.565
Sonication durations*Sonication durations	1	0.57	0.467	0.43	0.526
2-Way Interaction	3	7.27	0.007	3.39	0.062
SWNT:PSS*Sonication amp (%)	1	15.45	0.003	6.06	0.034
SWNT:PSS*Sonication durations	1	2.95	0.117	2.1	0.178
Sonication amp (%)*Sonication durations	1	3.42	0.094	2	0.187

Table 16- Analysis of variance for the resistance and particle size of the samples obtained under various preparation conditions for the PSS matrix solution diluted to 70%

		Resistance (ohm)		**Particle size (nm)**	
Source	DF	F-Value	P-Value	F-Value	P-Value
Model	9	10.37	0.001	2.55	0.081
Linear	3	16.56	0.001	3.47	0.059
SWNT:PSS	1	15.54	0.003	4.26	0.066
Sonication amp (%)	1	30.65	0.001	5.12	0.047
Sonication durations	1	3.47	0.092	1.02	0.336
Square	3	5.13	0.021	0.79	0.526
SWNT:PSS*SWNT:PSS	1	0.19	0.669	0.12	0.741
Sonication amp (%)*Sonication amp (%)	1	7.89	0.019	0.35	0.565
Sonication durations*Sonication durations	1	0.2	0.662	0.43	0.526

Table 16 - continued

2-Way Interaction	3	9.43	0.003	3.39	0.062
SWNT:PSS*Sonication amp (%)	1	20.25	0.001	6.06	0.034
SWNT:PSS*Sonication durations	1	3.49	0.091	2.1	0.178
Sonication amp (%)*Sonication durations	1	4.54	0.059	2	0.187

Table 17- Analysis of variance for the resistance and particle size of the samples obtained under various preparation conditions for the PSS matrix solution diluted to 40%

		Resistance (ohm)		**Particle size (nm)**	
Source	DF	F-Value	P-Value	F-Value	P-Value
Model	9	22.84	0.001	2.55	0.081
Linear	3	40.16	0.001	3.47	0.059
SWNT:PSS	1	23.06	0.001	4.26	0.066
Sonication amp (%)	1	90.47	0.001	5.12	0.047
Sonication durations	1	6.96	0.025	1.02	0.336
Square	3	15.04	0.001	0.79	0.526
SWNT:PSS*SWNT:PSS	1	0.06	0.81	0.12	0.741
Sonication amp (%)*Sonication amp (%)	1	28.89	0.001	0.35	0.565
Sonication durations*Sonication durations	1	0.07	0.795	0.43	0.526
2-Way Interaction	3	13.31	0.001	3.39	0.062
SWNT:PSS*Sonication amp (%)	1	30.04	0.001	6.06	0.034
SWNT:PSS*Sonication durations	1	0.76	0.403	2.1	0.178
Sonication amp (%)*Sonication durations	1	9.13	0.013	2	0.187

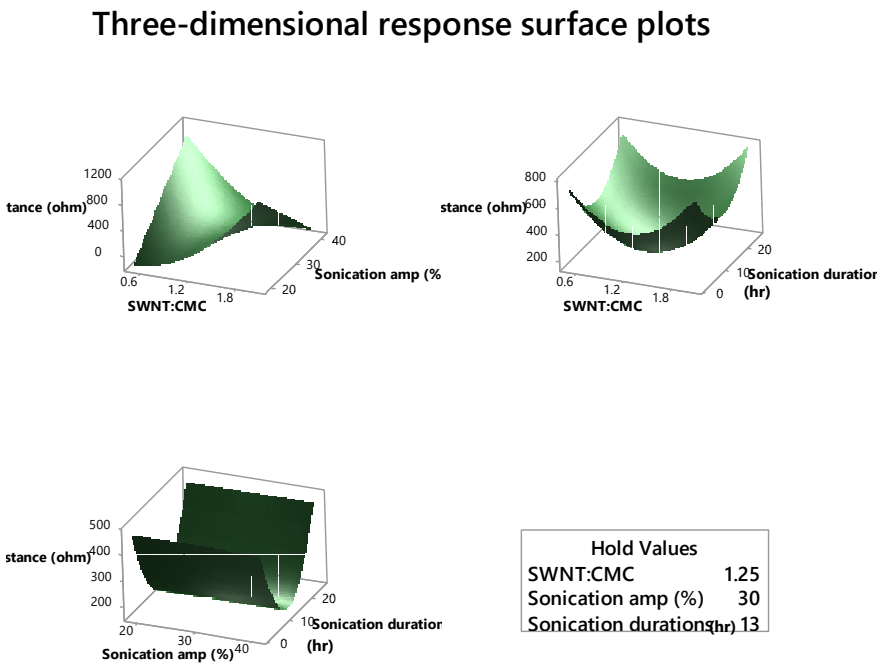
The predicted resistance from the models obtained from the prior analysis of variance, are shown in column 8 in Table 10 and Table 11. The predicted resistance values are in close agreement with the experimental results for resistance values less than 2000Ω (30 and 40 sonication amplitude data points). The surface and contour plots of the most significant process parameters (SWNT:CMC ratio, sonication amplitude, and sonication duration) are presented in Figure 25 to Figure 30. These figures show the effect of each factor on the resistance of the matrix solution. In general, intermediate to high values of

SWNT:CMC/PSS ratio and intermediate values of sonication amplitude and sonication duration provides the lowest resistance for the corresponding matrix solutions.

The effect of formulation dilution on dried matrix film resistance at low resistances appears to follow dilution closely, inversely proportional to the mass of conductor deposited per unit length. Resistance is inversely proportional to the conductor cross-sectional area. For instance the inverse of the ratio of the RSM predicted resistance values from run 5 in Table 18 for 70% dilution and 100% dilution (164Ω/235Ω) yields a value of 0.698. Since the mass concentration is diluted 70%, the expected value would be 0.700, suggesting that the dried matrix at low resistances is acting like a normal conductor with regard to mass dilution. The inverse of the ratio of the RSM predicted resistance values from run 5 in Table 18 for 40% dilution and 100% dilution (165Ω/333Ω) yields a value of 0.495, slight higher than the expect value 0.400.

The RSM model was not able to adequately predict dried matrix resistances at higher resistances above 2000 Ω and show these as outlier data points (even though we included them in the predicted results of the various tabulated tables). The difficulty in modeling this data is two-fold, the first and most significant is that this corresponds to all formulations performed at 20% sonication amplitude (the low level of the model for sonication). For instance, in Table 10, the four formulations (11, 6, 8, and 3) at 100% strength (dilution) in the section highlighted in red are the only 20% amplitude sonications run for this group and show dramatic effects (very large resistant changes) and in several cases opposite trends than what was observed in the low resistance data. Data sets 11 and 8 show a decrease in resistance with increasing sonication duration and data sets 6 and 3 show an increase in resistance with increasing sonication duration. These are opposing

trends just in this limited set. As a result it is difficult to model this data in the absence of a much larger experimental design (the second issue). Such a problem did not occur for modeling of resistances in the second phase of this research that is discussed in Chapter 3 where 20% sonication amplitudes were not used and where the model predicts resistance much better over a very large range of resistances. For this first research phase (Chapter 2), the models will focus on the lower resistance range due to the phenomena encountered with the lowest sonication amplitude that apparently is unpredictably affecting how the SWNT is being wrapped/not wrapped and dispersed/not dispersed by the CMC/PSS.



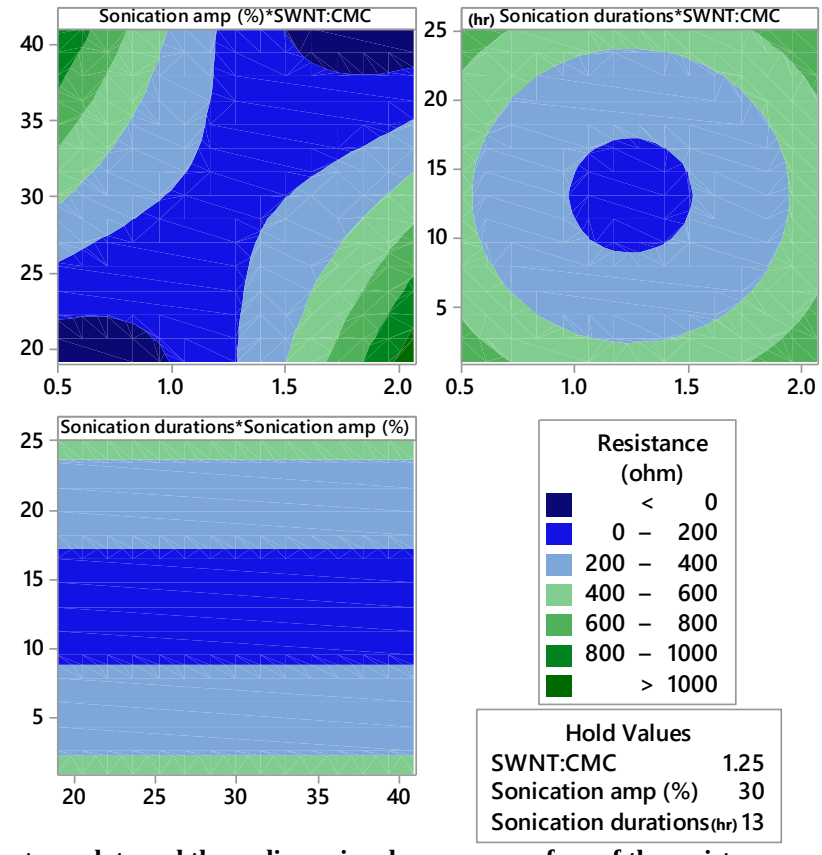


Figure 25. Contour plots and three-dimensional response surface of the resistance response for CMC at 100% (no dilution) corresponding to equation 5.

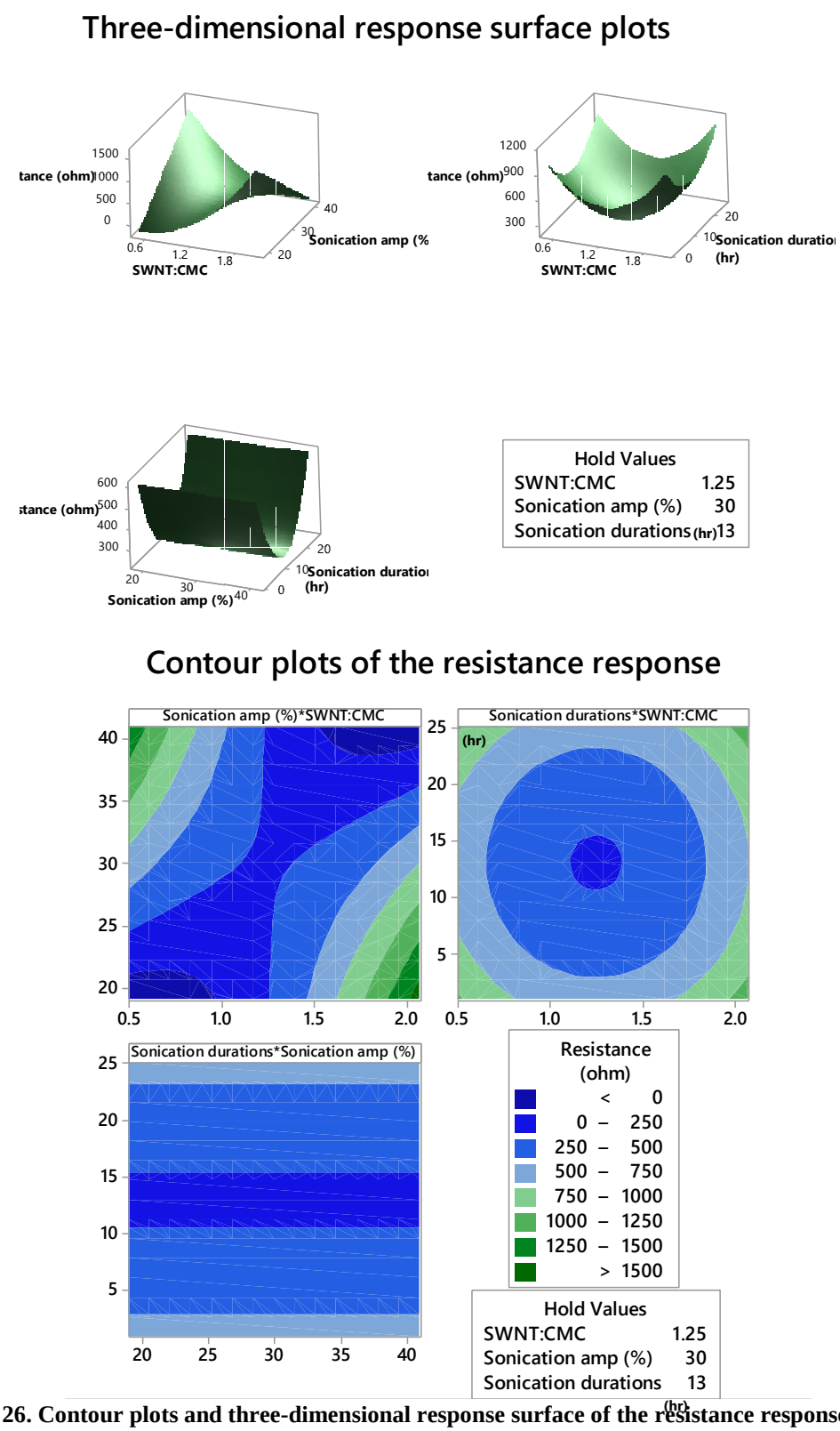


Figure 26. Contour plots and three-dimensional response surface of the resistance response for CMC diluted to 70%, corresponding to equation 6.

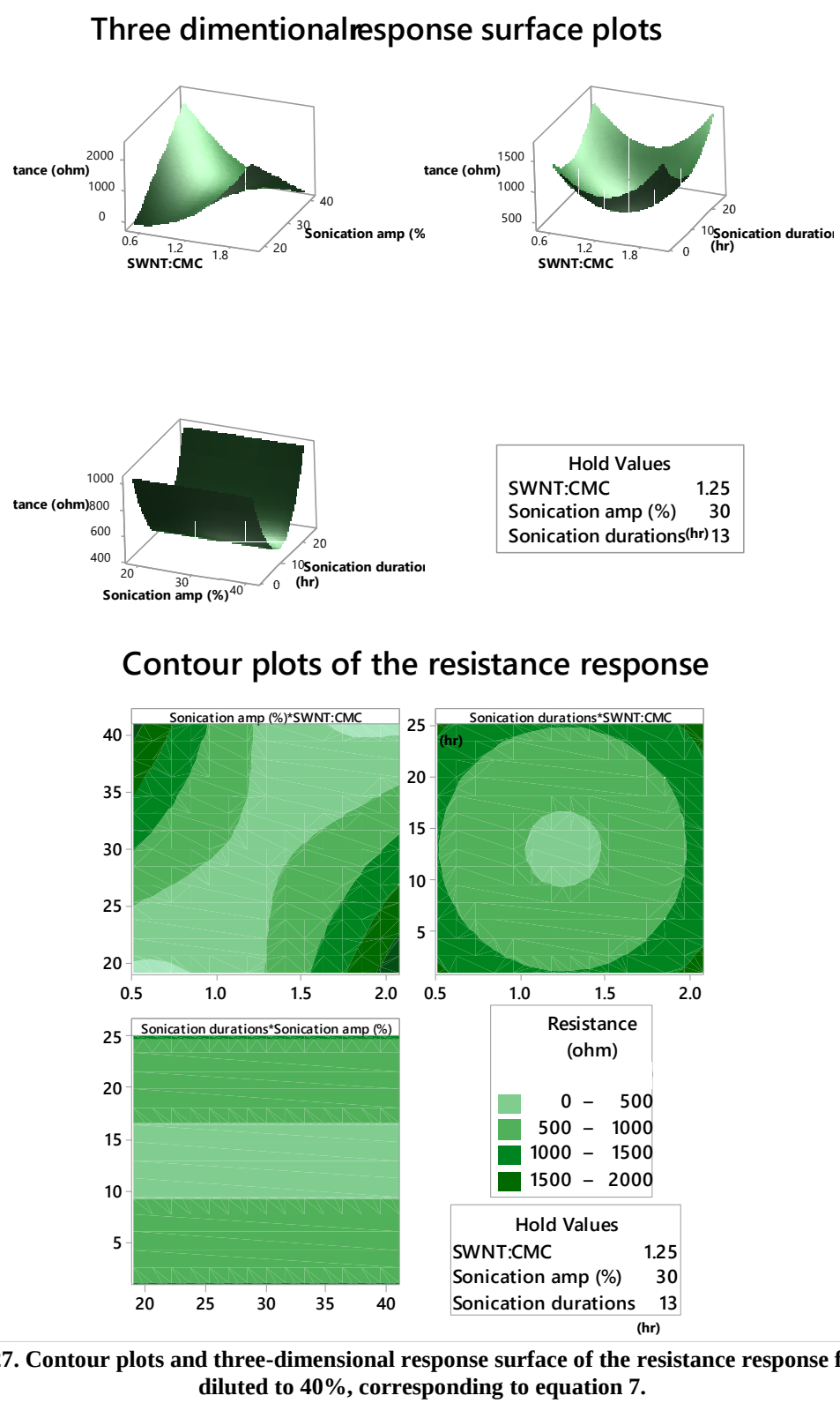


Figure 27. Contour plots and three-dimensional response surface of the resistance response for CMC diluted to 40%, corresponding to equation 7.

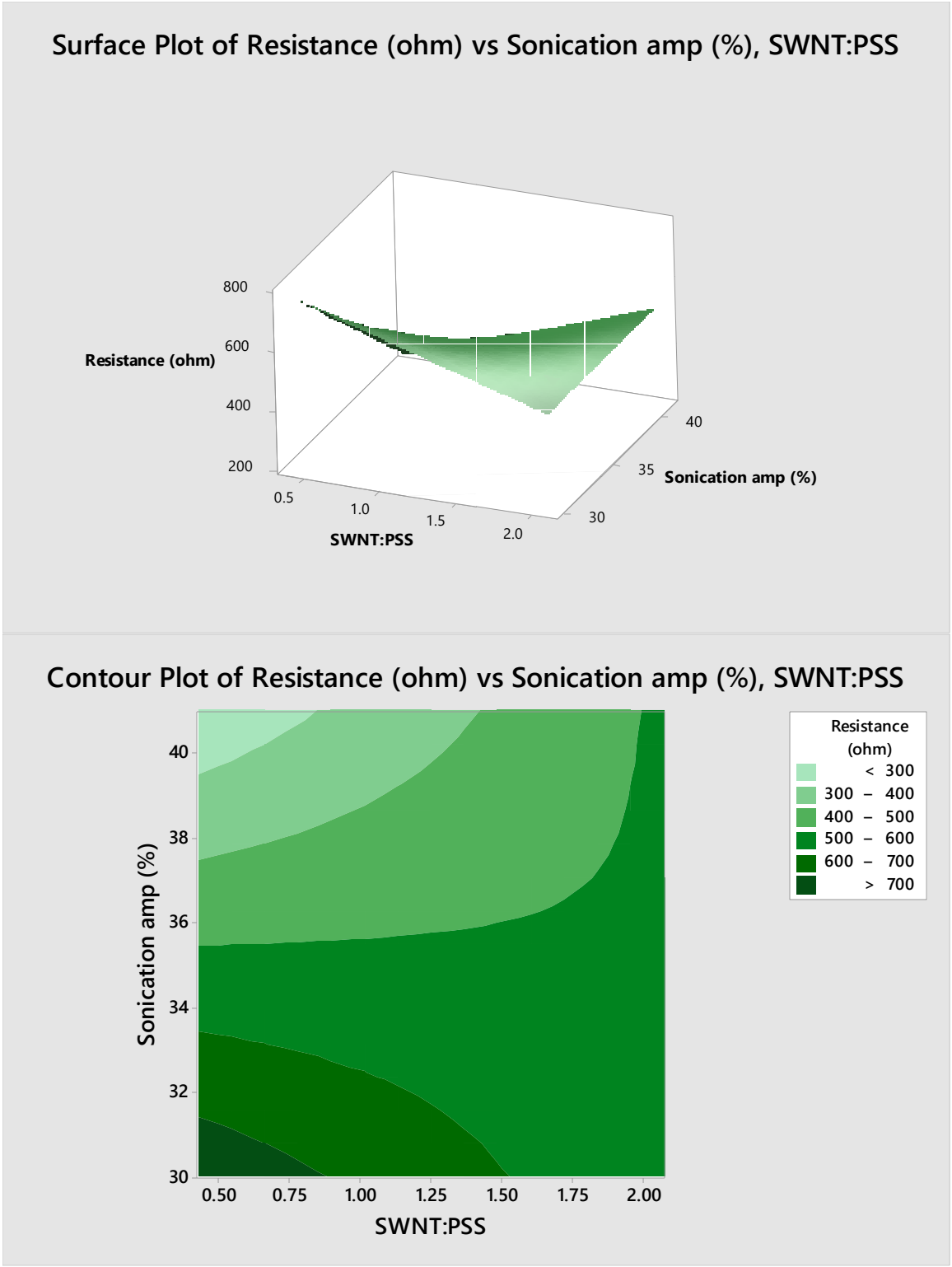


Figure 28. Contour plots and three-dimensional response surface of the resistance response for PSS at 100% (no dilution), corresponding to equation 8.

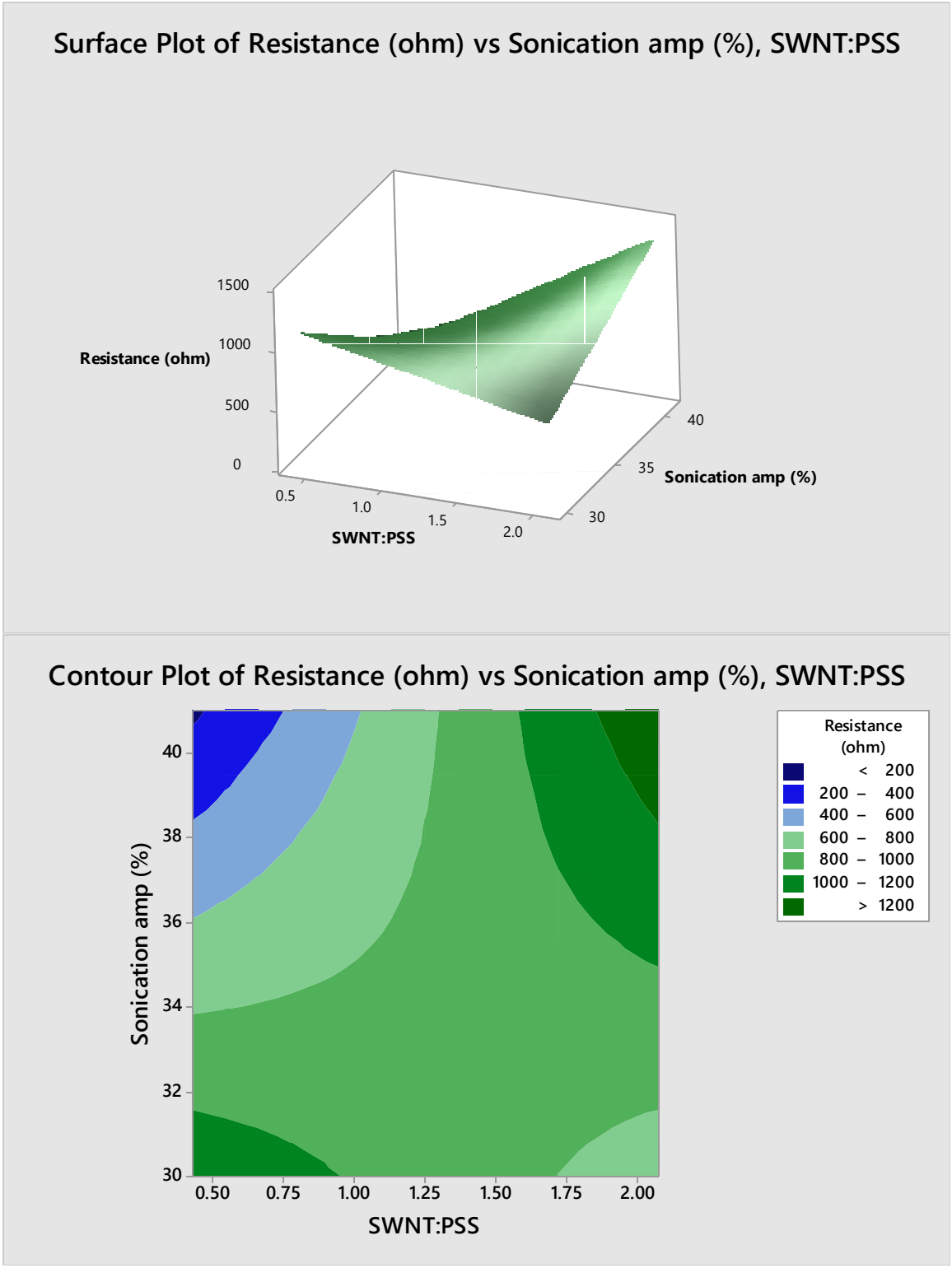


Figure 29. Contour plots and three-dimensional response surface of the resistance response for PSS diluted to 70%, corresponding to equation 9

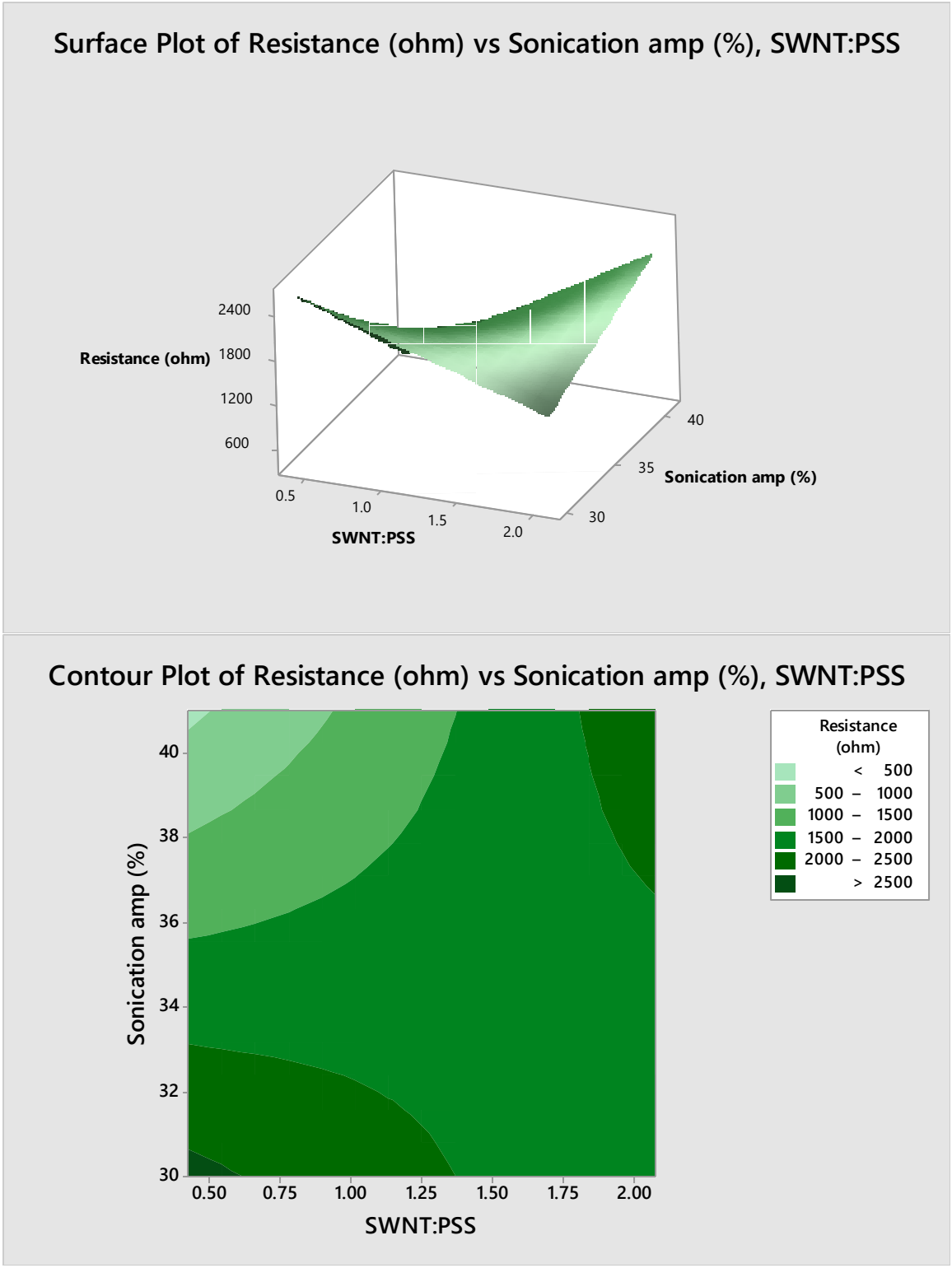


Figure 30. Contour plots and three-dimensional response surface of the resistance response for PSS diluted to 40%, corresponding to equation 10

2.3.3 Particle size analysis

Table 18 and Table 19 show the summary of the particle size analysis test results sorted from small to large for each of the matrix formulations (dilution percentages (100% (no dilution), 70%, and 40%), SWNT:CMC/PSS ratio (2 to 0.5), Sonication amplitude (40% to 20%), sonication duration (24 to 2 hr)), and color coded by particle size (green (low) to red (high)).

Table 18- Summary of particle size analysis for CMC matrix, color coded by particle size (green (low) to red (high)).

Runs	*X_1 (SWNT:CMC)*	*X_2 (Sonication amp (%))*	*X_3 (Sonication durations (h))*	*diluted to*	*particle size (nm)*	*Resistance (ohm)*	*Predicted Resistance (ohm)*	*Calculated coatings thickness (µm)*	*Measured coatings thickness (µm)*	*Coating resistivity (ohm.cm)*
5	1.25	30	13	100%	66	130	164	4.04	-	0.0131
1	1.25	30	13	100%	110	134	164	4.23	-	0.0141
2	1.25	30	13	100%	110	149	164	4.13	-	0.0153
6	0.5	20	24	100%	112	24231	*157**	4.27	-	2.580
15	2	40	24	100%	115	128	157	3.84	3.86	0.0123
20	1.25	41	13	100%	180	225	164	4.15	-	0.0234
8	2	20	24	100%	193	58878	*1211**	2.53	-	3.730
18	0.425	30	13	100%	213	6256	*493**	4.78	-	0.7470
13	1.25	30	13	100%	235	166	164	4.26	-	0.0177
17	1.25	30	13	100%	247	147	164	4.19	-	0.0154
7	1.25	30	25.1	100%	270	199	465	4.26	-	0.0212
10	1.25	19	13	100%	313	149	164	3.95	-	0.0147
16	1.25	30	13	100%	348	165	164	4.13	-	0.0170
19	1.25	30	0.9	100%	409	794	465	0.85	-	0.0169
12	2	40	2	100%	554	148	157	3.56	-	0.0131
11	2	20	2	100%	675	10914	*1211**	2.55	-	0.697
9	0.5	40	24	100%	932	1317	1212	4.81	-	0.1580
4	2.075	30	13	100%	2230	555	492	2.26	-	0.0313
14	0.5	40	2	100%	2731	1069	1212	4.60	-	0.1230
3	0.5	20	2	100%	4131	3868395	*157**	3.70	3.81	357.00
5	1.25	30	13	70%	66	174	235	2.83	-	0.0123
1	1.25	30	13	70%	110	190	235	2.96	-	0.014

Table 18 - continued

2	1.25	30	13	70%	110	214	235	2.89	-	0.0155
6	0.5	20	24	70%	112	28272	*238**	2.99	-	2.110
15	2	40	24	70%	115	200	238	2.69	2.81	0.0134
20	1.25	41	13	70%	180	331	235	2.91	-	0.0241
8	2	20	24	70%	193	71517	*1690**	1.77	-	3.170
18	0.425	30	13	70%	213	8141	*745**	3.34	-	0.6810
13	1.25	30	13	70%	235	244	235	2.98	-	0.0182
17	1.25	30	13	70%	247	195	235	2.93	-	0.0143
7	1.25	30	25.1	70%	270	254	608	2.98	-	0.0189
10	1.25	19	13	70%	313	210	235	2.76	-	0.0145
16	1.25	30	13	70%	348	223	235	2.89	-	0.0161
19	1.25	30	0.9	70%	409	1085	608	0.6	-	0.0161
12	2	40	2	70%	554	202	238	2.49	-	0.0126
11	2	20	2	70%	675	15109	*1690**	1.79	-	0.675
9	0.5	40	24	70%	932	1812	1692	3.36	-	0.1520
4	2.075	30	13	70%	2230	866	744	1.58	-	0.0342
14	0.5	40	2	70%	2731	1498	1692	3.22	-	0.1210
3	0.5	20	2	70%	4131	2812535	*238**	2.59	2.42	285.00
5	1.25	30	13	40%	66	333	448	1.62	-	0.0135
1	1.25	30	13	40%	110	362	448	1.69	-	0.0153
2	1.25	30	13	40%	110	410	448	1.65	-	0.0169
6	0.5	20	24	40%	112	36426	*469**	1.71	-	1.550
15	2	40	24	40%	115	401	468	1.54	1.63	0.0154
20	1.25	41	13	40%	180	595	448	1.66	-	0.0247
8	2	20	24	40%	193	122910	*2547**	1.01	-	3.110
18	0.425	30	13	40%	213	10685	*1152**	1.91	-	0.5110
13	1.25	30	13	40%	235	481	448	1.7	-	0.0205

Table 18 - continued

17	1.25	30	13	40%	247	423	448	1.68	-	0.0177
7	1.25	30	25.1	40%	270	463	1028	1.7	-	0.0197
10	1.25	19	13	40%	313	342	448	1.58	-	0.0135
16	1.25	30	13	40%	348	423	448	1.65	-	0.0175
19	1.25	30	0.9	40%	409	1862	1028	0.34	-	0.0158
12	2	40	2	40%	554	372	468	1.42	-	0.0132
11	2	20	2	40%	675	20437	*2547**	1.02	-	0.522
9	0.5	40	24	40%	932	2838	2548	1.92	-	0.1360
4	2.075	30	13	40%	2230	1420	1150	0.9	-	0.032
14	0.5	40	2	40%	2731	2095	2548	1.84	-	0.0963
3	0.5	20	2	40%	4131	4405986	*469*	1.48	1.18	104.00

*Fitted values in italic denotes an extremely unusual point relative to predictor levels used to fit the model

Dynamic light scattering system, Nicomp, was used to measure the particle size of the prepared formulations after the filtration. Figure 36 shows the particle size distribution of the matrix solution obtained for the Run 3 formulation using CMC dispersant. The largest particle size for the set of experiments in which CMC was used was observed in Run 3 (see Table 18) in which the maximum resistance was obtained. About 81% of the particles have an average particle size of ~5000 nm which is indicative of SWNT particle agglomeration.

Run 5 and 15 which resulted in matrix solutions with the minimum resistance (130 Ω and 128 Ω, respectively) possessed the minimum particle size (Figure 31 and Figure 32). The particle size distribution of the matrix solution obtained using Run 15 shows a monodisperse particle size distribution of about 115 nm (Figure 32). The matrix solution obtained using Run 5 has a bimodal particle size distribution with a small fraction of the particles (~15 %) having average particle size of ~210 nm and the larger fraction of the particles having average particle size of ~40 nm. These particles sizes are much greater than 20 times smaller than in Run 3 that demonstrated the highest resistance. In general, it can be seen from Table 18 that smaller particle sizes result in lower resistance. However, there are three runs with small particle size and very high resistance, runs 6, 8 and 18 (Table 18). These runs have the lowest sonication amplitude or the lowest SWNT:CMC ratio of the group thus suggesting potentially other factors other than particle size may be influencing resistivity. Regardless, the data in Table 18 suggests that agglomeration has an adverse effect on the conductivity of the nanotubes.

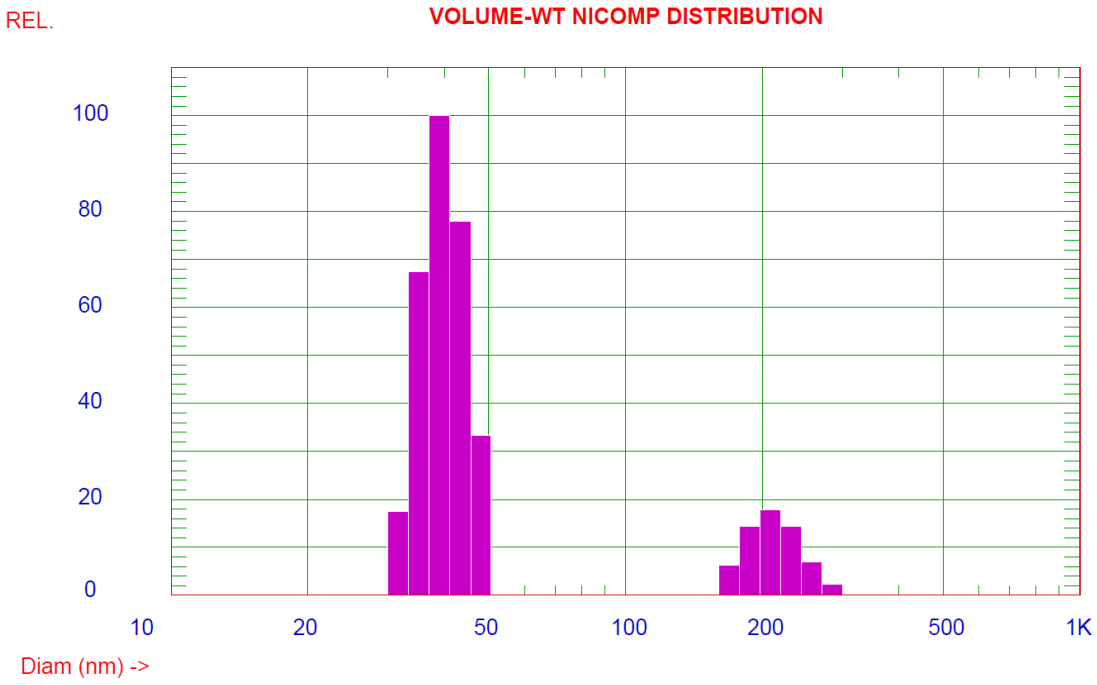
The topography of the deposited matrix solutions in the channels was investigated using an optical profiler.

The surface profile of Run 15 of the experiments in which CMC was used as the dispersant at 100% (no dilution), 70% dilution, and 40% dilution is presented in Figure 33 through Figure 35. In this run the minimum resistance for all formulations of 128 Ω (see Table 4) was achieved with a monodisperse particle size distribution and small average particle size of 115 nm (see Figure 32). As can be observed in Figure 33, a uniform coating with an average roughness of 67 nm was obtained for the matrix coating at 100% (no dilution). It can also be observed that the smoothness of the coating increased with dilution. The same formulation that was diluted down to 70% showed a roughness of 50 nm (Figure 34), and the coating that was diluted down to 40% showed a roughness of 34 nm (Figure 35). Note that as the thickness of the layer is reduced (with dilution) that some larger particles become more exposed and protrude from the smoother surrounding layer.

On the other hand, Run 3 (see Table 4), which was characterized by having the largest particle size (4131 nm) (Figure 36) and the maximum resistance 3.9 MΩ (see Table 6) among the set of experiments in which CMC was used, exhibits a rough surface. Figure 37 shows the surface morphology of the film obtained for Run 3 at 100% (no dilution) has an average roughness of 274 nm. The same formulation that was diluted down to 70% showed a slightly higher average roughness of 307 nm (one would expected it to be slightly lower) (Figure 38), and the coating that was diluted down to 40% showed an average roughness of 196 nm (Figure 39). This roughness is about 5 times larger than what run 15 (low resistance) showed.

Thus for matrix formulations with CMC, the surface topography of the dried matrix films shows some correlation with the resistance response of the matrix. Uniform and smooth surfaces can be translated to low SWNT agglomeration and low resistance of the

dried matrix solutions. Therefore it is desirable to obtain a uniform and smooth coating to lower resistivity of the matrix film.


REL.
VOLUME-WT NICOMP DISTRIBUTION
100
80
60
40
20
0
10
20
50
100
200
500
1K
Diam (nm) ->
REL.
VOLUME-WT NICOMP DISTRIBUTION
100
80
60
40
20
0
100
200
500
1K
2K
5K
10K
Diam (nm) ->
Figure 31. Particle size distribution of the matrix solution obtained through Run 5 (SWNT:CMC=1.25, sonication amplitude=30%, sonication duration=13 hr) using CMC dispersant, showing a low resistance. About 85% of the particles have an average particle size of ~40 nm.
Figure 32. Particle size distribution of the matrix solution obtained through Run 15 (SWNT:CMC=2, sonication amplitude=40%, sonication duration=24 hr) using CMC dispersant, showing a low resistance. A monodisperse average particle size of ~115 nm was obtained for this matrix solution.

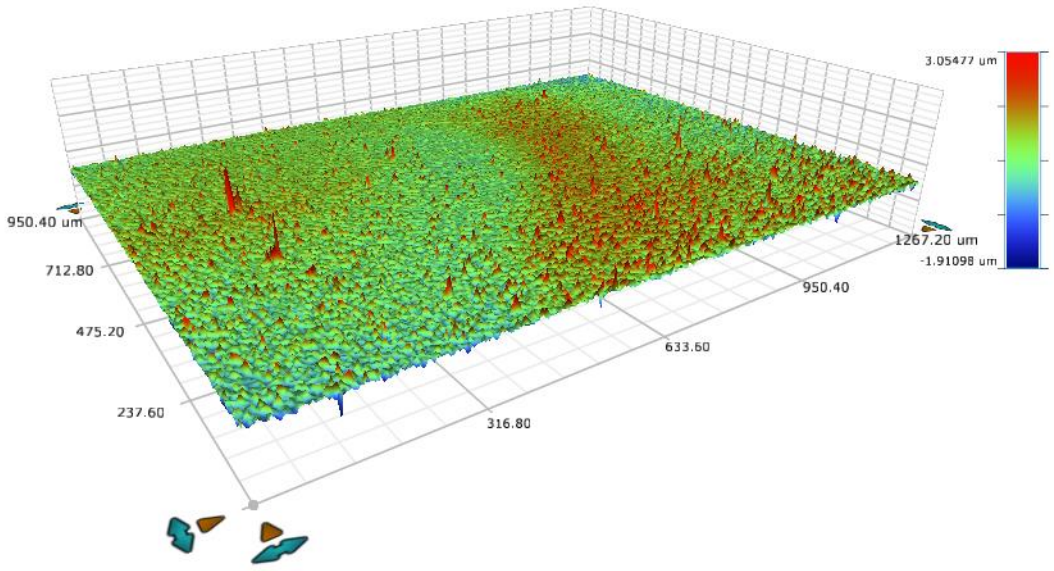


Figure 33. Profilometry of Run 15 (SWNT:CMC=2, sonication amplitude=40%, sonication duration=24 hr), showing a uniform CMC-dispersed coating at 100% (no dilution) with an average roughness of 0.067 µm.

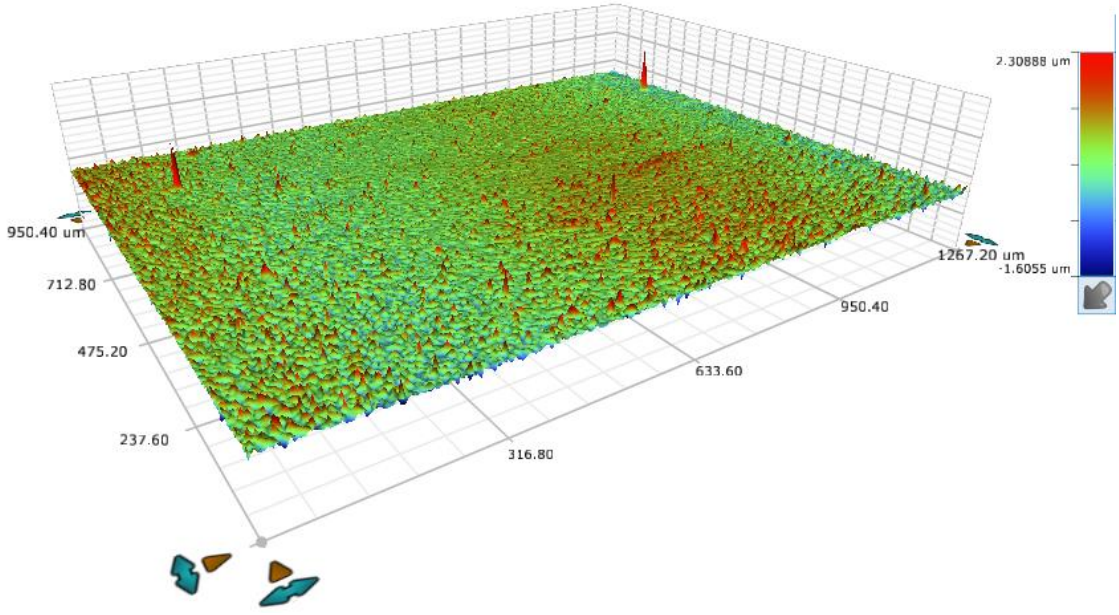


Figure 34. Profilometry of Run 15 (SWNT:CMC=2, sonication amplitude=40%, sonication duration=24 hr), showing a uniform CMC-dispersed coating diluted to 70% with an average roughness of 0.05 µm.

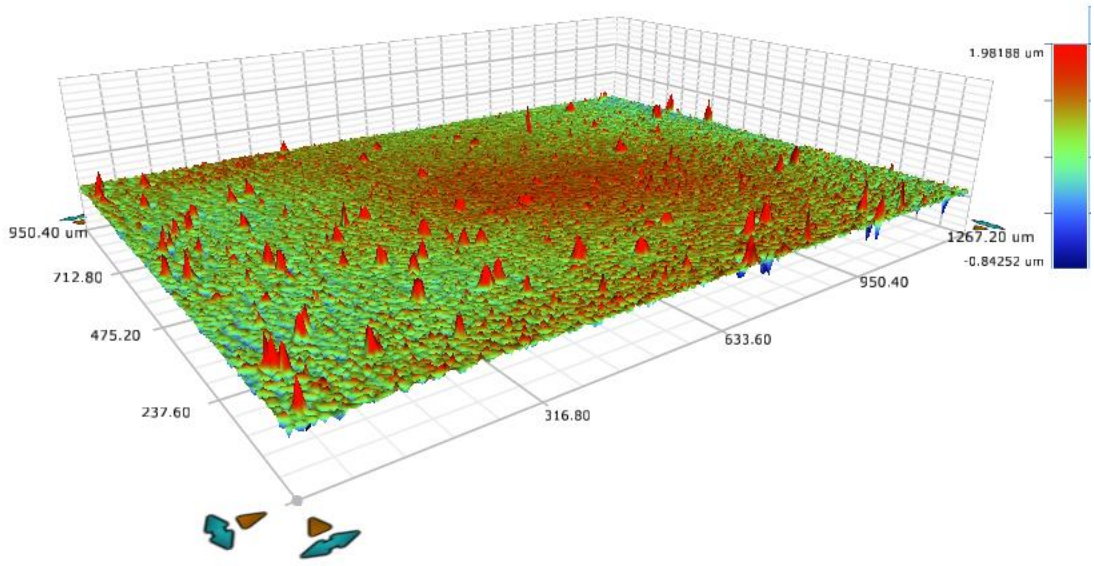


Figure 35. Profilometry of Run 15 (SWNT:CMC=2, sonication amplitude=40%, sonication duration=24 hr), showing a uniform CMC-dispersed coating diluted to 40% with an average roughness of 0.034 µm.

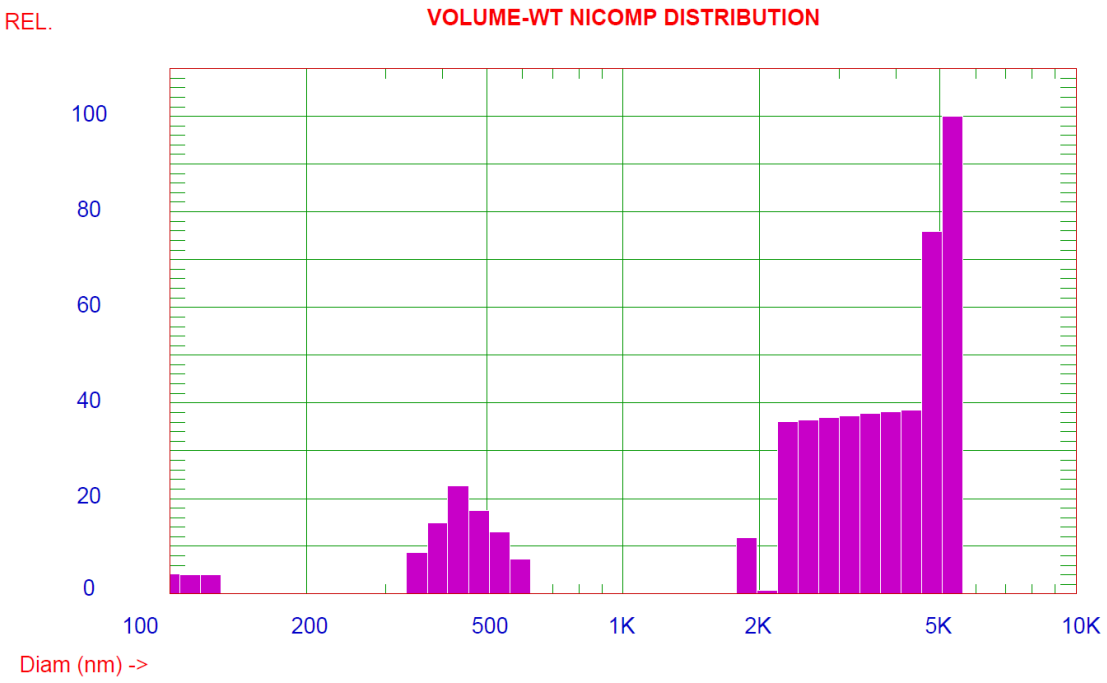


Figure 36. Particle size distribution of the matrix solution obtained through Run 3 (SWNT:CMC=0.5, sonication amplitude=20%, sonication duration=2 hr) using CMC dispersant, showing agglomeration. About 81% of the particles have an average particle size of ~5000 nm.

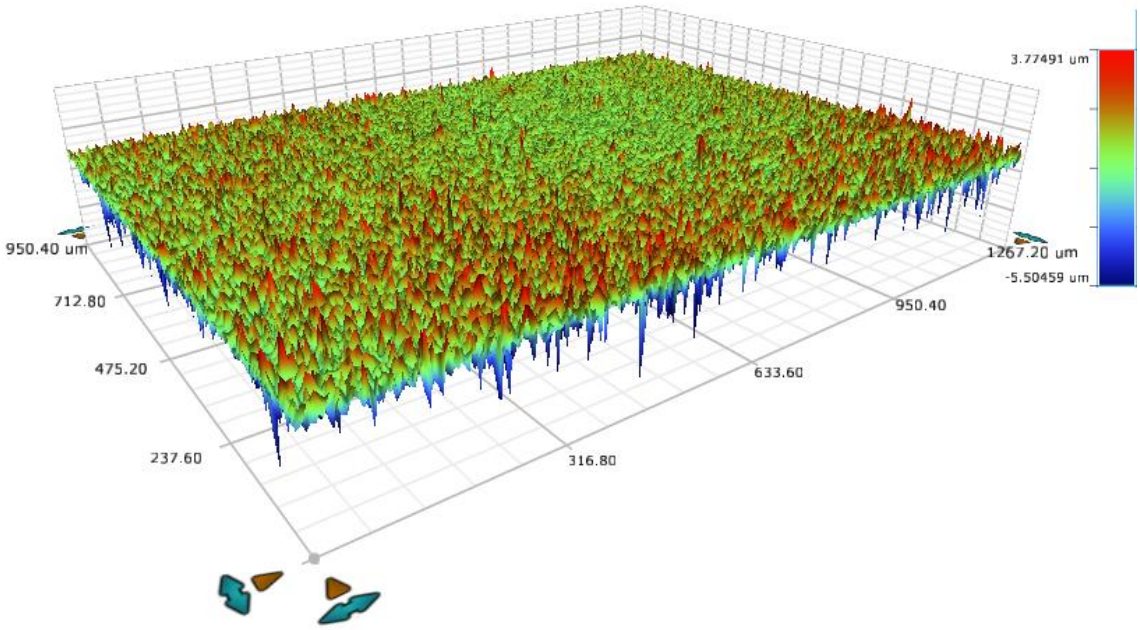


Figure 37. Profilometry of Run 3 (SWNT:CMC=0.5, sonication amplitude=20%, sonication duration=2 hr), showing a uniform CMC-dispersed coating at 100% (no dilution) with an average roughness of 0.274 µm.

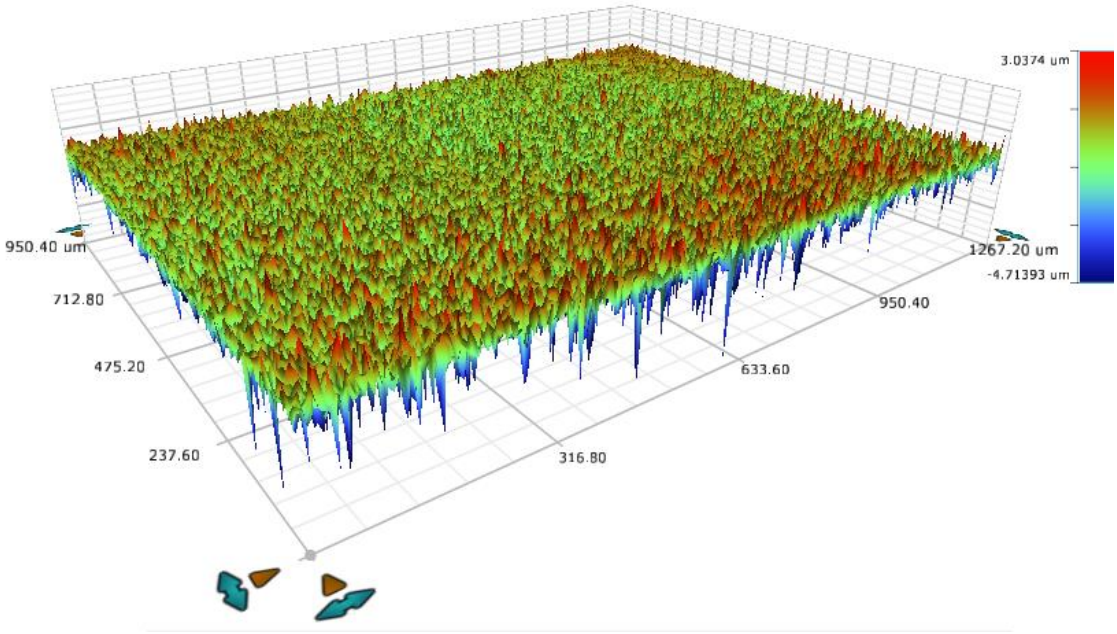


Figure 38. Profilometry of Run 3 (SWNT:CMC=0.5, sonication amplitude=20%, sonication duration=2 hr), showing a uniform CMC-dispersed coating diluted to 70% with an average roughness of 0.307 µm.

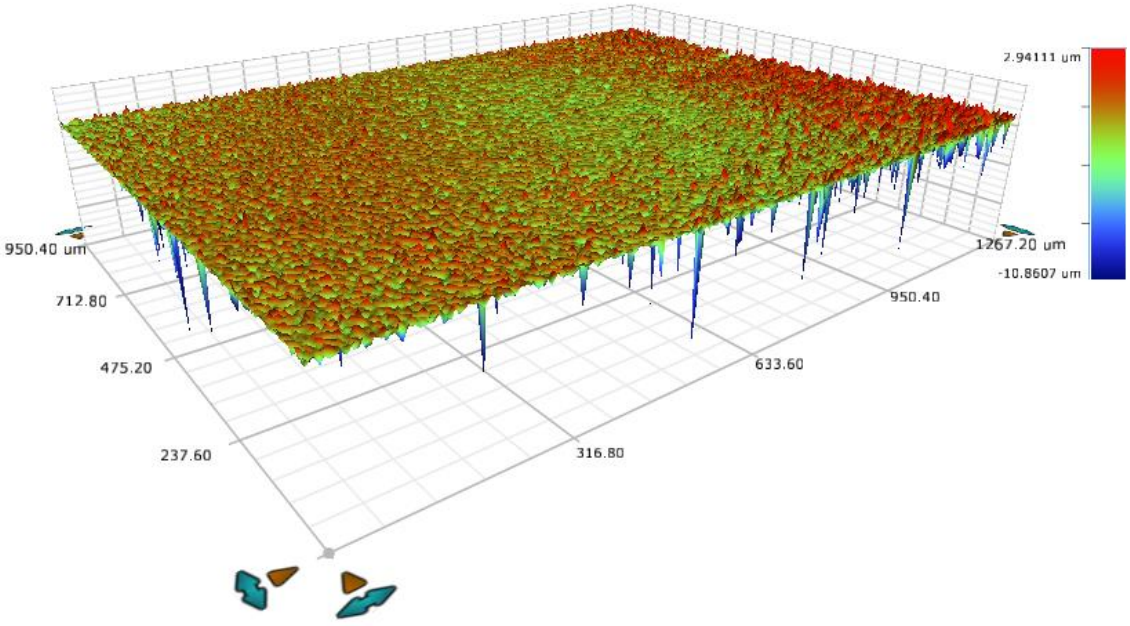


Figure 39. Profilometry of Run 3 (SWNT:CMC=0.5, sonication amplitude=20%, sonication duration=2 hr), showing a uniform CMC-dispersed coating diluted to 40% with an average roughness of 0.196 µm.

The behavior of the matrix solution in which PSS was used as the dispersant was found to be less predictable when compared to CMC-dispersed matrix solutions. Table 19 shows the summary of the particle size analysis test results sorted by particle size for all formulations within a given dilution percentage (100% (no dilution), 70%, and 40%), and color coded by particle size (green (low) to red (high)). The minimum particle size was observed for Run 4 with an average particle size of 15 nm. Run 5 had the next lowest average particle size, with average particle size of 18 nm (Figure 40) and the maximum particle size was observed in Run 15 with an average particle size of ~2880 nm (Figure 41).

Table 19. Summary of particle size analysis for PSS matrix, color coded by particle size (green (low) to red (high)).

Runs	*X_1 (SWNT:PSS)*	*X_2 (Sonication amp (%))*	*X_3 (Sonication durations (h))*	*diluted to*	*particle size (nm)*	*Resistance (ohm)*	*Predicted Resistance (ohm)*	*Calculated coatings thickness (µm)*	*Measured coatings thickness (µm)*	*Coating resistivity (ohm.cm)*
4	2.075	30	13	100%	15	304	515	3.82	-	0.0291
5	1.25	30	13	100%	18	393	643	4.29	-	0.0422
8	2	20	24	100%	53	701788	*550**	3.44	-	60.400
2	1.25	30	13	100%	107	749	643	4.23	-	0.0793
20	1.25	41	13	100%	110	125	370	6.23	5.66	0.0194
9	0.5	40	24	100%	110	277	286	8.11	-	0.0561
18	0.425	30	13	100%	110	560	770	8.51	-	0.1190
16	1.25	30	13	100%	122	365	643	4.87	-	0.0444
17	1.25	30	13	100%	127	1557	643	4.00	-	0.1560
6	0.5	20	24	100%	133	16316438	*1232**	6.57	6.15	2680.00
3	0.5	20	2	100%	152	6453796	*1232**	6.27	-	1010.00
7	1.25	30	25.1	100%	155	163	643	5.04	-	0.0206
19	1.25	30	0.9	100%	161	17817	*643**	0.66	-	0.2950
10	1.25	19	13	100%	169	2174028	*916**	3.71	-	202.00
1	1.25	30	13	100%	206	459	643	4.78	-	0.0549
11	2	20	2	100%	211	332381	*550**	3.57	-	29.700
14	0.5	40	2	100%	292	431	286	8.30	-	0.0894
12	2	40	2	100%	914	220	503	0.47	-	0.0026
13	1.25	30	13	100%	915	1211	643	4.61	-	0.1400
15	2	40	24	100%	2880	921	503	3.19	-	0.07
4	2.075	30	13	70%	15	390	707	2.67	-	0.0261
5	1.25	30	13	70%	18	544	922	3.00	-	0.0409

Table 19 - continued

8	2	20	24	70%	53	1141095	*202**	2.41	-	68.800
2	1.25	30	13	70%	107	1299	922	2.96	-	0.0962
20	1.25	41	13	70%	110	183	762	4.36	4.23	0.0199
9	0.5	40	24	70%	110	366	301	5.68	-	0.0519
18	0.425	30	13	70%	110	819	1136	5.96	-	0.1220
16	1.25	30	13	70%	122	502	922	3.41	-	0.0428
17	1.25	30	13	70%	127	2094	922	2.80	-	0.1470
6	0.5	20	24	70%	133	16505225	*1932**	4.60	4.29	1900.00
3	0.5	20	2	70%	152	6855038	*1932**	4.39	-	753.00
7	1.25	30	25.1	70%	155	241	922	3.53	-	0.0212
19	1.25	30	0.9	70%	161	21716	*922*	0.46	-	0.2520
10	1.25	19	13	70%	169	4977047	*1081**	2.60	-	323.00
1	1.25	30	13	70%	206	650	922	3.35	-	0.0544
11	2	20	2	70%	211	509977	*202**	2.50	-	31.900
14	0.5	40	2	70%	292	555	301	5.81	-	0.0807
12	2	40	2	70%	914	1339	1252	0.33	-	0.0109
13	1.25	30	13	70%	915	1698	922	3.23	-	0.1370
15	2	40	24	70%	2880	1484	1252	2.23	-	0.08
4	2.075	30	13	40%	15	770	1532	1.53	-	0.0294
5	1.25	30	13	40%	18	1202	2078	1.72	-	0.0516
8	2	20	24	40%	53	7231889	*1002**	1.38	-	249.000
2	1.25	30	13	40%	107	2176	2078	1.69	-	0.0921
20	1.25	41	13	40%	110	391	1358	2.49	2.54	0.0244
9	0.5	40	24	40%	110	801	685	3.24	-	0.0650
18	0.425	30	13	40%	110	1863	2625	3.41	-	0.1590
16	1.25	30	13	40%	122	1099	2078	1.95	-	0.0535
17	1.25	30	13	40%	127	5297	2078	1.60	-	0.2120

Table 19 - continued

6	0.5	20	24	40%	133	25362920	*4465**	2.63	2.46	1670.00
3	0.5	20	2	40%	152	14250756	*4465**	2.51	-	894.00
7	1.25	30	25.1	40%	155	575	2078	2.02	-	0.0290
19	1.25	30	0.9	40%	161	52246	*2078**	0.27	-	0.3470
10	1.25	19	13	40%	169	12746253	*2799**	1.48	-	473.00
1	1.25	30	13	40%	206	1464	2078	1.91	-	0.0700
11	2	20	2	40%	211	1099619	*1002**	1.43	-	39.300
14	0.5	40	2	40%	292	1100	685	3.32	-	0.0913
12	2	40	2	40%	914	2529	2162	0.19	-	0.0118
13	1.25	30	13	40%	915	4164	2078	1.84	-	0.1920
15	2	40	24	40%	2880	2326	2162	1.28	-	0.07

*Fitted values in italic denotes an extremely unusual point relative to predictor levels used to fit the model

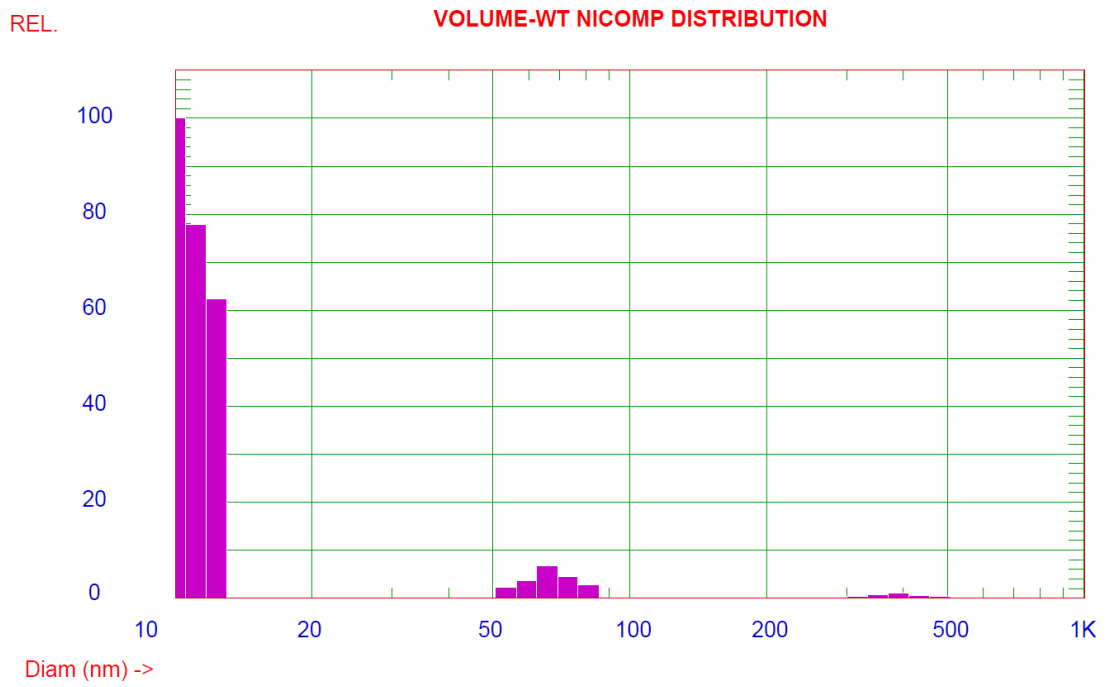


Figure 40. Particle size distribution of the matrix solution obtained through Run 5 (SWNT:PSS=1.25, sonication amplitude=30%, sonication duration=13 hr) using PSS dispersant, showing a low resistance of 393 Ω. The average particle size of ~18 nm was reported for this matrix solution.

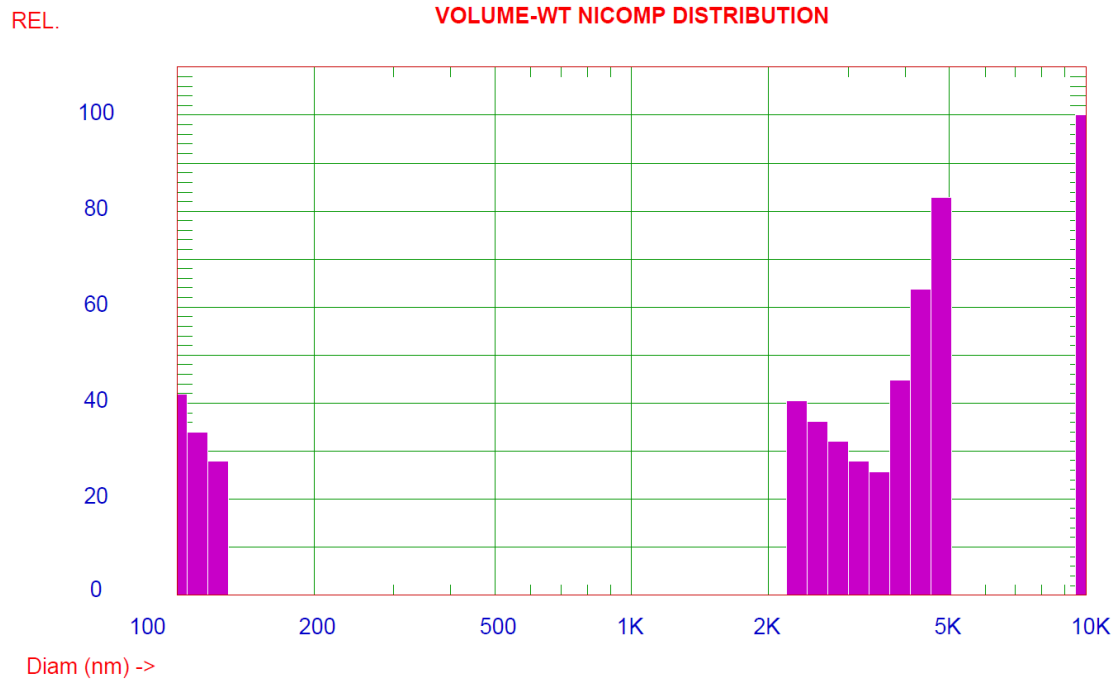


Figure 41. Particle size distribution of the matrix solution obtained through Run 15 (SWNT:PSS=2, sonication amplitude=40%, sonication duration=24 hr) using PSS dispersant, showing a high resistance of 2326 Ω. The average particle size of ~2880 nm was reported for this matrix solution.

The sample with the minimum average resistance of 125 Ω in Run 20 was found to have a monodisperse particle size distribution with an average particle size of 110 nm (Figure 42). The samples with the maximum average resistance of 25 KΩ in Run 6 also had a monodisperse particle size distribution with an average particle size of ~133 nm (Figure 46). This fact indicates that PSS is very sensitive to the sonication conditions. This may result in a portion of PSS wrapping around itself, forming bundles rather than wrapping around SWNTs and dispersing them, or wrapping in multiple layers around SWNTs which will hinder electron transport of conductive carbon nanotubes [92, 93, 96, 98]. This may also create larger particles which results in the removal of SWNTs from the solution after filtrations. This fact can also be observed through the analysis of variance of the particle sizes obtained in the PSS-dispersed matrix solutions (Table 15 through Table 17) as the sonication amplitude and its interaction with the concentration of PSS are the only significant factors among all (α=0.05). In contrast, the sonication duration is the most significant factor in the analysis of variance of the particle sizes obtained in the CMC-dispersed matrix solutions (see Table 12 through Table 14). No interaction is observed for the CMC-dispersed matrix solutions. Therefore, the interaction that exists between the PSS and the sonication amplitude will make PSS act even more unpredictable at various situations. This makes CMC as a superior, more predictably behaving dispersant for this application. Considering the t-statistics for each model term and the provisions of the RSM, the following first-order model can be used to predict the particle size of the CMC-dispersed matrix solutions:

$$\text{Particle size (nm)} = 1490 - 60.1\, X_3 \qquad (11)$$

The surface profile of Run 20 of the experiments in which PSS was used as the dispersant at 100% (no dilution), 70% dilution, and 40% dilution is presented in Figure 43 through Figure 45. As discussed earlier, in this run the minimum resistance of 125 Ω was achieved. As can be observed in Figure 43, a coating with an average roughness of 186 nm was obtained for the matrix coating at 100% (no dilution). This average roughness is almost three times more than its CMC counterpart (67 nm). The same formulation that was diluted down to 70% showed a roughness of 133 nm (Figure 44) (compare to 50 nm (Figure 34)), and the coating that was diluted down to 40% showed a roughness of 134 nm (Figure 45) (compare to 34 nm (Figure 35)).

On the other hand, Run 6, which was characterized by the maximum resistance among the set of experiments in which PSS was used, exhibit an even rougher surface. Figure 47 shows the surface morphology of the coating obtained from Run 6 at 100% (no dilution), revealing an average roughness of 601 nm (compare to the CMC counterpart at 274 nm). The coating non-uniformity of the PSS samples is obvious in the surface profiles of the all the PSS samples. The same formulation that was diluted down to 70% showed a roughness of 923 nm (Figure 48) (compare to 307 nm (Figure 38)), and the coating that was diluted down to 40% showed a roughness of 288 nm (Figure 49) (compared to 196 nm as shown in Figure 39).

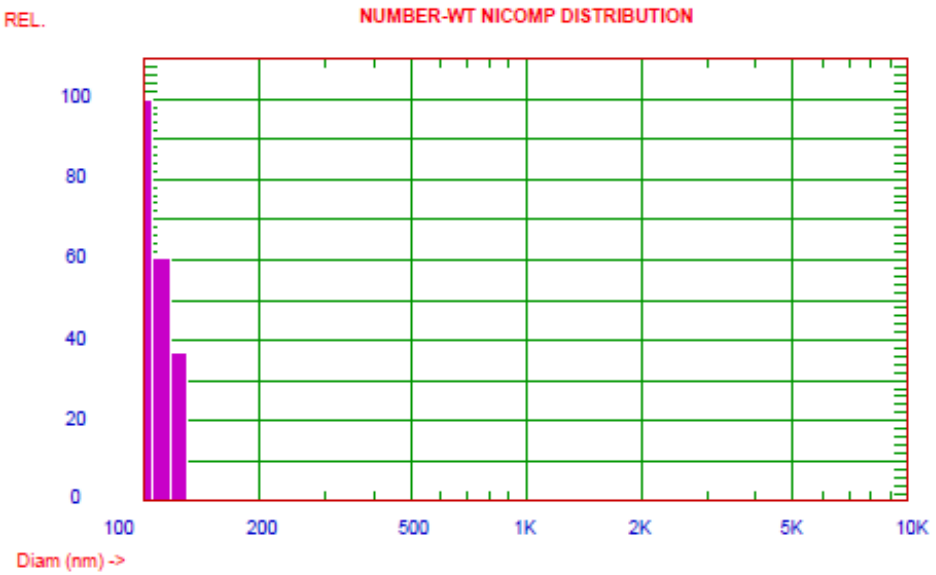


Figure 42. Particle size distribution of the matrix solution obtained through Run 20 (SWNT:PSS=1.25, sonication amplitude=41%, sonication duration=13 hr) using PSS dispersant, showing a resistance of 125 Ω. The average particle size of ~110 nm was reported for this matrix solution.

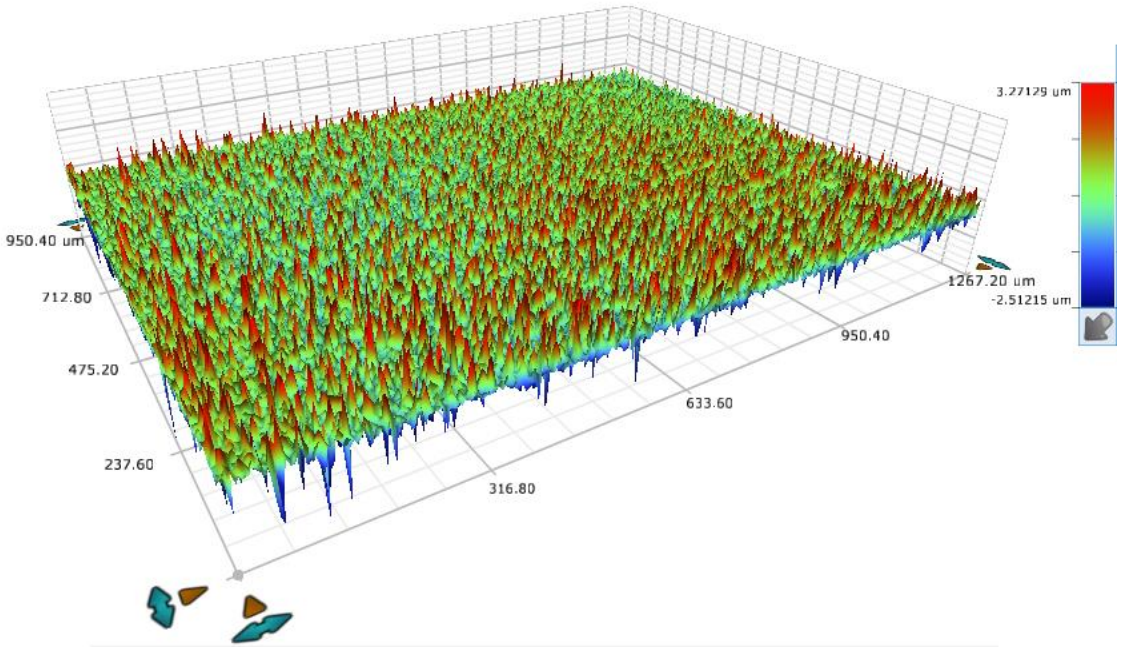


Figure 43. Profilometry of Run 20 (SWNT:PSS=1.25, sonication amplitude=41%, sonication duration=13 hr), showing a PSS-dispersed coating at 100% (no dilution) with an average roughness of 0.186 µm.

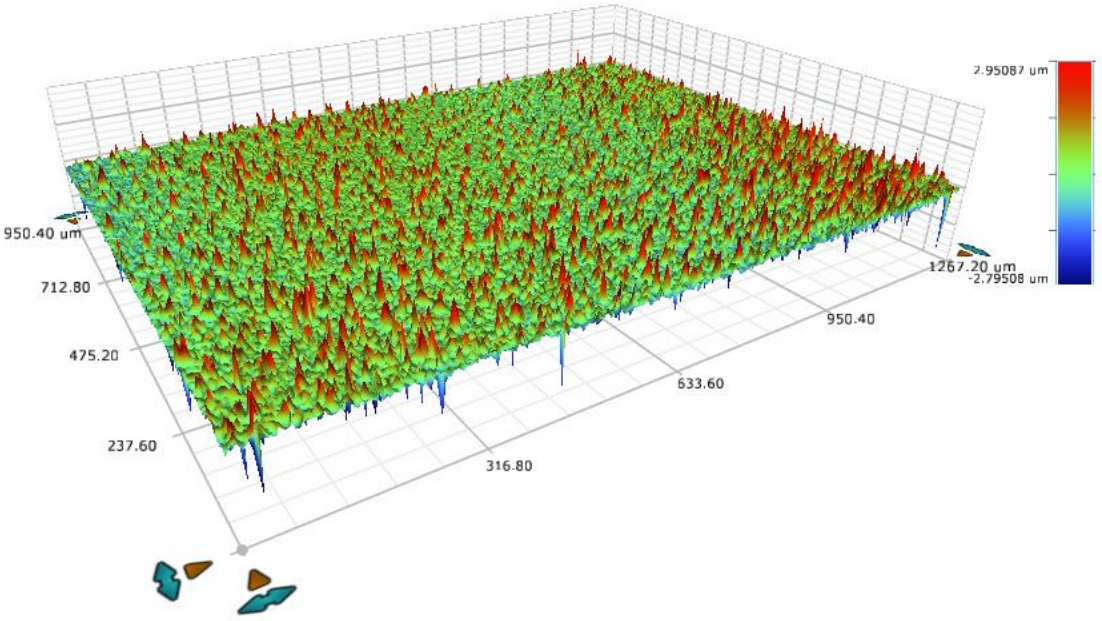


Figure 44. Profilometry of Run 20 (SWNT:PSS=1.25, sonication amplitude=41%, sonication duration=13 hr), showing a PSS-dispersed coating diluted to 70% with an average roughness of 0.133 µm.

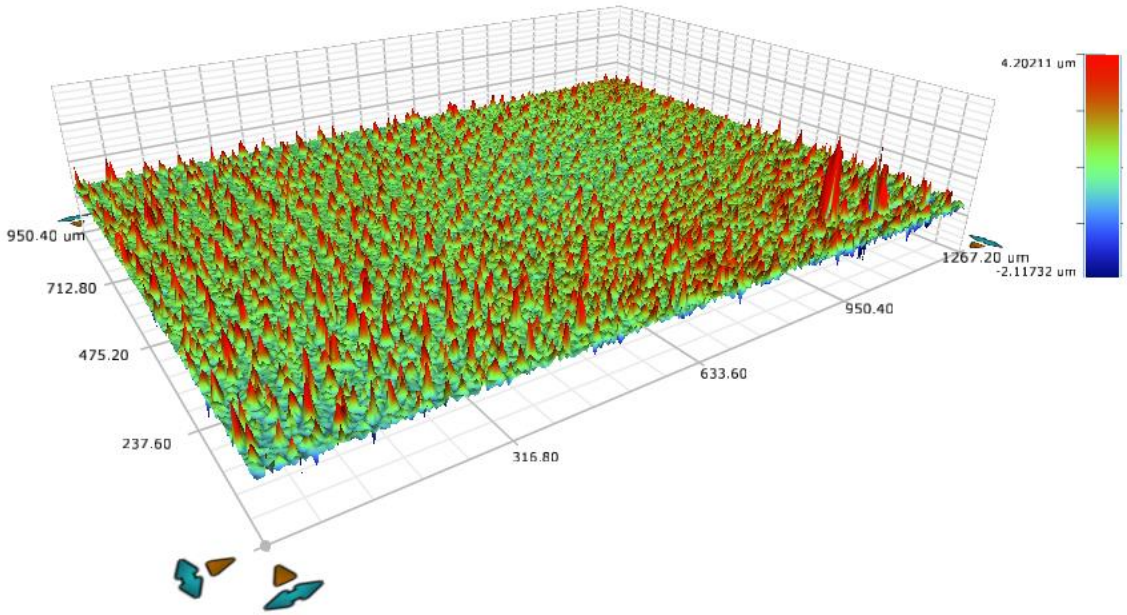


Figure 45. Profilometry of Run 20 (SWNT:PSS=1.25, sonication amplitude=41%, sonication duration=13 hr), showing a PSS-dispersed coating diluted to 40% with an average roughness of 0.134 µm.

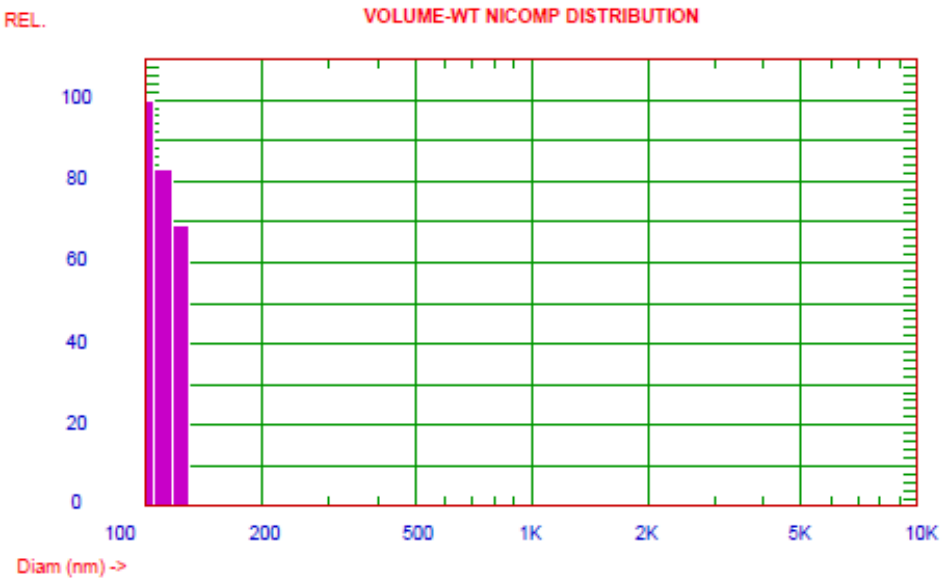


Figure 46. Particle size distribution of the matrix solution obtained through Run 6 (SWNT:PSS=0.5, sonication amplitude=20%, sonication duration=24 hr) using PSS dispersant, showing a high resistance of 25 KΩ. The average particle size of ~133 nm was reported for this matrix solution.

Figure 47. Profilometry of Run 6 (SWNT:PSS=0.5, sonication amplitude=20%, sonication duration=24 hr), showing a PSS-dispersed coating at 100% (no dilution) with an average roughness of 0.601 µm.

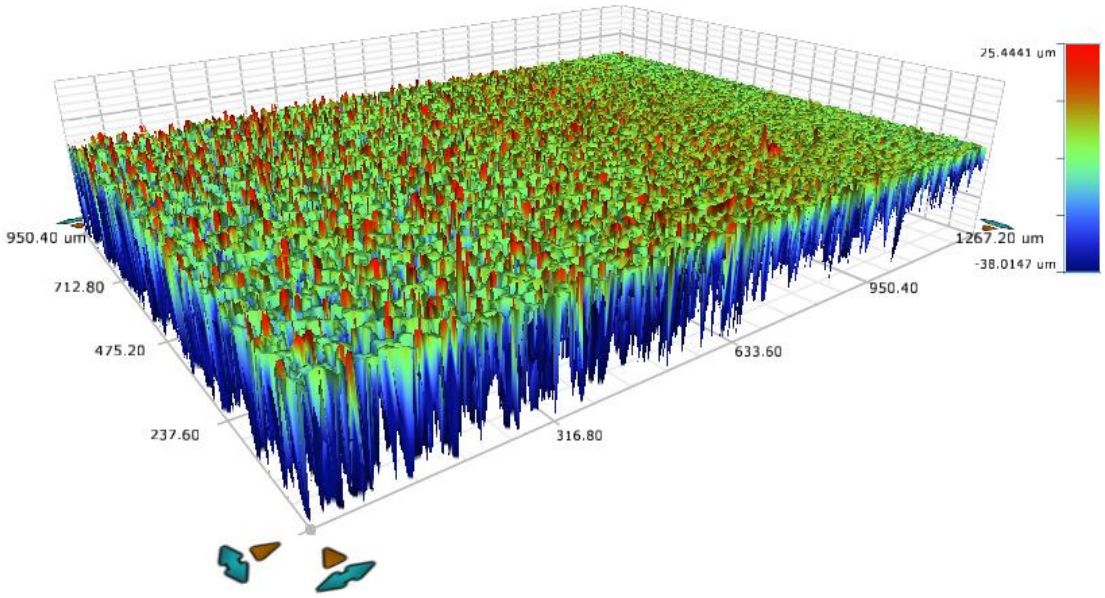


Figure 48. Profilometry of Run 6 (SWNT:PSS=0.5, sonication amplitude=20%, sonication duration=24 hr), showing a PSS-dispersed coating diluted to 70% with an average roughness of 0.923 µm.

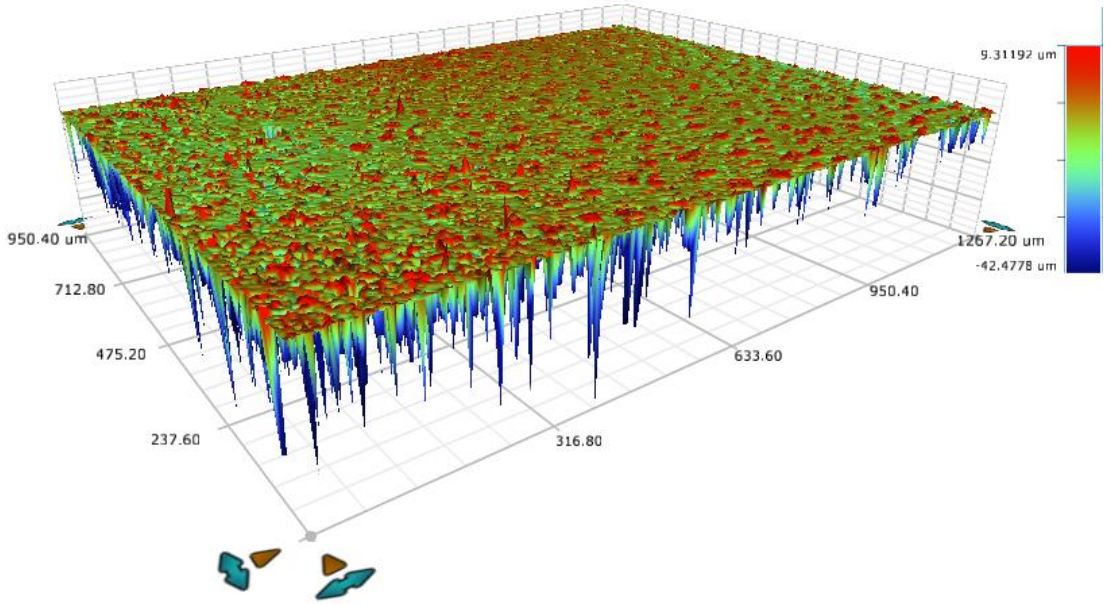


Figure 49. Profilometry of Run 6 (SWNT:PSS=0.5, sonication amplitude=20%, sonication duration=24 hr), showing a PSS-dispersed coating diluted to 40% with an average roughness of 0.288 µm.

Therefore, it can be concluded that a smoother surface can be achieved by using CMC as the dispersant for dispersing carbon nanotubes. Agglomerations and non-uniformity is obviously visible when SWNTs are dispersed using PSS at any concentration when compared to its CMC matrix solution counterparts. This makes CMC a superior, more predictable dispersant for SWNTs dispersion.

2.3.4 Mass balance and thickness

The thickness of the coatings is important because of their effect on the resistance of the obtained dried films. The higher the coating thickness is, the less the resistance of the coating will be. The thickness of the coatings can be experimentally and theoretically measured. The experimental measurements can be performed using optical profiler for each coating. Theoretical estimation of the coating is also possible through performing an accurate mass balance between the solid materials that were originally weighed for each formulation and the amount solids that were filtered out through filtration and centrifugation. For the purpose of theoretical thickness calculations, all the vials and filters used for each formulation were marked and weighed before the experiments. After the experiments, the left over matrix solution and their corresponding filters were dried in an oven for 2 days, under vacuum, until all the moisture was removed from the solution, leaving only solid particles in the vials. The vials were then weighed again and the amount of remaining solid that was eliminated from each solution was identified. This data was used to measure the theoretical thickness of the final coatings.

The density (ρ) of the materials in the matrix solution has the following relationship with the mass (m) and the volume of the solution:

$$\rho = \frac{m}{a \times b \times h} \tag{12}$$

Where (a) is the length, (b) is the width, and (h) is the thickness of the deposited matrix into each separate channels. This equation can be rearranged such that the thickness (h) represents the thickness of the deposited SWNT matrix solution after the solvent evaporation (dry thickness):

$$h = \frac{m}{a \times b \times \rho} \tag{13}$$

The theoretical thickness of the deposited matrix materials is presented in Table 20.

Table 20- Theoretical calculation of the coating thicknesses for different dilutions using the mass balance and the densities of each solution. Measured thicknesses by 2D microscopy profiling are shown in parentheses.

	CMC coatings thickness (µm)			PSS coatings thickness (µm)		
Sample	100%	70%	40%	100%	70%	40%
1	4.23	2.96	1.69	4.78	3.35	1.91
2	4.13	2.89	1.65	4.23	2.96	1.69
3	3.70 (3.81)	2.59 (2.42)	1.48(1.18)	6.27	4.39	2.51
4	2.26	1.58	0.90	3.82	2.67	1.53
5	4.04	2.83	1.62	4.29	3.00	1.72
6	4.27	2.99	1.71	6.57 (6.15)	4.60 (4.29)	2.63 (2.46)
7	4.26	2.98	1.70	5.04	3.53	2.02
8	2.53	1.77	1.01	3.44	2.41	1.38
9	4.81	3.36	1.92	8.11	5.68	3.24
10	3.95	2.76	1.58	3.71	2.60	1.48
11	2.55	1.79	1.02	3.57	2.50	1.43
12	3.56	2.49	1.42	0.47	0.33	0.19
13	4.26	2.98	1.70	4.61	3.23	1.84
14	4.60	3.22	1.84	8.30	5.81	3.32
15	3.84 (3.86)	2.69 (2.81)	1.54 (1.63)	3.19	2.23	1.28
16	4.13	2.89	1.65	4.87	3.41	1.95
17	4.19	2.93	1.68	4.00	2.80	1.60
18	4.78	3.34	1.91	8.51	5.96	3.41
19	0.85	0.60	0.34	0.66	0.46	0.27
20	4.15	2.91	1.66	6.23 (5.66)	4.36 (4.23)	2.49 (2.54)

The thickness of the dried matrix coating was also investigated using the optical profiler. For this purpose, the optical profile of the edge of the coatings was obtained using optical profiler for each sample. The thickness of matrix coatings obtained from Run 15 of the formulation in which CMC was used as the dispersant at 100% (no dilution), 70% dilution, and 40% dilution is presented in Figure 50 through Figure 52. The thickness of the deposited matrix solution is measured to be 3.86, 2.81, and 1.63 μm, respectively. As expected, the thickness of the coatings decreased by the dilution of the matrix solution.

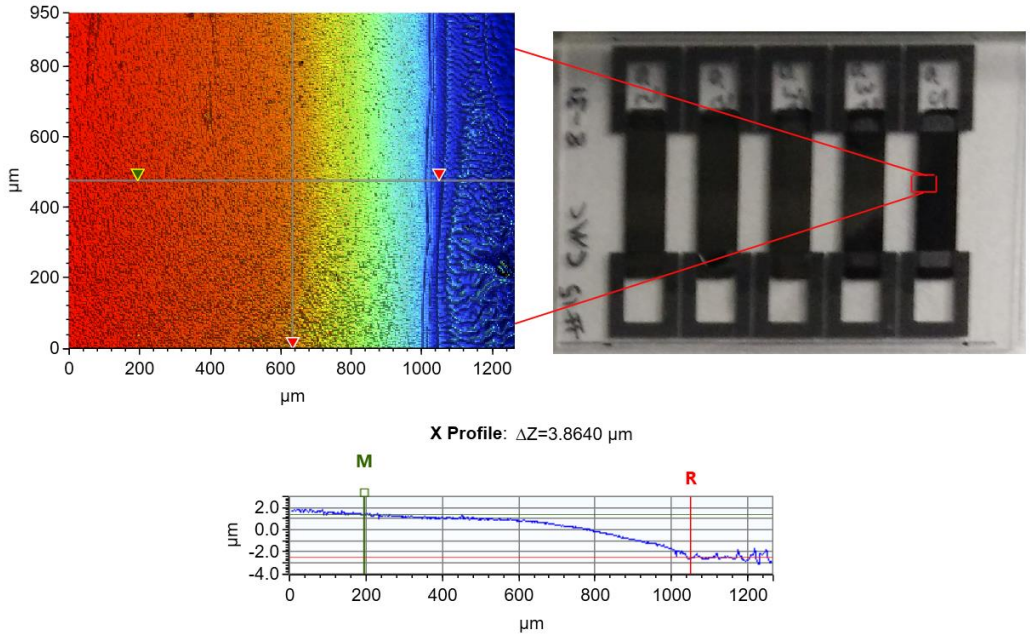


Figure 50. The thickness of the CMC-dispersed coating obtained from run 15 at 100% (no dilution) using 2D microscopy profile (1250 µm × 950 µm) showing a thickness of 3.864 µm.

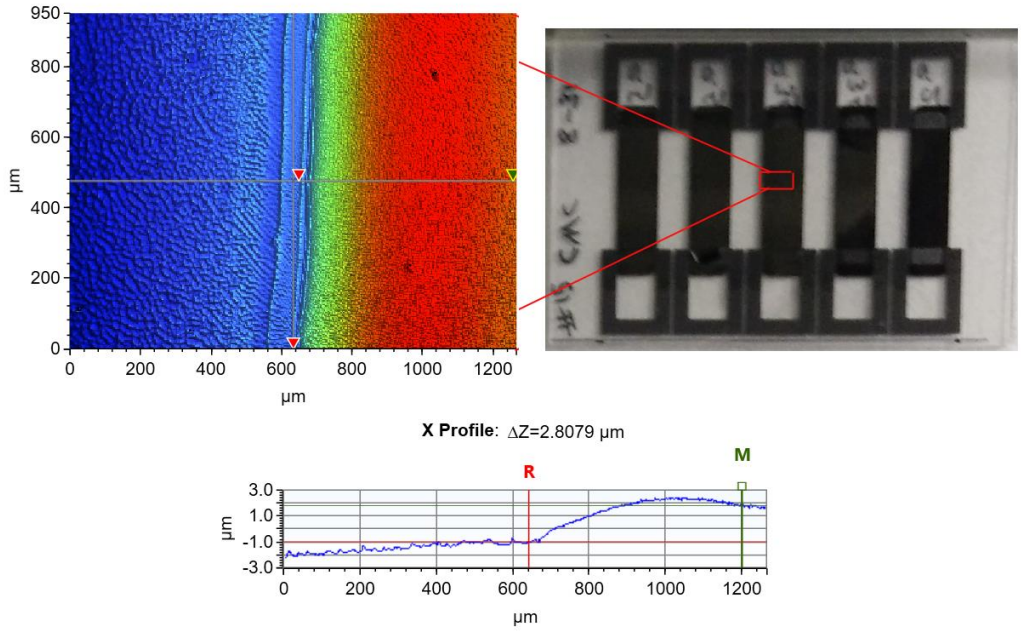


Figure 51. The thickness of the CMC-dispersed coating obtained from run 15 diluted to 70% using 2D microscopy profile (1250 µm × 950 µm) showing a thickness of 2.8079 µm.

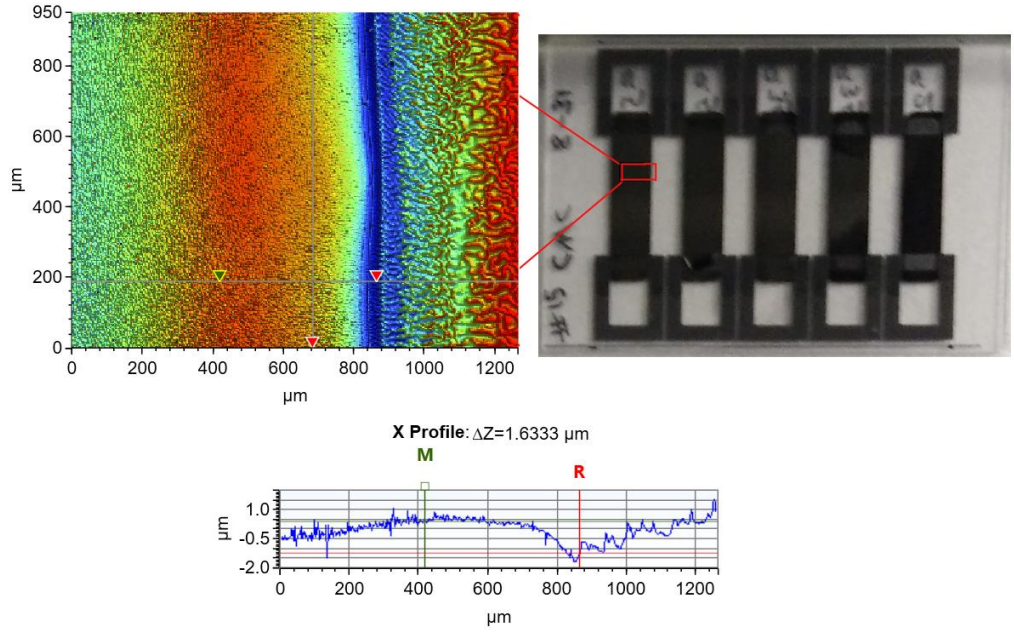


Figure 52. The thickness of the CMC-dispersed coating obtained from run 15 diluted to 40% using 2D microscopy profile (1250 µm × 950 µm) showing a thickness of 1.6333 µm.

The thickness of matrix coatings obtained from Run 3 of the formulation in which CMC was used as the dispersant at 100% (no dilution), 70% dilution, and 40% dilution is presented in Figure 53 through Figure 55. The thickness of the deposited matrix solution is measured to be 3.81, 2.42, and 1.18 µm, respectively.

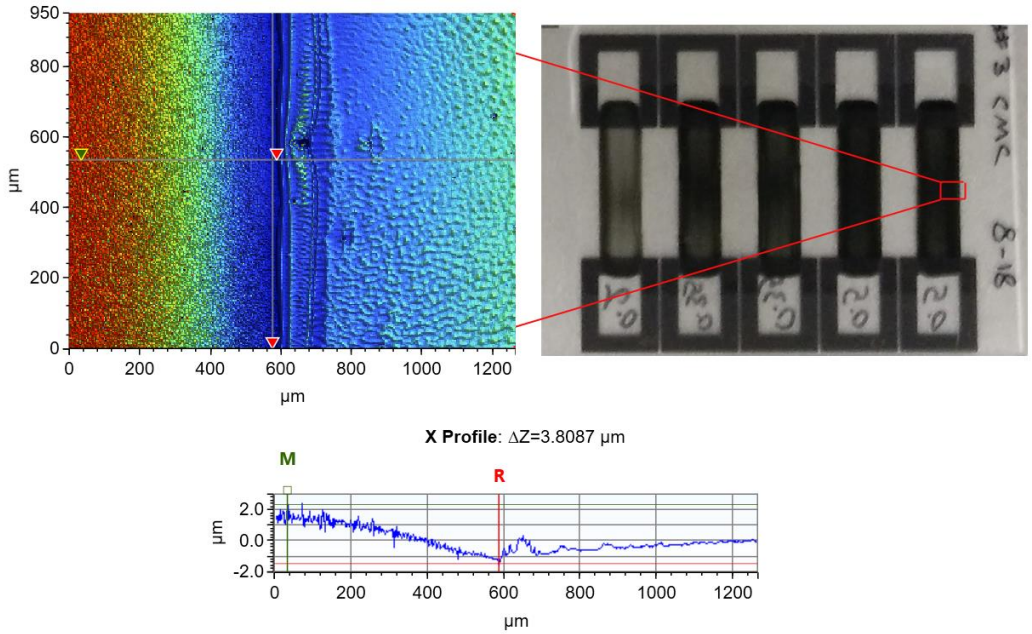


Figure 53. The thickness of the CMC-dispersed coating obtained from run 3 at 100% (no dilution) using 2D microscopy profile (1250 µm × 950 µm) showing a thickness of 3.8087 µm.

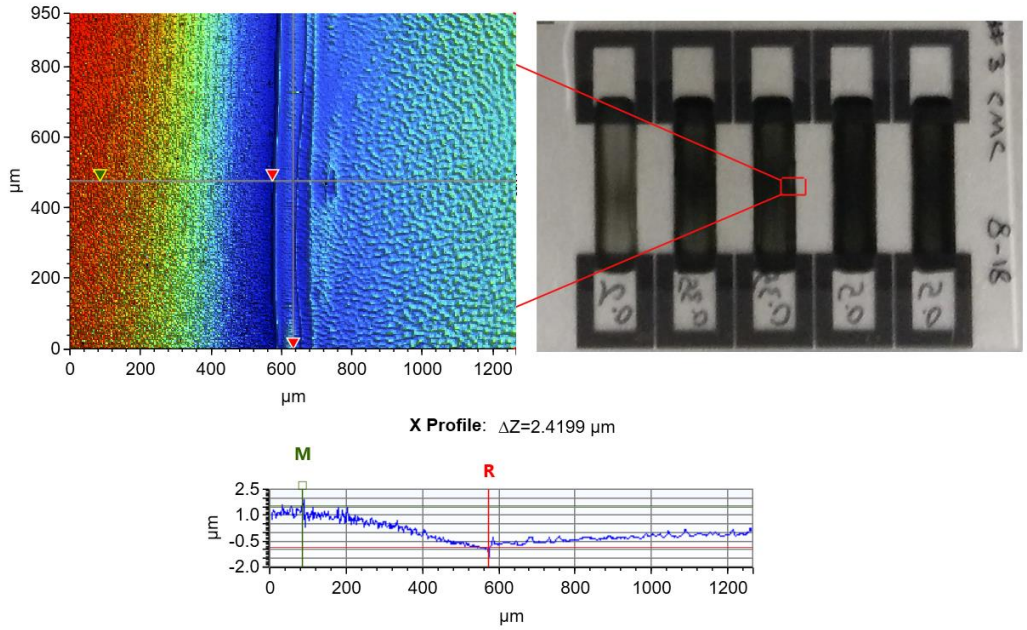


Figure 54. The thickness of the CMC-dispersed coating obtained from run 3 diluted to 70% using 2D microscopy profile (1250 µm × 950 µm) showing a thickness of 2.4199 µm.

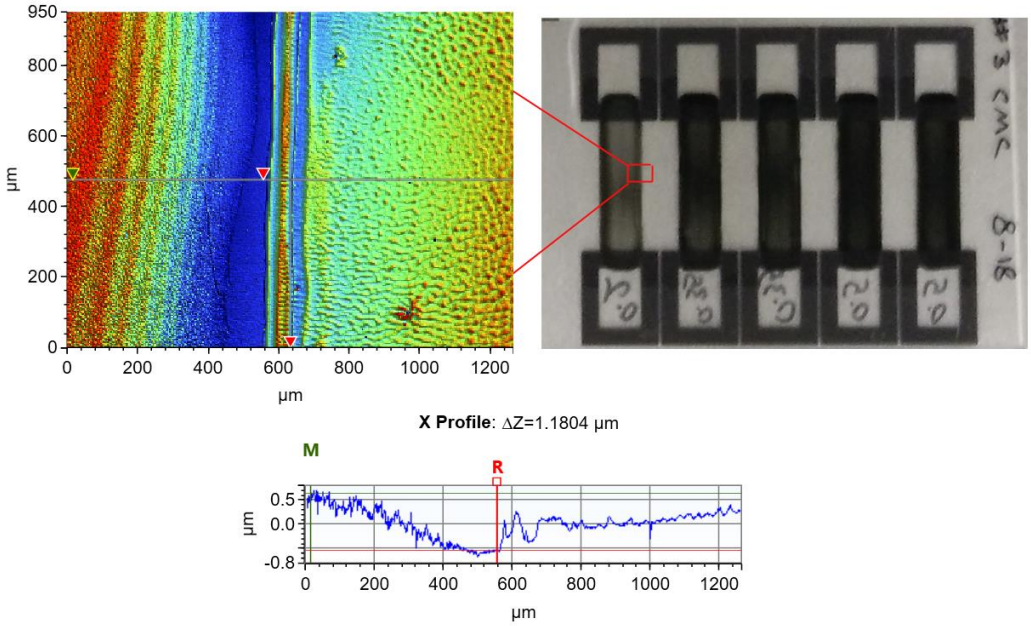


Figure 55. The thickness of the CMC-dispersed coating obtained from run 3 diluted to 40% using 2D microscopy profile (1250 µm × 950 µm) showing a thickness of 1.1804 µm.

The thickness of matrix coatings obtained from Run 20 of the formulation in which PSS was used as the dispersant at 100% (no dilution), 70% dilution, and 40% dilution is presented in Figure 56 through Figure 58. The thickness of the deposited matrix solution is measured to be 5.6645, 4.2286, and 2.5407 µm, respectively. As expected, the thickness of the dried matrix coatings decreased as the matrix solutions were diluted.

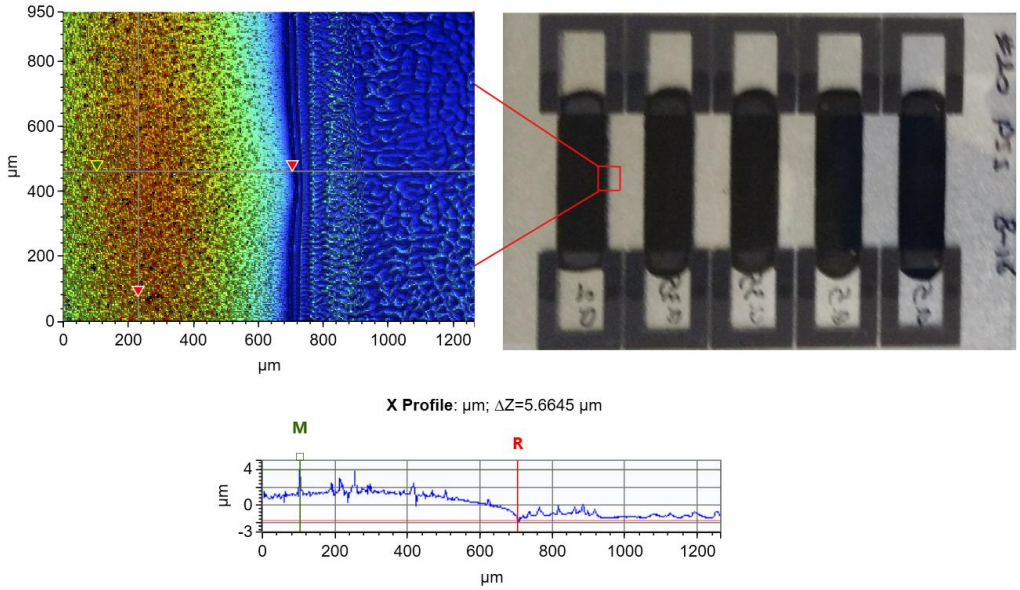


Figure 56. The thickness of the PSS-dispersed coating obtained from run 20 at 100% (no dilution) using 2D microscopy profile (1250 µm × 950 µm) showing a thickness of 5.6645 µm.

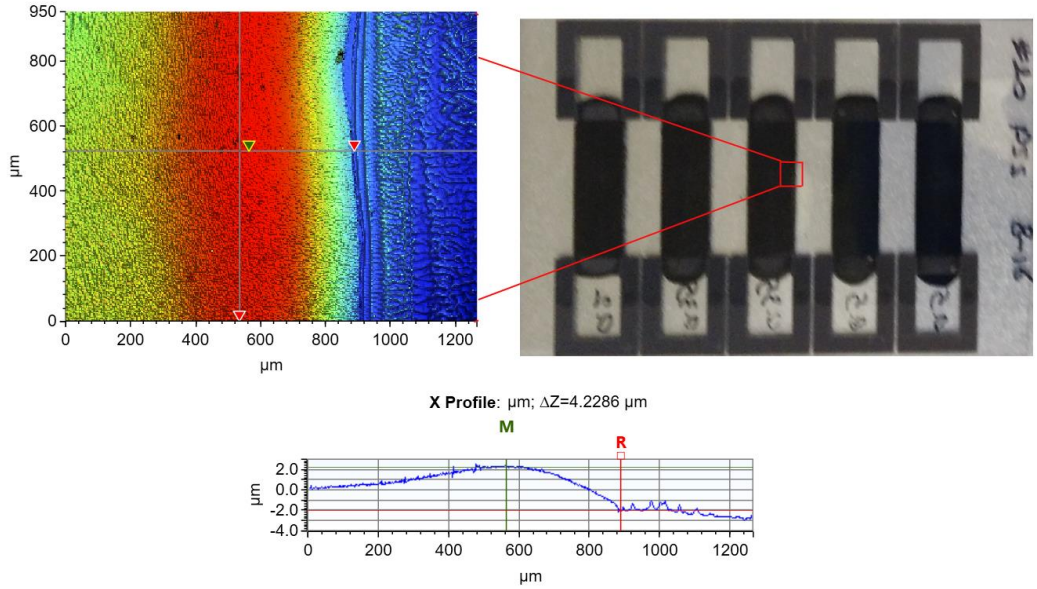


Figure 57. The thickness of the PSS-dispersed coating obtained from run 20 diluted to 70% using 2D microscopy profile (1250 µm × 950 µm) showing a thickness of 4.2286 µm.

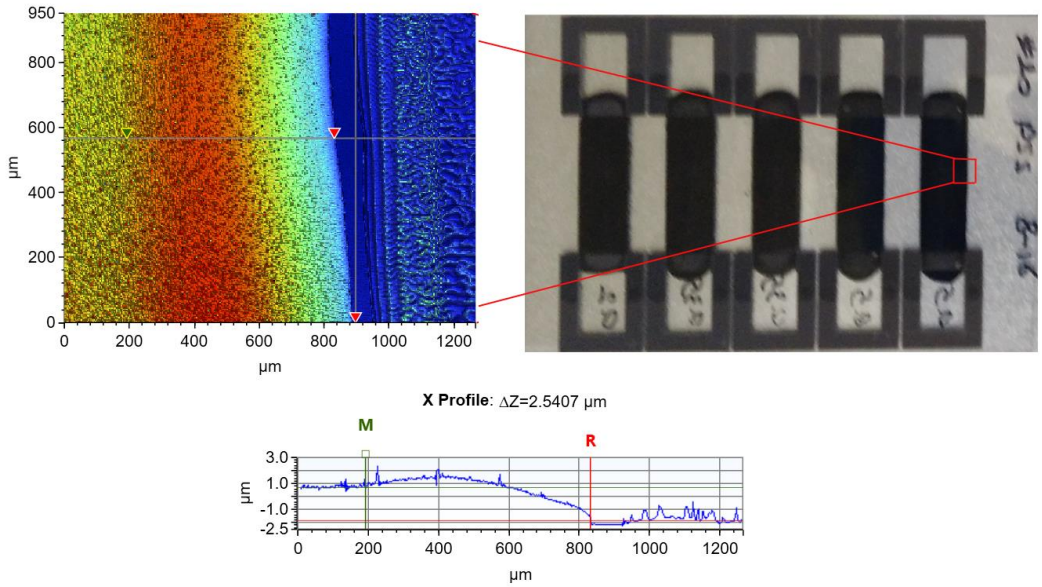


Figure 58. The thickness of the PSS-dispersed coating obtained from run 20 diluted to 40% using 2D microscopy profile (1250 µm × 950 µm) showing a thickness of 2.5407 µm.

The thickness of matrix coatings obtained from Run 6 of the formulation in which PSS was used as the dispersant at 100% (no dilution), 70% dilution, and 40% dilution is presented in Figure 59 through Figure 61. The thickness of the deposited matrix solution is measured to be 6.15, 4.29, and 2.46 µm, respectively.

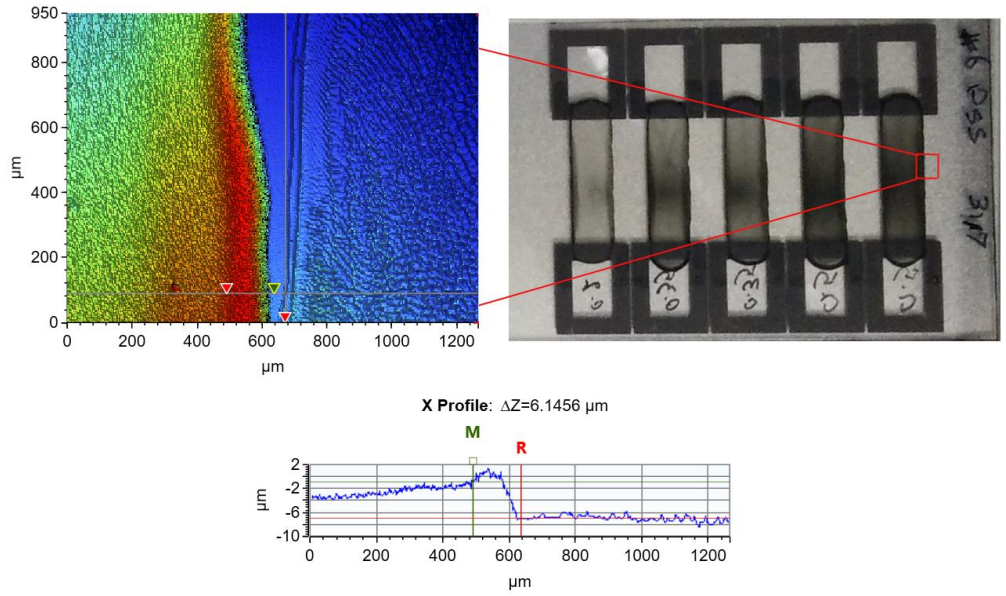


Figure 59. The thickness of the PSS-dispersed coating obtained from run 6 at 100% (no dilution) using 2D microscopy profile (1250 µm × 950 µm) showing a thickness of 6.1456 µm.

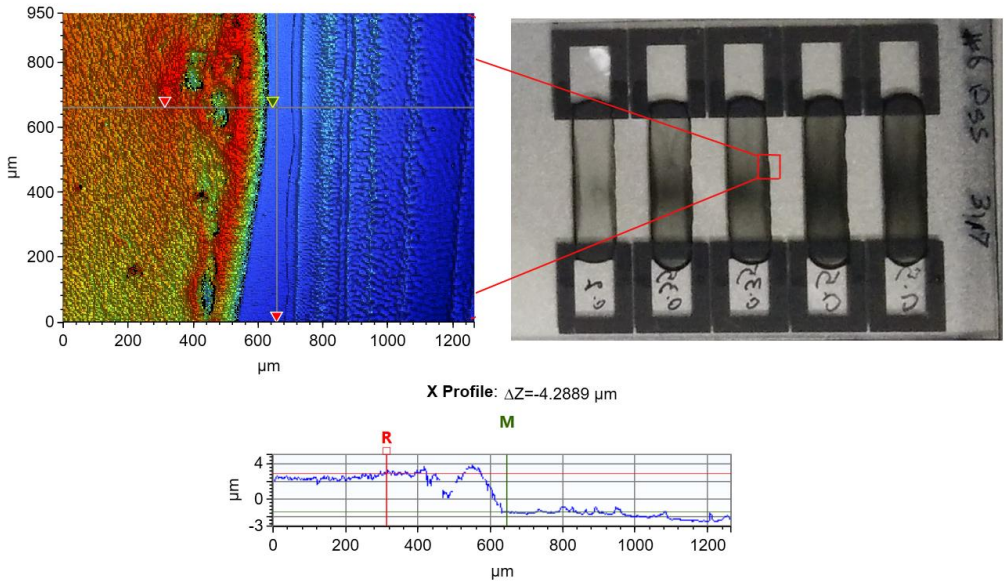


Figure 60. The thickness of the PSS-dispersed coating obtained from run 6 diluted to 70% using 2D microscopy profile (1250 µm × 950 µm) showing a thickness of 4.2889 µm.

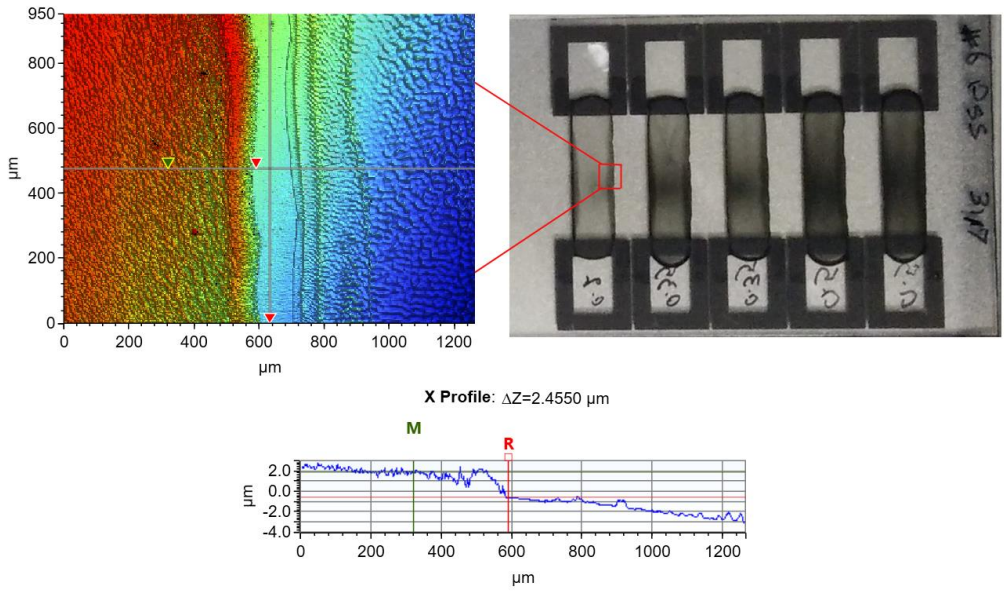


Figure 61. The thickness of the PSS-dispersed coating obtained from run 6 diluted to 40% using 2D microscopy profile (1250 µm × 950 µm) showing a thickness of 2.4550 µm.

The thickness values obtained from the empirical measurements using the surface profilometry with the theoretical values of the thickness presented in Table 20 are found to be in a close agreement (~±10%). Therefore the theoretical measurement of thickness can be used with a reasonable accuracy for prediction of the thickness for the deposited matrix solutions after drying.

2.3.5 Resistivity

By knowing the thickness of the deposited matrix solutions, and given that the dimensions of the deposited coatings are fixed for every channel, the resistivity of the coatings at different thicknesses can be calculated. The resistivity of such geometry can be obtained using the following equation [153, 154]:

$$\rho = \frac{V}{I}\frac{ah}{s} \tag{14}$$

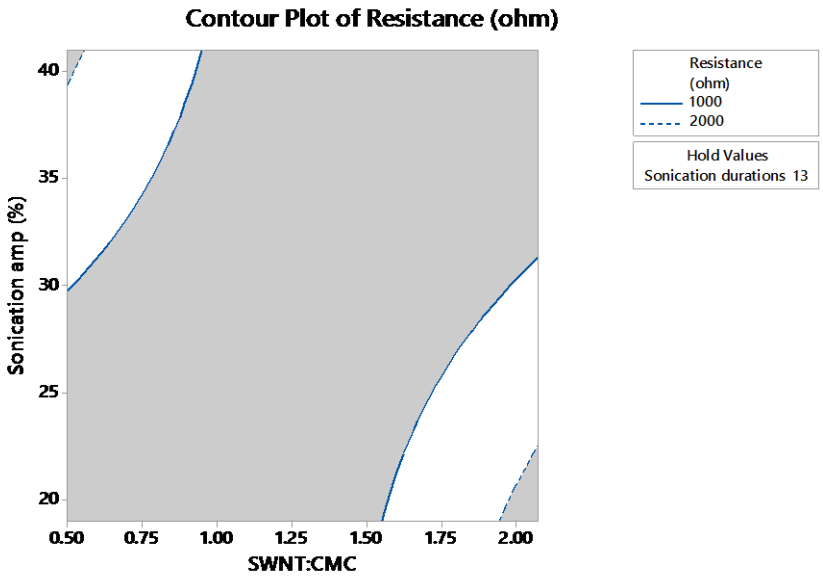
where ρ is the sample resistivity, V is the potential difference between the two voltage measurement probes, I is the current that passes through the sample, a and h are the sample width and height, and s is the length between the two probes. By using equation 14 the average resistivity of each sample has been calculated and presented in Table 21. Since the resistance of the electrodes/contacts are small compared to the resistance of the matrix coatings, a two point probe method was used to measure the resistance of the coatings [153, 154]. One would expect the resistivity of the film produced from each dilution of a sample to be similar, as they are in most cases.

Table 21- Resistivity of the coatings at 100% (no dilution), 70%, and 40% dilutions after drying sorted from low to high for CMC at 100%(no dilution)

Runs	*X1 (SWNT:CMC)*	*X2 (Sonication amp (%))*	*X3 (Sonication durations (h))*	CMC coating resistivity (ohm.cm)			PSS coating resistivity (ohm.cm)		
				100%	70%	40%	100%	70%	40%
15	2	40	24	0.0123	0.0134	0.0154	0.0735	0.0829	0.0742
12	2	40	2	0.0131	0.0126	0.0132	0.0026	0.0109	0.0118
5	1.25	30	13	0.0131	0.0123	0.0135	0.0422	0.0409	0.0516
1	1.25	30	13	0.0141	0.0140	0.0153	0.0549	0.0544	0.0700
10	1.25	19	13	0.0147	0.0145	0.0135	202.00	323.00	473.00
2	1.25	30	13	0.0153	0.0155	0.0169	0.0793	0.0962	0.0921
17	1.25	30	13	0.0154	0.0143	0.0177	0.1560	0.1470	0.2120
19	1.25	30	0.9	0.0169	0.0161	0.0158	0.2950	0.2520	0.3470
16	1.25	30	13	0.0170	0.0161	0.0175	0.0444	0.0428	0.0535
13	1.25	30	13	0.0177	0.0182	0.0205	0.1400	0.1370	0.1920
7	1.25	30	25.1	0.0212	0.0189	0.0197	0.0206	0.0212	0.0290
20	1.25	41	13	0.0234	0.0241	0.0247	0.0194	0.0199	0.0244
4	2.075	30	13	0.0313	0.0342	0.0320	0.0291	0.0261	0.0294
14	0.5	40	2	0.1230	0.1210	0.0963	0.0894	0.0807	0.0913
9	0.5	40	24	0.1580	0.1520	0.1360	0.0561	0.0519	0.0650
11	2	20	2	0.6970	0.6750	0.5220	29.700	31.900	39.300
18	0.425	30	13	0.7470	0.6810	0.5110	0.1190	0.1220	0.1590
6	0.5	20	24	2.5800	2.1100	1.5500	2680.0	1900.0	1670.00
8	2	20	24	3.7300	3.1700	3.1100	60.400	68.800	249.000
3	0.5	20	2	357.00	285.00	104.00	1010.0	753.00	894.00

2.3.6 RSM optimization

Thus far, as analyzed in the result and discussion section of this chapter, the predictability of the CMC-dispersed coatings, whether it be the resistance behavior or the particle size analysis, became apparent. The workability and the uniformity of the CMC-dispersed matrix solutions are also confirmed experimentally, as the CMC-dispersed SWNTs did not plug the filters and the coatings did not exhibit non-uniformity. These characteristics were not observed for the PSS-dispersed solution, leading the author to select the CMC as a superior dispersant for dispersing SWNTs in aqueous solutions. Using the response surface methodology (RSM) design of experiment, the behavior of the coatings can be modeled for dried matrix resistances up to several thousand ohms. As an example, the optimization of RSM was conducted based on the target resistance of ~2000 Ω. The optimized parameters for two possible solutions of achieving this goal are shown in the table insert in Figure 62. The unshaded areas on this plot identify several combinations of SWNT to CMC ratios and sonication amplitudes which result in a resistance between 1000 to 2000 Ω. Figure 63 also shows the overlay of the optimum conditions for Solution 1 at ~0.67 SWNT:CMC ratio, sonication amplitude of ~40%, and sonication duration of 23 hr. This modeling is valid for formulation sonication amplitudes in the 30-40% range.



Solution	SWNT:CMC	Sonication amp (%)	Sonication durations (hr)	Resistance (ohm) Fit	Composite Desirability
1	0.67	40	23	1995[1]	1.00
2	0.67	40	2	2061	0.93

[1](95% CI : 1590, 2400)

Figure 62. The condition optimized for the CMC solution at 40% showing the region of optimum (unshaded region) in which a resistance between 1000 to 2000 Ω can be achieved. The table insert shows the condition optimized for achieving a resistance of 2000 Ω, based on the response surface design. Composite desirability values close to 1 shows higher accuracy of the fit.

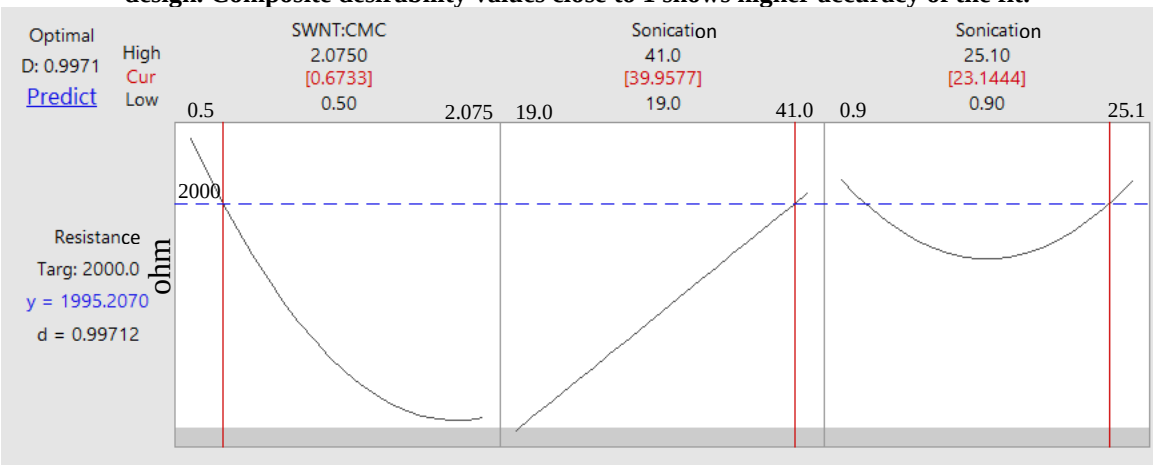


Figure 63. The main effect graph showing the optimized condition for achieving ~2000 ohm resistance using the CMC solution diluted to 40%. This figure refers to the Solution 1 in Figure 62 in order to achieve the target resistance of 2000 Ω, the parameters of SWNT:CMC, Sonication amp (%), and Sonication durations (hr) are set to 0.67, 40, and 23. Y axis represent resistance values (ohm).

2.4 Conclusion

Obtaining a uniform SWNT dispersion in aqueous solution using various sonication protocols along with poly(sodium 4-styrenesulfonate) (PSS) and carboxymethylcellulose (CMC) dispersants was investigated through a series of experiments designed with the aid of Response Surface Methodology (RSM). The resistance responses of the matrix solution formulations subjected to various conditions and coated and dried on UVO-treated PET substrate were modeled using this RSM design. The surface total free energy of the PET substrate used was increased from ~39 to 67 dyn/cm by UVO treatment for 5 minutes prior to use in these studies. From resistance measurements, the resistivity of the coatings was calculated by two methods, one using measured film thicknesses and the other using a thickness calculated from the mass of solids applied to the matrix film. The particle size distribution data using the dynamic light scattering technique was also correlated with the resistance response of each coating.

It was found that run 15 matrix solution (SWNT:CMC=2, sonication amplitude=40%, sonication duration=24 hr) resulted in dried matrix films with the lowest resistance (128 Ω) and possessed an average particle size of ~115 nm. In contrast, the largest particle size (81% of the particles have an average particle size of ~5000 nm) for the set of formulation experiments in which CMC was used was observed in Run 3 (SWNT:CMC=0.5, Sonication amplitude=20%, and sonication duration= 2 hr) in which the highest dried film resistance was obtained. This perhaps indicates that a lower SWNT:CMC ratio (lower conductive:insulating components) is contributing to larger SWNT particle size that together are contributing to higher film resistivity. Higher

concentration of dispersant in comparison with the SWNTs may result in the dispersant wrapping in multiple layers around SWNTs which will hinder electron transport of conductive carbon nanotubes. This may also create larger particles which results in the removal of SWNTs from the solution after filtrations. The sonication factor plays an important role in the dispersion and conductivity of SWNTs. The analysis of variance of the particle sizes obtained in the PSS-dispersed matrix solutions shows that the sonication amplitude and its interaction with the concentration of PSS and the sonication amplitude are the only significant factors (α=0.05) among all the factors. Moreover, the sonication duration is the most significant factor in the analysis of variance of the particle sizes obtained in the CMC-dispersed matrix solutions.

3D optical microscopy was performed on the dried matrix films to study the morphology and roughness of the dried films thickness of the coatings as well as to measure the thickness of the coatings. Profilometry of Run 3 (CMC-dispersed coating) at 100% (no dilution) showed an average roughness of 0.274 µm while profilometry of Run 15 at 100% (no dilution) showed an average roughness of 0.067 µm. The same trend was noted for matrix coatings at higher dilutions (70% and 40%). Therefore, increased particle size of the matrix formulations had a strong to correlation with increased roughness, and increased resistance of the CMC-dispersed coatings. Superior uniformity with low average roughness was observed for the coatings in which CMC was used as the dispersing agent in contrast to PSS.

The thickness of the coatings as measured by 3D optical microscope was found to decrease with the dilution of the matrix solution as would be expected due to reduced solids

content. As an example, the thickness of matrix coatings obtained from Run 15 of the formulation in which CMC was used as the dispersant at 100% (no dilution), 70% dilution, and 40% dilution was measured to be 3.86, 2.81, and 1.63 μm, respectively. Mass balance of each prepared solution was performed by determining the weight difference of the solids before and after the centrifugation and filtration and the thickness of the coatings after drying were calculated based on solids content, volume applied and areas. The results were compared with thickness measurements by the 3D optical microscope. The calculated values were found to be close to experimentally measured thickness measurements.

In conclusion, based on the coating quality and superior workability experimentally determined, CMC will be used in the matrix formulations as the dispersant for the next chapter (chapter 3) of this dissertation. An experiment will be designed to investigate several promising matrix formulations produced from stable SWNT/CMC dispersions in this chapter. Aliquots of the SWNT dispersion will be mixed with solutions of antibody, and glycerol. The resistance of dried matrix semi-solid films of these formulations with will be assessed with the same methodology and procedures as used in this chapter.

EFFECT OF ANTIBODY AND GLYCEROL ADDITION TO MATRIX FORMULATIONS

3.1 Objective

In chapter 2 of this dissertation, obtaining uniform SWNT dispersion in aqueous solution using various sonication protocols along with poly(sodium 4-styrenesulfonate) (PSS) and carboxymethylcellulose (CMC), two dispersing agents, and other components comprising sodium azide and phosphate buffer was studied. In this chapter, selected SWNT dispersions will be combined with antibody and other constituents (such as humectant glycerol) and deposited within test sensor channels, dried into a semi-solid/fluid film, and resistance tested using a constant microamp current. Once promising matrix solution formulations were identified, further characterizations were performed. These characterizations focused on selecting promising matrix films that could be further characterized by a combination of a 3D optical microscope (white light interferometer Contour GT-I) for profilometry, to look at gross features of the cured matrix layer formulation, and SEM to attempt to show physical interaction of micro-components of the formulations within the dried matrixes.

3.2 Methodology

3.2.1 Matrix formulation

3.2.1.1 Single-walled nano-tube (SWNT) dispersion

Three promising formulations from chapter 2 of this dissertation were selected based on the minimum resistance measurements obtained within each SWNT:CMC ratio categories (0.5, 1.25, and 2). The same procedures as explained in Research Phase 1 (Chapter 2) were employed to make 10 ml of each of these three solutions. These solutions were then used as the stock solutions for this research phase of the dissertation.

3.2.1.2 Matrix formulation materials (with SWNT, CMC, antibody and glycerol)

The purpose of the experiments in chapter 2 was to find matrix film formulations that had a dried resistance of less than 2000 ohms and to correlate resistance with film properties. Three matrix formulations produced from stable SWNT dispersions in phase 1 research (Chapter 2) were selected. Aliquots of the SWNT dispersion were mixed with solutions of antibody and glycerol. The resistance of dried matrix semi-solid films of these formulations with antibody was assessed with the same procedure as mentioned in in phase 1 research. Matrix formulation parameters investigated were:

1. Three composition ratios (1:1, 1:1.6, 1:4) of two matrix components (SWNT:glycerol);

2. Four levels of antibody (rabbit anti-mouse IgG), (1:0.1, 1:0.014, 1:0.0075) (SWNT:Ab);

3. And two different matrix film thicknesses achieved by using 100% strength formulations and dilution of formulations with water to 25% (75% dilution).

The dried channel matrices produced in this phase of the dissertation contained rabbit anti-mouse IgG – as this is a relatively inexpensive antibody to work with (all IgG antibodies have a molecular weight of ~150,000 daltons). In all cases the matrix antibody is physically adsorbed onto and entrapped by the nanotube matrix. The sensor and formulation materials needed for this study are presented in Table 2 (Research Phase 1). In addition, antibody (Sigma Aldrich) I-5006 rabbit anti-mouse-IgG and Glycerol (Sigma Aldrich) were used to prepare the matrix formulation for Research Phase 2.

Aliquots of dispersed nanotubes in solution (0.15 ml) were deposited on the test channels (see Figure 21 and Figure 22 and Figure 23) and let dry in a desiccant chamber. Two different matrix film thicknesses based on the theoretically calculated densities of the varying components in the formulations for the remaining solids (SWNT and CMC) was achieved by preparing diluted aliquots of the dispersions prepared in this section at 100% (no dilution), and 25 % (75% dilution) using water before coating.

The resistance of all matrix-coated plates/channels was measured following drying in a desiccant chamber.

3.2.2 RSM

In this experiment, the design was composed of two factors (SWNT:Glycerol ratio, and SWNT:antibody ratio), each with two levels (low, high), and a total of 13 runs were carried out to optimize the chosen variables. For the purpose of statistical computations,

the two independent variables were denoted as x_1, and x_2, respectively. The range of the values used for the levels of each factor investigated in the experiments was selected based on the preliminary experiments and are listed in Table 22. The quadratic equation can be used for this methodology to fit the response variables:

$$Y = \beta_0 + \sum_{i=1}^{k} k\, \beta_i x_i + \sum_{i=1}^{k} \beta_{ii}\, x_i^2 + \sum_{i}^{i<j} \sum_{j} \beta_{ij} x_i\, x_j \qquad (15)$$

where Y, k, β_0, β_i, β_{ii}, and β_{ij} are the predicted response variable, number of variables, a constant term, coefficients of the linear parameters, coefficients of the quadratic parameters, and coefficients of the interaction parameters, respectively. The coefficient of determination (R^2) can be estimated to test the certainty of the above polynomial model [151]. In this dissertation, RSM was employed to investigate the effect of SWNT:Glycerol ratio, and SWNT:antibody on the resistance of the prepared matrix solutions.

Table 22- Factors and levels used in this experimental design (DOE)

Factor	Low level (-1)	High level (+1)
SWNT:Glycerol (X_1)	0.25	1
SWNT:antibody (X_2)	10	133

Different mixtures using SWNT:Glycerol and SWNT:Antibody ratios were prepared for select matrix formulations developed in research phase 1 (formulations 12, 14, and 17 using CMC) and mixed with different ratios of SWNT:Glycerol (0.25 and 1) and SWNT:antibody (10 and 133). The matrix preparation parameters were set according to the response surface methodology (RSM) experimental design, with the parameters

tabulated in Table 23 through Table 28. Dilution of the prepared solutions (diluted to 25%), as explained earlier, and 0.15 ml of the resulting solutions were deposited into designated channels (in duplicate). The prepared templates were then dried in a desiccant chamber for 48 hr. Subsequently, the surface profile of the select dried matrix was obtained and analyzed.

Table 23- The design of experiment based on RSM showing the factor levels and their responses. The two independent variables were denoted as x_1, and x_2, which represent SWNT:Glycerol, and SWNT:antibody, respectively for the CMC Run 12 matrix solution (SWNT:CMC= 2, Sonication amp (%)=40, Sonication durations (h)=2) at 100% (no dilution)

Runs	***X_1 (SWNT:GLY)***	***X_2 (SWNT:Ab)***	***Resistance (ohm)***	***Predicted Resistance (ohm) (eq. 16)***
12-1	0.625	71.7	1827	2294
12-2	0.625	71.7	2322	2294
12-3	0.25	10.0	180753	145507
12-4	0.625	10.0	5283	4965
12-5	0.625	71.7	2421	2294
12-6	1	133.3	474	792
12-7	0.625	71.7	1902	2294
12-8	0.25	71.7	32026	3956*
12-9	1	71.7	1265	629
12-10	0.625	133.3	1634	1316
12-11	1	10.0	1841	2159
12-12	0.25	133.3	14718	*1841**
12-13	0.625	71.	2362	2294

*Fitted values in italic denotes an extremely unusual point relative to predictor levels used to fit the model

Table 24- The design of experiment based on RSM showing the factor levels and their responses. The two independent variables were denoted as x1, and x2, which represent SWNT:Glycerol, and SWNT:antibody, respectively for the CMC Run 12 matrix solution (SWNT:CMC= 2, Sonication amp (%)=40, Sonication durations (h)=2) diluted to 25%.

Runs	***X_1 (SWNT:GLY)***	***X_2 (SWNT:Ab)***	***Resistance (ohm)***	***Predicted Resistance (ohm) (eq. 17)***
12-1	0.625	71.7	3804	5869
12-2	0.625	71.7	7452	5869
12-3	0.25	10.0	184197	179903
12-4	0.625	10.0	6753	5869

Table 24 - continue

12-5	0.625	71.7	4355	5869
12-6	1	133.3	1135	1295
12-7	0.625	71.7	6753	5869
12-8	0.25	71.7	135247	*8666**
12-9	1	71.7	3392	3073
12-10	0.625	133.3	5637	5869
12-11	1	10.0	4692	4852
12-12	0.25	133.3	38606	*10443**
12-13	0.625	71.7	6331	5869

*Fitted values in italic denotes an extremely unusual point relative to predictor levels used to fit the model

Table 25- The design of experiment based on RSM showing the factor levels and their responses. The two independent variables were denoted as x_1, and x_2, which represent SWNT:Glycerol, and SWNT:antibody, respectively for the CMC Run 14 matrix solution (SWNT:CMC= 0.5, Sonication amp (%)=40, Sonication durations (h)=2) at 100% (no dilution)

Runs	***X_1 (SWNT:GLY)***	***X_2 (SWNT:Ab)***	***Resistance (ohm)***	***Predicted Resistance (ohm) (eq. 18)***
14-1	0.625	71.7	43576	45248
14-2	0.625	71.7	64756	45248
14-3	0.25	10.0	1650440	1283512
14-4	0.625	10.0	138495	145292
14-5	0.625	71.7	57602	45248
14-6	1	133.3	108749	4337*
14-7	0.625	71.7	28654	45248
14-8	0.25	71.7	4337	4337
14-9	1	71.7	5727	19322
14-10	0.625	133.3	8738	15535
14-11	1	10.0	13822	7024
14-12	0.25	133.3	97941	*137666*
14-13	0.625	71.7	17777	*45211*

*Fitted values in italic denotes an extremely unusual point relative to predictor levels used to fit the model

Table 26- The design of experiment based on RSM showing the factor levels and their responses. The two independent variables were denoted as x1, and x2, which represent SWNT:Glycerol, and SWNT:antibody, respectively for the CMC Run 14 matrix solution (SWNT:CMC= 0.5, Sonication amp (%)=40, Sonication durations (h)=2) diluted to 25%.

Runs	***X_1 (SWNT:GLY)***	***X_2 (SWNT:Ab)***	***Resistance (ohm)***	***Predicted Resistance (ohm) (eq. 19)***
14-1	0.625	71.7	17574	17838
14-2	0.625	71.7	21209	17838
14-3	0.25	10.0	356148	292113

Table 26 - continue

14-4	0.625	10.0	60731	142287
14-5	0.625	71.7	21104	17838
14-6	1	133.3	9190	7557
14-7	0.625	71.7	20363	17838
14-8	0.25	71.7	51550	*28118*
14-9	1	71.7	6862	7557
14-10	0.625	133.3	9890	17838
14-11	1	10.0	9983	7557
14-12	0.25	133.3	31483	28119
14-13	0.625	71.7	10159	17838

*Fitted values in italic denotes an extremely unusual point relative to predictor levels used to fit the model

Table 27- The design of experiment based on RSM showing the factor levels and their responses. The two independent variables were denoted as x_1, and x_2, which represent SWNT:Glycerol, and SWNT:antibody, respectively for the CMC Run 17 matrix solution (SWNT:CMC= 1.25, Sonication amp (%)=30, Sonication durations (h)=13) at 100% (no dilution)

Runs	***X_1 (SWNT:GLY)***	***X_2 (SWNT:Ab)***	***Resistance (ohm)***	***Predicted Resistance (ohm) (eq. 20)***
17-1	0.625	71.7	16360	21645
17-2	0.625	71.7	21138	21645
17-3	0.25	10.0	968476	921401
17-4	0.625	10.0	46313	43557
17-5	0.625	71.7	27339	21645
17-6	1	133.3	4162	3835
17-7	0.625	71.7	22043	21645
17-8	0.25	71.7	702175	*37042**
17-9	1	71.7	5570	6224
17-10	0.625	133.3	2488	*268*
17-11	1	10.0	8939	8612
17-12	0.25	133.3	551042	*4350**
17-13	0.625	71.7	15832	21645

*Fitted values in italic denotes an extremely unusual point relative to predictor levels used to fit the model

Table 28- The design of experiment based on RSM showing the factor levels and their responses. The two independent variables were denoted as x1, and x2, which represent SWNT:Glycerol, and SWNT:antibody, respectively for the CMC Run 17 matrix solution (SWNT:CMC= 1.25, Sonication amp (%)=30, Sonication durations (h)=13) diluted to 25%.

Runs	***X_1 (SWNT:GLY)***	***X_2 (SWNT:Ab)***	***Resistance (ohm)***	***Predicted Resistance (ohm) (eq. 21)***
17-1	0.625	71.7	59871	101831
17-2	0.625	71.7	273081	*23543*

Table 28 - continued

17-3	0.25	10.0	1376718	1041319
17-4	0.625	10.0	175400	101831
17-5	0.625	71.7	131665	101831
17-6	1	133.3	11912	23544
17-7	0.625	71.7	80214	*101831*
17-8	0.25	71.7	215690	101831
17-9	1	71.7	13971	23544
17-10	0.625	133.3	25774	101831
17-11	1	10.0	21869	23544
17-12	0.25	133.3	46424	23544
17-13	0.625	71.7	138061	101831

*Fitted values in italic denotes an extremely unusual point relative to predictor levels used to fit the model

3.3 Results and Discussion

3.3.1 Matrix solution selection

The stock matrix solution was selected based on the minimum resistance and minimum sonication duration for each SWNT to CMC ratios from the experiments in phase 1 research. Considering the factors mentioned and the resistance results from Table 4 trough Table 9, Run 14 was selected from set matrix solutions in which SWNT:CMC ratio was 0.5. Run 17 was selected from set matrix solutions in which SWNT:CMC ratio was 1.25. Run 12 was selected from set matrix solutions in which SWNT:CMC ratio was 2. *These selected solution will be referred to as CMC-14* (SWNT:CMC= 0.5, Sonication amp (%)=40, Sonication durations (h)=2), *CMC-17* (SWNT:CMC= 1.25, Sonication amp (%)=30, Sonication durations (h)=13), *and CMC-12* (SWNT:CMC= 2, Sonication amp (%)=40, Sonication durations (h)=2), *respectively, for phase 2 research discussion.* The corresponding resistance results were 1069, 794, and 148 Ω, respectively. The surface profile of run 12, 14, and 17 at 100%, 70%, and 40% is shown in Figure 64 through Figure 72. As mentioned earlier in phase 1, the surface roughness of the samples decreases with

the increase in the dilutions Table 29. This fact can also be observed of the samples from Run 12, 14, and 17.

Table 29- Summary of coating thickness and roughness of the selected matrix formulations from research phase 1.

	dilution	roughness (µm)	Thickness* (µm)	roughness/thickness ratio	Resistance (ohm)
CMC-12 (SWNT:CMC= 2, Sonication amp (%)=40, Sonication durations (h)=2)	100%	0.220	3.56	0.062	148
CMC-12	70%	0.189	2.49	0.076	202
CMC-12	40%	0.119	1.42	0.084	372
CMC-14 (SWNT:CMC= 0.5, Sonication amp (%)=40, Sonication durations (h)=2)	100%	0.258	4.60	0.056	1069
CMC-14	70%	0.208	3.22	0.065	1498
CMC-14	40%	0.168	1.84	0.091	2095
CMC-17 (SWNT:CMC= 1.25, Sonication amp (%)=30, Sonication durations (h)=13)	100%	0.113	4.19	0.027	147
CMC-17	70%	0.102	2.93	0.035	195
CMC-17	40%	0.066	1.68	0.039	423

**calculated thickness based on mass balance as described in chapter 2*

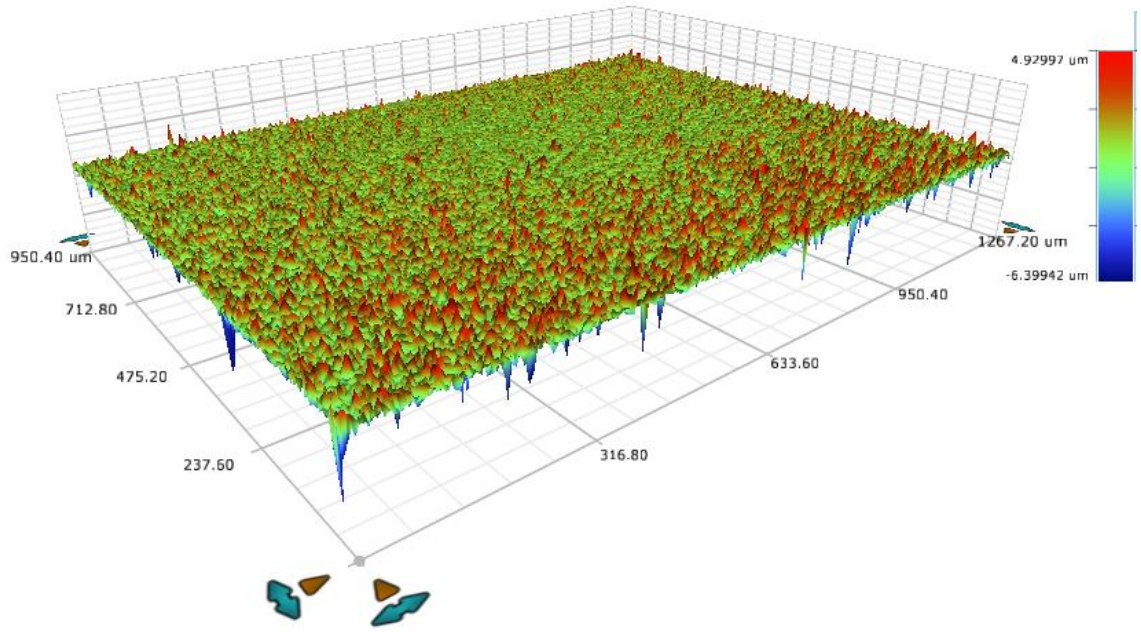


Figure 64. Profilometry of Run 12, showing a uniform CMC-dispersed coating at 100% (no dilution) with an average roughness of 0.220 µm.

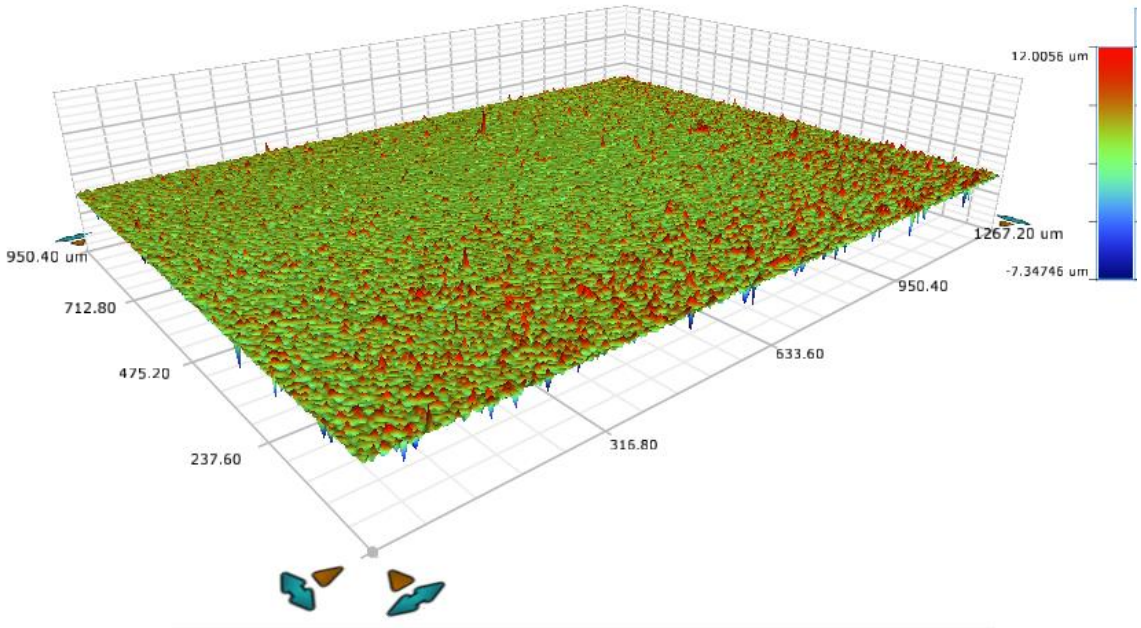


Figure 65. Profilometry of Run 12, showing a uniform CMC-dispersed coating diluted to 70% with an average roughness of 0.189 µm.

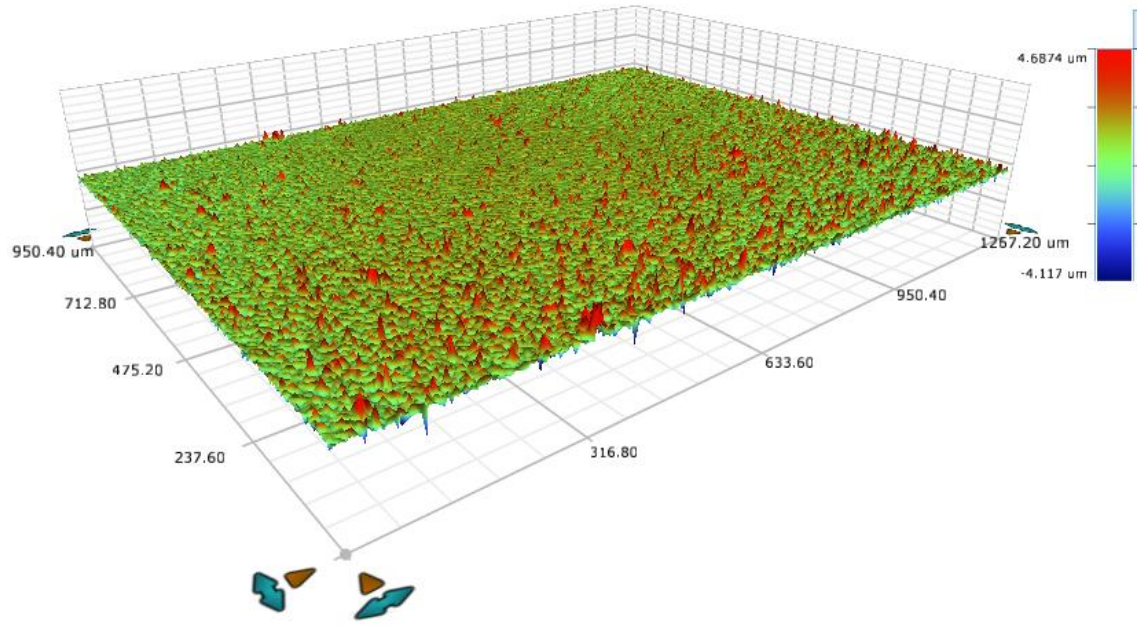


Figure 66. Profilometry of Run 12, showing a uniform CMC-dispersed coating diluted to 40% with an average roughness of 0.119 µm.

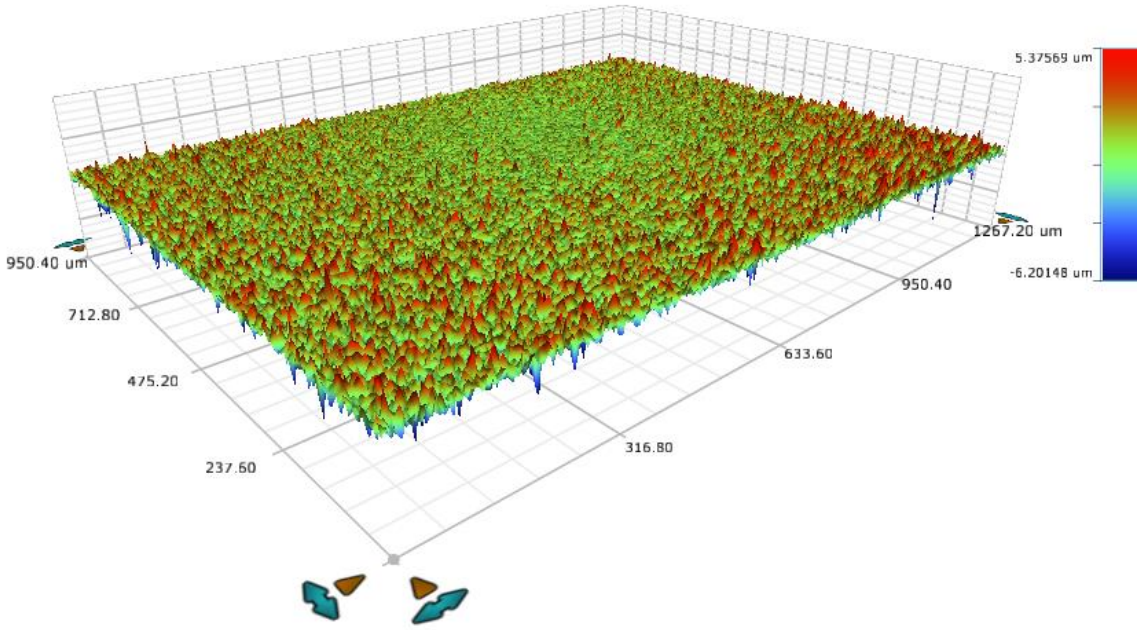


Figure 67. Profilometry of Run 14, showing a uniform CMC-dispersed coating at 100% (no dilution) with an average roughness of 0.258 µm.

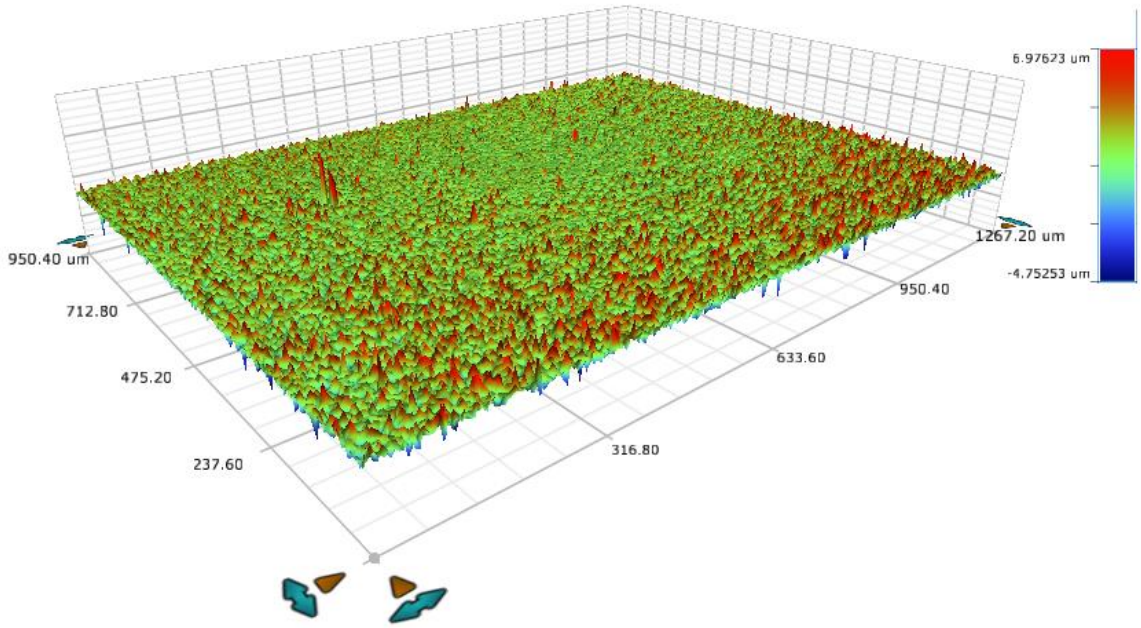


Figure 68. Profilometry of Run 14, showing a uniform CMC-dispersed coating diluted to 70% with an average roughness of 0.208 µm.

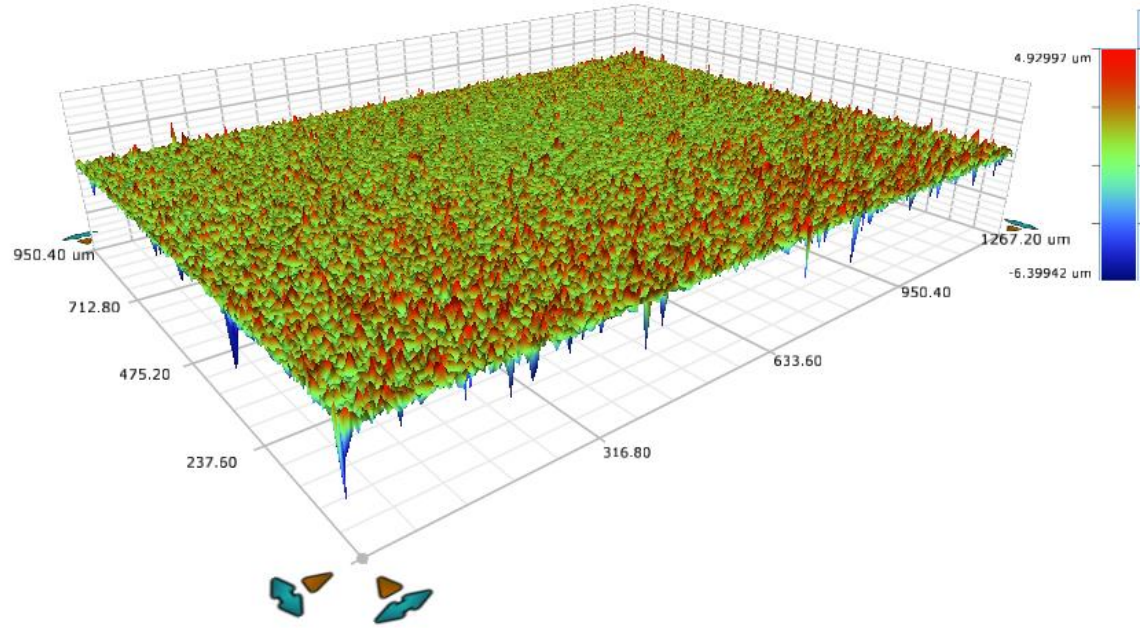


Figure 69. Profilometry of Run 14, showing a uniform CMC-dispersed coating diluted to 40% with an average roughness of 0.168 µm.

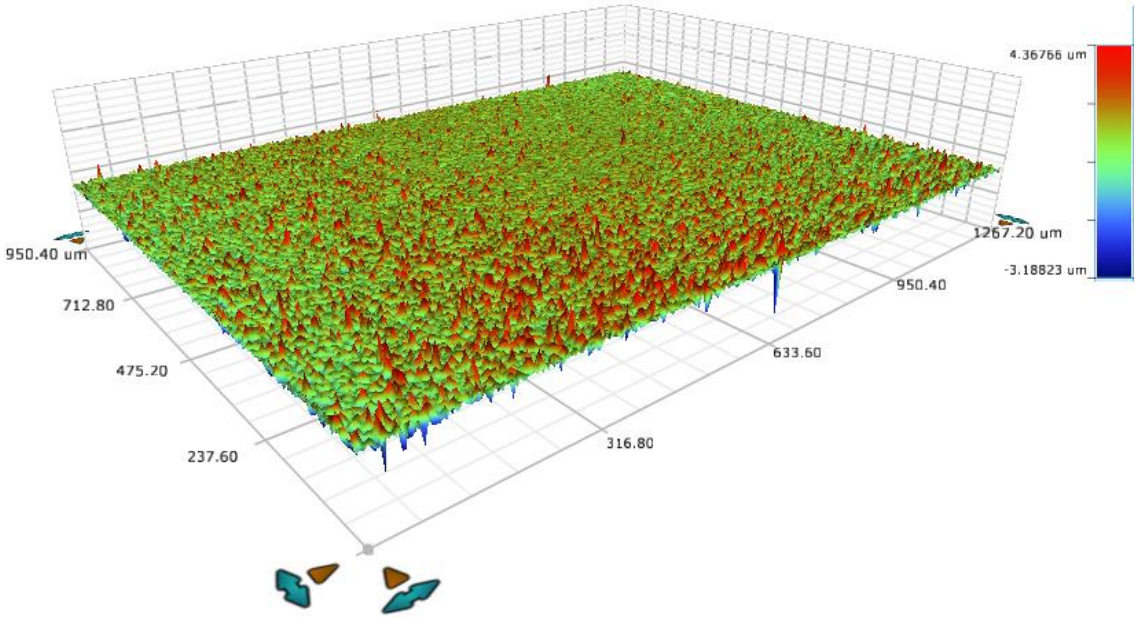


Figure 70. Profilometry of Run 17, showing a uniform CMC-dispersed coating at 100% (no dilution) with an average roughness of 0.113 µm.

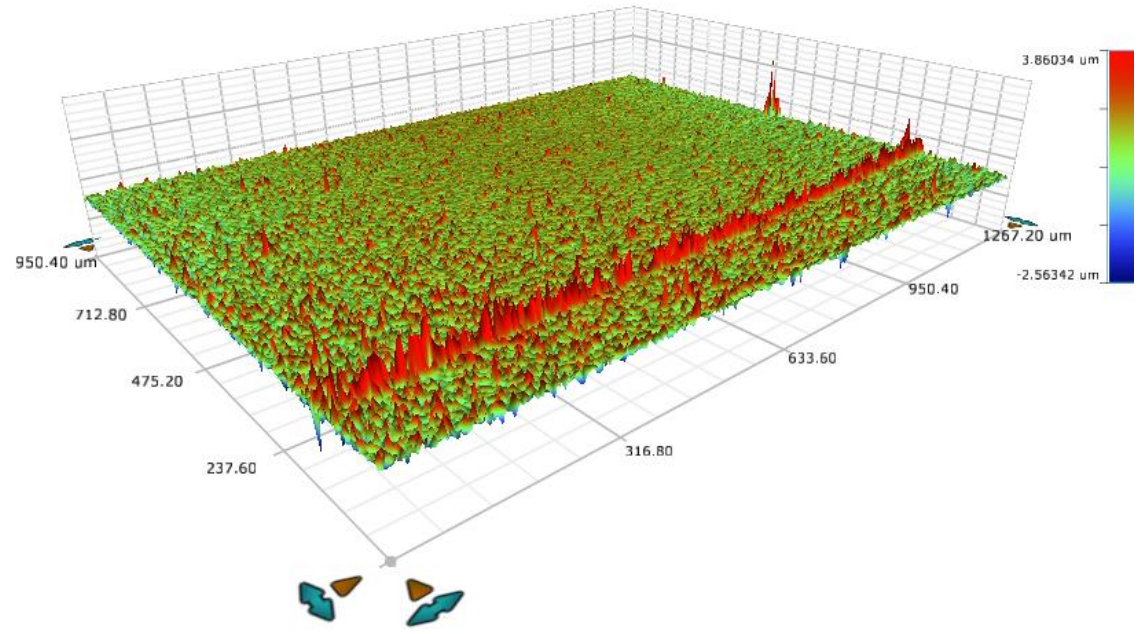


Figure 71. Profilometry of Run 17, showing a uniform CMC-dispersed coating diluted to 70% with an average roughness of 0.102 µm.

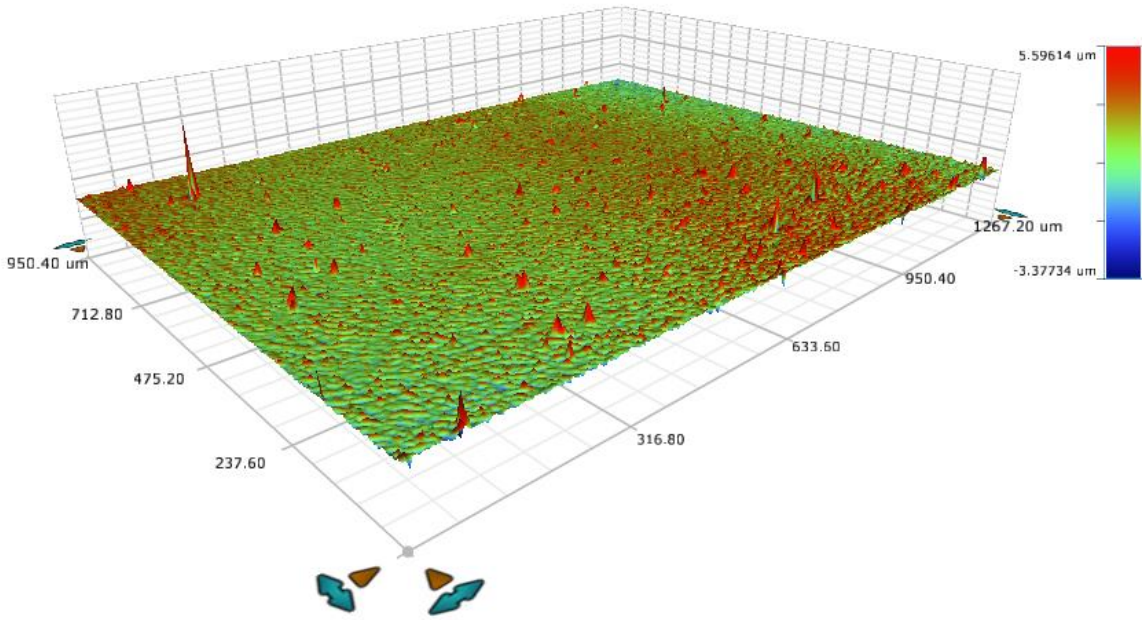


Figure 72. Profilometry of Run 17, showing a uniform CMC-dispersed coating diluted to 40% with an average roughness of 0.066 µm.

3.3.2 Resistance response analysis of variance

The dimensions of the test templates are all equal for all of the experiments, enabling us to use the resistance results as the basis of the electrical properties comparison for all the experiments. The minimum average resistance of 474 Ω for the set of experiments in which formulation CMC-12 was used at 100% (no dilution) was noted in Run 12-6 (see Table 23, 12-6) corresponding to the minimum concentration of glycerol and antibody at: SWNT:Gly ratio of 1, SWNT:Ab ratio of 133. The maximum average resistance of 1.65 MΩ for the set of experiments in which formulation CMC-14 was used at 100% was noted in Run 12-3 (see Table 25) corresponding to the maximum concentration of glycerol and antibody at: SWNT:Gly ratio of 0.25, and SWNT:Ab ratio

of 10. These results show that increasing concentrations of both glycerol and antibody increases the resistance of the matrix film.

The analysis of variance, presented in Table 30 through Table 35, shows that the resistance of the matrix solutions containing CMC as the dispersant are significantly dependent on the SWNT:Gly, and SWNT:Ab ratios as well as the interaction terms. Considering the t-statistics for each model term and the provisions of the RSM, the following models were generated from the data (coded values) and can be used to fit the resistance responses:

12 at 100% (no dilution):

$$\text{Resistance (ohm)} = 277540 - 546895\,X_1 - 1575\,X_2 + 255837\,X_1{\times}X_1 + 1780\,X_1{\times}X_2 \quad (16)$$

12 diluted to 25%

$$\text{Resistance (ohm)} = 354379 - 757014\,X_1 - 1366\,X_2 + 393546\,X_1{\times}X_1 + 1536\,X_1{\times}X_2 \quad (17)$$

14 at 100%

$$\text{Resistance (ohm)} = 1999590 - 1998354\,X_1 - 26903\,X_2 + 80.1\,X_2{\times}X_2 + 17811\,X_1{\times}X_2 \quad (18)$$

14 diluted to 25%

$$\text{Resistance (ohm)} = 444497 - 434550\,X_1 - 5403\,X_2 + 15.33\,X_2{\times}X_2 + 3501\,X_1{\times}X_2 \quad (19)$$

17 at 100%

$$\text{Resistance (ohm)} = 1900768 - 4425497\,X_1 - 4048\,X_2 + 2501328\,X_1{\times}X_1 + 4461\,X_1{\times}X_2 \quad (20)$$

17 diluted to 25%

$$\text{Resistance (ohm)} = 1567645 - 1730114\,X_1 - 12948\,X_2 + 14274\,X_1{\times}X_2 \quad (21)$$

Table 30- Analysis of variance for the resistance and particle size of the samples obtained under various preparation conditions for the CMC-12 matrix solution at 100% (no dilution)

	Resistance (ohm)		
Source	DF	F-Value	P-Value
Model	4	9.16	0.004
Linear	2	9.84	0.007
SWNT:GLY	1	12.34	0.008
SWNT:Ab	1	7.35	0.027
Square	1	6.37	0.036
SWNT:GLY*SWNT:GLY	1	6.37	0.036
2-Way Interaction	1	10.57	0.012
SWNT:GLY*SWNT:Ab	1	10.57	0.012

Table 31- Analysis of variance for the resistance and particle size of the samples obtained under various preparation conditions for the CMC-12 matrix solution diluted to 25%

	Resistance (ohm)		
Source	DF	F-Value	P-Value
Model	4	24.78	0.001
Linear	2	29.98	0.001
SWNT:GLY	1	50.37	0.001
SWNT:Ab	1	9.58	0.006
Square	1	25.35	0.001
SWNT:GLY*SWNT:GLY	1	25.35	0.001
2-Way Interaction	1	13.8	0.003
SWNT:GLY*SWNT:Ab	1	13.8	0.003

Table 32- Analysis of variance for the resistance and particle size of the samples obtained under various preparation conditions for the CMC-14 matrix solution at 100% (no dilution)

	Resistance (ohm)		
Source	DF	F-Value	P-Value
Model	4	17.45	0.012
Linear	2	18.73	0.023
SWNT:GLY	1	24	0.035
SWNT:Ab	1	13.46	0.039
Square	1	12.57	0.071
SWNT:GLY*SWNT:GLY	1	12.57	0.071
2-Way Interaction	1	19.78	0.014
SWNT:GLY*SWNT:Ab	1	19.78	0.014

Table 33- Analysis of variance for the resistance and particle size of the samples obtained under various preparation conditions for the CMC-14 matrix solution diluted to 25%

	Resistance (ohm)		
Source	DF	F-Value	P-Value
Model	4	8.46	0.003
Linear	2	9.37	0.004
SWNT:GLY	1	9.83	0.006
SWNT:Ab	1	8.92	0.010
Square	1	4.19	0.052
SWNT:GLY*SWNT:GLY	1	4.19	0.052
2-Way Interaction	1	10.93	0.008
SWNT:GLY*SWNT:Ab	1	10.93	0.008

Table 34- Analysis of variance for the resistance and particle size of the samples obtained under various preparation conditions for the CMC-17 matrix solution at 100% (no dilution)

	Resistance (ohm)		
Source	DF	F-Value	P-Value
Model	4	118.13	0.001
Linear	2	153.31	0.001
SWNT:GLY	1	291.23	0.001
SWNT:Ab	1	15.39	0.001
Square	1	145.05	0.001
SWNT:GLY*SWNT:GLY	1	145.05	0.001
2-Way Interaction	1	20.87	0.001
SWNT:GLY*SWNT:Ab	1	20.87	0.001

Table 35- Analysis of variance for the resistance and particle size of the samples obtained under various preparation conditions for the CMC-17 matrix solution diluted to 25%

	Resistance (ohm)		
Source	DF	F-Value	P-Value
Model	4	40.47	0.001
Linear	2	52.55	0.001
SWNT:GLY	1	68.33	0.001
SWNT:Ab	1	36.78	0.001
Square	1	18.34	0.003
SWNT:GLY*SWNT:GLY	1	18.34	0.003
2-Way Interaction	1	38.43	0.001
SWNT:GLY*SWNT:Ab	1	38.43	0.001

The surface and contour plots of the most significant process parameters are presented in Figure 73 to Figure 78. These figures show the effect of each factor on the resistance of the matrix solution. In general, the higher the SWNT:Glycerol/Antibody ratio, the lower the resistance of the corresponding matrix solution. This seems logical as more glycerol or antibody should act as insulator-like materials (low-conductivity) between SWNT-to-SWNT contacts. Table 36 shows the predicted resistances using the regression models equations (16) – (21) and the measured experimental resistances for select coatings. The predicted resistance values are in close agreement with the measured resistance for matrix solutions diluted to 25% as well as matrix solutions at no dilutions (100%) in majority of cases. Therefore, the fitted model can be used to predict the relative magnitude of the resistance of the dried matrix coatings.

Table 36- Comparison of the coatings' measured resistance and predicted resistance for select coatings

				Resistance (Ω)			**Predicted Resistance (ohm)**		
Run	SWNT:GLY	SWNT:Ab	dilution	CMC-12	CMC-17	CMC-14	CMC-12	CMC-17	CMC-14
3	0.25	10	100%	180753	968476	1650440	145507	921401	1283512
4	0.625	10	100%	5283	46313	138495	4965	43557	145292
11	1	10	100%	1841	8939	13822	2159	8612	7024
	∞	∞	100%	148	147	1069			
11	1	10	100%	1841	8939	13822	2159	8612	7024
9	1	71	100%	1265	5570	5727	629	6224	19322
6	1	133	100%	474	4162	4337	792	3835	4337
	∞	∞	100%	148	147	1069			
3	0.25	10	25%	184197	1376718	356148	179903	1041319	292113
4	0.625	10	25%	6753	175400	60731	5869	101831	142287
11	1	10	25%	4692	21869	9983	4852	23544	7557
	∞	∞	25%	n.d.	n.d.	n.d.			
		SWNT:CMC ratio =		**2.00**	**1.25**	**0.50**	**2.00**	**1.25**	**0.50**

Figure 73. Contour plots and three-dimensional response surface of the resistance response for CMC-12 (SWNT:CMC= 2, Sonication amp (%)=40, Sonication durations (h)=2) at 100% (no dilution)

Figure 74. Contour plots and three-dimensional response surface of the resistance response for CMC-12 (SWNT:CMC= 2, Sonication amp (%)=40, Sonication durations (h)=2) diluted to 25%

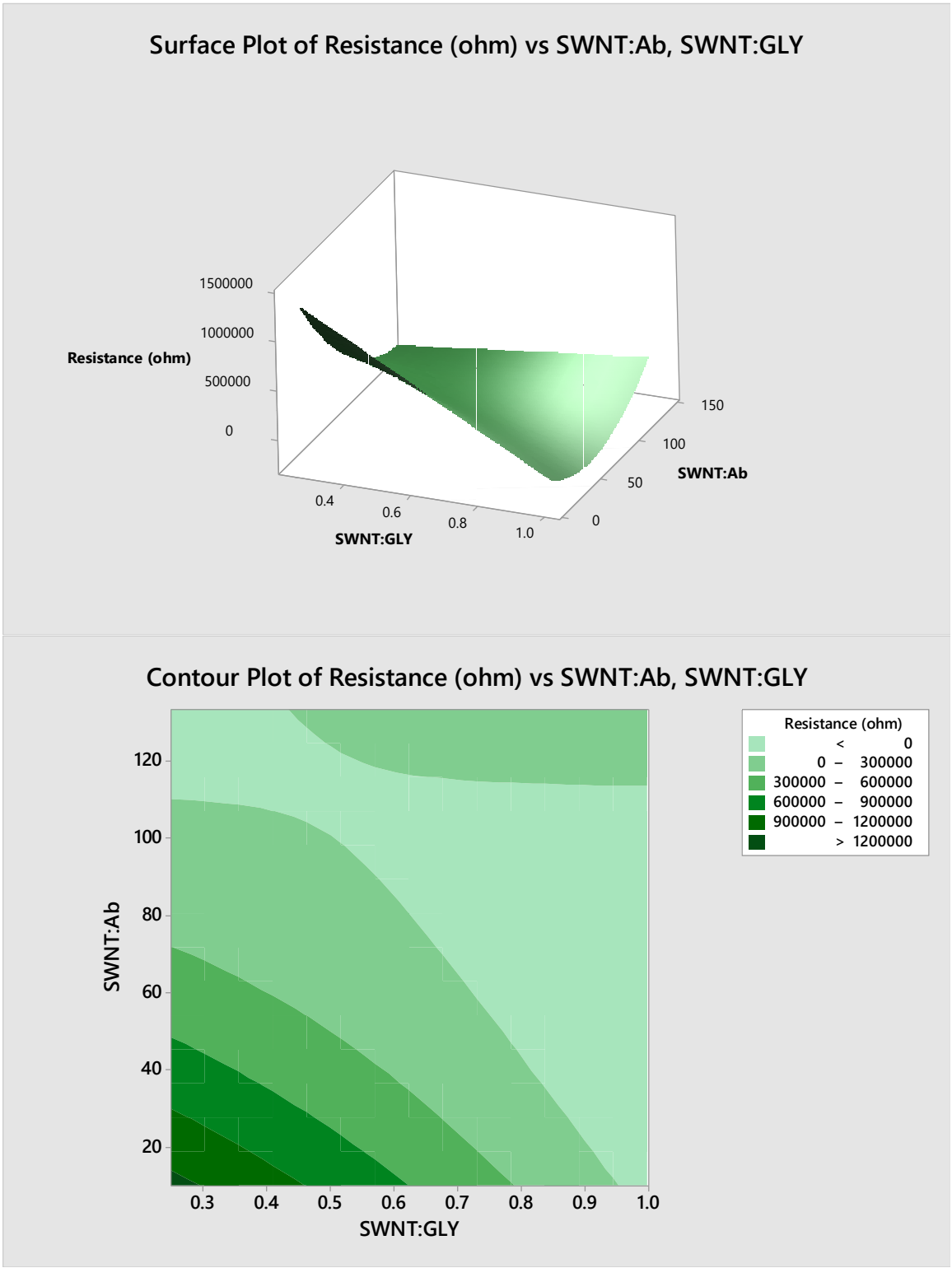


Figure 75. Contour plots and three-dimensional response surface of the resistance response for CMC-14 (SWNT:CMC= 0.5, Sonication amp (%)=40, Sonication durations (h)=2) at 100% (no dilution)

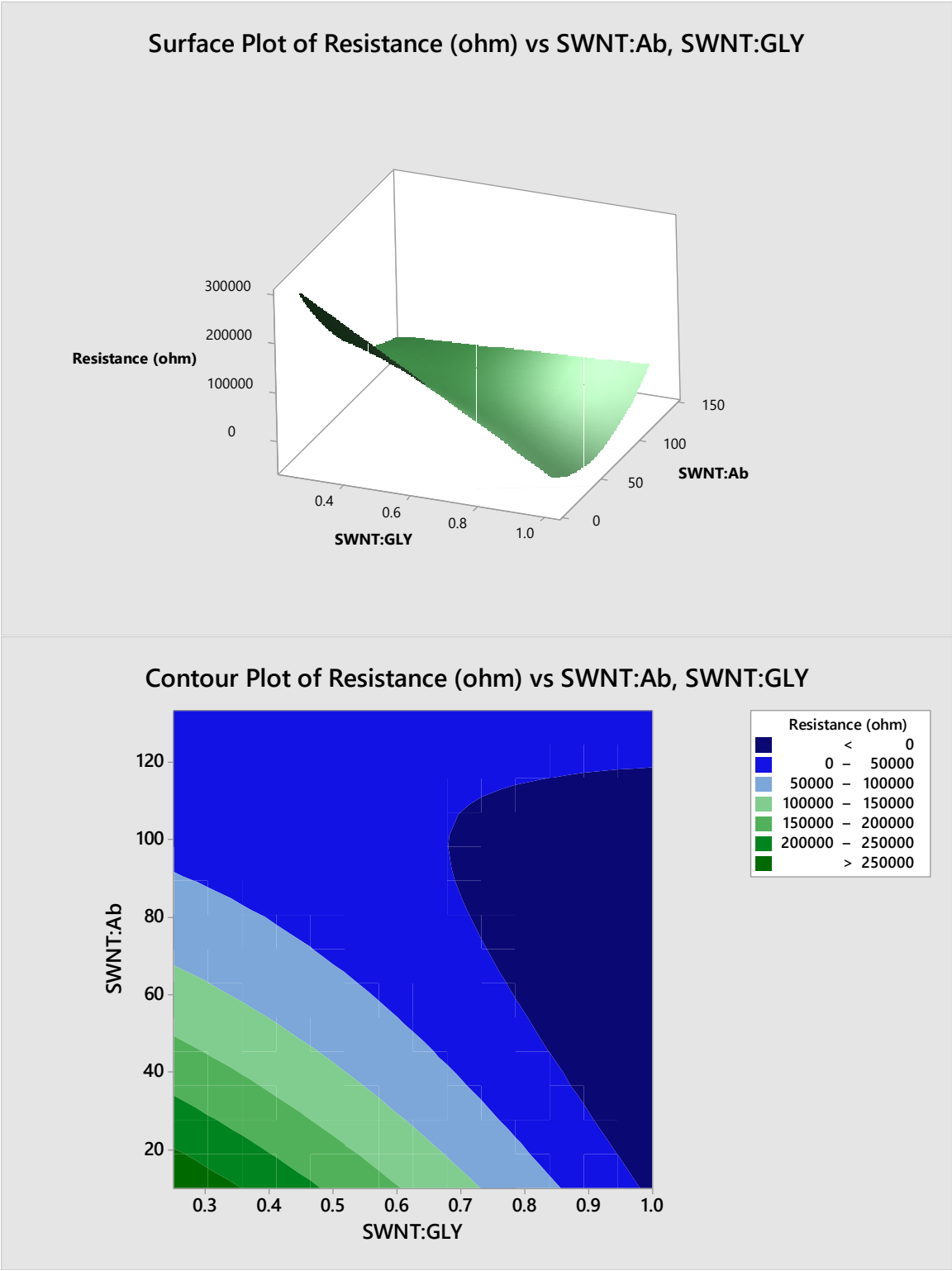


Figure 76. Contour plots and three-dimensional response surface of the resistance response for CMC-14 (SWNT:CMC= 0.5, Sonication amp (%)=40, Sonication durations (h)=2) diluted to 25%

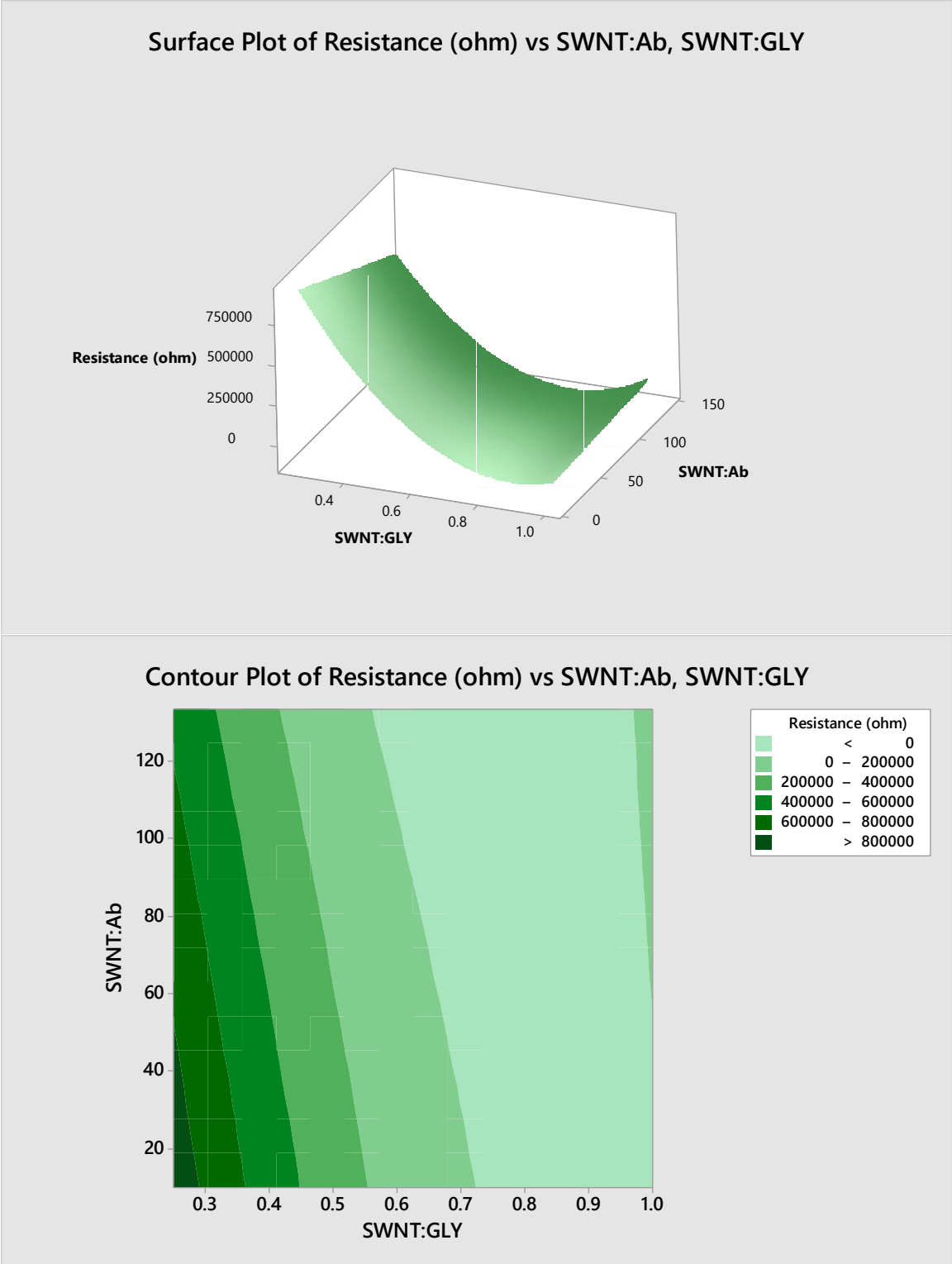


Figure 77. Contour plots and three-dimensional response surface of the resistance response for CMC-17 (SWNT:CMC= 1.25, Sonication amp (%)=30, Sonication durations (h)=13) at 100% (no dilution)

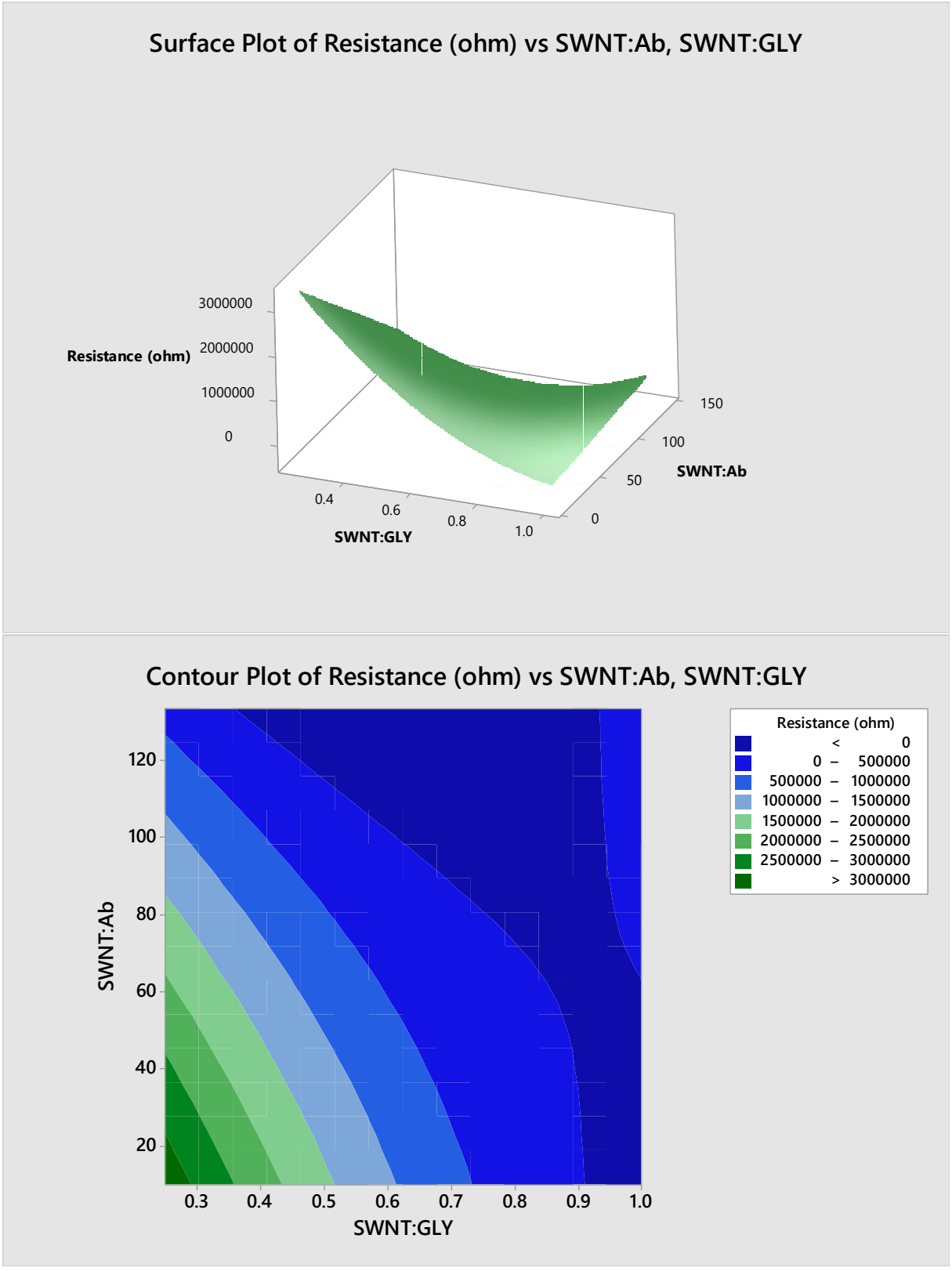


Figure 78. Contour plots and three-dimensional response surface of the resistance response for CMC-17 (SWNT:CMC= 1.25, Sonication amp (%)=30, Sonication durations (h)=13) diluted to 25%

3.3.3 Surface profile

The topography of the deposited matrix solutions in the channels was investigated using an optical profiler.

The average surface roughnesses of selected coatings are presented in Table 37 for comparison. In this table the coatings prepared from CMC-12, 17 and 14 formulations with select SWNT:Glycerol ratios, SWNT:antibody ratios, and water dilution were compared. The surface profile of the set of experiments in which CMC-12, CMC-14, and CMC-17 matrix formulations, at 100% (no dilution), and 25% dilution are presented in Figure 79 through Figure 94. From Table 37 and Figure 79 - Figure 94, the lowest resistances can be observed for the set of experiments in which the CMC-12 solution was used (see Table 23). The set of experiments in which solution CMC-17 was used resulted in the midrange resistances (see Table 25 and Table 37). CMC-14 solutions resulted in set of matrix samples with the highest resistances (see Table 27 and Table 37). It is important to note from these tables that the average roughness of the samples decreased with a decrease in the glycerol concentration. The roughness of the samples also decreased with an increase in the concentration of antibody. This is probably because antibody molecules can further disperse carbon nanotubes and therefore, they decrease aggregation, leading to a smoother surface. The roughness of the coating also decreased with matrix dilution. Interesting CMC-14 resistances decreased with dilution unlike other formulations and contrary to logic.

Table 37- Comparison of the coatings' average roughness and its effect on resistance for select coatings

				Resistance (Ω)			Roughness (µm)		
Run	SWNT:GLY	SWNT:Ab	dilution	CMC-12	CMC-17	CMC-14	CMC-12	CMC-17	**CMC-14**
3	0.25	10	100%	180753	968476	1650440	1.048		
4	0.625	10	100%	5283	46313	138495	0.816		
11	1	10	100%	1841	8939	13822	0.740	0.611	**0.504**
	∞	∞	100%	148	147	1069	0.220	0.113	**0.258**
11	1	10	100%	1841	8939	13822	0.740	0.611	**0.504**
9	1	71	100%	1265	5570	5727	0.624	0.455	**0.432**
6	1	133	100%	474	4162	4337	0.449	0.419	**0.387**
	∞	∞	100%	148	147	1069	0.220	0.113	**0.258**
3	0.25	10	25%	184197	1376718	356148	0.583		
4	0.625	10	25%	6753	175400	60731	0.424		
11	1	10	25%	4692	21869	9983	0.412	0.285	**0.192**
	∞	∞	25%	n.d.	n.d.	n.d.	n.d.	n.d.	**n.d.**
		SWNT:CMC ratio =		**2.00**	**1.25**	**0.50**	**2.00**	**1.25**	**0.50**

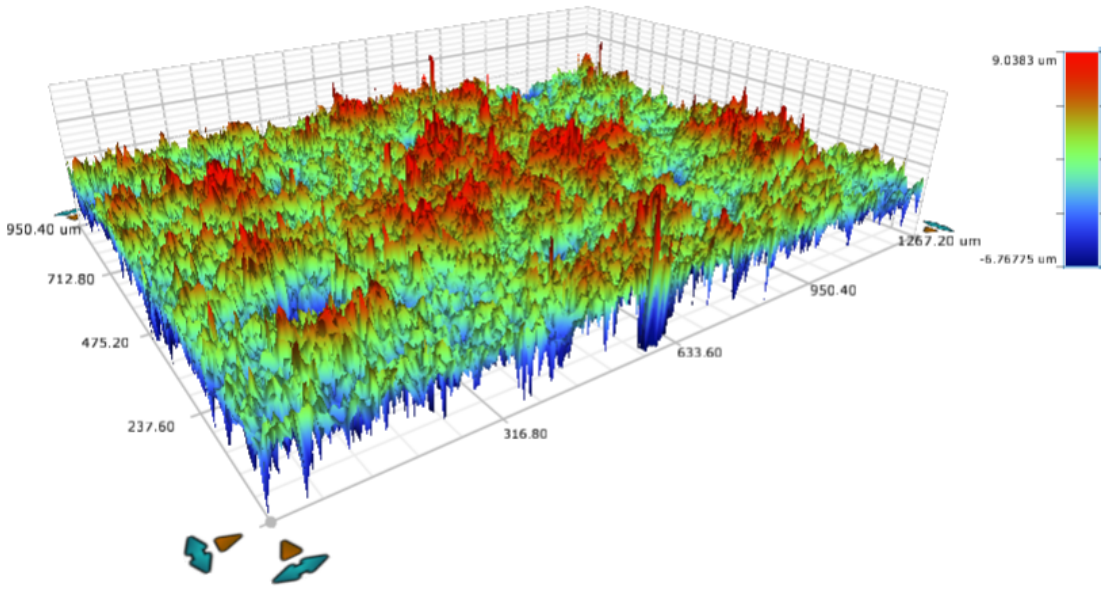


Figure 79. Profilometry of CMC-12 solution, Run 3 (SWNT:Gly = 0.25, SWNT:Ab = 10) at 100% (no dilution) with an average roughness of 1.048 µm.

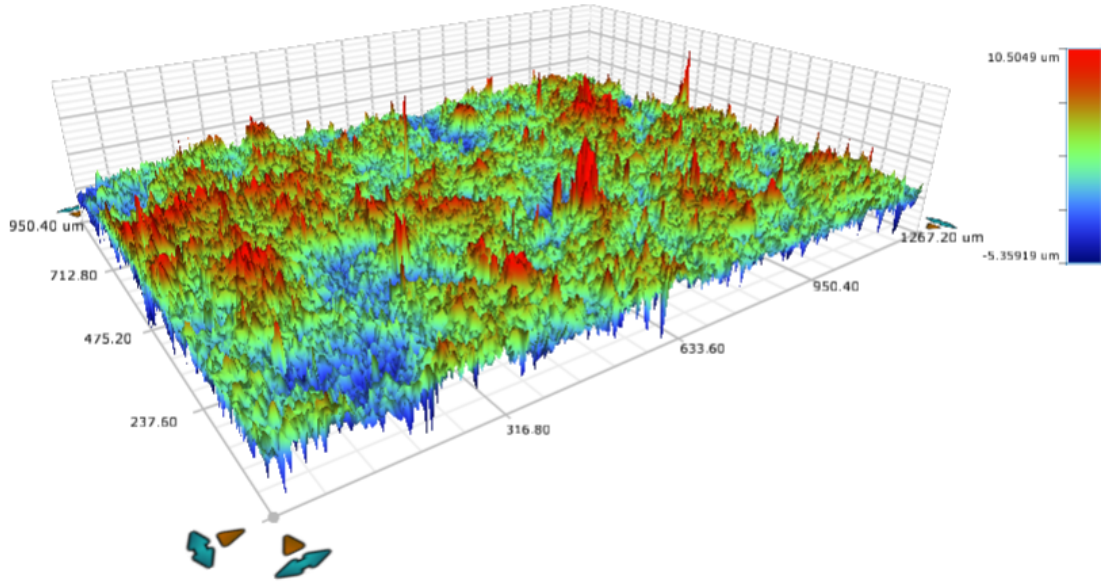


Figure 80. Profilometry of CMC-12 solution, Run 4 (SWNT:Gly = 0.625, SWNT:Ab = 10) at 100% (no dilution) with an average roughness of 0.816 µm.

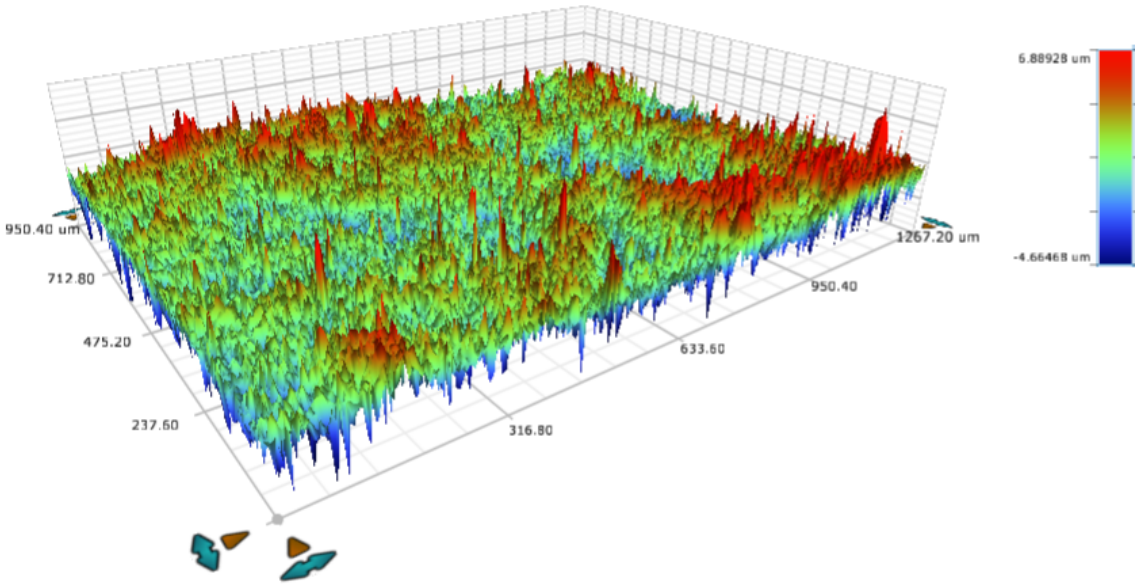


Figure 81. Profilometry of CMC-12 solution, Run 11 (SWNT:Gly = 1, SWNT:Ab = 10) at 100% (no dilution) with an average roughness of 0.74 µm.

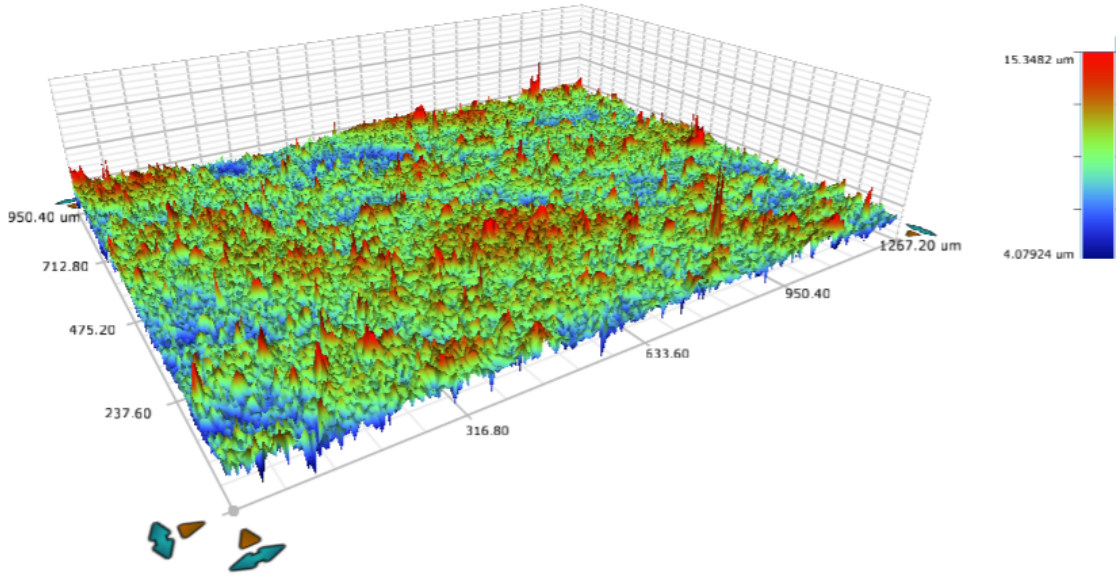


Figure 82. Profilometry of CMC-12 solution, Run 9 (SWNT:Gly = 1, SWNT:Ab = 71) at 100% (no dilution) with an average roughness of 0.624 µm.

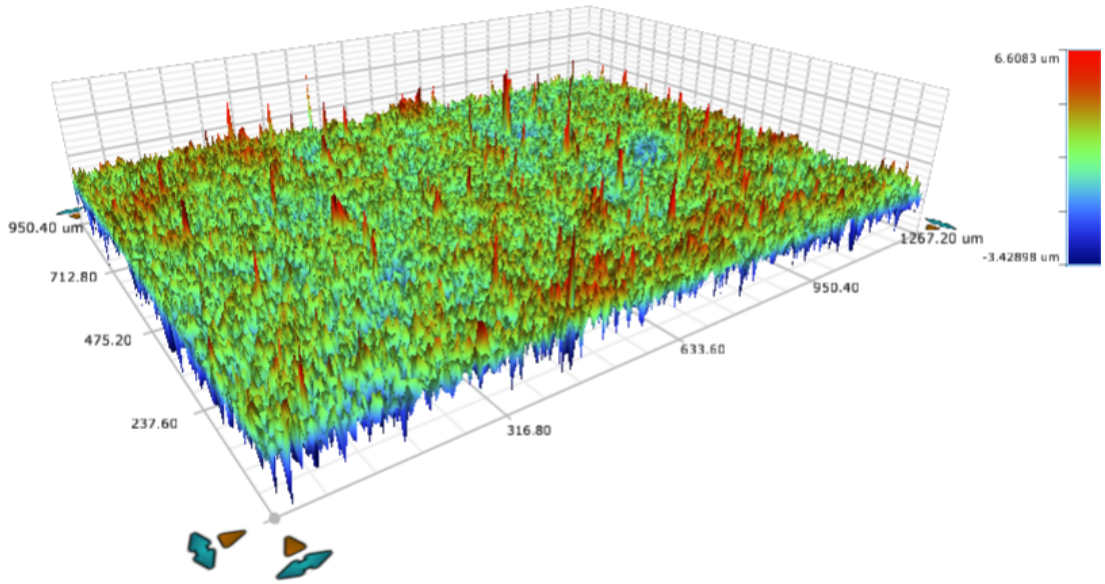


Figure 83. Profilometry of CMC-12 solution, Run 6 (SWNT:Gly = 1, SWNT:Ab = 133) at 100% (no dilution) with an average roughness of 0.449 µm.

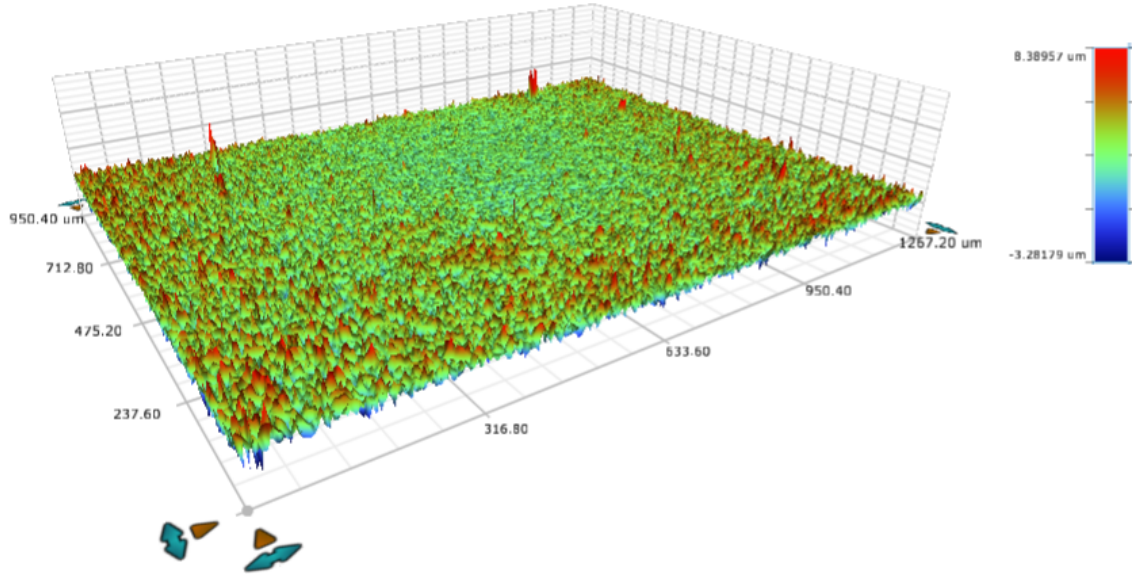


Figure 84. Profilometry of CMC-14 solution, Run 11 (SWNT:Gly = 1, SWNT:Ab = 10) at 100% (no dilution) with an average roughness of 0.504 µm.

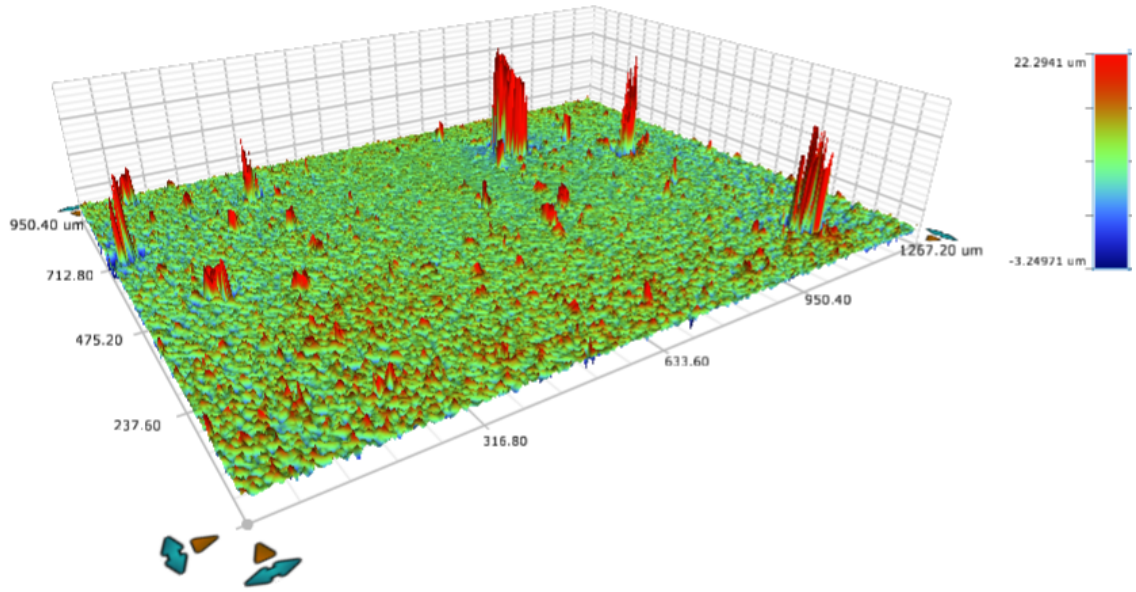


Figure 85. Profilometry of CMC-14 solution, Run 9 (SWNT:Gly = 1, SWNT:Ab = 71) at 100% (no dilution) with an average roughness of 0.432 µm.

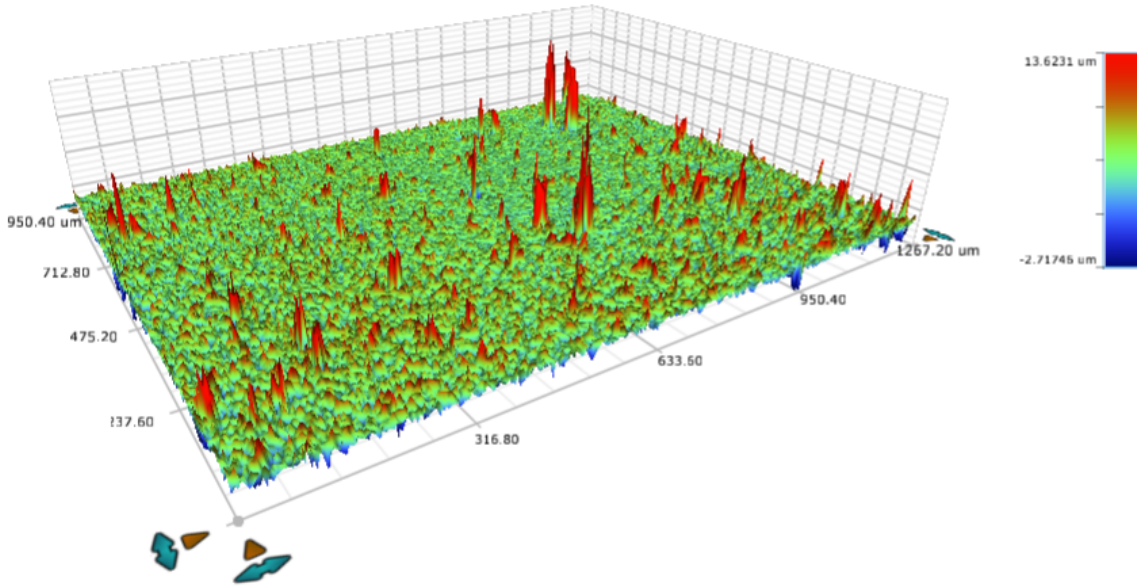


Figure 86. Profilometry of CMC-14 solution, Run 6 (SWNT:Gly = 1, SWNT:Ab = 133) at 100% (no dilution) with an average roughness of 0.387 µm.

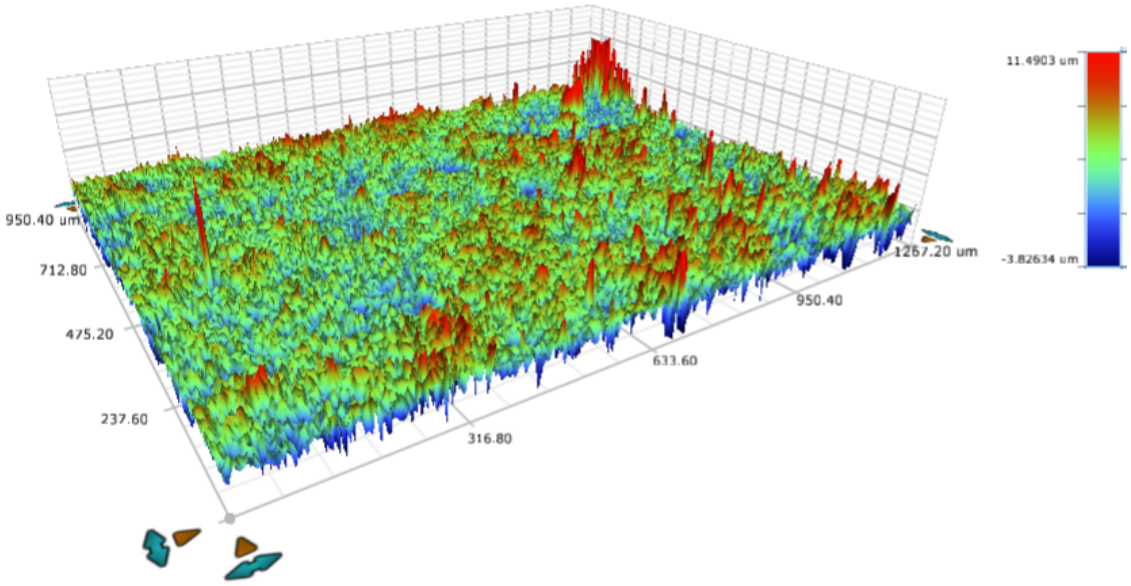


Figure 87. Profilometry of CMC-17 solution, Run 11 (SWNT:Gly = 1, SWNT:Ab = 10) at 100% (no dilution) with an average roughness of 0.611 µm.

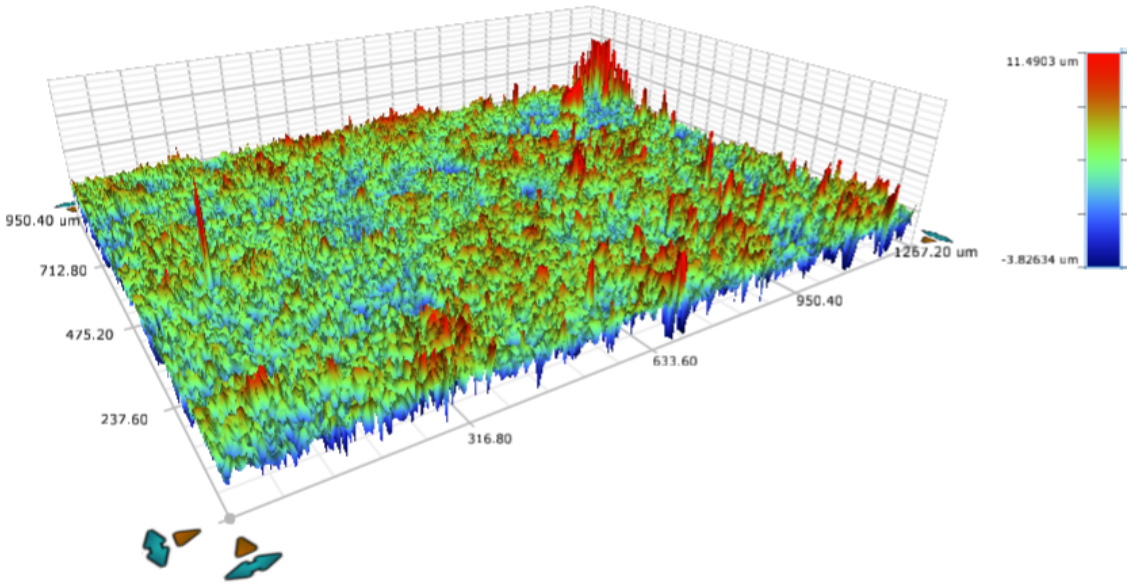


Figure 88. Profilometry of CMC-17 solution, Run 9 (SWNT:Gly = 1, SWNT:Ab = 71) at 100% (no dilution) with an average roughness of 0.455 µm.

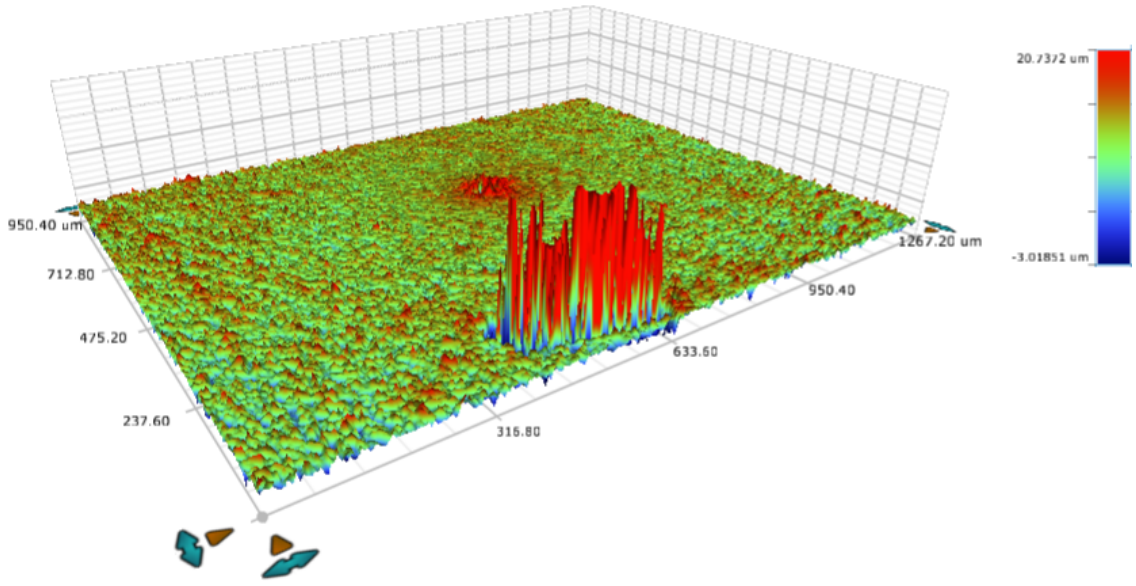


Figure 89. Profilometry of CMC-17 solution, Run 6 (SWNT:Gly = 1, SWNT:Ab = 133) at 100% (no dilution) with an average roughness of 0.419 µm.

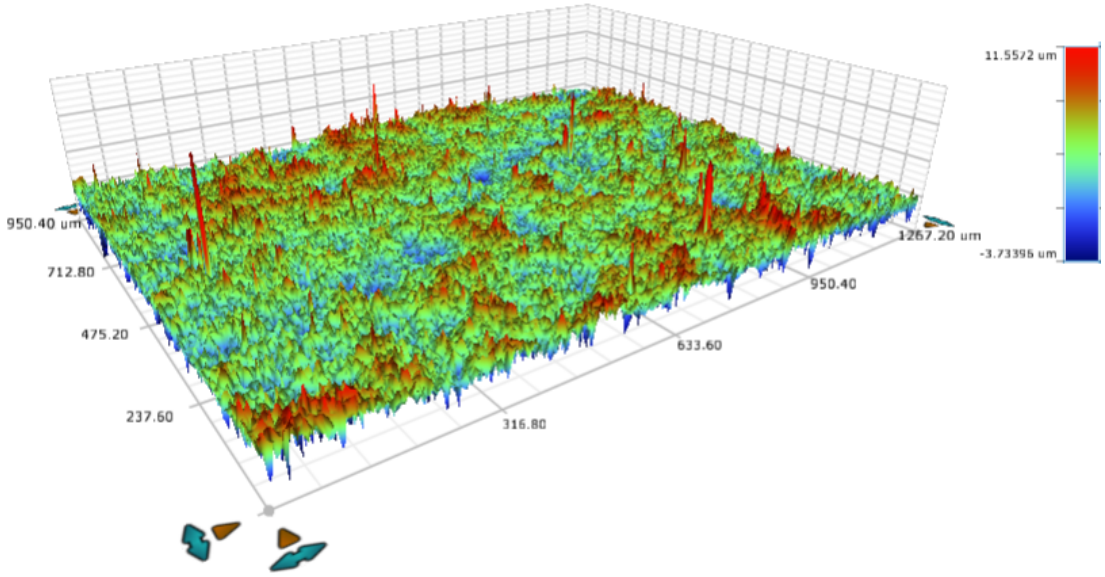


Figure 90. Profilometry of CMC-12 solution, Run 3 (SWNT:Gly = 0.25, SWNT:Ab = 10) diluted to 25% with an average roughness of 0.583 µm.

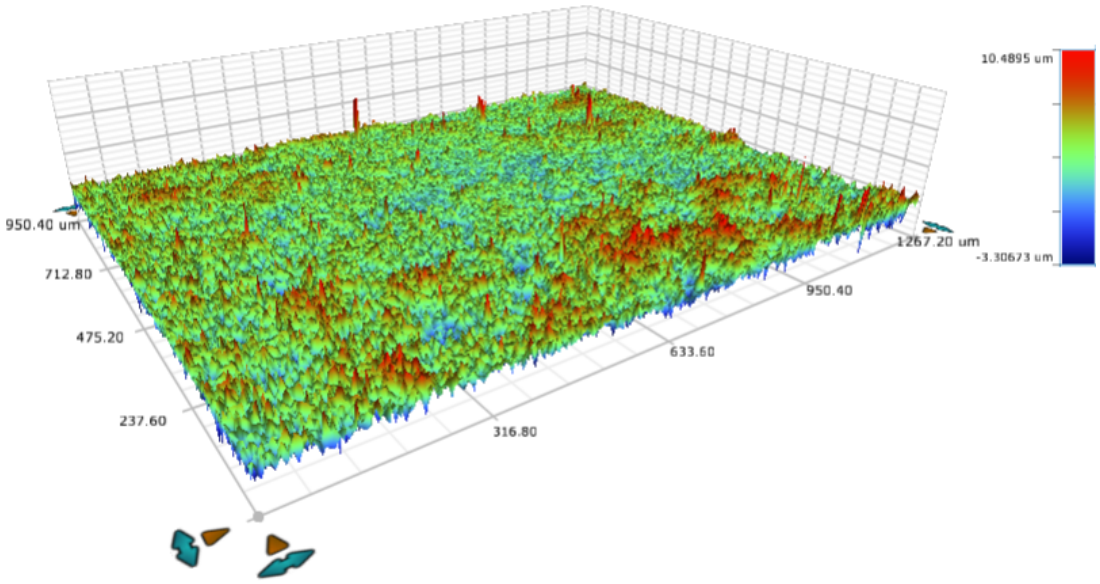


Figure 91. Profilometry of CMC-12 solution, Run 4 (SWNT:Gly = 0.625, SWNT:Ab = 10) diluted to 25% with an average roughness of 0.424 µm.

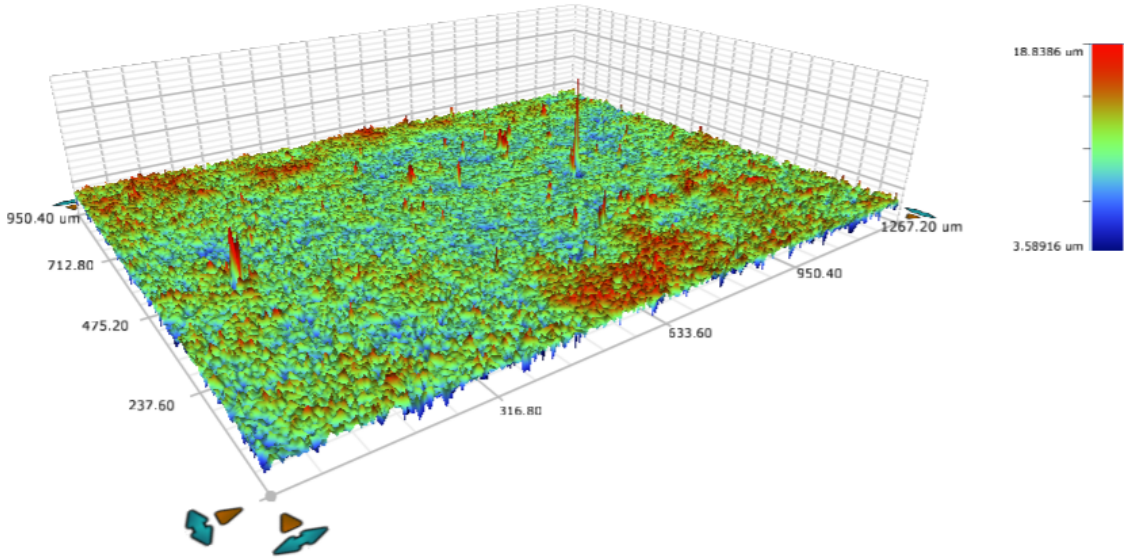


Figure 92. Profilometry of CMC-12 solution, Run 11 (SWNT:Gly = 1, SWNT:Ab = 10) diluted to 25% with an average roughness of 0.412 µm.

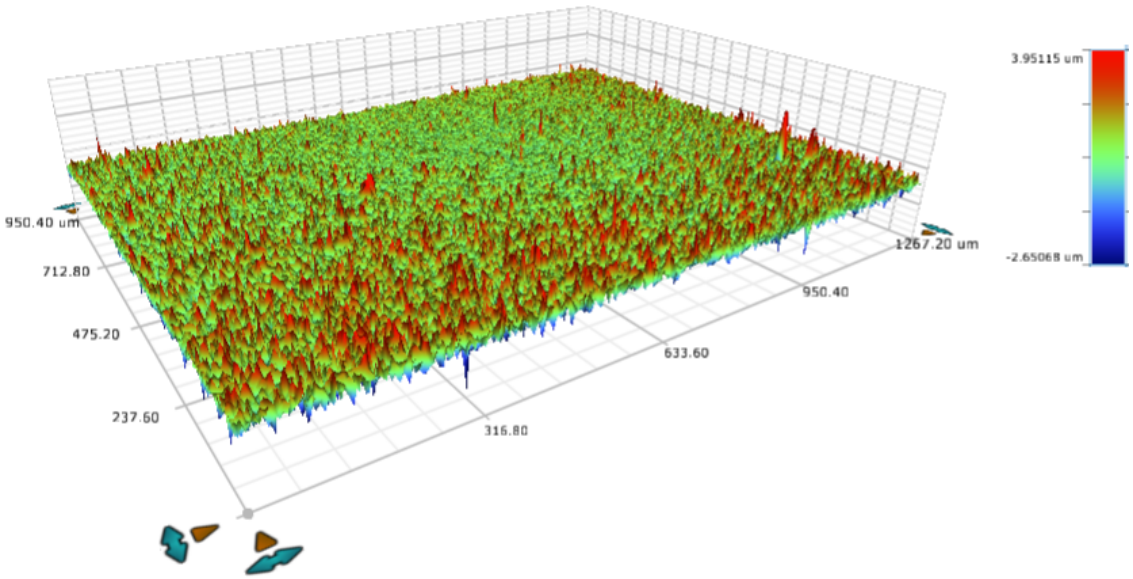


Figure 93. Profilometry of CMC-14 solution, Run 11 (SWNT:Gly = 1, SWNT:Ab = 10) diluted to 25% with an average roughness of 0.192 µm.

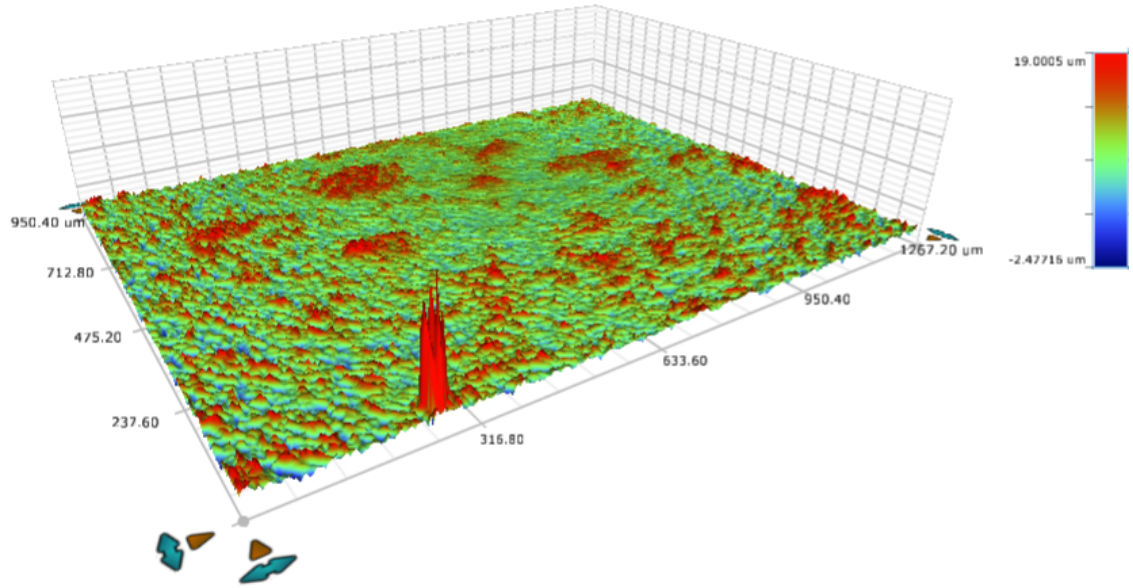


Figure 94. Profilometry of CMC-17 solution, Run 11 (SWNT:Gly = 1, SWNT:Ab = 10) diluted to 25% with an average roughness of 0.285 µm.

It can be concluded that the surface topography of the dried matrix films is in correlation with the resistance response of the matrix. Uniform and smooth surfaces can be translated to low SWNT agglomeration and low resistance of the dried matrix solutions. Therefore it is desirable to obtain a uniform and smooth coating.

3.3.4 Coating thickness

The thickness of the coatings is important because of their effect on the resistance of the obtained dried films. The higher the coating thickness is, the less the resistance of the coating will be. The thickness of the dried matrix coating was investigated using the optical profiler. For this purpose, the optical profile of the edge of the coatings was obtained using optical profiler for select samples. The thickness of matrix coatings from profilometry obtained for CMC-12, CMC-14, and CMC-17 dried matrix formulations at 100% (no dilution), and 25% dilution is presented in Figure 95 through Figure 110, and summarized in Table 38.

The thickness of the coatings was observed to decrease with an increase in the glycerol concentration. This trend suggests that the mass of material applied at higher glycerol concentrations may have been lower due to precipitates being filtered out during the matrix preparation (in phase 1 of this research it was shown that the measured thickness was consistent with mass balance calculated thickness). This would also be consistent with the increasing surface roughness trend that was observed with increasing glycerol, suggesting an increase in particle size.

The contribution of the concentration of antibody to the thickness is fairly small, showing a slight increase with antibody concentration for CMC-12 and slight decrease with concentration for CMC-17 and CMC-14, and perhaps statistically insignificant.

As expected, the thickness of the coatings is observed to decrease by slightly more than fourfold with the fourfold dilution of the matrix solution from 100% to 25%.

Resistivity, in contrast, did not increase with dilution as much as expected (4x or higher) and at highest glycerol ratios actually decreased slightly.

Table 38- Comparison of the coatings' average thickness and its effect on resistance for select coatings

				Resistance (Ω)			Thickness (µm)			Theoretical Thickness (µm)		
Run	SWNT: GLY	SWNT: Ab	dilution	CMC-12	CMC-17	CMC-14	CMC-12	CMC-17	CMC-14	CMC-12	CMC-17	CMC-14
3	0.25	10	100%	180753	968476	1650440	2.15			2.30		
4	0.625	10	100%	5283	46313	138495	2.43			2.59		
11	1	10	100%	1841	8939	13822	3.07	1.85	**1.24**	2.78	4.45	3.59
	∞	∞	100%	148	147	1069				3.56	4.19	4.6
11	1	10	100%	1841	8939	13822	3.07	1.85	**1.24**	2.78		
9	1	71	100%	1265	5570	5727	2.84	1.92	**1.31**	2.78		
6	1	133	100%	474	4162	4337	2.79	2	**1.46**	2.78	4.45	3.59
	∞	∞	100%	148	147	1069				3.56	4.19	4.6
3	0.25	10	25%	184197	1376718	356148	0.62			0.57		
4	0.625	10	25%	6753	175400	60731	0.63			0.65		
11	1	10	25%	4692	21869	9983				0.69	1.11	0.90
SWNT:CMC		**ratio =**		**2**	**1.25**	**0.5**	**2**	**1.25**	**0.5**	**2**	**1.25**	**0.5**

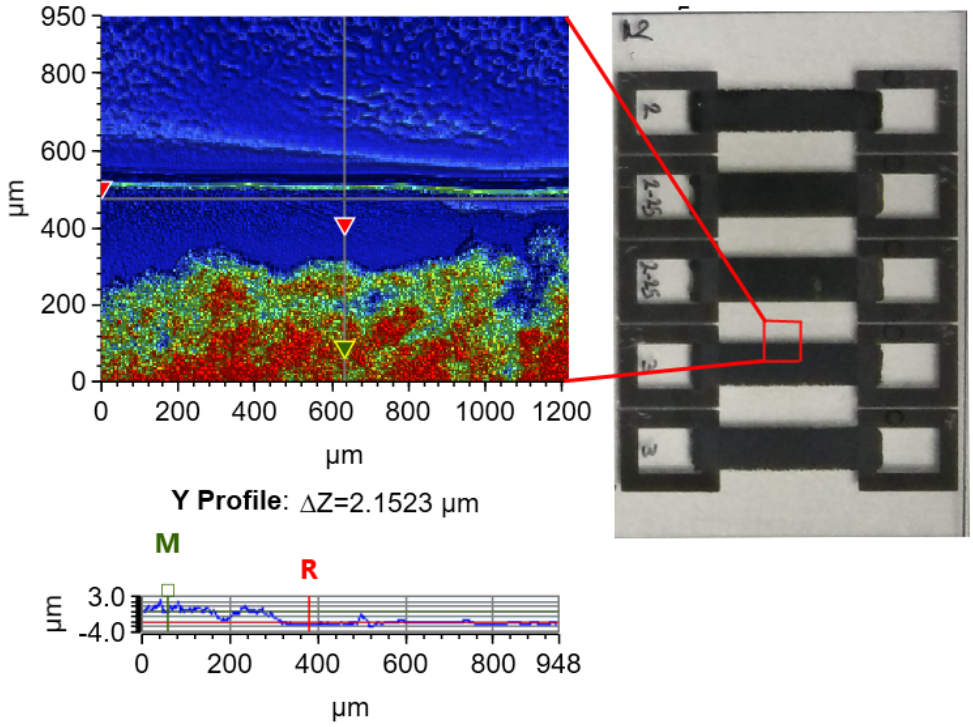


Figure 95. The thickness of Run 3 coating ((SWNT:Gly = 0.25, SWNT:Ab = 10) obtained from CMC-12 solution at 100% (no dilution) using 2D microscopy profile (1250 µm × 950 µm) showing a thickness of 2.15 µm.

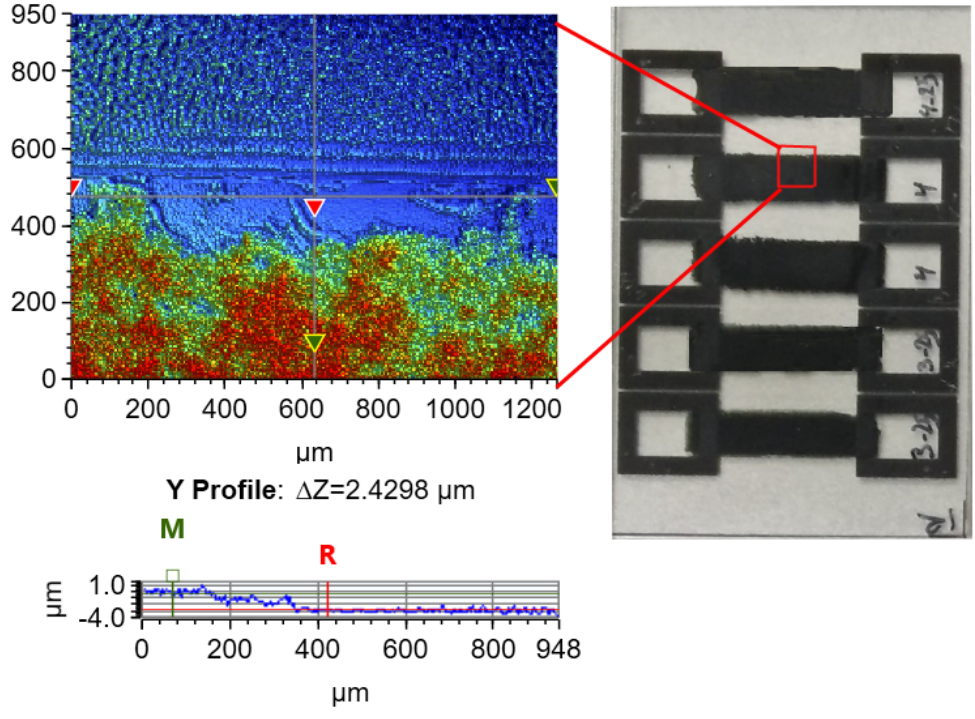


Figure 96. The thickness of Run 4 coating ((SWNT:Gly = 0.25, SWNT:Ab = 10) obtained from CMC-12 solution at 100% (no dilution) using 2D microscopy profile (1250 µm × 950 µm) showing a thickness of 2.43 µm.

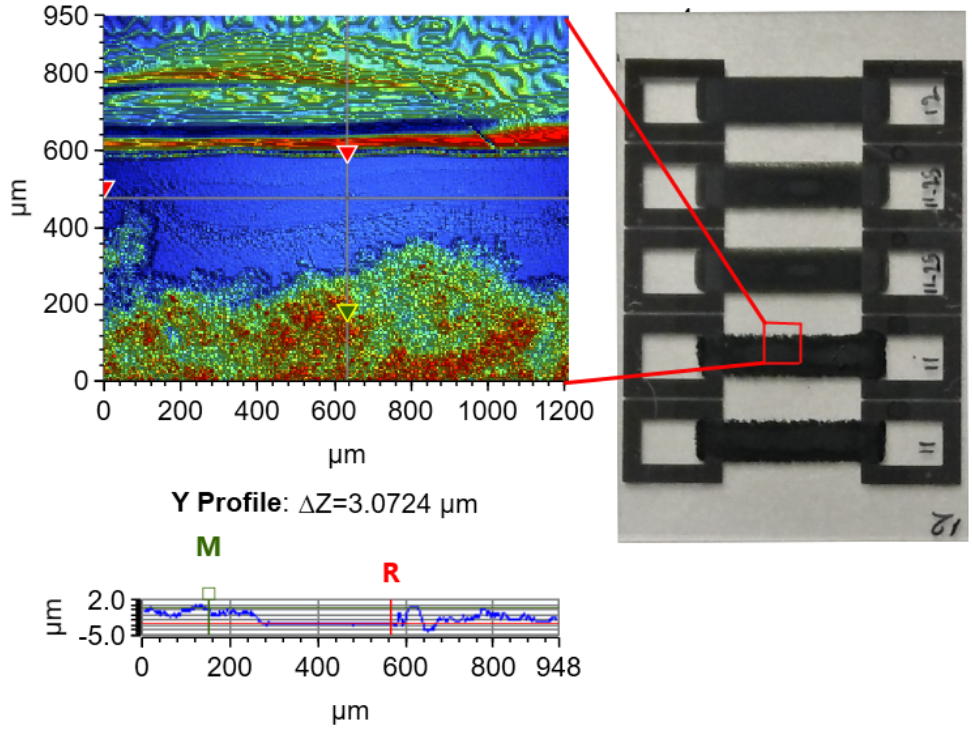


Figure 97. The thickness of Run 11 coating ((SWNT:Gly = 1, SWNT:Ab = 10) obtained from CMC-12 solution at 100% (no dilution) using 2D microscopy profile (1250 µm × 950 µm) showing a thickness of 3.07 µm.

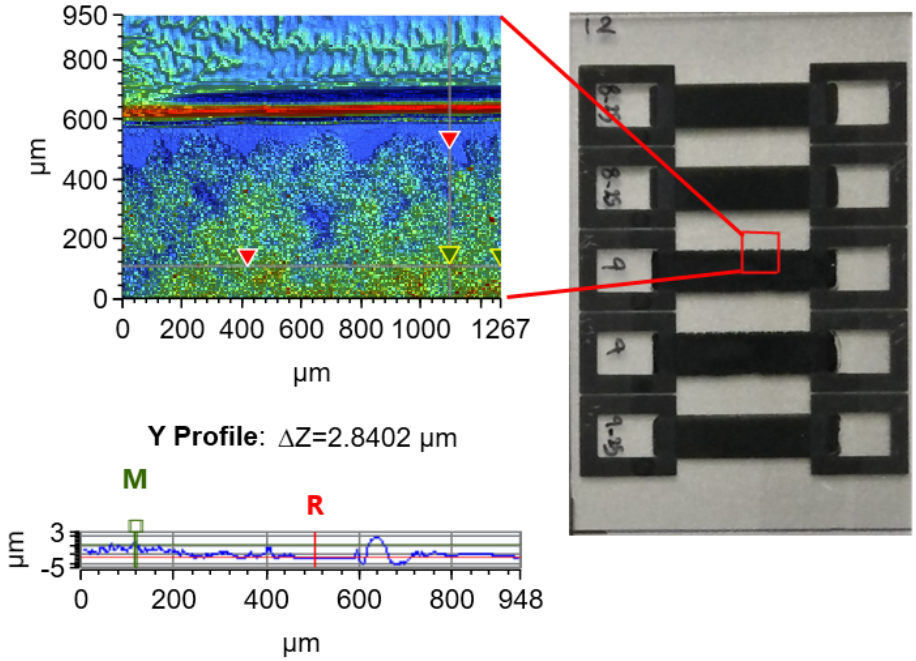


Figure 98. The thickness of Run 9 coating ((SWNT:Gly = 1, SWNT:Ab = 71) obtained from CMC-12 solution at 100% (no dilution) using 2D microscopy profile (1250 µm × 950 µm) showing a thickness of 2.84 µm.

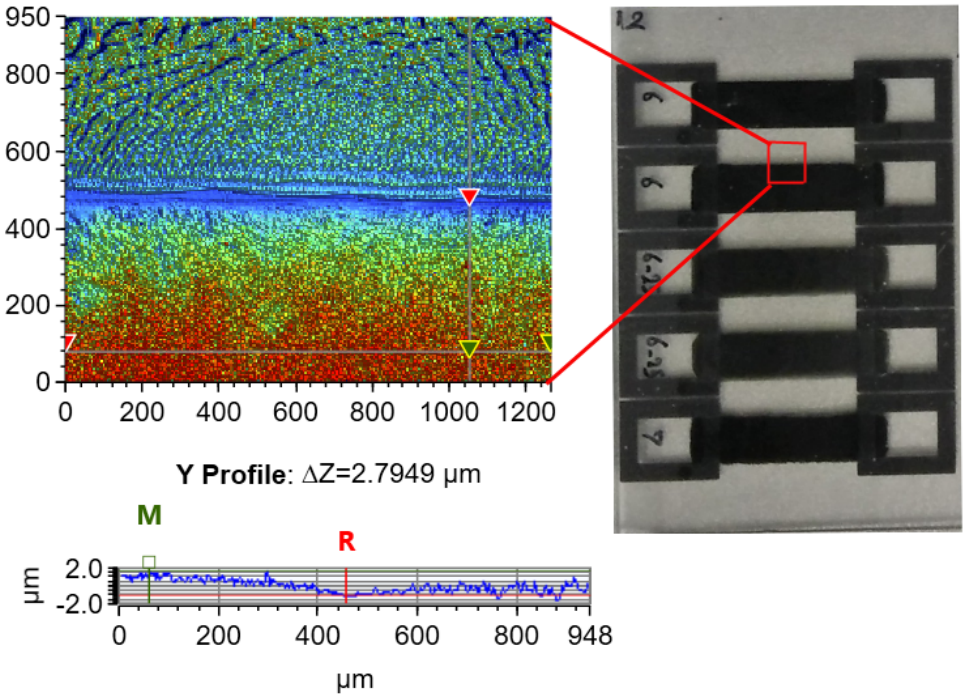


Figure 99. The thickness of Run 6 coating ((SWNT:Gly = 1, SWNT:Ab = 133) obtained from CMC-12 solution at 100% (no dilution) using 2D microscopy profile (1250 μm × 950 μm) showing a thickness of 2.79 μm.

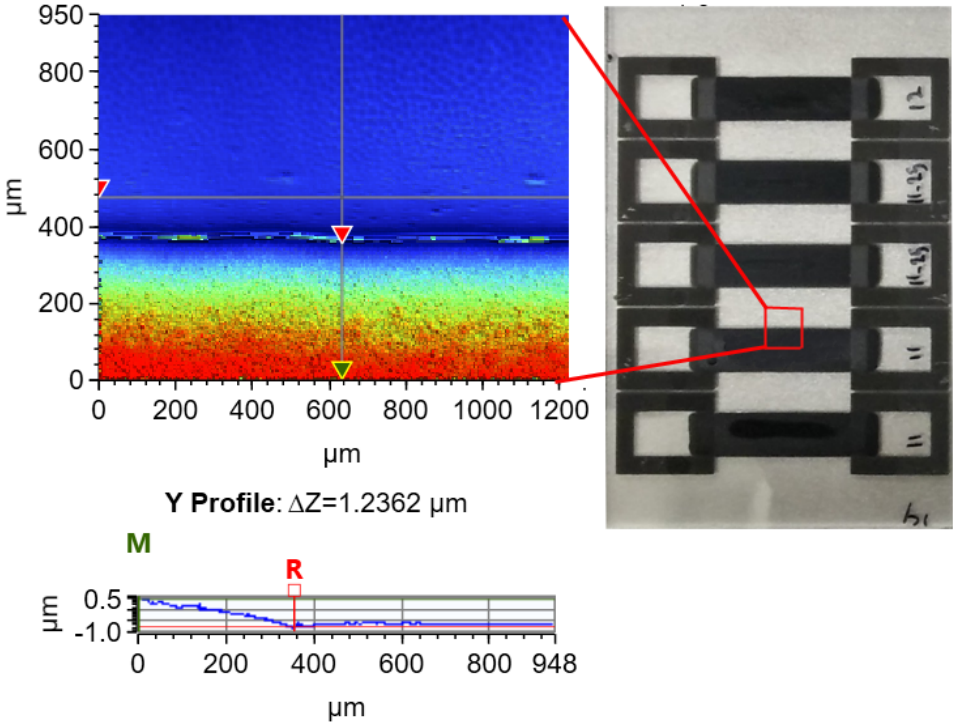


Figure 100. The thickness of Run 11 coating ((SWNT:Gly = 1, SWNT:Ab = 10) obtained from CMC-14 solution at 100% (no dilution) using 2D microscopy profile (1250 μm × 950 μm) showing a thickness of 1.24 μm.

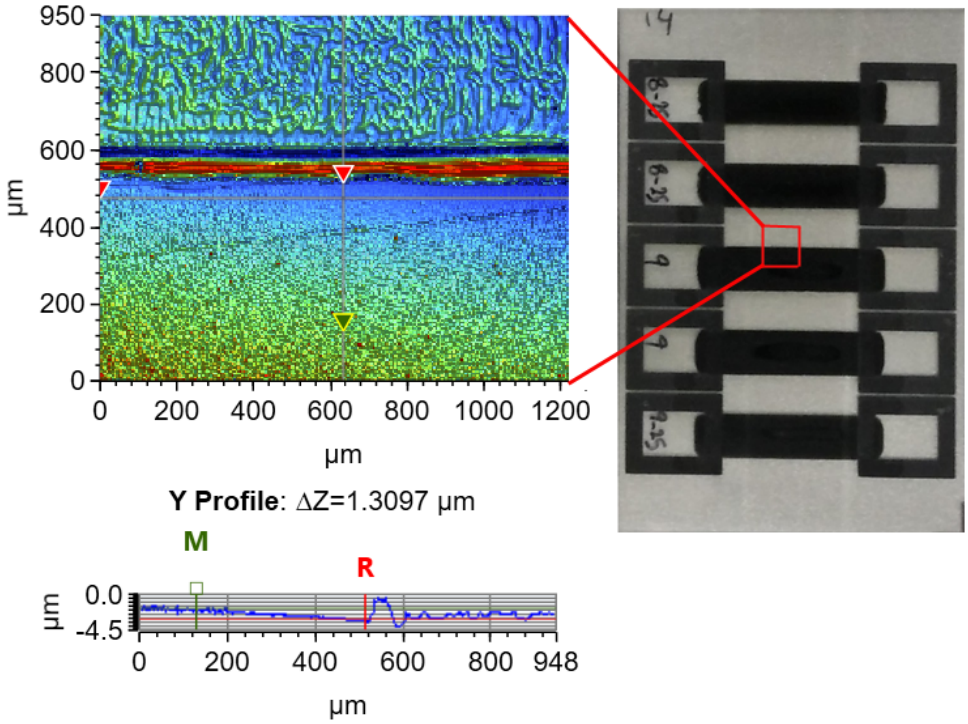


Figure 101. The thickness of Run 9 coating ((SWNT:Gly = 1, SWNT:Ab = 71) obtained from CMC-14 solution at 100% (no dilution) using 2D microscopy profile (1250 µm × 950 µm) showing a thickness of 1.31 µm.

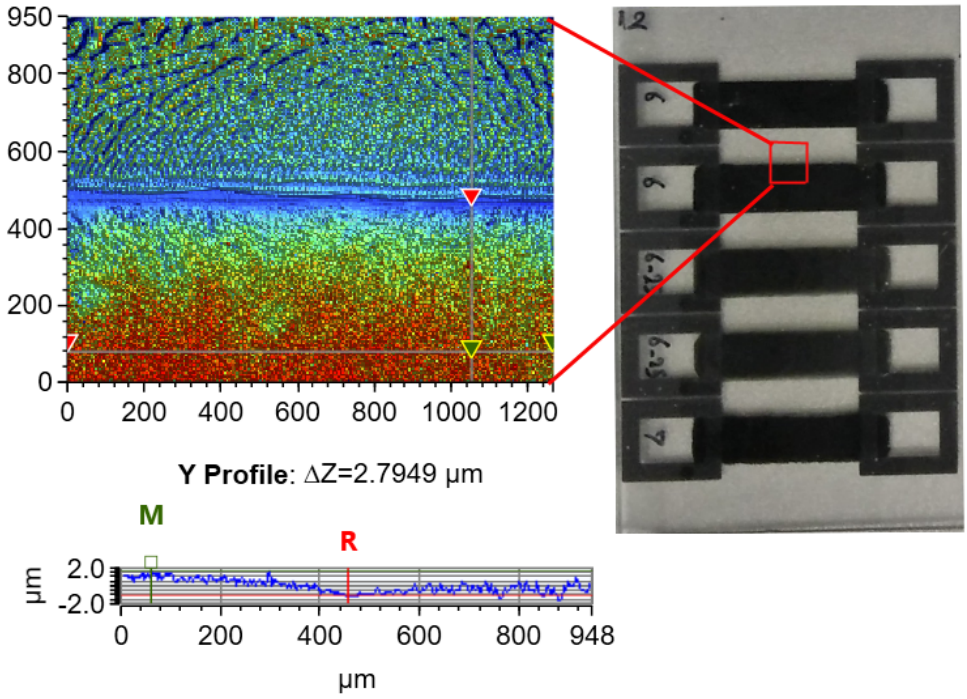


Figure 102. The thickness of Run 6 coating ((SWNT:Gly = 1, SWNT:Ab = 133) obtained from CMC-14 solution at 100% (no dilution) using 2D microscopy profile (1250 µm × 950 µm) showing a thickness of 2.79 µm.

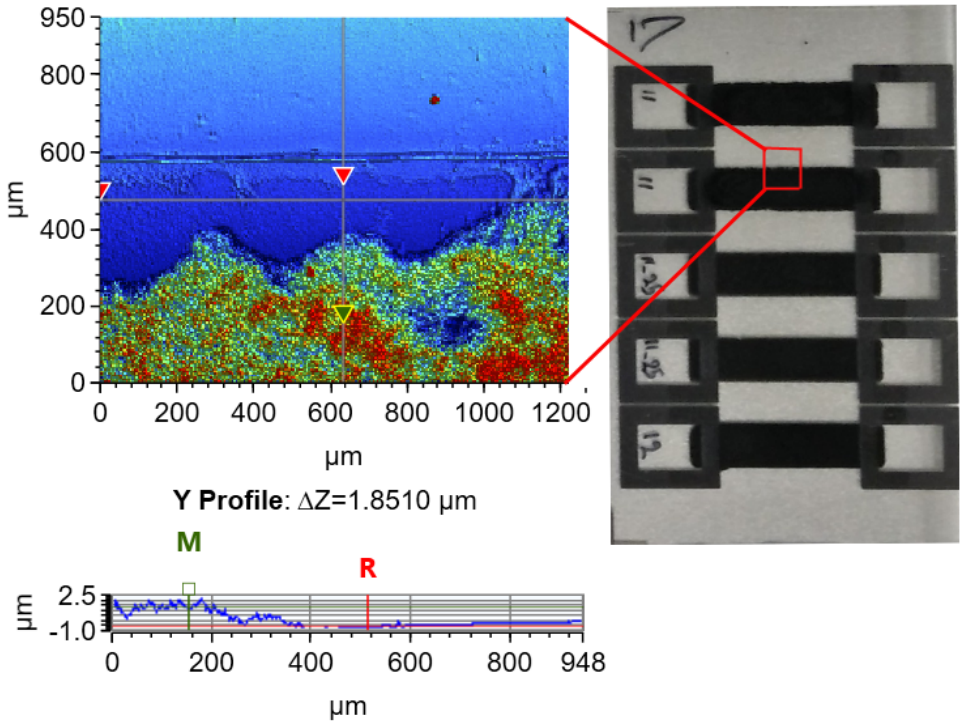


Figure 103. The thickness of Run 11 coating ((SWNT:Gly = 1, SWNT:Ab = 10) obtained from CMC-17 solution at 100% (no dilution) using 2D microscopy profile (1250 µm × 950 µm) showing a thickness of 1.85 µm.

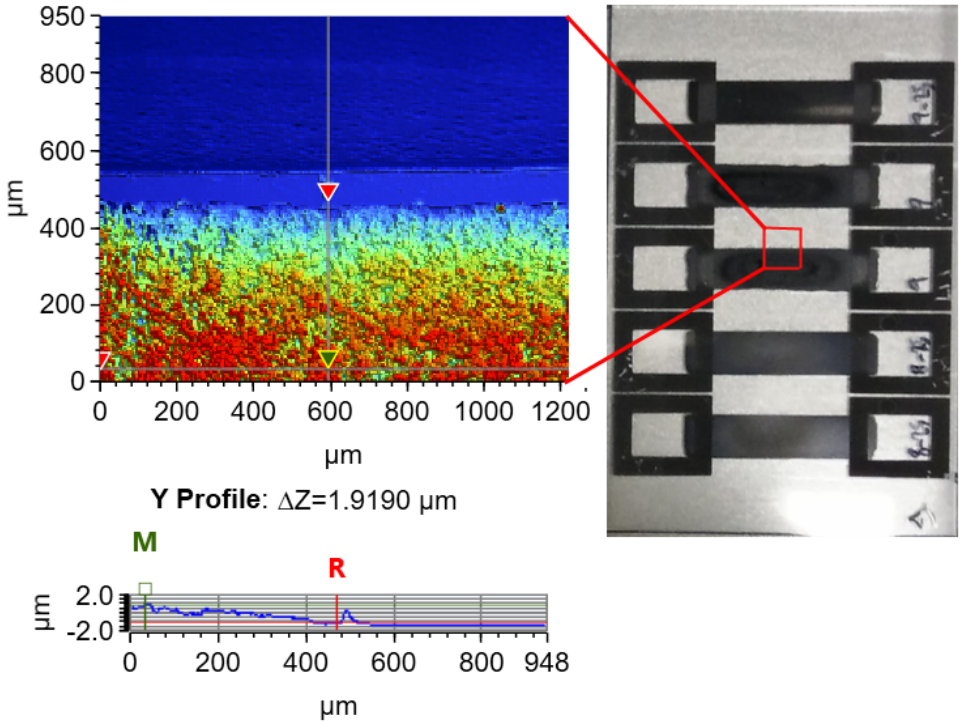


Figure 104. The thickness of Run 9 coating ((SWNT:Gly = 1, SWNT:Ab = 71) obtained from CMC-17 solution at 100% (no dilution) using 2D microscopy profile (1250 µm × 950 µm) showing a thickness of 1.92 µm.

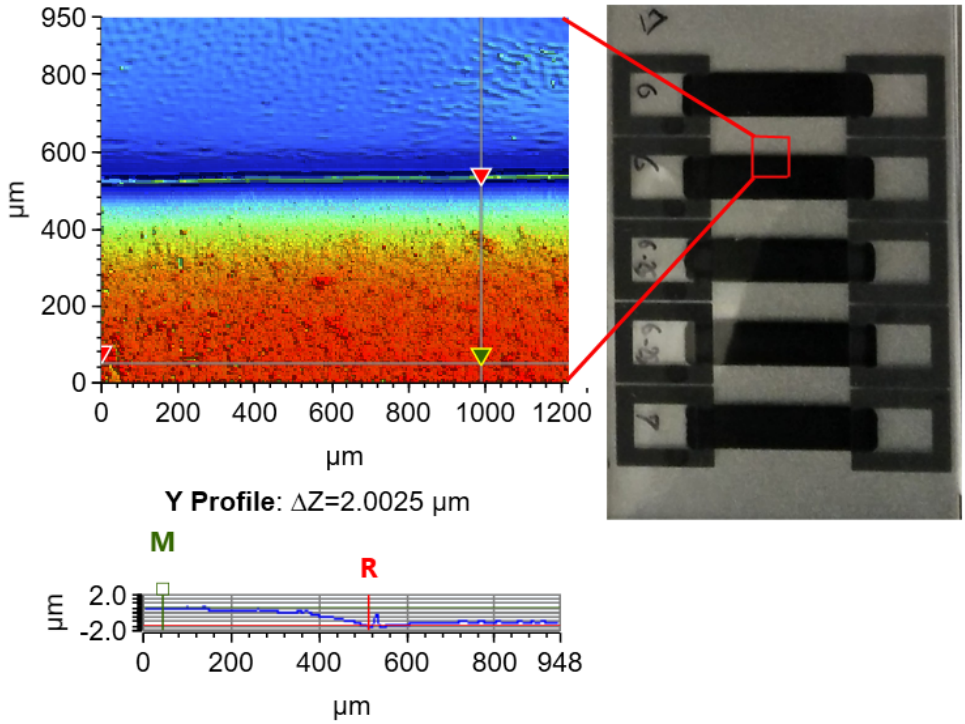


Figure 105. The thickness of Run 6 coating ((SWNT:Gly = 1, SWNT:Ab = 133) obtained from CMC-17 solution at 100% (no dilution) using 2D microscopy profile (1250 µm × 950 µm) showing a thickness of 2.00 µm.

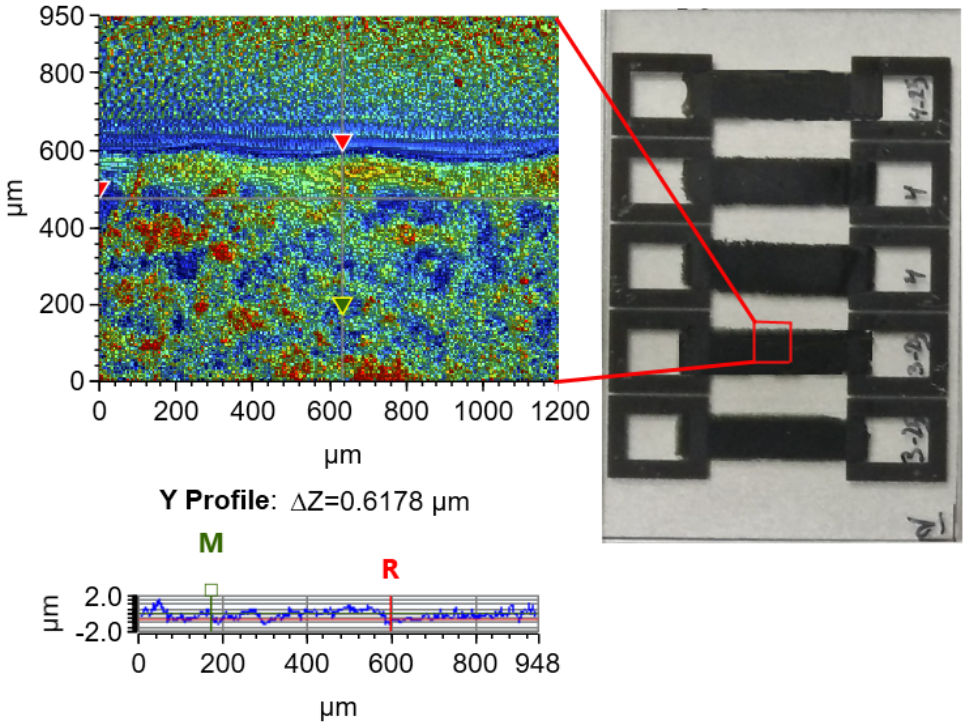


Figure 106. The thickness of Run 3 coating ((SWNT:Gly = 0.25, SWNT:Ab = 10) obtained from CMC-12 solution diluted to 25% using 2D microscopy profile (1250 µm × 950 µm) showing a thickness of 0.62 µm.

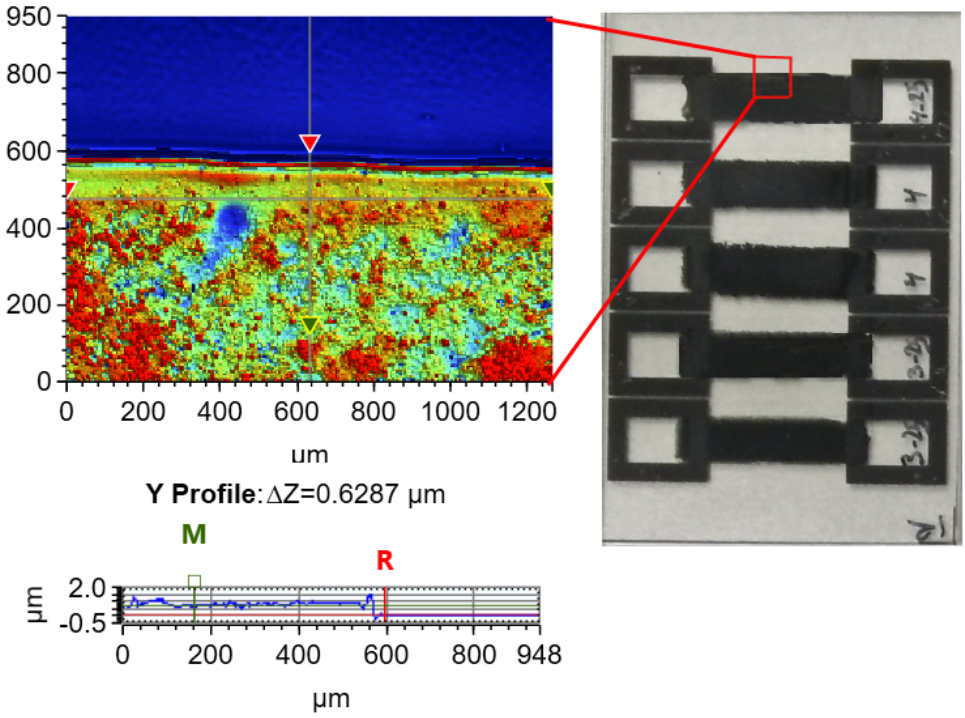


Figure 107. The thickness of Run 4 coating ((SWNT:Gly = 0.625, SWNT:Ab = 10) obtained from CMC-12 solution diluted to 25% using 2D microscopy profile (1250 µm × 950 µm) showing a thickness of 0.63 µm.

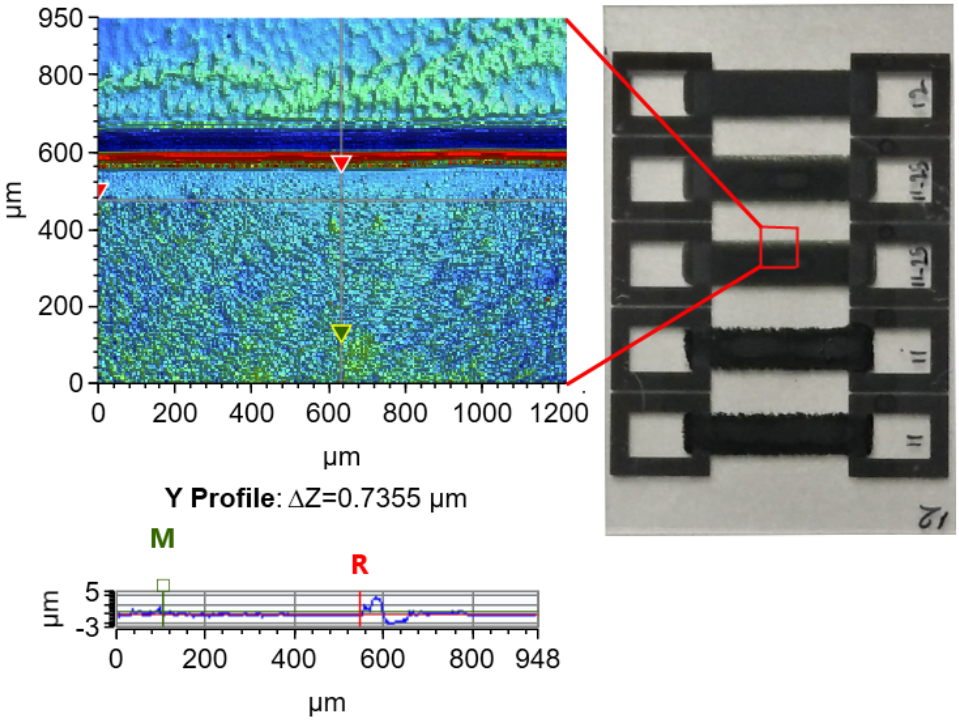


Figure 108. The thickness of Run 11 coating ((SWNT:Gly = 1, SWNT:Ab = 10) obtained from CMC-12 solution diluted to 25% using 2D microscopy profile (1250 µm × 950 µm) showing a thickness of 0.74 µm.

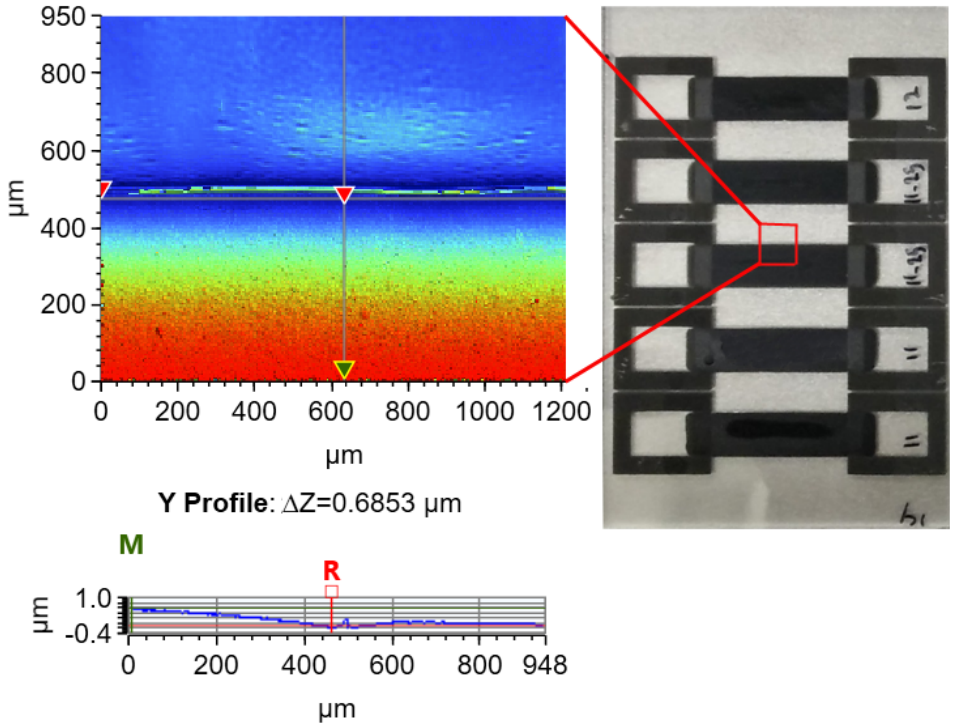


Figure 109. The thickness of Run 11 coating ((SWNT:Gly = 1, SWNT:Ab = 10) obtained from CMC-14 solution diluted to 25% using 2D microscopy profile (1250 µm × 950 µm) showing a thickness of 0.68 µm.

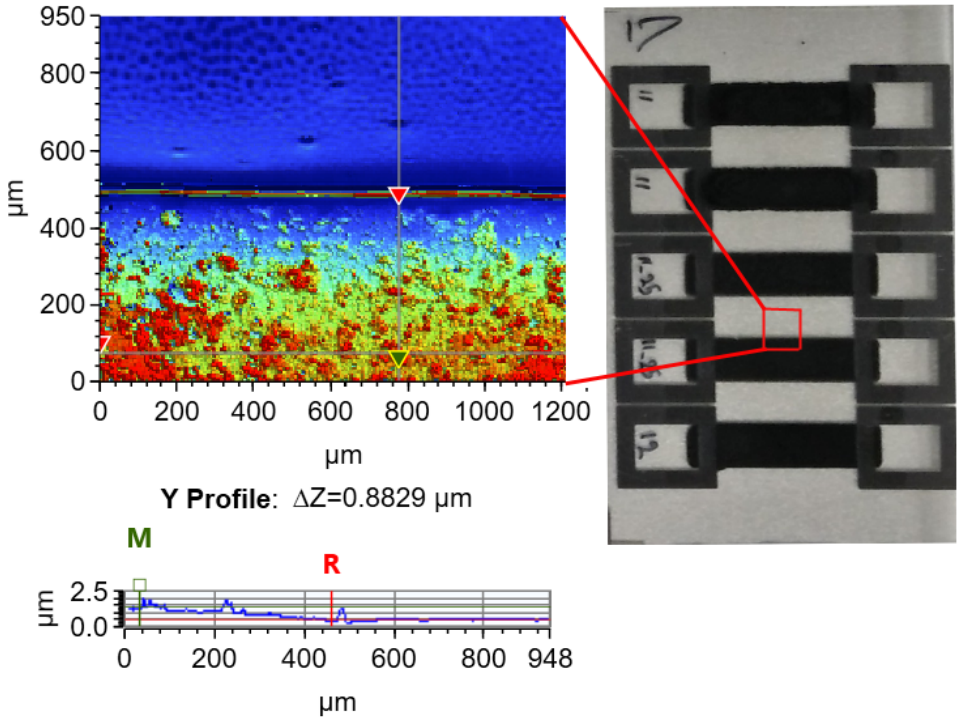


Figure 110. The thickness of Run 11 coating ((SWNT:Gly = 1, SWNT:Ab = 10) obtained from CMC-17 solution diluted to 25% using 2D microscopy profile (1250 µm × 950 µm) showing a thickness of 0.88 µm.

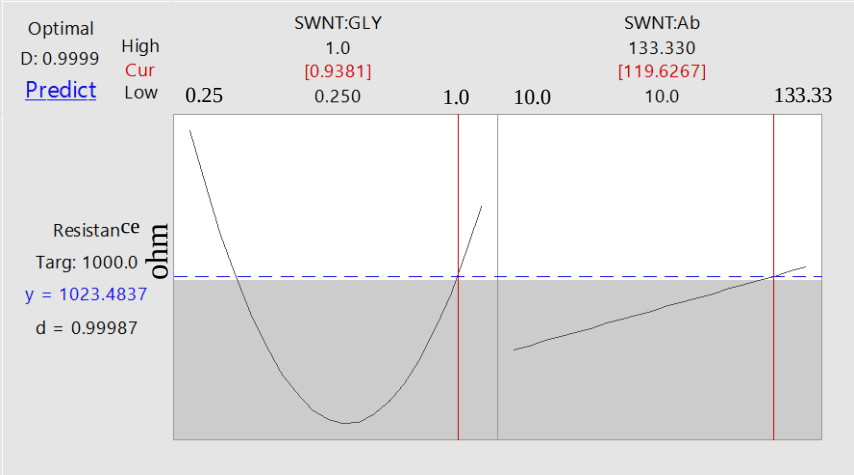
3.3.5 RSM optimization

Thus far, as analyzed in the result and discussion section of this chapter, the resistance behavior of coatings prepared from CMC-12 were found to be superior when compared to that of the coatings prepared from solutions CMC-14 and CMC-17. The workability and the uniformity of the coatings prepared from CMC-12 matrix solutions were also compared with other matrix coatings and were found to be superior, as the coatings exhibit the highest uniformity among different matrix solutions. These facts lead the author to select the CMC-12 matrix solution as a potential candidate for biosensing applications. Every 5 ml of the CMC-12 matrix solution comprise of 0.0134 g of SWCNT, 0.1674 g of CMC, 0.0321 g of azide, and 0.0045 grams of sodium phosphate dibasic dihydrate to adjust the pH to between 7 and 8. Among different ratio variations of SWNT:Glycerol, the highest ratio tested, 1:1, was found to lead to the minimum electrical resistance. Although the addition of antibody in the system results in an increase in the resistance of the matrix coating, any desired concentration of antibody, up to the SWNT:antibody ratio of 10, can be selected while maintaining the resistance below 2000 **Ω**, using matrix at full strength (no dilution with water). Therefore, it can be concluded that the matrix coating obtained using the CMC dispersant at the ratio of SWNT:CMC of 2.0 and the sonication amplitude of 40% for 2 hours can be potentially used for integration into immunodiagnostic biosensors. Glycerol at the ratio of SWNT:glycerol of 1.0 can be used as a humectant to help preserve the activity of the incorporated antibody (not yet evaluated).

Using the response surface methodology (RSM) design of experiment in the second phase of this study with antibody and glycerol, the behavior of the coatings were modeled.

The comparison between the experimental resistance values and the predicted values in section 3.3.2, Table 36, shows that the regression models can be used to predict the resistance behavior of the matrix coatings. 63% of the predicted resistances in the Table 36 fall within ±20% of the experimental values. The worst predicted value differs by 68% from the experimental value, however considering the range of resistances covered by this model in Table 36 was from 474Ω to 1.65MΩ, the model is fairly good.

As an example, the RSM models generated in this chapter can be used to identify formulation conditions that will result in dried matrix resistances of ~1000 Ω. The optimized parameters for one possible solution of achieving this goal using CMC-12 at 100% dilution is shown in the table insert in Figure 111. This figure also shows the overlay of the optimum conditions for Solution 1 at a SWNT:glycerol ratio of 1 and SWNT:antibody ratio of 120.



Solution	SWNT:Gly	SWNT:Ab	Resistance (ohm) Fit	Composite Desirability
1	1	120	1023	1

Figure 111. The main effect graph showing the optimized condition for achieving ~1000 ohm resistance using the CMC-12 solution at 100% (no dilution). The table insert shows the condition optimized for achieving a resistance of 1000 Ω, based on the response surface design.

3.3.6 Scanning electron microscopy

Efforts were made to obtain SEM micrographs of the matrix coatings. Five Institutions and Universities (Michigan State University, Western Michigan University (Dr. Eversole and Dr. Arigur's labs), Georgia Institute of Technology, and University of Georgia) have made effort to visualize a number of the samples of the prepared coating films. However, technical difficulties prohibited a successful visualization of the samples. Among the mentioned institutes, MSU obtained the best micrographs. Unfortunately, the SEM device used at MSU was not able to employ a higher magnification and sharper image due to a technical problem. Figure 112 shows SEM micrographs of Run 6 coating ((SWNT:Gly = 1, SWNT:Ab = 133) obtained from CMC-12 solution at 100% (no dilution). Uniformly dispersed individual SWNTs are visible in this figure. A larger clump of SWNT, representing SWNT agglomeration is visible in these two images, showing the

nature of SWNT bundles. The antibody and CMC molecules are not visible in these images due to insufficient magnification.

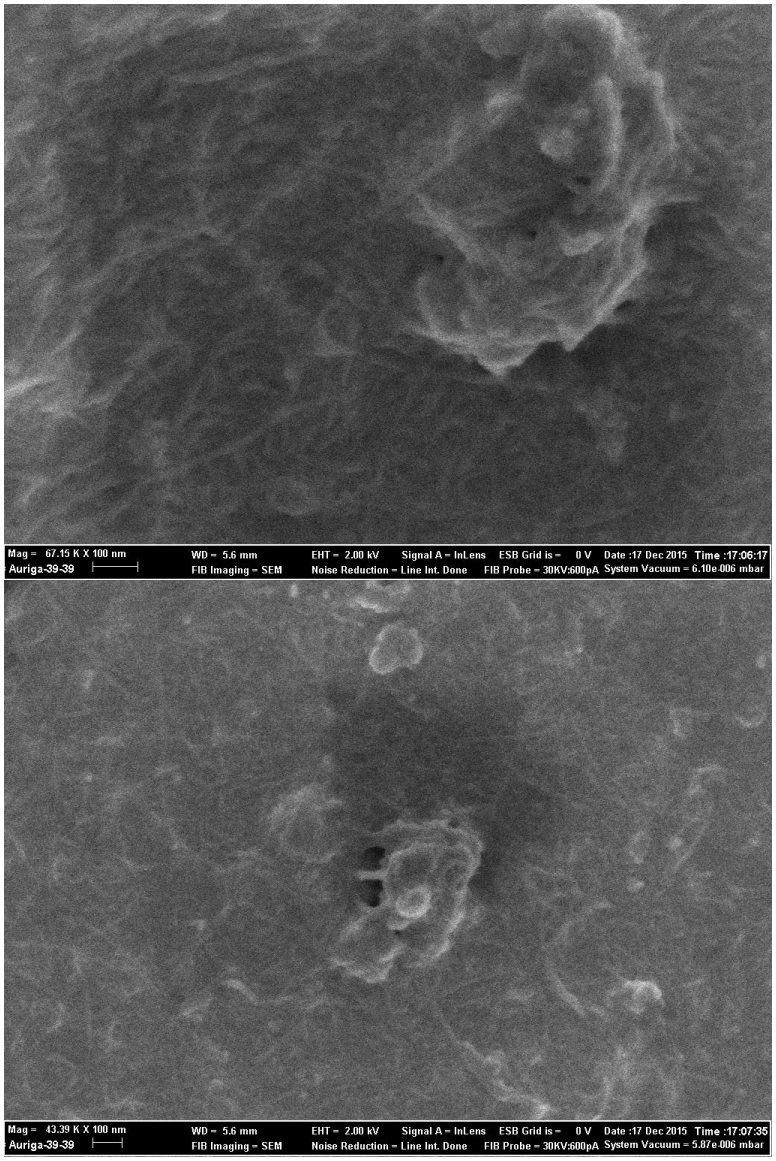


Figure 112. SEM micrographs of Run 6 coating ((SWNT:Gly = 1, SWNT:Ab = 133) obtained from CMC-12 solution at 100% (no dilution) at (top) 67KX and (bottom) 43KX. Images show fairly uniformly dispersed individual SWNTs and a larger agglomerated clump of SWNT.

3.4 Conclusion

The base matrix solution without glycerol and antibody was selected from the experiments the 1st phase of this research based on a set of matrix film formulations that achieved low resistance for each SWNT to CMC ratio. Matrix formulation protocols from

Run 14 (SWNT:CMC = 0.5), Run 17 (SWNT:CMC = 1.25), and Run 12 (SWNT:CMC = 2) were selected and labeled as CMC-14, CMC-17, and CMC-12, respectively. The corresponding resistance results for the dried matrices were 1069, 794, and 148 **Ω**, respectively. Seventy-eight different solutions were prepared using the CMC-14, CMC-17, and CMC-12 base matrix formulations based on an experimental design containing various SWNT:glycerol and SWNT:antibody ratios. Their resistance responses as well as surface morphologies were investigated using Profilometry. Although scanning electron microscopy of the prepared films with antibody/glycerol, the low quality of the SEM images at three different Universities (apparently due to technical difficulties as explained by the SEM technicians at each University) did not allow a comprehensive study of the coated matrix film morphology. However, the uniformly coated individualized SWNTs are still detectable in the lower magnification images obtained a Michigan State University.

The resistance behavior of coatings prepared from CMC-12 solution were found to be statistically more predictable when compared to that of the coatings prepared from solutions CMC-14 and CMC-17. 3D optical microscopy was performed on the dried matrix films to investigate the thickness of the coatings as well as to study the morphology of the dried films. The thickness of the coatings was found to increase with a decrease in the glycerol concentration. The uniformity of the dried films of antibody/glycerol formulations prepared from CMC-12 matrix solutions were found to be the best among the different matrix solutions and this superior uniformity helped achieve lower resistance. Therefore, CMC-12 matrix solution may be a potential candidate for biosensing applications.

The resistance response of different matrix dried film formulations were modeled using the RSM design. Among the three different ratio variations of SWNT:Glycerol, the

highest 1:1 ratio was found to lead to the lowest electrical resistance. Although the addition of antibody to the matrix results in an increase in the resistance of the matrix coating, increased levels of antibody up to the SWNT:antibody ratio of 10 can be added while maintaining the resistance below 2000 Ω if the formulation is not diluted. Therefore, it was determined that the matrix coating obtained using the CMC dispersant at the ratio of SWNT:CMC=2 and the sonication amplitude of 40% for 2 hours will lead to a relative low resistance, and uniform dried matrix film compared to others that were studied. Glycerol at the ratio of SWNT:glycerol of 1:1 is included in this matrix formulation and potentially could serve as a stabilizer to preserve the activity of antibodies after drying (not studied in this thesis). It is hoped that information from this research will be helpful in the design of immunodiagnostic biosensors relying on antibody-SWNT design elements.

FUTURE STUDY

4.1 Objective

A long-term research laboratory goal in Dr. Young's laboratory is to formulate a stable, sensitive and fast biosensor for immunodiagnostics application. Once developed, application of printing technology would be further pursued to streamline the matrix deposition process and avoid high expenses associated with traditional sensor manufacturing processing. A disposable biosensor suitable for point-of-care application is envisioned. With low fabrication cost and capability of miniaturization, this biosensor may find potential applications in both toxin detection and immunodiagnostics. Future studies beyond the scope of this dissertation would be required to develop multipurpose functional biosensors with reliable responses. Nevertheless, future work might be done using the results from the prior sections in this thesis to explore matrix resistance versus time of antigen solution exposure curves at different antigen solution concentrations to determine if specific antibody–antigen binding can be detected.

4.1.1 Experimental

The schematic picture of a fabricated laboratory test biosensor plate is depicted in Figure 113, Figure 114 and Figure 115. The biosensor is fabricated as follows (slightly modified from [1]), Ag silver ink will be deposited on DuPont Teijin Films™ (Melinex® ST505) polyester films using Western Michigan University's (WMU) MSP-485 screen printer (from Affiliated Manufacturers Inc.). Conductive Ag ink (Electrodag 7019) from Henkel is deposited as electrodes on Polyethylene terephthalate (PET) with 175 μm thickness. The resulting Ag electrode prints is cured for 10 min at 107°C. Carbon ink

(Electrodag 440B) is screen-printed on the silver layer to protect the silver layer from electron migration. The patterns on the screen used for this layer are deliberately slightly larger than that of the silver pattern to make sure that the carbon layer completely covers the silver. The carbon layer is also cured for 10 min at 107°C. SonoPlot® GIX Microplotter II is used to fabricate the channels as pictured in Figure 113. 3M™ Novec™ 2702 Electronic Grade Coating fluorochemical acrylic polymer carried in a hydrofluoroether solvent as a non-wetting polymer will be used for this purpose. This polymer is characterized as a low viscosity and low surface tension solution and comes in clear aqueous solution. The deposited channels are then cure at 100 °C for 1 hr for maximum attachment. The PET sheets are then UVO treated and attached to 75×50 mm microscope slides. 0.2 ml of matrix solution with different concentration (Figure 113) is deposited in the channels using a pipette and allowed to dry. Adhesive tape is placed on the sides of the PET. Then a glass cover slip is placed on the adhesive tape leaving a small gap between the channels and the cover slip to control the amount of analyte which will later be introduced to the channels for the resistivity measurement (Figure 114). A 1”x3" glass cover slide is attached to the double stick adhesive spacer so the slide is positioned directly above the matrices (see Figure 115). This slide has eight parallel lines of non-wetting polymer that lie directly above the 8 parallel lines of non-wetting polymer on the PET below. This allows the liquid sample to migrate into the gap above each of the matrix layers. With the spacer providing a narrow air gap (4 mils or less depending on the spacer, <100,000 nm) above the matrices and the glass cover slide (see Figure 115 side view), a controlled volume of liquid sample can be applied that will precisely coat each matrix with test sample.

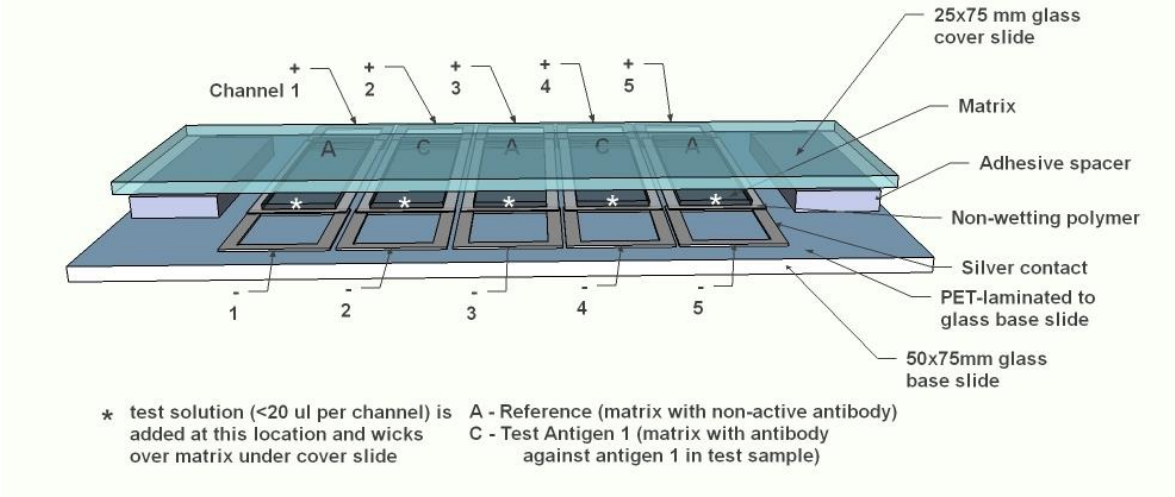


Figure 113. Side view of a five-channel test plate (adapted from [1]). The narrow gap between the bottom of the top glass slide and the top of the matrix for the five channels, through surface tension, draws the antigen containing test solution under the top glass slide when applied at the edge of the slide (see asterisk). The bottom of the top glass slide has lines of anti-wetting polymer strategically deposited to contain the applied liquid test sample over each matrix.

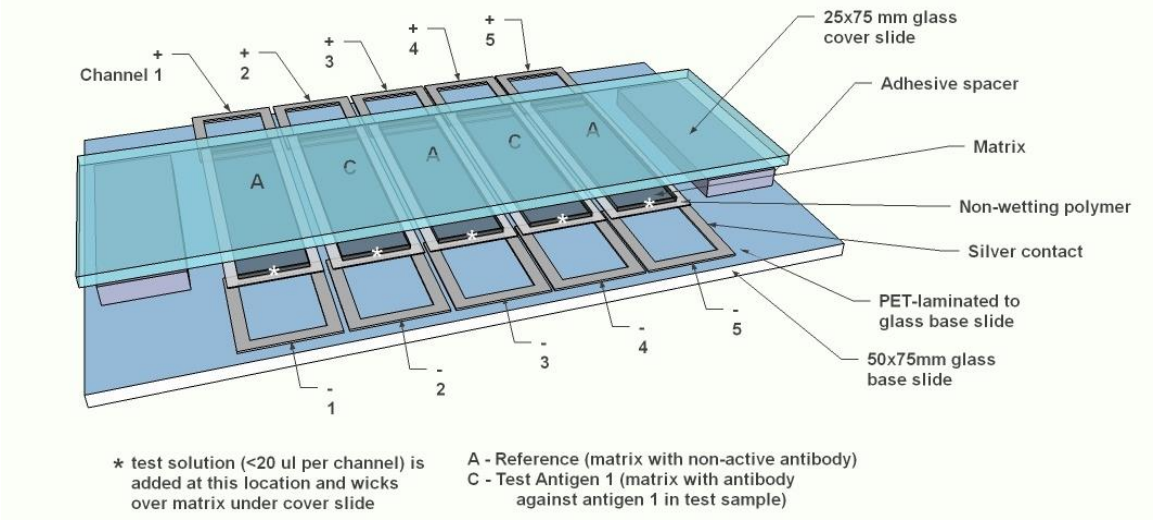


Figure 114. Schematic of five-channel test plate (adapted from [1]) for testing matrix formulations. Once connected to data acquisition system, the resistance of each matrix channel will be measured

every 10 sec upon addition of ~20 micro litter of the antigen-containing test solution to each matrix channel.

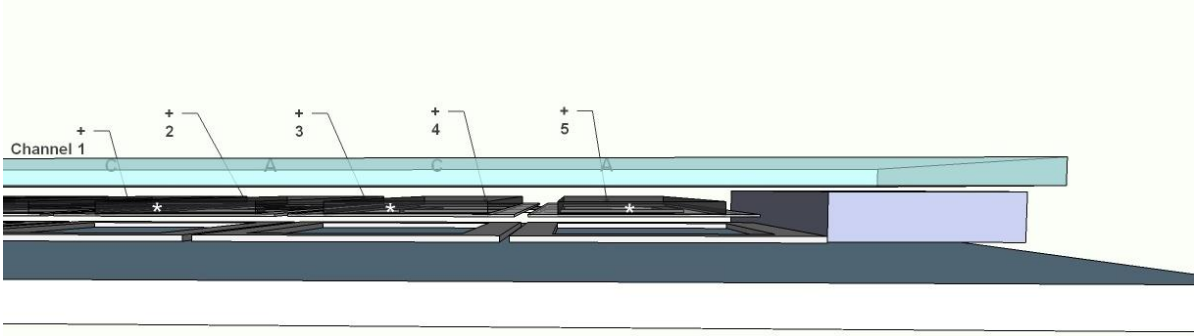


Figure 115. Enlarged view of the various layers that are affixed to the glass base slide of a test plate (adapted from [1]).

4.1.1.1 Matrix solution formulation

Preliminary work with the base matrix formulations, biosolutions and plate apparatus have been completed [1]. Matrix solutions containing different percentages of conducting Single Wall Carbon Nanotubes (SWNT) (SWeNT SG 76), Poly(sodium 4-styrenesulfonate) (PSS) 70,000 molecular weight, Glycerol (Sigma Aldrich), and IgG from rabbit serum (I5006) (Sigma Aldrich) and Anti-Rabbit IgG (R2004) (Sigma Aldrich) were used in this study. Sodium phosphate ($NaPO_4$) (Sigma Aldrich) and Sodium azide (Sigma Aldrich) were added to maintain a suitable condition for the proteins.

The matrix solution was prepared using the following method: different concentrations of SWNTs, glycerol, azide, sodium phosphate, PSS-water solution, and water were vortexed and completely dispersed with a sonicator at 1 watt/g for 2 hours. Then the I5006 protein was added to the vial and inverted 10 times for the proteins to mix completely into the solution. 0.15 or 0.2 ml of the solution was deposited in the channels using a pipette.

4.1.1.2 Test solution formulation

Test solutions containing 5, 1, 0.3, 0.08, 0.02, 0.005 and 0 mg/ml of antibody I5006 were prepared in buffer solution. Different concentrations of antigens were achieved by the dilution of the stock antigen solution with buffer of the same ionic strength. All solutions had the same ion conductivity as determined by a 3 point conductivity probe to minimize any chance of misinterpreting any apparent trends or correlations that could result if test solutions were of different salt/ion concentrations. R2004 will specifically bind I5006. Therefore the test solution which contains I5006 will specifically bind to the R2004 antibody in the channels. However the channels to which the I5006 protein was added in the matrix should not exhibit any specific binding. The latter channels were used as the control channels to be compared with the other channels. Buffer solutions without the presence of protein were used to evaluate the effect of buffer alone on the results. This way, it was possible to account for the effect of the buffer on the results. A total of 7 test plates with 2 "I" channel and 3 "R" channel replicates for each test solution concentration were used in the study for a given matrix formulation.

4.1.1.3 Characterization

2-point resistance measurements (Keithley 2602 Dual-Channel System Source-Meter) using a constant current resistance measurement of 0.7 uA were used. The resistance results were plotted. Once the test solution, 30 μL, was applied to the matrix-coated channels, the resistance values were recorded every 5 minutes and the change in the value of the resistance was correlated with the concentration of the antigen in the applied test solution. Analysis was performed to investigate the significance of the differences among the different concentrations of the antigen.

In this preliminary work, non-specific binding was shown to dominate the response and specific binding, if any, comparable to or less than inherent error in the resistance measurements.

4.1.1.4 Further Work

Future work could continue to explore antibody-antigen binding studies using this biosensor test-plate thin film matrix concept evaluated in the preliminary studies noted earlier but with CMC as the dispersant (rather than PSS) as it can be coated in more uniform coatings in a more predictable fashion compared to PSS as elucidated in the research reported in this thesis.

OVERALL CONCLUSIONS

Certain biosensors working on the basis of conductance/impedance changes have demonstrated their potential to detect various bacteria, enzymes, and biomolecules due to their enhanced electrical properties with incorporated single-walled carbon nanotubes (SWNT). One of the most challenging aspects in the development, characterization and optimization of biosensor material formulations for immunodiagnostic applications is uniformly dispersing SWNTs within the sensing component. In this study, this challenge has been addressed through a series of experiments varying the concentration of poly(sodium 4-styrenesulfonate) (PSS) or carboxymethylcellulose (CMC), two dispersing agents, glycerol (a protein protective/stability agent), and antibody formulated relative to the concentration of a conductive SWNT (at three concentrations of 0.21%, 15% and 8.4% by weight SWNT) in a phosphate buffered aqueous solution. Various sonication protocols (duration and intensity-% amplitude) were also evaluated. Formulated matrix solutions were characterized using dynamic light scattering. Dried composite "matrix" films deposited on test plate templates were characterized using 3D optical microscopy. Resistivity was determined for each dried composite matrix film.

A total of 198 experiments (120 experiments in Phase 1 and 78 experiments in Phase 2) were designed using Response Surface Methodology (RSM) in order to model the resistance of dried thin films of matrix solution produced under various conditions. Dispersed SWNT and aggregated/bundled SWNT present after various sonication protocols were separated by centrifugation and microfiltration, and percent dispersed was determined by weight difference of dried samples. This information was augmented with

particle size distribution data using the dynamic light scattering technique. Once characterized, the SWNTs matrix solutions were deposited within test sensor channels, dried into a semi-solid/fluid film, and resistance tested using a constant microamp current. Test sensor plates used in this study were prepared using printing technology consisting of screen printing and material plotting over PET base substrates. The surface total free energy of the PET substrate used was increased from ~39 to 67 dyn/cm by UVO treatment for 5 minutes prior to use in these studies.

The purpose of the Phase 1 on this study was to identify the role of the dispersing agents (CMC and PSS) at different SWNT:dispersant ratios under various sonication protocols (intensity/amplitude and duration). It was found that run 15 matrix solution (SWNT:CMC=2, sonication amplitude=40%, sonication duration=24 hr) resulted in dried matrix films with the lowest resistance (128 Ω) and possessed an average particle size of ~115 nm. In contrast, the largest particle size (where 81% of the particles have an average particle size of ~5000 nm), for the set of formulation experiments in which CMC was used, was observed in Run 3 (SWNT:CMC=0.5, Sonication amplitude=20%, and sonication duration= 2 hr) in which the highest dried film resistance was also obtained. From this it was concluded that a lower SWNT:CMC ratio (lower conductive:insulating components) is contributing to larger SWNT particle size that together are contributing to higher film resistivity. Higher concentration of dispersant in comparison with the SWNTs may result in the dispersant wrapping in multiple layers around SWNTs which hinders electron transport along the conductive carbon nanotubes. This may also create larger particles which results in the removal of SWNTs from the solution after filtration.

The sonication factor was found to play an important role in the dispersion and conductivity of SWNTs. The analysis of variance of the particle sizes obtained in the PSS-dispersed matrix solutions shows that the sonication amplitude and its interaction with the concentration of PSS are the only significant factors among all (α=0.05). Moreover, the sonication duration is the most significant factor in the analysis of variance of the particle sizes obtained in the CMC-dispersed matrix solutions (longer sonication, smaller particle size), although there are other interacting variables.

3D optical microscopy was performed on the dried matrix films to investigate the morphology, and roughness of the dried films as well as to measure the thickness of the coatings. Profilometry of Run 3 (CMC-dispersed coating) at 100% (no dilution) showed an average roughness of 0.274 μm while profilometry of Run 15 at 100% (no dilution) showed an average roughness of 0.067 μm. The same trend was noted for matrix coatings at higher dilutions (70% and 40%). Therefore, increased particle size of the matrix formulations had a strong correlation with increased roughness, and increased resistance of the CMC-dispersed coatings. Superior uniformity with low average roughness was observed for the coatings in which CMC was used as the dispersing agent in contrast to PSS.

The thickness of the dried matrix films as measured by 3D optical microscopy was found to decrease with the dilution of the matrix solution as would be expected due to reduced solids content. As an example, the thickness of matrix coatings obtained from Run 15 of the formulation in which CMC was used as the dispersant at 100% (no dilution), 70% dilution, and 40% dilution was measured to be 3.86, 2.81, and 1.63 μm, respectively. Mass balance of each prepared solution was performed by determining the weight difference of

the solids before and after the centrifugation and filtration and the thickness of the coatings after drying were calculated based on solids content, volume applied and area. The results were compared with thickness measurements by the 3D optical microscope. The calculated values were found to be very close to the experimentally measured thickness measurements.

Based on the experimentally-determined higher quality and superior workability of the formulations and resulting dried matrix films, it was concluded that CMC rather than PSS was more consistent and should be used as the dispersant in the matrix formulations developed in the 2nd phase (chapter 3) of this dissertation. The base matrix solution formulations carried forward to the 2nd research phase achieved low resistance for each SWNT to CMC ratio studied. Matrix formulation protocols from Run 14 (SWNT:CMC = 0.5), Run 17 (SWNT:CMC = 1.25), and Run 12 (SWNT:CMC = 2) were selected and labeled as CMC-14, CMC-17, and CMC-12, respectively. The corresponding resistance results for the dried matrices were 1069, 794, and 148 Ω, respectively. 78 different solutions were prepared using the CMC-14, CMC-17, and CMC-12 base matrix formulations based on an experimental design containing various SWNT:glycerol and SWNT:antibody ratios. Their resistance responses as well as surface morphologies of the dried matrix films were investigated using profilometry. The resistance responses of these antibody/glycerol-containing dried matrix films were modeled using the RSM design. The resistance behavior of coatings prepared from CMC-12 solution were found to be statistically more predictable when compared to that of the coatings prepared from solutions CMC-14 and CMC-17. 3D optical microscopy showed that the thickness of the coatings increased with a decrease in the glycerol concentration. The uniformity of the

coatings prepared from CMC-12 matrix solutions were found to be the highest among the different matrix solutions tested and the superior uniformity resulted in lower resistance.

Among the three different ratio variations of SWNT:Glycerol studied with CMC-12, the highest 1:1 ratio of the three ratios tested was found to lead to the lowest electrical resistance. Glycerol at the ratio of SWNT:Glycerol of 1:1 can be used as a stabilizer to perhaps preserve the activity of antibody after drying. Although the addition of antibody in the system results in an increase in the resistance of the matrix coating, a concentration of antibody, as high as SWNT:Antibody ratio of 10, can be selected while maintaining relative low resistance (below 2000 Ω for the geometry used in this research), with no dilution of the formulation. These levels of antibody and glycerol together with a base matrix formulation using the CMC dispersant at the ratio of SWNT:CMC=2 and the sonication amplitude of 40% for 2 hours was found to give the best properties. It is hoped that information from this research will be helpful in the design of immunodiagnostic biosensors relying on antibody-SWNT design elements.

REFERENCES

[1] B. Young, P. Aminayi, and T. young, "Evaluation of Thin Film Nanotube-Antibody Matrix Materials for Potential Integration into Immunodiagnostic Biosensors," in *WMU Research and Creative Scholars Day*, Kalamazoo, MI, 2014.

[2] L. Wang, W. Chen, D. Xu, B. S. Shim, Y. Zhu, F. Sun, *et al.*, "Simple, Rapid, Sensitive, and Versatile SWNT− Paper Sensor for Environmental Toxin Detection Competitive with ELISA," *Nano letters,* vol. 9, pp. 4147-4152, 2009.

[3] X. Wu, H. Kuang, C. Hao, C. Xing, L. Wang, and C. Xu, "Paper supported immunosensor for detection of antibiotics," *Biosensors and Bioelectronics,* vol. 33, pp. 309-312, 3/15/ 2012.

[4] J. S. Daniels and N. Pourmand, "Label-free impedance biosensors: Opportunities and challenges," *Electroanalysis,* vol. 19, pp. 1239-1257, // 2007.

[5] G. Evtugyn, "Introduction and Overview of History," in *Biosensors: Essentials*, ed: Springer, 2014, pp. 1-20.

[6] M. Vestergaard, K. Kerman, and E. Tamiya, "An overview of label-free electrochemical protein sensors," *Sensors,* vol. 7, pp. 3442-3458, 2007.

[7] X. Luo and J. J. Davis, "Electrical biosensors and the label free detection of protein disease biomarkers," *Chemical Society Reviews,* vol. 42, pp. 5944-5962, 2013.

[8] J. B. Beusink, A. M. C. Lokate, G. A. J. Besselink, G. J. M. Pruijn, and R. B. M. Schasfoort, "Angle-scanning SPR imaging for detection of biomolecular interactions on microarrays," *Biosensors and Bioelectronics,* vol. 23, pp. 839-844, // 2008.

[9] G. H. Cross, A. Reeves, S. Brand, M. J. Swann, L. L. Peel, N. J. Freeman, *et al.*, "The metrics of surface adsorbed small molecules on the young's fringe dual-slab waveguide interferometer," *Journal of Physics D: Applied Physics,* vol. 37, pp. 74-80, // 2004.

[10] G. H. Cross, A. A. Reeves, S. Brand, J. F. Popplewell, L. L. Peel, M. J. Swann, *et al.*, "A new quantitative optical biosensor for protein characterisation," *Biosensors and Bioelectronics,* vol. 19, pp. 383-390, // 2003.

[11] S. Lin, C. K. Lee, Y. H. Lin, S. Y. Lee, B. C. Sheu, J. C. Tsai, *et al.*, "Homopolyvalent antibody-antigen interaction kinetic studies with use of a dual-

polarization interferometric biosensor," *Biosensors and Bioelectronics,* vol. 22, pp. 715-721, // 2006.

[12] X. Cui, R. Pei, Z. Wang, F. Yang, Y. Ma, S. Dong, *et al.*, "Layer-by-layer assembly of multilayer films composed of avidin and biotin-labeled antibody for immunosensing," *Biosensors and Bioelectronics,* vol. 18, pp. 59-67, // 2003.

[13] C. Ayela, F. Roquet, L. Valera, C. Granier, L. Nicu, and M. Pugnière, "Antibody-antigenic peptide interactions monitored by SPR and QCM-D. A model for SPR detection of IA-2 autoantibodies in human serum," *Biosensors and Bioelectronics,* vol. 22, pp. 3113-3119, // 2007.

[14] X. Su, Y. J. Wu, and W. Knoll, "Comparison of surface plasmon resonance spectroscopy and quartz crystal microbalance techniques for studying DNA assembly and hybridization," *Biosensors and Bioelectronics,* vol. 21, pp. 719-726, // 2005.

[15] F. Huber, M. Hegner, C. Gerber, H. J. Güntherodt, and H. P. Lang, "Label free analysis of transcription factors using microcantilever arrays," *Biosensors and Bioelectronics,* vol. 21, pp. 1599-1605, // 2006.

[16] F. Tian, K. M. Hansen, T. L. Ferrell, T. Thundat, and D. C. Hansen, "Dynamic microcantilever sensor for discerning biomolecular interactions," *Analytical Chemistry,* vol. 77, pp. 1601-1606, // 2005.

[17] E. Komarova, K. Reber, M. Aldissi, and A. Bogomolova, "New multispecific array as a tool for electrochemical impedance spectroscopy-based biosensing," *Biosensors and Bioelectronics,* vol. 25, pp. 1389-1394, // 2010.

[18] A. E. Radi, X. Muñoz-Berbel, V. Lates, and J. L. Marty, "Label-free impedimetric immunosensor for sensitive detection of ochratoxin A," *Biosensors and Bioelectronics,* vol. 24, pp. 1888-1892, // 2009.

[19] V. Escamilla-Gómez, S. Campuzano, M. Pedrero, and J. M. Pingarrón, "Gold screen-printed-based impedimetric immunobiosensors for direct and sensitive Escherichia coli quantisation," *Biosensors and Bioelectronics,* vol. 24, pp. 3365-3371, // 2009.

[20] D. Grieshaber, R. MacKenzie, J. Vörös, and E. Reimhult, "Electrochemical biosensors - Sensor principles and architectures," *Sensors,* vol. 8, pp. 1400-1458, // 2008.

[21] I. E. Tothill, "Biosensors for cancer markers diagnosis," *Seminars in Cell & Developmental Biology*, vol. 20, pp. 55-62, 2// 2009.

[22] M. Varshney and Y. Li, "Interdigitated array microelectrodes based impedance biosensors for detection of bacterial cells," *Biosensors and Bioelectronics*, vol. 24, pp. 2951-2960, 6/15/ 2009.

[23] C. Berggren, B. Bjarnason, and G. Johansson, "Capacitive biosensors," *Electroanalysis*, vol. 13, pp. 173-180, // 2001.

[24] X. Chen, Y. Wang, J. Zhou, W. Yan, X. Li, and J. J. Zhu, "Electrochemical impedance immunosensor based on three-dimensionally ordered macroporous gold film," *Analytical Chemistry*, vol. 80, pp. 2133-2140, // 2008.

[25] N. De-los-Santos-Álvarez, M. J. Lobo-Castañón, A. J. Miranda-Ordieres, and P. Tuñón-Blanco, "Modified-RNA aptamer-based sensor for competitive impedimetric assay of neomycin B," *Journal of the American Chemical Society*, vol. 129, pp. 3808-3809, // 2007.

[26] J. R. Mcdonald, "Impedance spectroscopy: emphasizing solid materials and systems," *Impedance Spectroscopy Emphasizing Solid Materials and Systems*, 1987.

[27] V. Nandakumar, J. T. La Belle, J. Reed, M. Shah, D. Cochran, L. Joshi, *et al.*, "A methodology for rapid detection of Salmonella typhimurium using label-free electrochemical impedance spectroscopy," *Biosensors and Bioelectronics*, vol. 24, pp. 1039-1042, // 2008.

[28] T. Kurkina, A. Vlandas, A. Ahmad, K. Kern, and K. Balasubramanian, "Label-Free Detection of Few Copies of DNA with Carbon Nanotube Impedance Biosensors," *Angewandte Chemie International Edition*, vol. 50, pp. 3710-3714, 2011.

[29] Y. T. Long, C. Z. Li, H. B. Kraatz, and J. S. Lee, "AC impedance spectroscopy of native DNA and M-DNA," *Biophysical Journal*, vol. 84, pp. 3218-3225, // 2003.

[30] J. T. La Belle, K. Bhavsar, A. Fairchild, A. Das, J. Sweeney, T. L. Alford, *et al.*, "A cytokine immunosensor for multiple sclerosis detection based upon label-free electrochemical impedance spectroscopy," *Biosensors and Bioelectronics*, vol. 23, pp. 428-431, // 2007.

[31] S. J. Ding, B. W. Chang, C. C. Wu, M. F. Lai, and H. C. Chang, "Electrochemical evaluation of avidin-biotin interaction on self-assembled gold electrodes," *Electrochimica Acta*, vol. 50, pp. 3660-3666, // 2005.

[32] D. A. Mazzari and M. A. Seitz, "Biosensor," ed: Google Patents, 2012.

[33] P. Ajayan, T. Ebbesen, T. Ichihashi, S. Iijima, K. Tanigaki, and H. Hiura, "Opening carbon nanotubes with oxygen and implications for filling," *Nature*, vol. 362, pp. 522-525, 1993.

[34] A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, *et al.*, "Crystalline ropes of metallic carbon nanotubes," *Science-AAAS-Weekly Paper Edition*, vol. 273, pp. 483-487, 1996.

[35] J. Hone, B. Batlogg, Z. Benes, A. T. Johnson, and J. E. Fischer, "Quantized phonon spectrum of single-wall carbon nanotubes," *Science*, vol. 289, pp. 1730-1733, 2000.

[36] B. I. Yakobson and R. E. Smalley, "Fullerene nanotubes: C 1,000,000 and beyond," *American Scientist*, vol. 85, pp. 324-337, 1997.

[37] R. F. Service, "Superstrong nanotubes show they are smart, too," *Science*, vol. 281, pp. 940-942, 1998.

[38] R. Saito, G. Dresselhaus, and M. S. Dresselhaus, *Physical properties of carbon nanotubes* vol. 4: World Scientific, 1998.

[39] K. Koziol, B. O. Boskovic, and N. Yahya, "Synthesis of Carbon Nanostructures by CVD Method," in *Carbon and Oxide Nanostructures*, ed: Springer, 2011, pp. 23-49.

[40] Q. Chen, C. Saltiel, S. Manickavasagam, L. S. Schadler, R. W. Siegel, and H. Yang, "Aggregation behavior of single-walled carbon nanotubes in dilute aqueous suspension," *Journal of Colloid and Interface Science*, vol. 280, pp. 91-97, 12/1/ 2004.

[41] A. Elias, J. Rodriguez-Manzo, M. McCartney, D. Golberg, A. Zamudio, S. Baltazar, *et al.*, "Production and characterization of single-crystal FeCo nanowires inside carbon nanotubes," *Nano letters*, vol. 5, pp. 467-472, 2005.

[42] D. W. Schaefer, J. Zhao, J. M. Brown, D. P. Anderson, and D. W. Tomlin, "Morphology of dispersed carbon single-walled nanotubes," *Chemical Physics Letters*, vol. 375, pp. 369-375, 2003.

[43] P. Terech and Y. Talmon, "Aqueous suspensions of steroid nanotubules: Structural and rheological characterizations," *Langmuir*, vol. 18, pp. 7240-7244, 2002.

[44] T. Zhou, Q. Zhou, and Y. Yang, "An Acetylcholinesterase Biosensor Based on Platinum-Palladium Nanoparticles-Single Walled Carbon Nanotubes," *Advanced Materials Research,* vol. 850, pp. 102-106, 2014.

[45] J.-L. Gong, T. Sarkar, S. Badhulika, and A. Mulchandani, "Label-free chemiresistive biosensor for mercury (II) based on single-walled carbon nanotubes and structure-switching DNA," *Applied physics letters,* vol. 102, pp. 013701-013701-3, 2013.

[46] Y. Feng, N. Feng, Y. Bai, X. Wang, X. Zhou, and Y. Zhang, "Macroscopic Carbon Nanotube Fiber Film Based Glucose Biosensor," *International Journal of Electrochemical Science,* vol. 8, 2013.

[47] Y. Liu, G. Sun, C. Jiang, X. T. Zheng, L. Zheng, and C. M. Li, "Highly sensitive detection of hydrogen peroxide at a carbon nanotube fiber microelectrode coated with palladium nanoparticles," *Microchimica Acta,* pp. 1-8, 2013.

[48] J.-a. A. Ho, Y.-C. Lin, L.-S. Wang, K.-C. Hwang, and P.-T. Chou, "Carbon nanoparticle-enhanced immunoelectrochemical detection for protein tumor marker with cadmium sulfide biotracers," *Analytical chemistry,* vol. 81, pp. 1340-1346, 2009.

[49] A. Javey and J. Kong, *Carbon nanotube electronics*: Springer, 2009.

[50] C. Hierold, O. Brand, G. K. Fedder, J. G. Korvink, and O. Tabata, *Carbon Nanotube Devices: Properties, Modeling, Integration and Applications*: Wiley-VCH, 2008.

[51] V. N. Popov, "Carbon nanotubes: Properties and application," *Materials Science and Engineering R: Reports,* vol. 43, pp. 61-102, 2004.

[52] R. S. Ruoff and D. C. Lorents, "Mechanical and thermal properties of carbon nanotubes," *Carbon,* vol. 33, pp. 925-930, 1995.

[53] A. Kumar and C. Zhou, "The race to replace tin-doped indium oxide: Which material will win?," *ACS Nano,* vol. 4, pp. 11-14, 2010.

[54] M. C. LeMieux, M. Roberts, S. Barman, W. J. Yong, M. K. Jong, and Z. Bao, "Self-sorted, aligned nanotube networks for thin-film transistors," *Science,* vol. 321, pp. 101-104, 2008.

[55] B. Chandra, A. Afzali, N. Khare, M. M. El-Ashry, and G. S. Tulevski, "Stable charge-transfer doping of transparent single-walled carbon nanotube films," *Chemistry of Materials,* vol. 22, pp. 5179-5183, 2010.

[56] Q. Cao and J. A. Rogers, "Ultrathin films of single-walled carbon nanotubes for electronics and sensors: A review of fundamental and applied aspects," *Advanced Materials,* vol. 21, pp. 29-53, 2009.

[57] D. D. Tune and J. G. Shapter, "The potential sunlight harvesting efficiency of carbon nanotube solar cells," *Energy and Environmental Science,* vol. 6, pp. 2572-2577, 2013.

[58] K. Fu, O. Yildiz, H. Bhanushali, Y. Wang, K. Stano, L. Xue, *et al.*, "Aligned carbon nanotube-silicon sheets: A novel nano-architecture for flexible lithium ion battery electrodes," *Advanced Materials,* vol. 25, pp. 5109-5114, 2013.

[59] C. Journet, W. K. Maser, P. Bernier, A. Loiseau, M. Lamy de la Chapelle, S. Lefrant, *et al.*, "Large-scale production of single-walled carbon nanotubes by the electric-arc technique," *Nature,* vol. 388, pp. 756-758, 1997.

[60] R. H. Schmidt, I. A. Kinloch, A. N. Burgess, and A. H. Windle, "The Effect of Aggregation on the Electrical Conductivity of Spin-Coated Polymer/Carbon Nanotube Composite Films," *Langmuir,* vol. 23, pp. 5707-5712, 2007/05/01 2007.

[61] B. C. Satishkumar, A. Govindaraj, J. Mofokeng, G. N. Subbanna, and C. N. R. Rao, "Novel experiments with carbon nanotubes: Opening, filling, closing and functionalizing nanotubes," *Journal of Physics B: Atomic, Molecular and Optical Physics,* vol. 29, pp. 4925-4934, 1996.

[62] Y. Zhang, Z. Shi, Z. Gu, and S. Iijima, "Structure modification of single-wall carbon nanotubes," *Carbon,* vol. 38, pp. 2055-2059, // 2000.

[63] M. N. Tchoul, W. T. Ford, G. Lolli, D. E. Resasco, and S. Arepalli, "Effect of mild nitric acid oxidation on dispensability, size, and structure of single-walled carbon nanotubes," *Chemistry of Materials,* vol. 19, pp. 5765-5772, 2007.

[64] N. Nakashima and T. Fujigaya, "Fundamentals and Applications of Soluble Carbon Nanotubes," *Chemistry Letters,* vol. 36, pp. 692-697, 2007.

[65] T. Fujigaya and N. Nakashima, "Methodology for Homogeneous Dispersion of Single-walled Carbon Nanotubes by Physical Modification," *Polym. J,* vol. 40, pp. 577-589, 07/15/print 2008.

[66] A. Kuznetsova, I. Popova, J. T. Yates Jr, M. J. Bronikowski, C. B. Huffman, J. Liu, *et al.*, "Oxygen-containing functional groups on single-wall carbon nanotubes: NEXAFS and vibrational spectroscopic studies," *Journal of the American Chemical Society*, vol. 123, pp. 10699-10704, 2001.

[67] Y. T. Kim and T. Mitani, "Competitive effect of carbon nanotubes oxidation on aqueous EDLC performance: Balancing hydrophilicity and conductivity," *Journal of Power Sources*, vol. 158, pp. 1517-1522, 2006.

[68] M. S. Strano, V. C. Moore, M. K. Miller, M. J. Allen, E. H. Haroz, C. Kittrell, *et al.*, "The Role of Surfactant Adsorption during Ultrasonication in the Dispersion of Single-Walled Carbon Nanotubes," *Journal of Nanoscience and Nanotechnology*, vol. 3, pp. 81-86, // 2003.

[69] C. M. Sayes, F. Liang, J. L. Hudson, J. Mendez, W. Guo, J. M. Beach, *et al.*, "Functionalization density dependence of single-walled carbon nanotubes cytotoxicity in vitro," *Toxicology Letters*, vol. 161, pp. 135-142, 2006.

[70] Y. Bai, Y. Zhang, J. Zhang, Q. Mu, W. Zhang, E. R. Butch, *et al.*, "Repeated administrations of carbon nanotubes in male mice cause reversible testis damage without affecting fertility," *Nature Nanotechnology*, vol. 5, pp. 683-689, 2010.

[71] L. M. Pasquini, S. M. Hashmi, T. J. Sommer, M. Elimelech, and J. B. Zimmerman, "Impact of surface functionalization on bacterial cytotoxicity of single-walled carbon nanotubes," *Environmental Science and Technology*, vol. 46, pp. 6297-6305, 2012.

[72] L. Campagnolo, M. Massimiani, G. Palmieri, R. Bernardini, C. Sacchetti, A. Bergamaschi, *et al.*, "Biodistribution and toxicity of pegylated single wall carbon nanotubes in pregnant mice," *Particle and Fibre Toxicology*, vol. 10, pp. 1-13, 2013.

[73] L. Ren and W. Zhong, "Oxidation reactions mediated by single-walled carbon nanotubes in aqueous solution," *Environmental Science and Technology*, vol. 44, pp. 6954-6958, 2010.

[74] A. Galano, M. Francisco-Marquez, and A. Martínez, "Influence of point defects on the free-radical scavenging capability of single-walled carbon nanotubes," *Journal of Physical Chemistry C*, vol. 114, pp. 8302-8308, 2010.

[75] X. Qu, P. J. J. Alvarez, and Q. Li, "Photochemical transformation of carboxylated multiwalled carbon nanotubes: Role of reactive oxygen species," *Environmental Science and Technology*, vol. 47, pp. 14080-14088, 2013.

[76] B. Smith, J. Yang, J. L. Bitter, W. P. Ball, and D. H. Fairbrother, "Influence of surface oxygen on the interactions of carbon nanotubes with natural organic matter," *Environmental Science and Technology,* vol. 46, pp. 12839-12847, 2012.

[77] D. Tasis, N. Tagmatarchis, A. Bianco, and M. Prato, "Chemistry of carbon nanotubes," *Chemical Reviews,* vol. 106, pp. 1105-1136, 2006.

[78] H.-S. Hsieh and C. T. Jafvert, "Reactive oxygen species generation and dispersant-dependent electron transfer through single-walled carbon nanotubes in water," *Carbon,* vol. 89, pp. 361-371, 8// 2015.

[79] D. Douroumis, D. G. Fatouros, N. Bouropoulos, K. Papagelis, and D. Tasis, "Colloidal stability of carbon nanotubes in an aqueous dispersion of phospholipid," *International Journal of Nanomedicine,* vol. 2, pp. 761-766, 2007.

[80] Y. L. Zhao and J. F. Stoddart, "Noncovalent functionalization of single-walled carbon nanotubes," *Accounts of Chemical Research,* vol. 42, pp. 1161-1171, 2009.

[81] V. C. Moore, M. S. Strano, E. H. Haroz, R. H. Hauge, R. E. Smalley, J. Schmidt, *et al.*, "Individually Suspended Single-Walled Carbon Nanotubes in Various Surfactants," *Nano Letters,* vol. 3, pp. 1379-1382, 2003.

[82] C. J. Smith, B. J. Shaw, and R. D. Handy, "Toxicity of single walled carbon nanotubes to rainbow trout, (Oncorhynchus mykiss): Respiratory toxicity, organ pathologies, and other physiological effects," *Aquatic Toxicology,* vol. 82, pp. 94-109, 2007.

[83] C. A. Poland, R. Duffin, I. Kinloch, A. Maynard, W. A. H. Wallace, A. Seaton, *et al.*, "Carbon nanotubes introduced into the abdominal cavity of mice show asbestos-like pathogenicity in a pilot study," *Nature Nanotechnology,* vol. 3, pp. 423-428, 2008.

[84] I. Schwyzer, R. Kaegi, L. Sigg, R. Smajda, A. Magrez, and B. Nowack, "Long-term colloidal stability of 10 carbon nanotube types in the absence/presence of humic acid and calcium," *Environmental Pollution,* vol. 169, pp. 64-73, 2012.

[85] P. Wang, Q. Shi, H. Liang, D. W. Steuerman, G. D. Stucky, and A. A. Keller, "Enhanced environmental mobility of carbon nanotubes in the presence of humic acid and their removal from aqueous solution," *Small,* vol. 4, pp. 2166-2170, 2008.

[86] H. Hyung, J. D. Fortner, J. B. Hughes, and J. H. Kim, "Natural organic matter stabilizes carbon nanotubes in the aqueous phase," *Environmental Science and Technology,* vol. 41, pp. 179-184, 2007.

[87] D. Lifeng, L. J. Katherine, M. W. Colette, and M. C. Michael, "Cytotoxicity of single-walled carbon nanotubes suspended in various surfactants," *Nanotechnology,* vol. 19, p. 255702, 2008.

[88] Z. Liu, S. Tabakman, K. Welsher, and H. Dai, "Carbon nanotubes in biology and medicine: In vitro and in vivo detection, imaging and drug delivery," *Nano Research,* vol. 2, pp. 85-120, 2009.

[89] S. Azoz, L. M. Gilbertson, S. M. Hashmi, P. Han, G. E. Sterbinsky, S. A. Kanaan, *et al.*, "Enhanced dispersion and electronic performance of single-walled carbon nanotube thin films without surfactant: A comprehensive study of various treatment processes," *Carbon,* vol. 93, pp. 1008-1020, 11// 2015.

[90] J. Fu, D. Li, G. Li, F. Huang, and Q. Wei, "Carboxymethyl cellulose assisted immobilization of silver nanoparticles onto cellulose nanofibers for the detection of catechol," *Journal of Electroanalytical Chemistry,* vol. 738, pp. 92-99, 2/1/ 2015.

[91] L. Sanhueza, J. Castro, E. Urzúa, L. Barrientos, F. Oyarzun-Ampuero, H. Pesenti, *et al.*, "Photochromic Solid Materials Based on Poly(decylviologen) Complexed with Alginate and Poly(sodium 4-styrenesulfonate)," *The Journal of Physical Chemistry B,* 2015/09/23 2015.

[92] S. Paul, Y. S. Kang, J.-H. Yim, K. Y. Cho, and D.-W. Kim, "Effect of surfactant and coating method on the electrical and optical properties of thin conductive films prepared with single-walled carbon nanotubes," *Current Applied Physics,* vol. 10, pp. e101-e104, 11// 2010.

[93] M. Shimizu, S. Fujii, T. Tanaka, and H. Kataura, "Effects of surfactants on the electronic transport properties of thin-film transistors of single-wall carbon nanotubes," *Journal of Physical Chemistry C,* vol. 117, pp. 11744-11749, 2013.

[94] M. Monthioux, B. W. Smith, B. Burteaux, A. Claye, J. E. Fischer, and D. E. Luzzi, "Sensitivity of single-wall carbon nanotubes to chemical processing: An electron microscopy investigation," *Carbon,* vol. 39, pp. 1251-1272, 2001.

[95] A. G. Rinzler, J. Liu, H. Dai, P. Nikolaev, C. B. Huffman, F. J. Rodriguez-Macías, *et al.*, "Large-scale purification of single-wall carbon nanotubes: Process, product, and characterization," *Applied Physics A: Materials Science and Processing,* vol. 67, pp. 29-37, 1998.

[96] M. J. O'Connell, P. Boul, L. M. Ericson, C. Huffman, Y. Wang, E. Haroz, *et al.*, "Reversible water-solubilization of single-walled carbon nanotubes by polymer wrapping," *Chemical Physics Letters,* vol. 342, pp. 265-271, 7/13/ 2001.

[97] B. Vigolo, A. Penicaud, C. Coulon, C. Sauder, R. Pailler, C. Journet, *et al.*, "Macroscopic fibers and ribbons of oriented carbon nanotubes," *Science,* vol. 290, pp. 1331-1334, 2000.

[98] J. Pang and G. Xu, "Molecular dynamics simulations of the interactions between SWNT and surfactants," *Computational Materials Science,* vol. 65, pp. 324-330, 12// 2012.

[99] Z. Xu, X. Yang, and Z. Yang, "A Molecular Simulation Probing of Structure and Interaction for Supramolecular Sodium Dodecyl Sulfate/Single-Wall Carbon Nanotube Assemblies," *Nano Letters,* vol. 10, pp. 985-991, 2010/03/10 2010.

[100] N. R. Tummala, B. H. Morrow, D. E. Resasco, and A. Striolo, "Stabilization of Aqueous Carbon Nanotube Dispersions Using Surfactants: Insights from Molecular Dynamics Simulations," *ACS Nano,* vol. 4, pp. 7193-7204, 2010/12/28 2010.

[101] M. Yang, V. Koutsos, and M. Zaiser, "Interactions between Polymers and Carbon Nanotubes: A Molecular Dynamics Study," *The Journal of Physical Chemistry B,* vol. 109, pp. 10009-10014, 2005/05/01 2005.

[102] Q. Zheng, Q. Xue, K. Yan, L. Hao, Q. Li, and X. Gao, "Investigation of Molecular Interactions between SWNT and Polyethylene/Polypropylene/Polystyrene/Polyaniline Molecules," *The Journal of Physical Chemistry C,* vol. 111, pp. 4628-4635, 2007/03/01 2007.

[103] W. Liu, C.-L. Yang, Y.-T. Zhu, and M.-s. Wang, "Interactions between Single-Walled Carbon Nanotubes and Polyethylene/Polypropylene/Polystyrene/Poly(phenylacetylene)/Poly(p-phenylenevinylene) Considering Repeat Unit Arrangements and Conformations: A Molecular Dynamics Simulation Study," *The Journal of Physical Chemistry C,* vol. 112, pp. 1803-1811, 2008/02/01 2008.

[104] Zhao and J. K. Johnson, "Simulation of Adsorption of DNA on Carbon Nanotubes," *Journal of the American Chemical Society,* vol. 129, pp. 10438-10445, 2007/08/01 2007.

[105] C.-c. Chiu, M. C. Maher, G. R. Dieckmann, and S. O. Nielsen, "Molecular Dynamics Study of a Carbon Nanotube Binding Reversible Cyclic Peptide," *ACS Nano,* vol. 4, pp. 2539-2546, 2010/05/25 2010.

[106] T. Rungrotmongkol, U. Arsawang, C. Iamsamai, A. Vongachariya, S. T. Dubas, U. Ruktanonchai, *et al.*, "Increased dispersion and solubility of carbon nanotubes noncovalently modified by the polysaccharide biopolymer, chitosan: MD simulations," *Chemical Physics Letters,* vol. 507, pp. 134-137, 4/29/ 2011.

[107] J. Xie, Q. Xue, H. Chen, A. Keller, and M. Dong, "Different factors' effect on the SWNT-fluorocarbon resin interaction: A MD simulation study," *Computational Materials Science,* vol. 49, pp. 148-157, 6// 2010.

[108] G. Evtugyn, "Biochemical Components Used in Biosensor Assemblies," in *Biosensors: Essentials*. vol. 84, ed: Springer Berlin Heidelberg, 2014, pp. 21-97.

[109] Y. M. Newman, S. G. Ring, and C. Colaco, "The Role of Trehalose and Other Carbohydrates in Biopreservation," *Biotechnology and Genetic Engineering Reviews,* vol. 11, pp. 263-294, 1993/12/01 1993.

[110] K. B. Storey and J. M. Storey, "Frozen and alive," *Scientific American,* vol. 263, pp. 92-97, 1990.

[111] K. Fox, "Biopreservation. Putting proteins under glass," *Science,* vol. 267, pp. 1922-1923, March 31, 1995 1995.

[112] M. J. Pikal, "Freeze-drying of proteins. Part II: Formulation selection," *BioPharm,* vol. 3, pp. 26-30, 1990.

[113] G. Caliskan, A. Kisliuk, A. M. Tsai, C. L. Soles, and A. P. Sokolov, "Influence of solvent on dynamics and stability of a protein," *Journal of Non-Crystalline Solids,* vol. 307–310, pp. 887-893, 9// 2002.

[114] L. Chang, D. Shepherd, J. Sun, D. Ouellette, K. L. Grant, X. Tang, *et al.*, "Mechanism of protein stabilization by sugars during freeze-drying and storage: Native structure preservation, specific interaction, and/or immobilization in a glassy matrix?," *Journal of Pharmaceutical Sciences,* vol. 94, pp. 1427-1444, 2005.

[115] M. T. Cicerone and C. L. Soles, "Fast Dynamics and Stabilization of Proteins: Binary Glasses of Trehalose and Glycerol," *Biophysical Journal,* vol. 86, pp. 3836-3845, 6// 2004.

[116] F. Franks, R. H. M. Hatley, and S. F. Mathias, "MATERIALS SCIENCE AND THE PRODUCTION OF SHELF-STABLE BIOLOGICALS," *Biopharm-the Technology & Business of Biopharmaceuticals,* vol. 4, pp. 38-&, Oct 1991.

[117] L. Slade, H. Levine, and D. S. Reid, "Beyond water activity: Recent advances based on an alternative approach to the assessment of food quality and safety," *Critical Reviews in Food Science and Nutrition,* vol. 30, pp. 115-360, 1991/01/01 1991.

[118] J. F. Carpenter, S. J. Prestrelski, and T. Arakawa, "Separation of Freezing- and Drying-Induced Denaturation of Lyophilized Proteins Using Stress-Specific

Stabilization: I. Enzyme Activity and Calorimetric Studies," *Archives of Biochemistry and Biophysics,* vol. 303, pp. 456-464, 6// 1993.

[119] J. F. Carpenter and J. H. Crowe, "An infrared spectroscopic study of the interactions of carbohydrates with dried proteins," *Biochemistry,* vol. 28, pp. 3916-3922, 1989/05/01 1989.

[120] J. Crowe, L. Crowe, and J. Carpenter, "Preserving dry biomaterials: the water replacement hypothesis, part 1," *BIOPHARM-EUGENE-*, vol. 6, pp. 28-28, 1993.

[121] P. K. GhattyVenkataKrishna and G. A. Carri, "Effect of glycerol–water binary mixtures on the structure and dynamics of protein solutions," *Journal of Biomolecular Structure and Dynamics,* vol. 32, pp. 424-437, 2014/03/04 2014.

[122] J. C. Hulteen, D. A. Treichel, M. T. Smith, M. L. Duval, T. R. Jensen, and R. P. Van Duyne, "Nanosphere lithography: Size-tunable silver nanoparticle and surface cluster arrays," *Journal of Physical Chemistry B,* vol. 103, pp. 3854-3863, 1999.

[123] O. A. Louchev, Y. Sato, and H. Kanda, "Growth mechanism of carbon nanotube forests by chemical vapor deposition," *Applied Physics Letters,* vol. 80, pp. 2752-2754, 2002.

[124] G. S. Choi, Y. S. Cho, K. H. Son, and D. J. Kim, "Mass production of carbon nanotubes using spin-coating of nanoparticles," *Microelectronic Engineering,* vol. 66, pp. 77-82, 2003.

[125] D. Kim, S. Jeong, S. Lee, B. K. Park, and J. Moon, "Organic thin film transistor using silver electrodes by the ink-jet printing technology," *Thin Solid Films,* vol. 515, pp. 7692-7696, 2007.

[126] W. W. Yu and I. M. White, "Inkjet printed surface enhanced Raman spectroscopy array on cellulose paper," *Analytical chemistry,* vol. 82, pp. 9626-9630, 2010.

[127] S. H. Ko, H. Pan, C. P. Grigoropoulos, C. K. Luscombe, J. M. Fréchet, and D. Poulikakos, "All-inkjet-printed flexible electronics fabrication on a polymer substrate by low-temperature high-resolution selective laser sintering of metal nanoparticles," *Nanotechnology,* vol. 18, p. 345202, 2007.

[128] O. Brand, G. K. Fedder, C. Hierold, O. Tabata, J. G. Korvink, P. J. Smith, *et al.*, *Inkjet-based Micromanufacturing*: John Wiley & Sons, 2012.

[129] G. Li, R. C. Roberts, and N. C. Tien, "Interlacing method for micro-patterning silver via inkjet printing," in *SENSORS, 2014 IEEE,* 2014, pp. 1687-1690.

[130] H. Kipphan, *Handbook of Print Media: Technologies and Production Methods*: Springer Berlin Heidelberg, 2014.

[131] X. Zhu, L. Zhu, H. Chen, Z. Li, and W. Zhang, "Fabrication of high numerical aperture micro-lens array based on drop-on-demand generating of water-based molds," *Optics & Laser Technology,* vol. 68, pp. 23-27, 5// 2015.

[132] J. Sakai, E. Fujinaka, T. Nishimori, N. lto, J. Adachi, S. Nagano, *et al.*, "High efficiency organic solar cells by screen printing method," in *Photovoltaic Specialists Conference, 2005. Conference Record of the Thirty-first IEEE,* 2005, pp. 125-128.

[133] P. Aminayi, M. Rezaei, and M. Z. Atashbar, "A Novel Inkjet Printed Surface Enhanced Raman Spectroscopy (SERS) Substrate Based on Marangoni Effect for the Detection of Heavy Metal Compounds," in *IMCS,* Buenos Aires, Argentina, 2014.

[134] P. Aminayi, M. Rezaei, and M. Z. Atashbar, "Detection of Heavy Metal Compounds Using a Novel Inkjet Printed Surface Enhanced Raman Spectroscopy (SERS) Substrate Based on Metallic Triangular Nano Structures," in *IMCS,* Buenos Aires, Argentina, 2014.

[135] H. Cheun, P. P. Rugheimer, B. J. Larson, P. Gopalan, M. G. Lagally, and M. J. Winokur, "Polymer light emitting diodes and poly(di-n-octylfluorene) thin films as fabricated with a microfluidics applicator," *Journal of Applied Physics,* vol. 100, p. 073510, 2006.

[136] "GIX Microplotter II User Manual," ed: SonoPlot, Inc., 2015.

[137] J. A. Owczarek and F. Howland, "A study of the off-contact screen printing process. I. Model of the printing process and some results derived from experiments," *Components, Hybrids, and Manufacturing Technology, IEEE Transactions on,* vol. 13, pp. 358-367, 1990.

[138] V. Serafín, L. Agüí, P. Yáñez-Sedeño, and J. M. Pingarrón, "A novel hybrid platform for the preparation of disposable enzyme biosensors based on poly(3,4-ethylenedioxythiophene) electrodeposition in an ionic liquid medium onto gold nanoparticles-modified screen-printed electrodes," *Journal of Electroanalytical Chemistry,* vol. 656, pp. 152-158, 2011.

[139] S. V. Pereira, F. A. Bertolino, M. A. Fernandez-Baldo, G. A. Messina, E. Salinas, M. I. Sanz, *et al.*, "A microfluidic device based on a screen-printed carbon electrode with electrodeposited gold nanoparticles for the detection of IgG anti-Trypanosoma cruziantibodies," *Analyst,* vol. 136, pp. 4745-4751, 2011.

[140] Ó. A. Loaiza, S. Campuzano, M. Pedrero, and J. M. Pingaron, "Designs of Enterobacteriaceae Lac Z Gene DNA Gold Screen Printed Biosensors," *Electroanalysis,* vol. 20, pp. 1397-1405, 2008.

[141] Yean, B. Kamarudin, D. A. Ozkan, L. S. Yin, P. Lalitha, A. Ismail, *et al.*, "Enzyme-Linked Amperometric Electrochemical Genosensor Assay for the Detection of PCR Amplicons on a Streptavidin-Treated Screen-Printed Carbon Electrode," *Analytical Chemistry,* vol. 80, pp. 2774-2779, 2008/03/18 2008.

[142] Z. Zou, J. Kai, M. J. Rust, J. Han, and C. H. Ahn, "Functionalized nano interdigitated electrodes arrays on polymer with integrated microfluidics for direct bio-affinity sensing using impedimetric measurement," *Sensors and Actuators, A: Physical,* vol. 136, pp. 518-526, 2007.

[143] M. Basu, S. Seggerson, J. Henshaw, J. Jiang, R. D. A. Cordona, C. Lefave, *et al.*, "Nano-biosensor development for bacterial detection during human kidney infection: Use of glycoconjugate-specific antibody-bound gold NanoWire arrays (GNWA)," *Glycoconjugate Journal,* vol. 21, pp. 487-496, 2004.

[144] M. Li, Y.-T. Li, D.-W. Li, and Y.-T. Long, "Recent developments and applications of screen-printed electrodes in environmental assays—A review," *Analytica Chimica Acta,* vol. 734, pp. 31-44, 7/13/ 2012.

[145] Y. H. Tse, P. Janda, H. Lain, and A. B. P. Lever, "Electrode with Electropolymerized Tetraaminophthalocyanatocobalt(II) for Detection of Sulfide Ion," *Analytical Chemistry,* vol. 67, pp. 981-985, 1995.

[146] Y. Hori, R. Takahashi, Y. Yoshinami, and A. Murata, "Electrochemical reduction of CO at a copper electrode," *Journal of Physical Chemistry B,* vol. 101, pp. 7075-7081, 1997.

[147] P. Kaushik and A. Malik, "Process optimization for efficient dye removal by< i> Aspergillus lentulus</i> FJ172995," *Journal of hazardous materials,* vol. 185, pp. 837-843, 2011.

[148] S. A. Jabasingh and G. Pavithra, "Response surface approach for the biosorption of Cr6+ ions by Mucor racemosus," *CLEAN–Soil, Air, Water,* vol. 38, pp. 492-499, 2010.

[149] J. Mehrabani, M. Noaparast, S. Mousavi, R. Dehghan, and A. Ghorbani, "Process optimization and modelling of sphalerite flotation from a low-grade Zn-Pb ore using response surface methodology," *Separation and Purification Technology,* vol. 72, pp. 242-249, 2010.

[150] B. Ebrahimi, S. Shojaosadati, S. Ranaie, and S. Mousavi, "Optimization and evaluation of acetylcholine esterase immobilization on ceramic packing using response surface methodology," *Process Biochemistry,* vol. 45, pp. 81-87, 2010.

[151] W. Li, B. Li, W. Ding, J. Wu, C. Zhang, and D. Fu, "Response surface methodology as a tool to optimize the electrochemical incineration of bromophenol blue on boron-doped diamond anode," *Diamond and Related Materials,* vol. 50, pp. 1-8, 2014.

[152] F. C. Krebs, "Fabrication and processing of polymer solar cells: A review of printing and coating techniques," *Solar Energy Materials and Solar Cells*, vol. 93, pp. 394-412, 4// 2009.

[153] L. J. Swartzendruber, "Calculations for comparing two-point and four-point probe resistivity measurements on rectangular bar-shaped semiconductor samples(Fortran programs for calculation of four-point probe resistivity measurements on bar-shaped semiconductor samples)," 1964.

[154] H. Topsoe, *Geometric Factors in Four Point Resistivity Measurement*: Semiconductor division, 1968.

APPENDIX

SPRINGER LICENSE
TERMS AND CONDITIONS

Apr 02, 2016

This is a License Agreement between Payam Aminayi ("You") and Springer ("Springer") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Springer, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

License Number	3841110343289
License date	Apr 02, 2016
Licensed content publisher	Springer
Licensed content publication	Springer eBook
Licensed content title	Introduction and Overview of History
Licensed content author	Gennady Evtugyn
Licensed content date	Jan 1, 2014
Type of Use	Thesis/Dissertation
Portion	Figures/tables/illustrations
Number of figures/tables/illustrations	2
Author of this Springer article	No
Order reference number	3
Original figure numbers	Fig. 1.3 and Fig. 1.4
Title of your thesis / dissertation	Development and Evaluation of Matrix Material Formulations for Potential Integration into Immunodiagnostic Biosensors
Expected completion date	Jun 2016
Estimated size(pages)	200
Total	0.00 USD
Terms and Conditions	

Introduction
The publisher for this copyrighted material is Springer. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).
Limited License
With reference to your request to reuse material on which Springer controls the copyright, permission is granted for the use indicated in your enquiry under the following conditions:
- Licenses are for one-time use only with a maximum distribution equal to the number stated in your request.

- Springer material represents original material which does not carry references to other sources. If the material in question appears with a credit to another source, this permission is not valid and authorization has to be obtained from the original copyright holder.
- This permission
• is non-exclusive
• is only valid if no personal rights, trademarks, or competitive products are infringed.
• explicitly excludes the right for derivatives.
- Springer does not supply original artwork or content.
- According to the format which you have selected, the following conditions apply accordingly:
• **Print and Electronic:** This License include use in electronic form provided it is password protected, on intranet, or CD-Rom/DVD or E-book/E-journal. It may not be republished in electronic open access.
• **Print:** This License excludes use in electronic form.
• **Electronic:** This License only pertains to use in electronic form provided it is password protected, on intranet, or CD-Rom/DVD or E-book/E-journal. It may not be republished in electronic open access.
For any electronic use not mentioned, please contact Springer at permissions.springer@spi-global.com.
- Although Springer controls the copyright to the material and is entitled to negotiate on rights, this license is only valid subject to courtesy information to the author (address is given in the article/chapter).
- If you are an STM Signatory or your work will be published by an STM Signatory and you are requesting to reuse figures/tables/illustrations or single text extracts, permission is granted according to STM Permissions Guidelines: http://www.stm-assoc.org/permissions-guidelines/
For any electronic use not mentioned in the Guidelines, please contact Springer at permissions.springer@spi-global.com. If you request to reuse more content than stipulated in the STM Permissions Guidelines, you will be charged a permission fee for the excess content.
Permission is valid upon payment of the fee as indicated in the licensing process. If permission is granted free of charge on this occasion, that does not prejudice any rights we might have to charge for reproduction of our copyrighted material in the future.
-If your request is for reuse in a Thesis, permission is granted free of charge under the following conditions:
This license is valid for one-time use only for the purpose of defending your thesis and with a maximum of 100 extra copies in paper. If the thesis is going to be published, permission needs to be reobtained.
- includes use in an electronic form, provided it is an author-created version of the thesis on his/her own website and his/her university's repository, including UMI (according to the definition on the Sherpa website: http://www.sherpa.ac.uk/romeo/);
- is subject to courtesy information to the co-author or corresponding author.
Geographic Rights: Scope
Licenses may be exercised anywhere in the world.
Altering/Modifying Material: Not Permitted
Figures, tables, and illustrations may be altered minimally to serve your work. You may not alter or modify text in any manner. Abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of the author(s).
Reservation of Rights
Springer reserves all rights not specifically granted in the combination of (i) the license

details provided by you and accepted in the course of this licensing transaction and (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

License Contingent on Payment

While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by Springer or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received by the date due, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and Springer reserves the right to take any and all action to protect its copyright in the materials.

Copyright Notice: Disclaimer

You must include the following copyright and permission notice in connection with any reproduction of the licensed material:

"Springer book/journal title, chapter/article title, volume, year of publication, page, name(s) of author(s), (original copyright notice as given in the publication in which the material was originally published) "With permission of Springer"

In case of use of a graph or illustration, the caption of the graph or illustration must be included, as it is indicated in the original publication.

Warranties: None

Springer makes no representations or warranties with respect to the licensed material and adopts on its own behalf the limitations and disclaimers established by CCC on its behalf in its Billing and Payment terms and conditions for this licensing transaction.

Indemnity

You hereby indemnify and agree to hold harmless Springer and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.

No Transfer of License

This license is personal to you and may not be sublicensed, assigned, or transferred by you without Springer's written permission.

No Amendment Except in Writing

This license may not be amended except in a writing signed by both parties (or, in the case of Springer, by CCC on Springer's behalf).

Objection to Contrary Terms

Springer hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and Springer (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

Jurisdiction

All disputes that may arise in connection with this present License, or the breach thereof, shall be settled exclusively by arbitration, to be held in the Federal Republic of Germany, in

accordance with German law.

Other conditions:

V 12AUG2015

ELSEVIER LICENSE
TERMS AND CONDITIONS

Apr 02, 2016

This is a License Agreement between Payam Aminayi ("You") and Elsevier ("Elsevier") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Elsevier, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

Supplier	Elsevier Limited The Boulevard,Langford Lane Kidlington,Oxford,OX5 1GB,UK
Registered Company Number	1982084
Customer name	Payam Aminayi
Customer address	3740 Club Drive DULUTH, GA 30096
License number	3841111197244
License date	Apr 02, 2016
Licensed content publisher	Elsevier
Licensed content publication	Seminars in Cell & Developmental Biology
Licensed content title	Biosensors for cancer markers diagnosis
Licensed content author	Ibtisam E. Tothill
Licensed content date	February 2009
Licensed content volume number	20
Licensed content issue number	1
Number of pages	8
Start Page	55
End Page	62
Type of Use	reuse in a thesis/dissertation
Intended publisher of new work	other
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	2
Format	electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No

Order reference number	19
Original figure numbers	Table 3. and Fig. 1
Title of your thesis/dissertation	Development and Evaluation of Matrix Material Formulations for Potential Integration into Immunodiagnostic Biosensors
Expected completion date	Jun 2016
Estimated size (number of pages)	200
Elsevier VAT number	GB 494 6272 12
Permissions price	0.00 USD
VAT/Local Sales Tax	0.00 USD / 0.00 GBP
Total	0.00 USD
Terms and Conditions	

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:
"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com)
6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed

use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.
9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.
10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.
11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.
12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).
13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.
14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:
15. **Translation**: This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.
16. **Posting licensed content on any Website**: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx or the Elsevier homepage for books at http://www.elsevier.com; Central Storage: This license does not include permission for a

scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.
Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at http://www.elsevier.com . All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.
17. **For journal authors:** the following clauses are applicable in addition to the above:
Preprints:
A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).
Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).
If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.
Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.
Authors can share their accepted author manuscript:

- immediately
  - via their non-commercial person homepage or blog
  - by updating a preprint in arXiv or RePEc with the accepted manuscript
  - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
  - directly by providing copies to their students or to research collaborators for their personal use
  - for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- after the embargo period
  - via non-commercial hosting platforms such as their institutional repository
  - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.
Policies for sharing publishing journal articles differ for subscription and gold open access articles:
Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version.
Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.
If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.
Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a CrossMark logo, the end user license, and a DOI link to the formal publication on ScienceDirect.
Please refer to Elsevier's posting policy for further information.
18. **For book authors** the following clauses are applicable in addition to the above:
Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.
19. **Thesis/Dissertation**: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions
You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our open access license policy for more information.
Terms & Conditions applicable to all Open Access articles published with Elsevier:
Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.
The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.
If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.
Additional Terms & Conditions applicable to each Creative Commons user license:

ELSEVIER LICENSE
TERMS AND CONDITIONS

Apr 02, 2016

This is a License Agreement between Payam Aminayi ("You") and Elsevier ("Elsevier") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Elsevier, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

Supplier	Elsevier Limited The Boulevard,Langford Lane Kidlington,Oxford,OX5 1GB,UK
Registered Company Number	1982084
Customer name	Payam Aminayi
Customer address	3740 Club Drive DULUTH, GA 30096
License number	3841120428765
License date	Apr 02, 2016
Licensed content publisher	Elsevier
Licensed content publication	Journal of Colloid and Interface Science
Licensed content title	Aggregation behavior of single-walled carbon nanotubes in dilute aqueous suspension
Licensed content author	Quan Chen,Craig Saltiel,Siva Manickavasagam,Linda S. Schadler,Richard W. Siegel,Hoichang Yang
Licensed content date	1 December 2004
Licensed content volume number	280
Licensed content issue number	1
Number of pages	7
Start Page	91
End Page	97
Type of Use	reuse in a thesis/dissertation
Intended publisher of new work	other
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	2
Format	both print and electronic
Are you the author of this Elsevier article?	No

Will you be translating?	No
Order reference number	39
Original figure numbers	Fig. 1. and Fig. 2
Title of your thesis/dissertation	Development and Evaluation of Matrix Material Formulations for Potential Integration into Immunodiagnostic Biosensors
Expected completion date	Jun 2016
Estimated size (number of pages)	200
Elsevier VAT number	GB 494 6272 12
Permissions price	0.00 USD
VAT/Local Sales Tax	0.00 USD / 0.00 GBP
Total	0.00 USD
Terms and Conditions	

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:
"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com)
6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the

transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.
9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.
10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.
11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.
12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).
13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.
14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:
15. **Translation**: This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.
16. **Posting licensed content on any Website**: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx or the Elsevier homepage for books at

http://www.elsevier.com; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.
Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at http://www.elsevier.com . All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.
17. **For journal authors:** the following clauses are applicable in addition to the above:
Preprints:
A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).
Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).
If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.
Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.
Authors can share their accepted author manuscript:

- immediately
  - via their non-commercial person homepage or blog
  - by updating a preprint in arXiv or RePEc with the accepted manuscript
  - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
  - directly by providing copies to their students or to research collaborators for their personal use
  - for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- after the embargo period
  - via non-commercial hosting platforms such as their institutional repository
  - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to

appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.
Policies for sharing publishing journal articles differ for subscription and gold open access articles:
Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version.
Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.
If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.
Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a CrossMark logo, the end user license, and a DOI link to the formal publication on ScienceDirect.
Please refer to Elsevier's posting policy for further information.
18. **For book authors** the following clauses are applicable in addition to the above:
Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.
19. **Thesis/Dissertation**: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions
You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our open access license policy for more information.
Terms & Conditions applicable to all Open Access articles published with Elsevier:
Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.
The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.
If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.

Additional Terms & Conditions applicable to each Creative Commons user license:
CC BY: The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by/4.0.
CC BY NC SA: The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. Further, any new works must be made available on the same conditions. The full details of the license are available at http://creativecommons.org/licenses/by-nc-sa/4.0.
CC BY NC ND: The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by-nc-nd/4.0.
Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.
Commercial reuse includes:

- Associating advertising with the full text of the Article
- Charging fees for document delivery or access
- Article aggregation
- Systematic distribution via e-mail lists or share buttons

Posting or linking by commercial companies for use by customers of those companies.

20. **Other Conditions**:

v1.8

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

ELSEVIER LICENSE
TERMS AND CONDITIONS

Apr 02, 2016

This is a License Agreement between Payam Aminayi ("You") and Elsevier ("Elsevier") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Elsevier, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

Supplier	Elsevier Limited The Boulevard,Langford Lane Kidlington,Oxford,OX5 1GB,UK
Registered Company Number	1982084
Customer name	Payam Aminayi
Customer address	3740 Club Drive DULUTH, GA 30096
License number	3841120733547
License date	Apr 02, 2016
Licensed content publisher	Elsevier
Licensed content publication	Chemical Physics Letters
Licensed content title	Morphology of dispersed carbon single-walled nanotubes
Licensed content author	Dale W. Schaefer,Jian Zhao,Janis M. Brown,David P. Anderson,David W. Tomlin
Licensed content date	3 July 2003
Licensed content volume number	375
Licensed content issue number	3-4
Number of pages	7
Start Page	369
End Page	375
Type of Use	reuse in a thesis/dissertation
Intended publisher of new work	other
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Format	both print and electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No

Order reference number	41
Original figure numbers	Fig. 2.
Title of your thesis/dissertation	Development and Evaluation of Matrix Material Formulations for Potential Integration into Immunodiagnostic Biosensors
Expected completion date	Jun 2016
Estimated size (number of pages)	200
Elsevier VAT number	GB 494 6272 12
Permissions price	0.00 USD
VAT/Local Sales Tax	0.00 USD / 0.00 GBP
Total	0.00 USD
Terms and Conditions	

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:
"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com)
6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed

use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.
9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.
10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.
11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.
12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).
13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.
14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:
15. **Translation**: This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.
16. **Posting licensed content on any Website**: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx or the Elsevier homepage for books at http://www.elsevier.com; Central Storage: This license does not include permission for a

scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.
Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at http://www.elsevier.com . All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.
17. **For journal authors:** the following clauses are applicable in addition to the above:
Preprints:
A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).
Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).
If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.
Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.
Authors can share their accepted author manuscript:

- immediately
  - via their non-commercial person homepage or blog
  - by updating a preprint in arXiv or RePEc with the accepted manuscript
  - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
  - directly by providing copies to their students or to research collaborators for their personal use
  - for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- after the embargo period
  - via non-commercial hosting platforms such as their institutional repository
  - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.
Policies for sharing publishing journal articles differ for subscription and gold open access articles:
Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version.
Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.
If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.
Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a CrossMark logo, the end user license, and a DOI link to the formal publication on ScienceDirect.
Please refer to Elsevier's posting policy for further information.
18. **For book authors** the following clauses are applicable in addition to the above:
Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.
19. **Thesis/Dissertation**: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions
You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our open access license policy for more information.
Terms & Conditions applicable to all Open Access articles published with Elsevier:
Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.
The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.
If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.
Additional Terms & Conditions applicable to each Creative Commons user license:

Title: Aqueous Suspensions of Steroid Nanotubules: Structural and Rheological Characterizations

Author: Pierre Terech, Yeshayahu Talmon

Publication: Langmuir

Publisher: American Chemical Society

Date: Sep 1, 2002

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

If credit is given to another source for the material you requested, permission must be obtained from that source.

BACK | CLOSE WINDOW

AW: WG: request permission

From : Rights DE <RIGHTS-and-LICENCES@wiley-vch.de> Thu, Apr 21, 2016 02:40 AM
Subject : AW: WG: request permission 1 attachment
To : 'Payam Aminayi' <payam.aminayi@wmich.edu>

Dear Payam Aminayi,

About the Wiley-VCH Journal	
Journal Title	ChemInform
Year of Publication	2007
Volume and Issue Number	38, 40
Article Title (please include page numbers)	Fundamentals and Applications of Soluble Carbon Nanotubes
Author	Naotoshi Nakashima, Tsuyohiko Fujigaya
Figure and Page Reference	graphical abstract
Do you or your institute hold a current subscription to this journal?	No
Are you the originial author of the requested material?	No

Where would you like to include our material?

About Your Publication	
Author / Editor	Payam Aminayi
Title of Publication	Development and Evaluation of Matrix Material Formulations for Potential Integration into Immunodiagnostic Biosensors
Rights Required (eg. Print/ Electronic/ Translation, etc.)	Print and electronic
Publisher	N/A
Publication Date	30.05.2016
Medium (e.g. Book/Journal, Handout, CD Rom, Internet, etc.)	Thesis/Dissertation
Print Run (hard back / paper back)	Paper back
If Making Copies Please Include the Number of Copies You Wish to Make	N/A
Retail Price	N/A
Web address material will be posted on	http://scholarworks.wmich.edu/dissertations/
Is the website password-protected?	No

Tell us how to get in touch with you (Please note that this will be where your invoice and/or permission will be addressed to. We are unable to send documents to more than one address):

Please provide your full address details:

Name	Payam Aminayi
Salutation	Mr.
Department	Paper and Printing Science
Job title	Student
Organisation	Western Michigan University
Street	3740 Club Drive #8109
Town	Duluth
State / Province	GA
Zip / Postal Code	30096
Country	USA
Telephone	8063195656
Fax	N/A
Email	payam.aminayi@wmich.edu

We hereby grant permission for the requested use expected that due credit is given to the original source.

If material appears within our work with credit to another source, authorisation from that source must be obtained.

Credit must include the following components:

- Books: Author(s)/ Editor(s) Name(s): Title of the Book. Page(s). Publication year. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.
- Journals: Author(s) Name(s): Title of the Article. Name of the Journal. Publication year. Volume. Page(s). Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.
- Online Portal: Author(s): Title of the Online portal. Link or DOI. Publication year. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

Kind regards

Bettina Loycke
Senior Rights Manager
Rights & Licenses

Wiley-VCH Verlag GmbH & Co. KGaA
Boschstraße 12
69469 Weinheim
Germany
www.wiley-vch.de

T +(49) 6201 606-280
F +(49) 6201 606-332
rightsDE@wiley.com

WILEY

ELSEVIER LICENSE
TERMS AND CONDITIONS

Apr 03, 2016

This is a License Agreement between Payam Aminayi ("You") and Elsevier ("Elsevier") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Elsevier, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

Supplier	Elsevier Limited The Boulevard,Langford Lane Kidlington,Oxford,OX5 1GB,UK
Registered Company Number	1982084
Customer name	Payam Aminayi
Customer address	3740 Club Drive DULUTH, GA 30096
License number	3841170533534
License date	Apr 03, 2016
Licensed content publisher	Elsevier
Licensed content publication	Chemical Physics Letters
Licensed content title	Reversible water-solubilization of single-walled carbon nanotubes by polymer wrapping
Licensed content author	Michael J. O'Connell,Peter Boul,Lars M. Ericson,Chad Huffman,Yuhuang Wang,Erik Haroz,Cynthia Kuper,Jim Tour,Kevin D. Ausman,Richard E. Smalley
Licensed content date	13 July 2001
Licensed content volume number	342
Licensed content issue number	3-4
Number of pages	7
Start Page	265
End Page	271
Type of Use	reuse in a thesis/dissertation
Intended publisher of new work	other
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Format	both print and electronic
Are you the author of this	No

Elsevier article?	
Will you be translating?	No
Order reference number	95
Original figure numbers	Fig. 4.
Title of your thesis/dissertation	Development and Evaluation of Matrix Material Formulations for Potential Integration into Immunodiagnostic Biosensors
Expected completion date	Jun 2016
Estimated size (number of pages)	200
Elsevier VAT number	GB 494 6272 12
Permissions price	0.00 USD
VAT/Local Sales Tax	0.00 USD / 0.00 GBP
Total	0.00 USD
Terms and Conditions	

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:
"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com)
6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
8. License Contingent Upon Payment: While you may exercise the rights licensed

immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.

9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.

10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.

11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.

12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).

13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:

15. **Translation**: This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.

16. **Posting licensed content on any Website**: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at

http://www.sciencedirect.com/science/journal/xxxxx or the Elsevier homepage for books at http://www.elsevier.com; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.
Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at http://www.elsevier.com . All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.
17. **For journal authors:** the following clauses are applicable in addition to the above:
Preprints:
A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).
Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).
If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.
Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.
Authors can share their accepted author manuscript:

- immediately
  - via their non-commercial person homepage or blog
  - by updating a preprint in arXiv or RePEc with the accepted manuscript
  - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
  - directly by providing copies to their students or to research collaborators for their personal use
  - for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- after the embargo period
  - via non-commercial hosting platforms such as their institutional repository
  - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be

shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.
Policies for sharing publishing journal articles differ for subscription and gold open access articles:
Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version.
Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.
If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.
Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a CrossMark logo, the end user license, and a DOI link to the formal publication on ScienceDirect.
Please refer to Elsevier's posting policy for further information.
18. **For book authors** the following clauses are applicable in addition to the above:
Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.
19. **Thesis/Dissertation**: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions
You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our open access license policy for more information.
Terms & Conditions applicable to all Open Access articles published with Elsevier:
Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.
The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.
If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to

ensure their reuse complies with the terms and conditions determined by the rights holder.
Additional Terms & Conditions applicable to each Creative Commons user license:
CC BY: The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by/4.0.
CC BY NC SA: The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. Further, any new works must be made available on the same conditions. The full details of the license are available at http://creativecommons.org/licenses/by-nc-sa/4.0.
CC BY NC ND: The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by-nc-nd/4.0.
Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.
Commercial reuse includes:

- Associating advertising with the full text of the Article
- Charging fees for document delivery or access
- Article aggregation
- Systematic distribution via e-mail lists or share buttons

Posting or linking by commercial companies for use by customers of those companies.

20. **Other Conditions**:

v1.8

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

ELSEVIER LICENSE
TERMS AND CONDITIONS

Apr 03, 2016

This is a License Agreement between Payam Aminayi ("You") and Elsevier ("Elsevier") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Elsevier, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

Supplier	Elsevier Limited The Boulevard,Langford Lane Kidlington,Oxford,OX5 1GB,UK
Registered Company Number	1982084
Customer name	Payam Aminayi
Customer address	3740 Club Drive DULUTH, GA 30096
License number	3841170703948
License date	Apr 03, 2016
Licensed content publisher	Elsevier
Licensed content publication	Computational Materials Science
Licensed content title	Molecular dynamics simulations of the interactions between SWNT and surfactants
Licensed content author	Jinyu Pang,Guiying Xu
Licensed content date	December 2012
Licensed content volume number	65
Licensed content issue number	n/a
Number of pages	7
Start Page	324
End Page	330
Type of Use	reuse in a thesis/dissertation
Intended publisher of new work	other
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Format	both print and electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No

Order reference number	97
Original figure numbers	Fig. 2
Title of your thesis/dissertation	Development and Evaluation of Matrix Material Formulations for Potential Integration into Immunodiagnostic Biosensors
Expected completion date	Jun 2016
Estimated size (number of pages)	200
Elsevier VAT number	GB 494 6272 12
Permissions price	0.00 USD
VAT/Local Sales Tax	0.00 USD / 0.00 GBP
Total	0.00 USD
Terms and Conditions	

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:
"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com)
6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed

use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.
9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.
10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.
11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.
12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).
13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.
14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:
15. **Translation**: This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.
16. **Posting licensed content on any Website**: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx or the Elsevier homepage for books at http://www.elsevier.com; Central Storage: This license does not include permission for a

scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.
Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at http://www.elsevier.com . All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.
17. **For journal authors:** the following clauses are applicable in addition to the above:
Preprints:
A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).
Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).
If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.
Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.
Authors can share their accepted author manuscript:

- immediately
  - via their non-commercial person homepage or blog
  - by updating a preprint in arXiv or RePEc with the accepted manuscript
  - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
  - directly by providing copies to their students or to research collaborators for their personal use
  - for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- after the embargo period
  - via non-commercial hosting platforms such as their institutional repository
  - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.
Policies for sharing publishing journal articles differ for subscription and gold open access articles:
Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version.
Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.
If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.
Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a CrossMark logo, the end user license, and a DOI link to the formal publication on ScienceDirect.
Please refer to Elsevier's posting policy for further information.
18. **For book authors** the following clauses are applicable in addition to the above:
Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.
19. **Thesis/Dissertation**: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions
You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our open access license policy for more information.
Terms & Conditions applicable to all Open Access articles published with Elsevier:
Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.
The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.
If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.

Additional Terms & Conditions applicable to each Creative Commons user license:

SPRINGER LICENSE
TERMS AND CONDITIONS

Apr 03, 2016

This is a License Agreement between Payam Aminayi ("You") and Springer ("Springer") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Springer, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

License Number	3841491381716
License date	Apr 03, 2016
Licensed content publisher	Springer
Licensed content publication	Springer eBook
Licensed content title	Printing Technologies without a Printing Plate (NIP Technologies)
Licensed content author	Prof. Dr.-Ing. habil. Helmut Kipphan
Licensed content date	Jan 1, 2001
Type of Use	Thesis/Dissertation
Portion	Figures/tables/illustrations
Number of figures/tables/illustrations	1
Author of this Springer article	No
Order reference number	129
Original figure numbers	Fig. 5.5-17
Title of your thesis / dissertation	Development and Evaluation of Matrix Material Formulations for Potential Integration into Immunodiagnostic Biosensors
Expected completion date	Jun 2016
Estimated size(pages)	200
Total	0.00 USD
Terms and Conditions	

Introduction

The publisher for this copyrighted material is Springer. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

Limited License

With reference to your request to reuse material on which Springer controls the copyright, permission is granted for the use indicated in your enquiry under the following conditions:

- Licenses are for one-time use only with a maximum distribution equal to the number stated in your request.

- Springer material represents original material which does not carry references to other sources. If the material in question appears with a credit to another source, this permission is not valid and authorization has to be obtained from the original copyright holder.
- This permission
• is non-exclusive
• is only valid if no personal rights, trademarks, or competitive products are infringed.
• explicitly excludes the right for derivatives.
- Springer does not supply original artwork or content.
- According to the format which you have selected, the following conditions apply accordingly:
• **Print and Electronic:** This License include use in electronic form provided it is password protected, on intranet, or CD-Rom/DVD or E-book/E-journal. It may not be republished in electronic open access.
• **Print:** This License excludes use in electronic form.
• **Electronic:** This License only pertains to use in electronic form provided it is password protected, on intranet, or CD-Rom/DVD or E-book/E-journal. It may not be republished in electronic open access.
For any electronic use not mentioned, please contact Springer at permissions.springer@spi-global.com.
- Although Springer controls the copyright to the material and is entitled to negotiate on rights, this license is only valid subject to courtesy information to the author (address is given in the article/chapter).
- If you are an STM Signatory or your work will be published by an STM Signatory and you are requesting to reuse figures/tables/illustrations or single text extracts, permission is granted according to STM Permissions Guidelines: http://www.stm-assoc.org/permissions-guidelines/
For any electronic use not mentioned in the Guidelines, please contact Springer at permissions.springer@spi-global.com. If you request to reuse more content than stipulated in the STM Permissions Guidelines, you will be charged a permission fee for the excess content.
Permission is valid upon payment of the fee as indicated in the licensing process. If permission is granted free of charge on this occasion, that does not prejudice any rights we might have to charge for reproduction of our copyrighted material in the future.
-If your request is for reuse in a Thesis, permission is granted free of charge under the following conditions:
This license is valid for one-time use only for the purpose of defending your thesis and with a maximum of 100 extra copies in paper. If the thesis is going to be published, permission needs to be reobtained.
- includes use in an electronic form, provided it is an author-created version of the thesis on his/her own website and his/her university's repository, including UMI (according to the definition on the Sherpa website: http://www.sherpa.ac.uk/romeo/);
- is subject to courtesy information to the co-author or corresponding author.
Geographic Rights: Scope
Licenses may be exercised anywhere in the world.
Altering/Modifying Material: Not Permitted
Figures, tables, and illustrations may be altered minimally to serve your work. You may not alter or modify text in any manner. Abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of the author(s).
Reservation of Rights
Springer reserves all rights not specifically granted in the combination of (i) the license

details provided by you and accepted in the course of this licensing transaction and (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

License Contingent on Payment

While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by Springer or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received by the date due, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and Springer reserves the right to take any and all action to protect its copyright in the materials.

Copyright Notice: Disclaimer

You must include the following copyright and permission notice in connection with any reproduction of the licensed material:

"Springer book/journal title, chapter/article title, volume, year of publication, page, name(s) of author(s), (original copyright notice as given in the publication in which the material was originally published) "With permission of Springer"

In case of use of a graph or illustration, the caption of the graph or illustration must be included, as it is indicated in the original publication.

Warranties: None

Springer makes no representations or warranties with respect to the licensed material and adopts on its own behalf the limitations and disclaimers established by CCC on its behalf in its Billing and Payment terms and conditions for this licensing transaction.

Indemnity

You hereby indemnify and agree to hold harmless Springer and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.

No Transfer of License

This license is personal to you and may not be sublicensed, assigned, or transferred by you without Springer's written permission.

No Amendment Except in Writing

This license may not be amended except in a writing signed by both parties (or, in the case of Springer, by CCC on Springer's behalf).

Objection to Contrary Terms

Springer hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and Springer (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

Jurisdiction

All disputes that may arise in connection with this present License, or the breach thereof, shall be settled exclusively by arbitration, to be held in the Federal Republic of Germany, in

accordance with German law.
Other conditions:
V 12AUG2015

ELSEVIER LICENSE
TERMS AND CONDITIONS

Apr 03, 2016

This is a License Agreement between Payam Aminayi ("You") and Elsevier ("Elsevier") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Elsevier, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

Supplier	Elsevier Limited The Boulevard,Langford Lane Kidlington,Oxford,OX5 1GB,UK
Registered Company Number	1982084
Customer name	Payam Aminayi
Customer address	3740 Club Drive DULUTH, GA 30096
License number	3841170888744
License date	Apr 03, 2016
Licensed content publisher	Elsevier
Licensed content publication	Optics & Laser Technology
Licensed content title	Fabrication of high numerical aperture micro-lens array based on drop-on-demand generating of water-based molds
Licensed content author	Xiaoyang Zhu,Li Zhu,Hejuan Chen,Zongan Li,Weiyi Zhang
Licensed content date	May 2015
Licensed content volume number	68
Licensed content issue number	n/a
Number of pages	5
Start Page	23
End Page	27
Type of Use	reuse in a thesis/dissertation
Intended publisher of new work	other
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Format	both print and electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No

Order reference number	130
Original figure numbers	Fig. 4.
Title of your thesis/dissertation	Development and Evaluation of Matrix Material Formulations for Potential Integration into Immunodiagnostic Biosensors
Expected completion date	Jun 2016
Estimated size (number of pages)	200
Elsevier VAT number	GB 494 6272 12
Permissions price	0.00 USD
VAT/Local Sales Tax	0.00 USD / 0.00 GBP
Total	0.00 USD
Terms and Conditions	

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:
"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com)
6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed

use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.
9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.
10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.
11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.
12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).
13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.
14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:
15. **Translation**: This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.
16. **Posting licensed content on any Website**: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx or the Elsevier homepage for books at http://www.elsevier.com; Central Storage: This license does not include permission for a

scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.
Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at http://www.elsevier.com . All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.
17. **For journal authors:** the following clauses are applicable in addition to the above:
Preprints:
A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).
Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).
If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.
Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.
Authors can share their accepted author manuscript:

- immediately
  - via their non-commercial person homepage or blog
  - by updating a preprint in arXiv or RePEc with the accepted manuscript
  - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
  - directly by providing copies to their students or to research collaborators for their personal use
  - for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- after the embargo period
  - via non-commercial hosting platforms such as their institutional repository
  - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.
Policies for sharing publishing journal articles differ for subscription and gold open access articles:
Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version.
Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.
If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.
Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a CrossMark logo, the end user license, and a DOI link to the formal publication on ScienceDirect.
Please refer to Elsevier's posting policy for further information.
18. **For book authors** the following clauses are applicable in addition to the above:
Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.
19. **Thesis/Dissertation**: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions
You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our open access license policy for more information.
Terms & Conditions applicable to all Open Access articles published with Elsevier:
Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.
The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.
If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.

Additional Terms & Conditions applicable to each Creative Commons user license:

Title:	High efficiency organic solar cells by screen printing method
Conference Proceedings:	Photovoltaic Specialists Conference, 2005. Conference Record of the Thirty-first IEEE
Author:	J. Sakai; E. Fujinaka; T. Nishimori; N. Ito; J. Adachi; S. Nagano; K. Murakami
Publisher:	IEEE
Date:	3-7 Jan. 2005

Thesis / Dissertation Reuse

The IEEE does not require individuals working on a thesis to obtain a formal reuse license, however, you may print out this statement to be used as a permission grant:

Requirements to be followed when using any portion (e.g., figure, graph, table, or textual material) of an IEEE copyrighted paper in a thesis:

1) In the case of textual material (e.g., using short quotes or referring to the work within these papers) users must give full credit to the original source (author, paper, publication) followed by the IEEE copyright line © 2011 IEEE.
2) In the case of illustrations or tabular material, we require that the copyright line © [Year of original publication] IEEE appear prominently with each reprinted figure and/or table.
3) If a substantial portion of the original paper is to be used, and if you are not the senior author, also obtain the senior author's approval.

Requirements to be followed when using an entire IEEE copyrighted paper in a thesis:

1) The following IEEE copyright/ credit notice should be placed prominently in the references: © [year of original publication] IEEE. Reprinted, with permission, from [author names, paper title, IEEE publication title, and month/year of publication]
2) Only the accepted version of an IEEE copyrighted paper can be used when posting the paper or your thesis on-line.
3) In placing the thesis on the author's university website, please display the following message in a prominent place on the website: In reference to IEEE copyrighted material which is used with permission in this thesis, the IEEE does not endorse any of [university/educational entity's name goes here]'s products or services. Internal or personal use of this material is permitted. If interested in reprinting/republishing IEEE copyrighted material for advertising or promotional purposes or for creating new collective works for resale or redistribution, please go to http://www.ieee.org/publications_standards/publications/rights/rights_link.html to learn how to obtain a License from RightsLink.

If applicable, University Microfilms and/or ProQuest Library, or the Archives of Canada may supply single copies of the dissertation.

AIP PUBLISHING LLC LICENSE TERMS AND CONDITIONS

Apr 03, 2016

This Agreement between Payam Aminayi ("You") and AIP Publishing LLC ("AIP Publishing LLC") consists of your license details and the terms and conditions provided by AIP Publishing LLC and Copyright Clearance Center.

License Number	3841480129066
License date	Apr 03, 2016
Licensed Content Publisher	AIP Publishing LLC
Licensed Content Publication	Journal of Applied Physics
Licensed Content Title	Polymer light emitting diodes and poly(di-n-octylfluorene) thin films as fabricated with a microfluidics applicator
Licensed Content Author	H. Cheun,P. P. Rugheimer,B. J. Larson, et al.
Licensed Content Date	Oct 9, 2006
Licensed Content Volume Number	100
Licensed Content Issue Number	7
Type of Use	Thesis/Dissertation
Requestor type	Student
Format	Print and electronic
Portion	Figure/Table
Number of figures/tables	1
Order reference number	134
Title of your thesis / dissertation	Development and Evaluation of Matrix Material Formulations for Potential Integration into Immunodiagnostic Biosensors
Expected completion date	Jun 2016
Estimated size (number of pages)	200
Requestor Location	Payam Aminayi 3740 Club Drive #8109 DULUTH, GA 30096 United States Attn: Payam Aminayi
Billing Type	Invoice
Billing Address	Payam Aminayi 3740 Club Drive #8109 DULUTH, GA 30096 United States

	Attn: Payam Aminayi
Total	0.00 USD

Terms and Conditions

AIP Publishing LLC -- Terms and Conditions: Permissions Uses

AIP Publishing hereby grants to you the non-exclusive right and license to use and/or distribute the Material according to the use specified in your order, on a one-time basis, for the specified term, with a maximum distribution equal to the number that you have ordered. Any links or other content accompanying the Material are not the subject of this license.

1. You agree to include the following copyright and permission notice with the reproduction of the Material:"Reprinted from [FULL CITATION]. with the permission of AIP Publishing." For an article, the credit line and permission notice must be printed on the first page of the article or book chapter. For photographs, covers, or tables, the notice may appear with the Material, in a footnote, or in the reference list.
2. If you have licensed reuse of a figure, photograph, cover, or table, it is your responsibility to ensure that the material is original to AIP Publishing and does not contain the copyright of another entity, and that the copyright notice of the figure, photograph, cover, or table does not indicate that it was reprinted by AIP Publishing, with permission, from another source. Under no circumstances does AIP Publishing purport or intend to grant permission to reuse material to which it does not hold appropriate rights.
   You may not alter or modify the Material in any manner. You may translate the Material into another language only if you have licensed translation rights. You may not use the Material for promotional purposes.
3. The foregoing license shall not take effect unless and until AIP Publishing or its agent, Copyright Clearance Center, receives the Payment in accordance with Copyright Clearance Center Billing and Payment Terms and Conditions, which are incorporated herein by reference.
4. AIP Publishing or Copyright Clearance Center may, within two business days of granting this license, revoke the license for any reason whatsoever, with a full refund payable to you. Should you violate the terms of this license at any time, AIP Publishing, or Copyright Clearance Center may revoke the license with no refund to you. Notice of such revocation will be made using the contact information provided by you. Failure to receive such notice will not nullify the revocation.
5. AIP Publishing makes no representations or warranties with respect to the Material. You agree to indemnify and hold harmless AIP Publishing, and their officers, directors, employees or agents from and against any and all claims arising out of your use of the Material other than as specifically authorized herein.
6. The permission granted herein is personal to you and is not transferable or assignable without the prior written permission of AIP Publishing. This license may not be amended except in a writing signed by the party to be charged.
7. If purchase orders, acknowledgments or check endorsements are issued on any forms containing terms and conditions which are inconsistent with these provisions, such inconsistent terms and conditions shall be of no force and effect. This document, including the CCC Billing and Payment Terms and Conditions, shall be the entire agreement between the parties relating to the subject matter hereof.

This Agreement shall be governed by and construed in accordance with the laws of the State of New York. Both parties hereby submit to the jurisdiction of the courts of New York County for purposes of resolving any disputes that may arise hereunder.

V1.1

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Thesis / Dissertation Reuse

The IEEE does not require individuals working on a thesis to obtain a formal reuse license, however, you may print out this statement to be used as a permission grant:

Requirements to be followed when using any portion (e.g., figure, graph, table, or textual material) of an IEEE copyrighted paper in a thesis:

1) In the case of textual material (e.g., using short quotes or referring to the work within these papers) users must give full credit to the original source (author, paper, publication) followed by the IEEE copyright line © 2011 IEEE.
2) In the case of illustrations or tabular material, we require that the copyright line © [Year of original publication] IEEE appear prominently with each reprinted figure and/or table.
3) If a substantial portion of the original paper is to be used, and if you are not the senior author, also obtain the senior author's approval.

Requirements to be followed when using an entire IEEE copyrighted paper in a thesis:

1) The following IEEE copyright/ credit notice should be placed prominently in the references: © [year of original publication] IEEE. Reprinted, with permission, from [author names, paper title, IEEE publication title, and month/year of publication]
2) Only the accepted version of an IEEE copyrighted paper can be used when posting the paper or your thesis on-line.
3) In placing the thesis on the author's university website, please display the following message in a prominent place on the website: In reference to IEEE copyrighted material which is used with permission in this thesis, the IEEE does not endorse any of [university/educational entity's name goes here]'s products or services. Internal or personal use of this material is permitted. If interested in reprinting/republishing IEEE copyrighted material for advertising or promotional purposes or for creating new collective works for resale or redistribution, please go to http://www.ieee.org/publications_standards/publications/rights/rights_link.html to learn how to obtain a License from RightsLink.

If applicable, University Microfilms and/or ProQuest Library, or the Archives of Canada may supply single copies of the dissertation.

ELSEVIER LICENSE
TERMS AND CONDITIONS

Apr 03, 2016

This is a License Agreement between Payam Aminayi ("You") and Elsevier ("Elsevier") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Elsevier, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

Supplier	Elsevier Limited The Boulevard,Langford Lane Kidlington,Oxford,OX5 1GB,UK
Registered Company Number	1982084
Customer name	Payam Aminayi
Customer address	3740 Club Drive DULUTH, GA 30096
License number	3841180343443
License date	Apr 03, 2016
Licensed content publisher	Elsevier
Licensed content publication	Analytica Chimica Acta
Licensed content title	Recent developments and applications of screen-printed electrodes in environmental assays—A review
Licensed content author	Meng Li,Yuan-Ting Li,Da-Wei Li,Yi-Tao Long
Licensed content date	13 July 2012
Licensed content volume number	734
Licensed content issue number	n/a
Number of pages	14
Start Page	31
End Page	44
Type of Use	reuse in a thesis/dissertation
Intended publisher of new work	other
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Format	both print and electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No

Order reference number	143
Original figure numbers	Fig. 3.
Title of your thesis/dissertation	Development and Evaluation of Matrix Material Formulations for Potential Integration into Immunodiagnostic Biosensors
Expected completion date	Jun 2016
Estimated size (number of pages)	200
Elsevier VAT number	GB 494 6272 12
Permissions price	0.00 USD
VAT/Local Sales Tax	0.00 USD / 0.00 GBP
Total	0.00 USD
Terms and Conditions	

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:
"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com)
6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed

use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.
9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.
10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.
11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.
12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).
13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.
14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:
15. **Translation**: This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.
16. **Posting licensed content on any Website**: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx or the Elsevier homepage for books at http://www.elsevier.com; Central Storage: This license does not include permission for a

scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.
Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at http://www.elsevier.com . All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.
17. **For journal authors:** the following clauses are applicable in addition to the above:
Preprints:
A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).
Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).
If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.
Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.
Authors can share their accepted author manuscript:

- immediately
  - via their non-commercial person homepage or blog
  - by updating a preprint in arXiv or RePEc with the accepted manuscript
  - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
  - directly by providing copies to their students or to research collaborators for their personal use
  - for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- after the embargo period
  - via non-commercial hosting platforms such as their institutional repository
  - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.
Policies for sharing publishing journal articles differ for subscription and gold open access articles:
Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version.
Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.
If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.
Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a CrossMark logo, the end user license, and a DOI link to the formal publication on ScienceDirect.
Please refer to Elsevier's posting policy for further information.
18. **For book authors** the following clauses are applicable in addition to the above:
Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.
19. **Thesis/Dissertation**: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions
You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our open access license policy for more information.
Terms & Conditions applicable to all Open Access articles published with Elsevier:
Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.
The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.
If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.
Additional Terms & Conditions applicable to each Creative Commons user license: