Size-Dependent Interactions of Metal Nanoparticles with Fluorophores and Semiconductors

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SIZE-DEPENDENT INTERACTIONS OF METAL NANOPARTICLES WITH FLUOROPHORES AND SEMICONDUCTORS

by

Liyana A Wajira Ariyadasa

A dissertation submitted to the Graduate College in partial fulfilment of the requirements for the degree of Doctoral Philosophy Chemistry Western Michigan University April 2014

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SIZE-DEPENDENT INTERACTIONS OF METAL NANOPARTICLES WITH FLUOROPHORES AND SEMICONDUCTORS

Liyana A. Wajira Ariyadasa, Ph.D.
Western Michigan University, 2014

In recent years, nanoscale metallic particles have gained considerable interest due to their potential applications in advanced technology. Despite such interest, synthetic procedures that produce gram-scale, well-defined metallic nanoparticles with controlled size and shape, especially with diameters less than 5 nm remains a challenge. Our work has focused on developing synthetic procedures that produce well-defined platinum and palladium metal nanoparticles in the 1-5 nm size range. Thioether ligands were used as stabilizers and resulted in metal nanoparticles with controlled size. The nanoparticles were characterized using transmission electron microscopy (TEM), x-ray diffraction (XRD), selected area electron diffraction (SAED), x-ray photoelectron spectroscopy (XPS), electrochemistry and high-resolution transmission electron microscopy (HRTEM). Unique size-dependent electronic properties were found to arise when the particle diameter was less than 5 nm. We studied the changes in electronic properties of fluorophores and semiconductor nanoparticles brought in close proximity to the metal nanoparticles. The interaction of metal nanoparticles with the fluorophores was found to be size-dependent involving a surface energy transfer mechanism. Furthermore, the metal nanoparticles were found to store multiple electrons that were effective in the catalytic reduction of environmental pollutants.
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Liyana A. Wajira Ariyadasa
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1.1 Nanoscale materials

Nanoscale particles are defined as materials whose dimensions lie within the 1-100 nanometer (nm) range. Within this size range, materials exhibit unique and tunable chemical and physical properties.\textsuperscript{1,2} As a result of their unique properties nanoscale particles and the field of nanoscale science and technology have impacted several areas including chemistry, physics, biology, agriculture, food science, environmental science and medicine.

G. Schmid explained the concept of materials with nanoscale dimensions by considering an inorganic nanocrystal containing a few atoms.\textsuperscript{3} He explained that the properties of the crystal varied significantly from that of the single atom as well as that of the bulk solid. Since the number of atoms exposed to the surface of the nanocrystal is a considerable fraction of the total number of atoms, the nanocrystal’s properties are highly influenced by the atomic and molecular features. As a result, nanoscale materials are highly reactive relative to their bulk counterparts. The properties of atoms and molecules are well explained by quantum chemistry while the properties of bulk materials are well explained by the principles in solid-state physics (Figure 1.1). However, significant
differences in properties arise when the size of materials is reduced to the nanoscale, some of which are well understood, while others remain to be uncovered.

**Figure 1.1:** Size relationship of nanoscale materials with atoms, molecules and condensed matter.

1.2 Nanoscale metals

Metals at the nanoscale have gained significant attention due to their unique properties and immense applications. The electronic structure of metals on the nanoscale can be explained using molecular orbital (MO) theory. The highest occupied molecular orbital (HOMO) is defined as the Fermi energy level \( E_f \). The \( E_f \) is highly dependent on the electron density \( \rho \), which can be calculated using the formula \( \rho = N/V \),

\[
\delta \propto \frac{E_f}{L^3}
\]

Since volume \( V \) is three-dimensional it can be considered as the cubic side length \( L \) of a particle and thus, \( V = L^3 \)

The average energy level spacing \( \delta \) can be calculated as \( E_f/N \). The energy level spacing \( \delta \) is inversely proportional to the volume \( L^3 \). Therefore, \( \delta \) is proportional to \( E_f (\lambda_f/L)^3 \),
where \( \lambda_f \) corresponds to the wavelength of the electron in the Fermi energy level. Therefore, when the length of the particle \( (L) \) decreases, the energy level spacing becomes large, resulting in discrete energy levels.

Figure 1.2 is a representation of the formation of energy bands for molecules, nanoscale materials and bulk materials.

Figure 1.2: Band structure formation for metals (a) at molecular level, (b) nanoscale level, and (c) bulk level. Taken with permission from reference [2].

1.2.1 Physical and chemical properties of metallic nanoparticles

The properties of a material strongly depend on its electronic structure. Nanoscale metallic particles display narrow energy levels which govern their properties.\(^4\)\(^-\)\(^6\) The presence of a large fraction of high-energy surface atoms on the metallic nanoparticles further influences their properties and function.\(^7\)\(^-\)\(^9\) Of all the metallic nanoparticles described in the scientific literature, gold (Au) nanoparticles have gained the most
attention. While gold as a bulk material is unreactive and known for its stability, at the nanoscale, gold has been found to be highly catalytic. Its unique optical properties have also been utilized in various electronic, sensor and optoelectronic applications.

Besides optical properties, metals on the nanoscale exhibit significant differences in physical and chemical properties relative to their molecular and bulk counterparts. Often these properties depend on the particle size, shape and composition. Examples of tunable properties include melting point, magnetism, conductivity and surface reactivity.

1.3 Synthesis of metallic nanostructures

The synthesis of metallic nanoparticles is central to nanoscale science and technology. The procedures used as well and the type of particles formed govern how the resulting nanoparticles can be applied for technological applications. There are two general approaches used for producing nanoscale metal particles: the top-down approach and the bottom up approach (Figure 1.3). The top-down approach involves physically decreasing and breaking down the bulk metal to obtain metals with nanoscale dimensions. The major advantage of this approach is the ability to produce nanoparticles in large scale. However, one of the limitations is the difficulty in achieving monodisperse nanoparticles and controlling the overall particle size. In the ‘bottom-up’ approach, solution-phase colloidal chemistry is used to combine and shape atoms to form nanoparticles. A major goal in the bottom-up approach is controlling the reaction so that the size and shape of the resulting nanoparticles can be controlled. One of the limitations
of the bottom-up approach is the difficulty in scaling up the nanoparticle production for projected industrial usage.\textsuperscript{12}

![Diagram of top-down and bottom-up approaches]

**Figure 1.3:** Schematic diagram to illustrate top-down and bottom-up approaches.

### 1.3.1 Chemical synthesis of metal nanoparticles

Chemical synthetic methods for the production of metal nanoparticles are classified as bottom-up approaches. Chemical synthesis methods generally require the use of metal precursors, a suitable solvent, a stabilizer to prevent uncontrollable nanoparticle growth and agglomeration, and a reducing agent.\textsuperscript{7,12–17} Obtaining well-defined metal nanoparticles requires development of reaction conditions where all the
aforementioned reagents are tailored to produce the desired nanoparticles. Reaction conditions including temperature, pH, pressure, and reaction time play a significant role in the nucleation and growth processes. Common solution phase chemical methods that have been used to synthesize metal nanoparticles include redox processes\textsuperscript{18–20}, thermal decomposition,\textsuperscript{21–24} electrochemical synthesis,\textsuperscript{25,26} sol-gel, and galvanic exchange/replacement.\textsuperscript{7,15,16}

### 1.3.1.1 Reduction

Reduction is a process in which a chemical species decreases its oxidation number by accepting electrons. There are several reduction methods available for synthesizing metal nanoparticles. Reduction from metal salt precursors, and reduction of organic ligands bonded to organometallic precursors, are the popular methods.\textsuperscript{27}

**Reduction from metal salt precursors:** Reduction of metal salt precursors have been performed in three different media: in the aqueous phase, in the organic phase and in reverse micelles (surfactant – stabilized water-in-oil microemulsions).\textsuperscript{28} Synthesizing metal nanocrystals in the aqueous phase via reduction dates back to the 19\textsuperscript{th} century. In 1853, Michael Faraday prepared colloidal Au using HAuCl\textsubscript{4} as the precursor and phosphorous as the reducing agent. This procedure is called the ‘wet chemical’ method.\textsuperscript{29} In 1950, Turkevich and his co-workers reported synthesizing spherical 10-20 nm Au nanoparticles.\textsuperscript{30–32} The equation below explains the reduction approach.

\[
xM^{n+} + nxe^- + stabilizer \rightarrow M^0 \quad n (Cluster)
\]
where $M$ is the metal precursor and $nxe^-$ is the reducing agent.

Commonly used reducing agents include metal borohydrides, alcohol, hydrazine or hydrogen. Stabilizing agents such as surfactants, ligands and polymers prevent uncontrollable growth of the nanoparticles and particle agglomeration (Figure 1.4).

![Figure 1.4](image)

**Figure 1.4:** Formation of nanoparticles by reduction of metal precursors. Taken with permission from reference [27].

*Reduction in Organic phase:* The synthesis of metal nanoparticles in organic solvents is often required when high temperature is needed for the synthesis reaction to undergo completion. Common reducing agents used in the organic phase include super hydrides or alcohols.33–35

*Reverse micelle method:* The reverse micelle method is another procedure that is widely used for synthesizing uniform metal nanoparticles. In this method, an aqueous solution of metal salt with excess surfactant is mixed with a non-polar organic solvent to form spherical inverted micelles around the desired particle.36 Metal precursors are dissolved in the aqueous media and are surrounded by organic micelles. The metal ions are reduced to zero-valent metals and undergo nucleation and growth processes to form metal
nanoparticles. In 1994, Klabunde et al. synthesized cobalt (Co) nanoparticles using two different microemulsion systems involving the reverse micelle process. Pilleni and her co-workers also used the reverse micelle process to synthesize copper (Cu), silver (Ag), platinum (Pt) and Co nanoparticles.

1.3.1.2 Thermal decomposition

Chemical decomposition of a compound using heat as a form of energy, is called thermal decomposition or thermolysis. Most transition metal based organometallic compounds are capable undergoing decomposition to the corresponding metal upon mild heating. In fact organometallic precursors are ideal for producing nanoparticles. Smith et al. reported the use of carbonyl complexes of rhodium (Rh), iridium (Ir), ruthenium (Ru), osmium (Os), palladium (Pd) and Pt to produce the corresponding metal nanoparticles. Furthermore, colloidal solutions of Pd and Pt nanoparticles have been prepared by the thermal decomposition of palladium acetate, palladium acetylacetonate and platinum acetylacetonate in the organic phase. Bimetallic Cu-Pd nanoparticles were prepared by thermal decomposition of a mixture of their acetates in the organic phase. Nakamato et al. reported size controlled synthesis of monodisperse Ag nanoparticles capped with long chain alkyl carboxylates via thermal decomposition of silver carboxylate in the presence of tertiary amines stabilizers. Recently, microwave techniques have been found to be efficient in the thermal decomposition of metal salts to form nanoscale particles.
1.3.1.3 Electrochemical synthesis

Electrochemical reduction of metal ions to form their corresponding nanoparticles has been an efficient method for nanoparticle preparation. For example, Reetz et al. developed a five step electrochemical method for synthesizing single metal and bimetallic nanoparticles as described in Figure 1.5.25,26,28,47:

1. Oxidative dissolution of bulk metal anode.
   For Ag nanoparticles: \( Ag^0 - e^- \rightarrow Ag^{+1} \)
   Oxygen gas releases and at the same time \( Ag_2O \) deposits on the anode.

2. Metal ion migration to the cathode.

3. At the cathode, reduction of the metal ion to the zero-valent metal.
   For Ag nanoparticles: \( Ag^{+1} + e^- \rightarrow Ag^0 \)

4. Formation of metal nanoparticles by nucleation and growth, which involves van der Waals forces between metal atoms.

5. Controlling the growth and protecting the nanoparticles using stabilizing ligands.

There are several advantages of electrochemical synthesis of metal nanoparticles.

1. Since the system is free from reducing agents, it avoids the contamination of nanoparticles with byproducts formed from reducing agents.

2. Nanoparticles are easy to isolate as they are precipitated.

3. Particle size can be controlled by modulating the current density, distance between the electrodes, the reaction time, temperature and solvent polarity. High current densities result in the formation of small nanoparticles.
Recently Pd, Ni, Ag and Au single metal nanoparticles and Pd-Ni, Fe-Co, Fe-Ni bimetallic particles were successfully synthesized via electrochemically.\textsuperscript{25,26,48–53}

1.3.2 Mechanism of nanoparticle formation

Well-defined and monodisperse nanoparticles are required for advanced technological applications. While there are numerous colloidal chemical synthetic methods that have been developed to produce metal nanoparticles, an understanding of the mechanisms of nanoparticle formation is limited.\textsuperscript{54,7} According to the limited existing literature, it is thought that the mechanism of nanoparticle growth involves nucleation and growth processes.\textsuperscript{4,7,55,56} The first study describing the preparation of uniform colloidal particles was reported by Victor K. LaMer and Robert H. Dinegar in 1950.\textsuperscript{57} They developed the concept of “burst nucleation” for preparing various hydrosols.

\textbf{Figure 1.5}: Electrochemical formation of Pd nanoparticles. Taken with permission from reference [27].
and oil aerosols. According to their explanation, a number of nuclei are produced simultaneously during a ‘nucleation’ process, which is followed by a ‘growth’ process in which the nuclei grow.\textsuperscript{12,57} The “burst nucleation” process allows the control of particle size during the synthesis and has been used to understand the mechanism of formation of monodisperse nanoparticles.\textsuperscript{54,58,59}

1.3.2.1 Nucleation

Nucleation is the first event that occurs during the nanoparticle synthesis process. Studying the nucleation mechanism is crucial and to date a few advances have been made.\textsuperscript{60} During the synthesis process, it is important to control the kinetic and thermodynamic processes so that nanoparticles with desired size, shape and uniformity are obtained. The nucleation and growth steps must be separated from each other during the reaction process.\textsuperscript{59,61–63} In an early study by LaMer and coworkers, the nucleation and growth processes were separated using homogeneous nucleation. However, once the nuclei were introduced to the homogeneous solution, it became heterogeneous. In this process, there is a high-energy barrier caused by the sudden phase change from homogeneous to heterogeneous. In the system, the concentration of atoms is increased as the reaction time increases. Consequently, the atoms aggregate through self-nucleation until the solution reaches super-saturation. Once the solution is super-saturated with monomers or atoms, the nucleation process begins. If the monomer concentration is low in the solution, the nucleation process is decelerated. After the formation of stable nuclei,
particle growth occurs, which can be controlled kinetically or thermodynamically, depending on the desired nanoparticles.\textsuperscript{64,65}

1.3.2.2 Growth

There are two types of growth processes: (i) size focusing process, and (ii) size defocusing process. The size focusing process involves diffusion of monomers to the surface of the nuclei. Size defocusing processes involve the reaction between the monomers and the surface of nuclei. According to a study done by Xie \textit{et al.}, these two processes are driven by the Gibbs-Thompson effect, which explains the relationship between the solubility of a particle and the solubility of its bulk, as a function of size.\textsuperscript{58,13,66}

\[ S_r = S_b \exp\left(\frac{2\sigma V_m}{rRT}\right) \]

where \( S_r = \) solubility of the particle, \( S_b = \) solubility of bulk, \( \sigma = \) specific surface energy, \( V_m = \) molar volume of the material, \( r = \) the radius of the particle, \( R = \) gas constant, \( T = \) temperature.\textsuperscript{66,67}

When \( (2\sigma V_m/rRT) < 1 \) and the thickness of the diffusion \( \sim \infty \) (infinity), the rate of growth of a particle is given by,

\[ \frac{dr}{dt} = K\left(\frac{1}{r}\right)\left(\frac{1}{r^*} - \frac{1}{r}\right) \]

where \( K = \) rate constant, \( r^* = \) critical particle size for which the growth rate is zero at the current monomer concentration.\textsuperscript{66,67}
1.3.3 Stabilization of metal nanoparticles

The particles formed during the nucleation and growth processes are kinetically unstable. Therefore, surface stabilization or surface passivation using an appropriate ligand is required. The role of the stabilizing ligands is to adsorb onto the nanoparticle surface and protect the particle from further agglomeration. There are three types of stabilization processes: (i) electrostatic, (ii) steric and (iii) electro-steric stabilization.27

Electrostatic stabilization: Positive and negative ions in solution act as an electrical double layer to protect the nanoparticles. Figure 1.6 shows the Columbic repulsion resulting from an electrical double layer and how it protects the nanoparticles from aggregation.

![Figure 1.6: Electrostatic stabilization of metal nanoparticles. Taken with permission from reference[27].](image-url)
**Steric stabilization:** Adsorption of large molecules such as surfactants and polymers onto the nanoparticle surface is called steric stabilization. Figure 1.7 shows a metal nanocluster surrounded by large surfactant molecules to create high local concentration, which causes them to be apart.

![Figure 1.7: Steric stabilization of metal nanoparticle. Taken with permission from reference [27].](image)

### 1.4 Characterization of metal nanoparticles

The chemical and physical properties of nanoparticles depend on their size, shape and structure. Whenever a nanoparticle is synthesized, careful measures need to be taken to determine the structural features. There are several techniques that are useful for the structural characterization of nanoparticles including x-ray diffraction (XRD), atomic pair distribution function (PDF), x-ray absorbance fine structure (XAFS), x-ray photoelectron spectroscopy (XPS), Raman spectroscopy, transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), selected area electron
diffraction (SAED), scanning electron microscopy (SEM), scanning tunneling microscopy (STM), and atomic force microscopy (AFM). For the characterization of electronic properties, x-ray absorption near edge spectroscopy (XANES), optical absorption and valence and core-level photoemission are useful.\textsuperscript{68,7} Specifically, for characterization of colloidal metal nanoparticles, UV-visible absorbance spectroscopy, electrochemical methods, TEM, HRTEM, XRD and SAED are widely used.\textsuperscript{7,42,69} In this dissertation, metal nanoparticles were synthesized and characterized using electron microscopy, XRD and SAED, which are briefly described below.

1.4.1 X-ray diffraction

X-ray diffraction is used to determine the composition and size of the nanoparticles.\textsuperscript{70,71} In an XRD spectrum, the position of each peak indicates the spacing between the crystal planes of the particle. In the case of metal nanoparticles, the crystal planes enable confirmation of the identity of the metal by matching the lattice parameters. If the particles are bimetallic, the ratio of two metals can be calculated by obtaining lattice parameters from the spectrum. The width of the peaks in the spectrum depends on the particle size. If the particle size is large, the peak width is small and \textit{vice versa} (Figure 1.8). To calculate the particle size, the Scherrer equation and Bragg equation are used.\textsuperscript{71}

Scherrer equation: \( \Delta s = 0.9 \left( \frac{1}{D} \right) \), where \( D \) = particle diameter and \( s = 2 \sin \theta / \lambda \)
1.4.2 Electron microscopic methods

Microscopic imaging of nanoscale materials is important as it is the only technique that provides direct visual evidence of the material. Electron microscopic methods are powerful tools for characterization of metal nanoparticles, because they provide visual real space images of the particle surface, thus allowing determination of the nanoparticle morphology, topography and composition. There are several important electron microscopic methods: TEM, HRTEM, SEM, STM and AFM. Nanoparticle imaging can be obtained by TEM, which allows direct imaging making it possible to determine the size, shape and dispersity. Using HRTEM, an operating mode of TEM whereby an image is formed by collecting scattered beams and the central beam, one can obtain information on material crystallinity. As a result of the high resolution, individual atoms and small crystalline defects can be visualized. Particularly in

Figure 1.8: X-ray diffraction of powder samples of (a) 2 nm and (b) 5 nm Au nanoparticles. Taken with permission from reference [71].
nanoparticles, HRTEM provides interatomic distance.\textsuperscript{68,72} Additional analytical techniques that provide morphological information include SEM and AFM.

1.4.3 Selected area electron diffraction (SAED)

Selected area electron diffraction is usually measured using a HRTEM with electron beam energy of 100-400 keV. Crystallographic information of a single nanoparticle can be elucidated by SAED. The high electron beam energy allows electrons to pass through the nanoparticle being analyzed. Since the energy of the electron beam is high, the wavelength of the beam is within the nanometer range. Some of the energy of the beam that does not pass through the crystal structure is scattered and the rest of the beam passes through the nanoparticle. This phenomenon leads to the formation of images that consist of a series of spots called selected area diffraction patterns. To image only the selected area of the specimen or a single particle, a selected area aperture is used to block the beam used.\textsuperscript{73} In the case of nanoparticles, SAED consists of ring patterns that are expected to match the XRD of the material (Figure 1.9).\textsuperscript{74,75}
1.5 Summary and major focus of the research

The unique chemical and physical properties of metal nanoparticles have opened new avenues in various technological fields including catalysis, environmental science, biomedical applications, alternative energy, optoelectronics, electronics and photochemistry. Despite such advancements, fundamental questions about the interactions of metal nanoparticles with other materials are not well understood. Furthermore, synthetic procedures that produce well-defined metallic nanoparticles with controlled size and shape are still a challenge. The work in this dissertation focuses on developing synthetic procedures that produce well-defined Pt and Pd metal nanoparticles in the 1-5 nm size range. The electrochemical properties of the Pt and Pd nanoparticles were studied. The interaction of Pd nanoparticles with fluorescent molecules and semiconductor nanoparticles were investigated with an emphasis on determining the size-dependent interactions. It was found that when Pd nanoparticles were brought in close
proximity to semiconductor nanoparticles, electron transfer took place. On the other hand when fluorescent molecules were brought in close proximity to the metal nanoparticles, there was transfer of energy. The fluorescent quenching of the fluorophores caused by metal nanoparticles was found to be a result of a mechanism known as nanoparticle surface energy transfer (NSET).
1.6 References


CHAPTER II

SYNTHESIS, CHARACTERIZATION AND EVALUATION OF THE CATALYTIC ACTIVITY OF PALLADIUM NANOPARTICLES

2.1 Introduction

Over the past two decades, metal nanoparticles have gained increasing interest in the field of nanoscale science and technology.\textsuperscript{1-4} This interest stems from unique chemical and physical properties that arise due to discrete energy levels when the particle size is reduced to the nanoscale.\textsuperscript{5} As a result of the particle size, nanoparticles exhibit properties that lie between those of the bulk materials and the molecular level.\textsuperscript{3} The physical and chemical properties of metal nanoparticles including color, melting point and surface reactivity depend highly on the particle size, shape and composition.\textsuperscript{6} For instance, studies have shown that the melting point of 1.5 nm gold (Au) nanoparticles is 500 °C while the melting point of 2.2 nm gold nanoparticles is 700 °C.\textsuperscript{6} Therefore, it is crucial to tailor the nanoparticle size and shape to obtain homogeneous samples in order to obtain a precise understanding of their properties.\textsuperscript{7} One of the biggest challenges in nanoscale science is synthesizing nanoparticles that are size-controlled and in the 1-5 nm size range where unique properties arise.\textsuperscript{8-11} The synthesis of Pd nanoparticles in the size 1-5 nm range of has gained much attention due to their applications as catalysis including
carbon-carbon cross coupling reactions, and hydrogenation. Therefore, in this chapter, a synthesis procedure to obtain monodisperse, size-controlled Pd nanoparticles is discussed.

2.1.1 Ligands for Pd nanoparticles

As described in Chapter I, the synthesis of metallic nanoparticles involves the use of various reagents including the metal precursor, solvent, stabilizing ligands and reducing agents. Several parameters must also be controlled including temperature, pH, pressure, and reagent amounts in order to obtain well-defined nanoparticles. Common stabilizers that have been used for the synthesis of Pd nanoparticles include surfactants, dendrimers, phosphine ligands, thiols, and polymers.

Nanoparticle formation includes nucleation and growth processes. Stabilizing ligands play an important role in the growth process by averting particle agglomeration and surface passivation that aids in particle size control. The use of thiols has been prevalent in the design of nanoparticles containing soft metals, for example Au, silver (Ag) and platinum (Pt). Thiols are the most common sulfur based ligands for nanoparticle synthesis, and they attach to the metal surface via covalent bonding. Other suitable stabilizing ligands containing heteroatoms such as nitrogen and phosphorus are also used.

In this Chapter, we study the use of the sulfur containing thioether ligands as Pd nanoparticle stabilizers. Sulfur based ligands are efficient stabilizers for soft metals including Pd and Pt, because of the soft-soft acid-base interactions. In 1990, Burst and
his co-workers reported that thiols were excellent stabilizers in the synthesis of Au nanoparticles.\textsuperscript{21} The Brust method has been modified and has led to the successful synthesis of metal nanoparticles though many of these exhibit polydispersity.\textsuperscript{19} Thioether ligands are advantageous relative to thiols because they attach to the metal surface via dative bonding rather than covalent bonding. Thioethers are generally more stable and less toxic relative to phosphine ligands and are therefore easier to handle.\textsuperscript{19}

The use of sulfur-based ligands as stabilizers for catalytic metals such as Pd have raised some concerns in that the sulfur containing ligands would be expected to poison the Pd catalysts.\textsuperscript{22} A few reports have indicated that some nanoparticles stabilized by sulfur-based ligands are effective catalysts. For example, in 2005, Miyake and co-workers reported that dodecylthiolate stabilized Pd nanoparticles were effective catalysts for synthesizing carbon nanotubes.\textsuperscript{23} Astruc \textit{et al.} similarly showed that thiolate-stabilized Pd nanoparticles were stable and recyclable in the Suzuki-Miyaura reaction for the conversion of aryl halides.\textsuperscript{24} Furthermore, thiolated cyclodextrin stabilized Pd nanoparticles were found to show excellent catalytic activity toward hydrogenation reactions.\textsuperscript{25} It is important to examine the catalytic activity of newly synthesized nanoparticles to ensure that the stabilizer does not prevent surface reactivity.

In this chapter, we describe the synthesis of monodisperse Pd and Pt nanoparticles via a thermal decomposition method. The nanoparticles were characterized using XRD, TEM, HRTEM and SAED. We also examined the catalytic activity of the synthesized Pd nanoparticles in a hydrogenation reaction.
2.2 Experimental section

2.2.1 Chemicals: Platinum (II) acetylacetonate (97%), \( n \)-dodecyl sulfide (93%), palladium acetate (97%), silica gel [high purity grade (Davisil Grade 633), pore size 60 Å, 200-425 mesh particle size], \( trans \)-cinnamaldehyde (90 %), citral (95%) and chloroform-\( d \) [\(^{100}\%\), 99.96 atom%] were purchased from the Sigma Aldrich Company and used as received. Diphenyl ether, toluene and absolute ethanol were HPLC grade and purchased from the Sigma Aldrich Company.

2.2.2 Synthesis of Pt nanoparticles: Platinum acetylacetonate (0.050 g, \( 1.27 \times 10^{-4} \) moles) and \( n \)-dodecyl sulfide (0.235 g, \( 6.35 \times 10^{-4} \) moles) were added to a 100 mL round-bottom flask with 50 mL of phenyl ether. The round-bottom flask and its contents were immersed into a silicon oil bath, and fitted to a condenser. The flask was heated at 210 °C for 45 minutes. After approximately 30 minutes of heating, the solution color changed from yellow to dark brown, indicating reduction of \( \text{Pt}^{2+} \rightarrow \text{Pt}^0 \) and consequently, the formation of the Pt nanoparticles. After a total of 45 minutes of refluxing, the flask was removed from the silicon oil bath and allowed cool to room temperature.

2.2.3 Synthesis of Pd nanoparticles: Palladium acetate (0.1 g, \( 1.48 \times 10^{-4} \) moles) and \( n \)-dodecyl sulfide (0.2750 g, \( 7.4 \times 10^{-4} \) moles) were added to a 100 mL round-bottom flask and dissolved in 30 mL of toluene. The round bottom flask and its contents were fitted to a condenser, immersed in an oil bath, and stirred magnetically. The flask was then heated at 90-95 °C for 1 hour, 2 hours and 3 hours, respectively, to obtain the three different sizes.
2.2.4 Characterization of Pd and Pt nanoparticles

2.2.4.1 UV-visible absorbance spectroscopy: UV-visible absorbance spectra were recorded using Varian Cary 50 Bio spectrophotometer in the range of 200-1100 nm.

2.2.4.2 XRD: Powder X-ray diffraction (XRD) data was collected on a Scientag XDS model 2000 diffractometer. For XRD measurement, the Pd nanoparticle sample was dried and mixed with 325 mesh Si powder and was placed on a Si wafer sample holder.

2.2.4.3 Transmission electron microscopy (TEM): TEM images of Pd and Pt nanoparticles were obtained using a JOEL JEM-1230 TEM. Sample preparation was done by placing a 1 µL drop of nanoparticle solution on a Formvar/carbon-coated copper grid and drying it in a desiccator. Each sample was imaged at 400 K, 500 K and 600 K magnification. Histograms for the core-size of the nanoparticles were prepared by manual reading.

2.2.5 Immobilization of Pd nanoparticles on SiO₂ to prepare Pd/SiO₂

A sample of 1 gram of silica gel was calcinated at 400 °C for 12 hours to remove adsorbed water. The Pd nanoparticles (30 mL in toluene) were mixed with the calcinated silica and mixture was stirred overnight. Stirring was stopped and the mixture was allowed to sit undisturbed for 6 hours for the silica gel with Pd adsorbed on it to settle at the bottom of the flask. The solid consisting of Pd nanoparticles adsorbed onto silica was vacuum filtered and washed with ethanol 3 times. The precipitate was dried in a desiccator for one day.
2.2.6 Hydrogenation reaction using Pd/SiO$_2$

Cinnamaldehyde and citral were used as model compounds for $\alpha$, $\beta$-unsaturated aldehydes. 0.5 mL of each aldehyde, 10 mL of ethanol and 0.2 g of Pd/SiO$_2$ were mixed in a 25 mL round bottom flask. The mixture was stirred in the presence of a steady flow of hydrogen gas at room temperature. After every 2 hours, 0.5 mL of the sample was withdrawn from the reaction mixture and excess ethanol was evaporated using a rotary evaporator. The dried product was mixed with 0.5 mL of CDCl$_3$ to prepare a sample for $^1$H NMR analysis. The reaction products were identified by $^1$H NMR spectroscopy (JEOL Eclipse 400 MHz).

2.3 Results and discussion

Size control during the synthesis procedure in order to obtain a homogeneous colloidal solution of nanoparticles is crucial toward understanding the size-dependent properties of materials at the nanoscale. The scientific literature contains numerous reports for procedures that lead to well-defined plasmonic nanoparticles (Au and Ag)$^{26-31}$ For other transition metals, the methods are not well established. It is desirable to obtain synthetic procedures that are not labor intensive, straightforward and most importantly produce monodisperse particles so that separation of size or shape is avoided or minimized.
2.3.1 Synthesis of Pd nanoparticles

Three different sizes of monodisperse, \( n \)-dodecyl sulfide stabilized Pd nanoparticles were synthesized by thermal decomposition of palladium acetate (\( \text{Pd}_3(\text{OAc})_6 \)) in toluene.\(^{32}\) A bright yellow solution of \( \text{Pd}_3(\text{OAc})_6 \) and \( n \)-dodecyl sulfide (M:L=1:5) were dissolved in toluene and heated at 95 °C while stirring. After 20 minutes, the color of the solution changed to dark brown indicating the reduction of \( \text{Pd}^{2+} \) to \( \text{Pd}^0 \) and the formation of Pd nanoparticles.

![Figure 2.1: UV-visible absorbance spectrum of \( \text{Pd}_3(\text{OAc})_6 \) dissolved in toluene.](image)

To obtain three different sizes of nanoparticles samples were withdrawn from the reaction after 1, 2, and 3 hours of heating. UV-visible spectra were recorded before and after heating (Figure 2.1, 2.2). The UV-visible spectrum of \( \text{Pd}_3(\text{OAc})_6 \) showed a peak at 430 nm (Figure 2.1) corresponding to the \( d-d \) transitions of \( \text{Pd}^{2+} \) in \( \text{Pd}_3(\text{OAc})_6 \).\(^{20}\) The
430 nm peak was no longer observable after 20 minutes of reaction time, further indicating the reduction of the metal ions from Pd$^{2+}$ to Pd$^0$.

![UV-visible absorbance spectrum of Pd nanoparticles](image)

**Figure 2.2:** UV-visible absorbance spectrum of Pd nanoparticles withdrawn from the reaction after 1 hr, 2 hrs and 3 hrs, respectively.

2.3.2 Characterization of Pd nanoparticles

*TEM analysis:* Particle analysis by TEM allows determination of their size, shape and dispersity. Figure 2.3 shows TEM images of 1.9 ± 0.1 nm, 2.3 ± 0.1 nm and 2.5 ± 0.1 nm Pd nanoparticles and their corresponding histograms. The particles were spherical in shape and not aggregated. All the images were obtained without a size selection process.
Figure 2.3: TEM images of Pd nanoparticles of (A) 1.9 ± 0.1 nm, (C) 2.3 ± 0.1 nm, (E) 2.5 ± 0.1 nm and their corresponding histograms (B), (D) and (F). The images were taken directly from the reaction flask without a size selection process.
Figure 2.4: HRTEM of 2.5 nm Pd nanoparticles.

Figure 2.5: (A) XRD and (B) SAED of Pd nanoparticles.
**HRTEM analysis:** HRTEM allows imaging of the lattice fringes and the determination of the inter-fringe distance of the crystal planes.\(^{33,34}\) Figure 2.4 shows the HRTEM image of 2.5 nm Pd nanoparticles where the lattice fringes are visible and \{111\} is the most dominant. The inter-planner distance was calculated to be 0.215 nm which was consistent with the inter-planner distance of \{111\} planes. The HRTEM of 2.5 nm Pd nanoparticles showed twinning which is a common phenomenon in metal nanoparticles.

**XRD and SAED analysis:** Figure 2.5A shows the XRD pattern for 2.5 nm Pd nanoparticles. The diffraction peaks were observed at \(2\theta\) values of 40.49°, 46.97°, 68.39°, 82.31° and 86.83° corresponding to the planes the \{111\}, \{200\}, \{220\}, \{311\} and \{222\} of a face-centered cubic metal structure. The XRD results indicate that the nanoparticles are single metals and that they are not contaminated with any other metal. The SAED image of 2.5 nm Pd nanoparticles is shown in Figure 2.5B and it consists of five diffused ring patterns which can be assigned to the diffraction peaks shown in the XRD data. The SAED data was used to confirm the crystallographic data obtained from XRD.\(^{35,36}\) The visibly possible Miller indices are assigned to fcc indices. The SAED data was in good agreement with the XRD.

### 2.3.3 Synthesis of Pt nanoparticles

Monodisperse Pt nanoparticles stabilized by \(n\)-dodecyl sulfide were produced in phenyl ether. Platinum acetylacetonate was dissolved in diphenyl ether forming a bright orange solution. The stabilizer \(n\)-dodecyl sulfide was added to the precursor in a 1:5 metal to stabilizer ratio and the solution was heated at 210 °C while stirring. After 40
minutes of reaction time, the solution color changed from orange to dark brown indicating reduction of Pt\textsuperscript{2+} to Pt\textsuperscript{0}.

2.3.4 Characterization of Pt nanoparticles

Figure 2.6: (A) TEM image of Pt nanoparticle of size 2.5 ± 0.1 nm (B) Histogram of corresponding nanoparticles.
Figure 2.7: HRTEM of Pt nanoparticles.

Figure 2.8: (A) XRD and (B) SAED of Pt nanoparticles.
Figure 2.6 shows the TEM image and the corresponding histogram of 2.5 ± 0.1 nm Pt nanoparticles. The image is shown particles with a narrow size distribution and the image was obtained without a size selection process. The particles were found to be spherical in shape.

Figure 2.7 shows the HRTEM image of the Pt nanoparticles with clear lattice fringes in the {111} plane. The inter-planner distance was calculated to be 0.28 nm. Figure 2.8B shows the SAED of the Pt nanoparticles with five diffused rings which could be assigned to the {111}, {200}, {220}, {311} and the {222} reflections of a face-centered cubic structure. The XRD measurements shown in Figure 2.8A shows five peaks at a $2\theta$ value of 39.8°, 46.3°, 67.6°, 81.5° and 85.9° characteristic of the {111}, {200}, {220}, {311} and {222}, patterns, respectively. Crystal structure information from both techniques is in agreement with the fcc structure.

### 2.3.5 Supported Pd catalyst for hydrogenation reactions

There are concerns that arise when stabilizers are used to passivate the surface of catalytic metal nanoparticles. The main concern is the poisoning of the catalyst by the stabilizer. Since our Pd nanoparticles are stabilized by a sulfur-based ligand it was important to access the nature of the overall nanoparticle activity. Therefore, the synthesized colloidal Pd nanoparticles were tested as catalysts in a hydrogenation reaction. Colloidal metal nanoparticles have been extensively used as catalysts for different types of reactions such as cross-coupling, electron transfer, hydrogenation and
oxidation reactions.\textsuperscript{37} Catalytic hydrogenation of C-C double bond has gained much attention due to their involvement in the production of commodity chemicals.\textsuperscript{37} We used cinnamaldehyde and citral as model compounds and Pd nanoparticles immobilized on the silica as a heterogeneous catalyst (Scheme 2.1). The products obtained were identified using \textsuperscript{1}H NMR spectroscopy.

\textbf{Scheme 2.1:} Reaction for hydrogenation of C=C of cinnamaldehyde and citral

\textsuperscript{1}H NMR analysis for hydrogenation of cinnamaldehyde: Figure 2.9 shows time dependent \textsuperscript{1}H NMR analysis for hydrogenation of cinnamaldehyde. Hydrogenation of
cinnamaldehyde in the presence of Pd nanoparticles was monitored over an 8 hour time period. $^1$H NMR spectra of the reaction mixture confirmed the formation of hydrocinnamaldehyde. A doublet at $\delta = 9.7$ ppm corresponding to the aldehyde proton of cinnamaldehyde decreased in intensity and disappeared after 7 hours.

**Figure 2.9:** $^1$H NMR spectrum for cinnamaldehyde hydrogenation: composition of the reaction mixture (a) 0 hrs, (b) 3 hrs, (c) 5 hrs, (d) 7 hrs, (e) 8 hrs and (f) 3 days.

This observation confirmed the complete consumption of cinnamaldehyde. Furthermore, a new peak appeared at $\delta = 9.8$ ppm corresponding to the aldehyde proton of hydrocinnamaldehyde. The hydrogenation of the double bond was further confirmed
by the appearance of two triplets at $\delta = 2.77$ ppm and $\delta = 2.95$ ppm for the two methylene groups of hydrocinnamaldehyde.

**Figure 2.10:** Conversion of cinnamaldehyde during the 8 hrs reaction time.

Figure 2.10 shows a graph of conversion percentage of cinnamaldehyde vs. time. At the end of 8 hours, all the cinnamaldehyde was converted into hydrocinnamaldehyde and 3-phenylpropanol. More than 80% of mixture was hydrocinnamaldehyde.

$^1H$ NMR analysis for hydrogenation of citral: Citral is a mixture of two isomers (E and Z). Two doublets at $\delta = 9.8$ ppm and $\delta = 10.0$ ppm for the two aldehyde peaks confirm
the presence of two isomers in the starting reaction mixture (Figure 2.11). In the presence of the Pd catalyst the intensity of the above mentioned peaks decreased due to the consumption of citral.

**Figure 2.11:** $^1$H NMR spectrum of pure-citral.

**Figure 2.12:** $^1$H NMR spectrum of the mixture of citral and citronellal after 8 hrs of hydrogenation.
Appearance of a new peak at $\delta = 9.7$ ppm (triplet) corresponding to the aldehyde proton of citronellal confirmed the reduction of double bond adjacent to aldehyde group (Figure 2.12).

### 2.4 Conclusion

Three different sizes of monodisperse Pd nanoparticles (1.9, 2.3 and 2.5 nm) and one size of monodisperse Pt nanoparticles (2.5 nm) were prepared. The colloidal nanoparticle solution was found to contain well-defined particles that had a narrow size distribution. The procedure established in this work shows that Pd and Pt metal nanoparticles could be prepared using a facile synthetic procedure. The characterization data showed that the nanoparticles were crystalline. Catalytic activity of Pd nanoparticles was examined in the hydrogenation of cinnamaldehyde and citral at room temperature. These studies were conducted to ensure that the thioether stabilizer did not poison the catalyst. The Pd nanoparticles converted cinnamaldehyde to hydrocinnamaldehyde while citral was converted to citronellal. The results showed that $n$-dodecyl sulfide is a useful stabilizer for the synthesis of Pd nanoparticles.
2.5 References


CHAPTER III

ELECTRON TRANSFER FROM NANOCRYSTALLINE SEMICONDUCTORS TO PALLADIUM AND PLATINUM NANOPARTICLES

3.1 Introduction

The interaction between semiconductor nanoparticles and metal nanoparticles is a significant area of scientific research.\textsuperscript{1-6} The major driving force for studying such systems is that metals at semiconductor interfaces have been found to enhance the semiconductor photocatalytic efficiency by improving charge separation.\textsuperscript{7-19} Studies involving the interactions of well-defined quantized metal nanoparticles at semiconductor interfaces are less prevalent. The role of metal nanoparticles in metal-semiconductor systems is not completely understood, and many studies need to be done. According to the early studies, electrons and holes generated by light excitation of semiconductors are transferable via the interface in picoseconds.\textsuperscript{20-22} Also coupling metal nanoparticles to the semiconductor nanoparticles is one of the most popular ways to enhance the efficiency of semiconductor photocatalysts.\textsuperscript{1,5,17,18,13,23} Recent studies have shown that metal co-catalyst improves the process of electron transfer by three steps\textsuperscript{5}: (a) improves the charge separation in the semiconductor nanoparticle (b) discharge photoinduced electrons via the interface (c) allows reduction and oxidation pathways with low potential. Enhanced photocatalytic activity of metal coupled semiconductors is due to the shift of Fermi level
of semiconductor into more negative potentials.\textsuperscript{7,9,10,24} Fermi level shifting to negative potentials makes the interfacial charge transfer process more favorable.

The unique properties of metal nanoparticles with discrete energy levels such as quantized double layer charging ability make them ideal for reaching Fermi level equilibration. Size of the metal nanoparticle is also reported as a key factor that influences the electrical properties of nanocomposite.\textsuperscript{7}

In this Chapter, the electrochemical properties of Pd and Pt nanoparticles and their interaction with titanium dioxide (TiO\textsubscript{2}) semiconductor nanoparticles is discussed. Both Pd and Pt nanoparticles showed charging and discharging ability which is useful in various chemical reactions.

### 3.1.1 Semiconductor nanoparticles

Semiconductors can undergo charge separation upon irradiation with energy equal to or greater than the bandgap. The distance between the conduction and valence band is called bandgap. Titanium dioxide is a large bandgap semiconductor with bandgap energy of 3.2 eV that is used in several photocatalytic studies. Irradiation of TiO\textsubscript{2} with energy equal to or greater than 3.2 eV, results in the promotion of an electron from the valence band to the conduction band and leaves a positively charged hole in the valence band as shown in Equation 3.1. Figure 3.1 illustrates the charge separation process (Equation 3-1).
**Figure 3.1:** Mechanism of electron/hole pair generation of TiO$_2$ in the presence of light. Taken with permission from reference [26].

- **Charge separation:**  
  \[ \text{TiO}_2 + h\nu \rightarrow \text{TiO}_2(e + h) \quad (3-1) \]

- **Oxidation:**  
  \[ \text{TiO}_2(e + h) + 0x \rightarrow \text{TiO}_2(e) + 0x^+ \quad (3-2) \]

- **Reduction:**  
  \[ \text{TiO}_2(e + h) + \text{Red} \rightarrow \text{TiO}_2(h) + \text{Red}^- \quad (3-3) \]

- **Recombination:**  
  \[ \text{TiO}_2(e + h) \rightarrow \text{TiO}_2 \quad (3-4) \]

The generated electrons (conduction band) and holes (valence band) are useful in reduction (Equation 3-3) and oxidation (Equation 3-2) reactions, respectively. However, most of the charge carriers tend to recombine (Equation 3-4). Using a scavenger for holes or electrons, trapped electrons or holes can be created.\textsuperscript{26}
Trapping electrons in the conduction band using ethanol as a holes scavenger:

\[
\text{TiO}_2(e + h) + C_2H_5OH \rightarrow \text{TiO}_2(e_t) + C_2H_5O^- \quad (3-5)
\]

The electrons get trapped in titanium(IV) sites.\textsuperscript{27} The behavior of trapped electrons in the Ti\textsuperscript{4+} can be elucidated using electron paramagnetic resonance (EPR)\textsuperscript{28,29} and transient absorption (TA) spectroscopy.\textsuperscript{30,31} Also, it is important to note that dissolved oxygen in the system can scavenge the accumulated electrons in the conduction band according to Equation 3-6.

\[
e^- + O_2 \rightarrow O_2^- \quad (3-6)
\]

Therefore, trapping electrons in the conduction band requires two important steps: removing dissolved oxygen from the system and utilization of a hole scavenger.

### 3.1.2 Electrochemical properties of metal nanoparticles

Monolayer protected metal clusters are known to exhibit interesting electrochemistry and electron transfer chemistry.\textsuperscript{32} Studies have focused on three types of electrochemical properties of metal nanoparticles: 1. Electronic Double Layer Charging of the metal nanoparticles dissolved in the electrolyte, 2. Electrical conductivity of dried films of metal nanoparticles, 3. The electrochemistry of active protecting groups of metal nanoparticles.\textsuperscript{32} Metal nanoparticles such as gold and palladium stabilized by alkanethiolate have been reported to show quantized double layer (QDL) charging which were measured by electrochemical techniques.\textsuperscript{33–40} It was first introduced under the name of Coulomb Staircase behavior.\textsuperscript{41} In 1997, Ingram et al.
reported the electron transfer behavior of pure 28 kDa alkanethiolate protected Au nanoparticles using a Coulomb Staircase experiment performed at 83 K using scanning tunneling microscopy.\textsuperscript{33}

**Coulomb Staircase characteristics:** Electron transfer between an electron source and monolayer protected metal cores shows characteristic staircase like current to voltage relationship. The potential barrier to transfer one electron is equal to the division of the charge of one electron by one coulomb (\( \frac{e}{c} \)) (Figure 3.2). The following electron transfers take place at the voltage of \( \frac{2e}{c}, \frac{3e}{c}, \ldots \) etc. One step of the staircase corresponds to a single electron transfer between the electron source and the nanoparticle. The work was followed by studies conducted in Murray’s group who developed a theoretical model, the concentric sphere capacitor model, based on electrostatic interactions to explain the peaks observed in the voltammetric studies of monolayer protected Au particles. They showed that the metal nanoparticle core could act as a capacitor as result of the combination of small metal like core size while the stabilizer served as the dielectric layer (Figure 3.3).\textsuperscript{38,35,37}
Figure 3.2: Illustration to show characteristic staircase like current vs. voltage relationship.

Figure 3.3: Schematic diagram of concentric sphere capacitor model.

According to the concentric sphere capacitor model, the electrical double layer capacitance is clearly observed for monolayer-protected clusters, which are small enough to show coulomb staircase features when they are in an electrochemical system and are charged by a working electrode. Electron transfers take place to equilibrate the
nanoparticle metallic core with the Fermi level of the working electrode.\textsuperscript{32} As a result, there is a measurable current flow. Upon gaining or losing an electron from the nanoparticle core, an electrochemical double layer forms on the protected core. In that case nanoparticles act as tiny capacitors with the capacitance of sub attofarad (aF). The change in potential associated with this event is given by the equation, $\Delta V = \frac{e}{C_{CLU}}$ (3-7)

where $e$=charge of the electron and $C_{CLU}$= capacitance per metal core.

Since the $C_{CLU}$ is a subattofarad value, the division of the charge of an electron by $C_{CLU}$ results in a fairly high $\Delta V$ value. As a result, single electron transfer reactions provide voltammogram which consist of highly resolved and well-separated waves (Figure 3.4).\textsuperscript{42} To observe the double layer charging features in the voltammetric measurements, the nanoparticles must have a narrow size distribution and be small in size (i.e. a small $C_{CLU}$). If the particles are polydisperse the resulting voltammetric waves have no feature.\textsuperscript{33,43} For bigger size nanoparticles associated with larger capacitance, single electron transfer peaks in the voltammogram are not well separated even though they are monodisperse because $\Delta V < k_B T$ ($k_B$ is the Boltzman constant, $1.38 \times 10^{-23}$ J/K, and $T$ is the absolute temperature). Figure 3.4 shows the regular spacing of peaks which exhibit double layer charging process.\textsuperscript{42} If the metal core consists of a smaller number of metal atomic units, it develops molecular properties.\textsuperscript{25} The HOMO-LUMO gap or bandgap is one of those properties and can be determined electrochemically.\textsuperscript{39} Electrochemical bandgap is the potential difference between the initial oxidation and the reduction relative to the potential of zero charge of nanoparticles (Figure 3.4).\textsuperscript{42}
Figure 3.4: DPV shows a HOMO-LUMO gap of 1.2 V for monolayer Protected Gold nanoparticles. Taken with permission from reference [42].

The capacitance of spherical nanoparticles protected by a uniform monolayer is given by the relationship below,\(^{39}\)

\[
C_{CLU} = \frac{4\pi \varepsilon \varepsilon_0}{d} \cdot r(r + d) \quad (3-8)
\]

Where \(C_{CLU}\) = capacitance of the nanoparticle with the radius \(r\),

d = thickness of the protecting dielectric layer

\(\varepsilon\) = dielectric constant of the protecting monolayer

\(\varepsilon_0\) = Permittivity of free space

According to the above equation, the nanoparticle capacitance increases as the radius increases. On the other hand, \(C_{CLU}\) decreases with increasing thickness of the protecting layer.\(^{35}\)
3.1.3 Spectroscopic properties of metal nanoparticles

Metal nanoparticles display unique optical, chemical and electrochemical properties. For the determination of optical properties of metal nanoparticles, UV-visible absorbance spectroscopic measurements are used. Nanoscale Au, Ag, and Cu particles are known to display strong surface plasmon resonance bands, which can be measured by UV-visible absorbance spectroscopy. The surface Plasmon resonance bands can be explained according to the theory of Mie Scattering which is an exponential-decay profile observed with decreasing photon energy. The surface plasmon resonance of metal nanoparticles allows them to have several important potential applications in biology, imaging, drug delivery, cell targeting, and sensor design to name but a few. Thus, several researchers have invested much time in the development of synthetic techniques that produce plasmonic nanoparticles with well-defined size, shape and dispersity. In the case of other transition metals, such protocols are not well developed and thus the development of metal nanoparticles with QDL charging is not well established. It is important to study the quantized double layer charging especially for transition metal nanoparticles that are expected to have strong catalytic properties, as such properties could be significantly enhanced if well studied and understood.

In this chapter, we describe the interaction between the large bandgap semiconductor, TiO$_2$ and Pd and Pt nanoparticles. We examine the effect of size relative to electron storage and examine the ability of transfer of the stored electrons. We note that Pt and Pd are not plasmonic nanoparticles but are well known effective catalysts for hydrogenation reactions.
3.2 Experimental section

3.2.1 Chemicals: Titanium(IV) isopropoxide (Ti[OCH(CH₃)₂]₄) (97%), acetic acid (99%, glacial), tetrabutylammonium hexafluorophosphate (C₁₆H₃₆F₆NP) (99%), methyl viologen dichloride hydrate (C₁₂H₁₄Cl₂N₂.xH₂O) (98%) were purchased from the Sigma Aldrich Company and used as received. Diphenyl ether, dimethyl sulfoxide (DMSO) and absolute ethanol were of HPLC grade and were also purchased from the Sigma Aldrich Company.

3.2.2 Synthesis of TiO₂ nanoparticles: TiO₂ nanoparticles were synthesized by a previously reported method.³⁰ Briefly, 98.5 ml of absolute ethanol was stirred vigorously and 1.5 ml of glacial acetic acid was added to while stirring. Titanium isopropoxide was added dropwise to the solution. After 3-4 hours, a transparent colloidal solution was obtained and stirring was continued overnight. The concentration of the stock solution of TiO₂ was 0.049 M. A diluted sample of TiO₂ in a cuvette was prepared as the final concentration of was 3.42 x 10⁻³ M.

3.2.3 Synthesis of palladium and platinum nanoparticles: A detailed procedure for the synthesis of Pd and Pt nanoparticles that were used in this work is described in Chapter II.

3.2.4 Charge transfer experiments. A quartz cuvette with a 20/40 attachment was filled with 4 mL of colloidal TiO₂ nanoparticles, sealed with a septum and purged with nitrogen for 20 minutes. The purged TiO₂ solution was irradiated using a solar simulator (Newport model H66921) with a KV 370 cut-off filter. After 15 minutes of irradiation, it was observed that the clear color of the TiO₂ solution had changed to dark blue indicating
electron accumulation in the TiO$_2$ conduction band. The Pd nanoparticles were titrated to the charged TiO$_2$.

**3.2.5 Electron discharge:** Once all the TiO$_2$ electrons were transferred to the Pd nanoparticles, we studied the electron discharge process from the Pd nanoparticles using an electron acceptor. Methyl viologen (0.01 M) was used as the electron acceptor and was prepared in pure ethanol then purged with nitrogen to remove dissolved oxygen. The methyl viologen was added to the stored electrons in the Pd nanoparticles in 5 µL increments. Changes in the UV-visible absorbance spectra of methyl viologen were recorded using the UV-visible absorbance spectrophotometer.

**3.2.6 Measurements:** *Electrochemical Measurements:* Differential pulse voltammetry (DPV) was performed using a Bioanalytical system, Inc. (BAS) CV 50W electrochemical analyzer. Tetrabutylammonium hexafluorophosphate (TBAPF$_6$) (0.1 M) was used as the supporting electrolyte and prepared in DMSO. All samples were purged with nitrogen gas before measurements were taken. The working electrode, counter electrode and reference electrode were glassy carbon, Pt wire and the Ag/AgCl (aqueous) electrode respectively. These three electrodes were cleaned with an alumina slurry and polished on carbon pads. DPV was performed with the parameters: scan rate of 20 mV/sec, pulse amplitude of 50 mV, sample width of 17 mS, pulse width of 50 mS, pulse period of 200 mS, quiet time of 2 S.

*UV-Vis spectroscopy:* UV-visible absorbance spectra were recorded using a Varian Cary 50 spectrophotometer.
Transmission Electron Microscopy (TEM): TEM images of Pd, Pt and TiO₂ nanoparticles were obtained with transmission electron microscope (JEM-1230). Each sample was prepared by placing a 1 µL drop of nanoparticle on a Formvar/carbon-coated copper grid and drying it in a desiccator. Each sample was imaged at 400 K, 500 K and 600 K magnification. Histograms for the core-size of the nanoparticles were prepared by manual reading.

3.3 Results and discussion

3.3.1 Electrochemical properties of metal nanoparticles: Since there is a significant correlation between capacitance and the size of the metal nanoparticles we first discuss the electrochemical studies. A few literature reports have described the electrochemical properties of Pd nanoclusters. Most show poor signal to noise ratio relative to Au nanoclusters. This may arise due to the difficulty in obtaining monodisperse Pd nanoparticles in the range of 1-5 nm size, as well as the tendency of Pd nanoparticles to oxidize in the presence of air. The ability to generate Pd nanoparticles in the range of 1-5 nm size using our pyrolysis procedure, and the lack of requirement for a size selection process provides an opportunity to investigate the electrochemical properties in an inert atmosphere. The differential pulse voltammogram (DPV) (Figure 3.5) of colloidal solutions of Pd and (Figure 3.6) Pt nanoparticles in 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) electrolyte were measured.
Figure 3.5: Differential pulse voltammogram of (a) 1.9 nm (b) 2.3 nm Pd nanoparticles obtained at potential scan rate 25 mV.

The Pd nanoparticle concentration in each case was 0.6 mM. The DPV represents the solution electrochemistry of the monodisperse Pd nanoparticles. The DPV of Pd nanoparticles in DMSO shows fairly-defined peaks which are quite evenly spaced.
Capacitance ($C_{CLU}$) is determined by dividing the charge of the electron ($e$) by the spacing ($\Delta V$) between adjacent single electron charging peaks:

$$C_{CLU} = \frac{e}{\Delta V}$$

Each current peak in Figure 3.6 (a) and (b) corresponds to a single electron charging of nanoparticles that diffuse to the electrode or are attached to the electrode. The peak spacing for 1.9 nm was calculated to be $\Delta V= 480 \pm 75$ mV, thus a $C_{CLU} = 0.33$ aF.

$$C_{CLU} = \frac{1.602 \times 10^{-19}}{480 \times 10^{-3}} \cdot \frac{C}{V}$$

Since $\frac{C}{V} = F$,

$$C_{CLU} = \frac{1.602 \times 10^{-19}}{480 \times 10^{-3}} \cdot F$$

$$C_{CLU} = 0.0033375 \times 10^{-16} \text{ F} = 0.33 \text{ aF}$$

But for 2.3 nm Pd nanoparticles calculations showed that $\Delta V = 35 \pm 12$ mV, thus $C_{CLU}$ is 4.5 aF. 2.5 nm Pd nanoparticles did not show distinct peaks in their DPV. A few studies have briefly reported the electrochemical properties of Pd nanoparticles.\textsuperscript{40,45,49} In these reports, the particles were stabilized using either alkanethiolate ligands or dendrimers. We have studied the electrochemical properties of thioether protected Pd nanoparticles for the first time. Since the $C_{CLU}$ value is strongly dependent on the protecting layer, the values obtained from different synthetic methods are not expected to be similar to this study. However, the $C_{CLU}$ value obtained for 1.9 nm Pd nanoparticle (0.33 aF) is fairly close to the capacitance of monolayer protected Pd nanoparticles (1.3
nm) prepared by dendrimer templating which is 0.39 aF.\textsuperscript{40} Table 3.1 shows the calculated peak spacing and capacitance for 1.9 nm and 2.3 nm Pd nanoparticles. The capacitance increases with increasing Pd nanoparticle size.

**Table 3.1:** Calculated capacitance of Pd nanoparticles

<table>
<thead>
<tr>
<th>Pd nanoparticle size/nm</th>
<th>ΔV/mV</th>
<th>$C_{CLU}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9</td>
<td>480 ± 75 mV</td>
<td>0.33 aF</td>
</tr>
<tr>
<td>2.3</td>
<td>35 ± 12 mV</td>
<td>4.50 aF</td>
</tr>
</tbody>
</table>

**Figure 3.6:** Differential pulse voltammogram of 2.5 nm Pt nanoparticles obtained at potential scan rate 25 mV.
Figure 3.6 shows the DPV of 2.5 nm Pt nanoparticles. The QDL peaks are fairly resolved and roughly evenly spaced with $\Delta V = 0.113 \pm 0.002$ V vs. Ag/AgCl. Thus, given that $\Delta V = e/C_{CLU}$, for the 2.5 ± 0.1 nm Pt nanoparticles, $C_{CLU}$ is equal to 1.4 aF and is consistent with the fact that larger particles have larger quantized double layer capacitance.\(^{35}\)

### 3.3.2 Investigation of charge transfer ability between TiO\(_2\) and metal (Pd, Pt) nanoparticles

As described in the introduction, there are two important steps in the charge transfer process: (a) charge separation, and (b) charge accumulation in the conduction band. Irradiation of a deaerated colloidal TiO\(_2\) nanoparticle (3.42 x 10\(^{-3}\) M) in ethanol solution for 15 minutes resulted in a change in solution color from colorless to blue (Figure 3.7). The observed color change is an indication of electron accumulation in the TiO\(_2\) conduction band according to the Equation 3-1. The blue color is only stable in an inert environment, Equation 3-6. The excited electrons were trapped in the conduction band while the holes were scavenged by ethanol, according to Equation 3-5.
Figure 3.7: Color change for accumulation of conduction band electrons in the TiO$_2$ by UV light irradiation in deaerated ethanol.

The concentration of electrons trapped in Ti$^{4+}$ sites is easily monitored by UV-visible absorbance spectroscopy by measuring the absorbance peak at 700 nm. Figure 3.8 shows changes in the UV-visible absorption spectrum of TiO$_2$ in ethanol after steady-state UV irradiation (wavelength > 370 nm).

Figure 3.8: UV-visible absorbance spectra of deaerated colloidal TiO$_2$ in ethanol before the UV light irradiation and after different times of irradiation.
The broad absorption band with a wavelength maximum at 650 nm corresponds to trapped electrons in the TiO$_2$ conduction band [TiO$_2$(e$_{CB}$)]. The trapped electrons are stable in an inert atmosphere. Irradiation of the colloidal TiO$_2$ sample for 20 minutes was found to be sufficient for accumulating electrons in the conduction band.

### 3.3.3 Interaction between [TiO$_2$(e$_{CB}$)] and Pd nanoparticles

Figure 3.9 shows the concept of charge separation in TiO$_2$ and transfer of electrons to the metal nanoparticles. In order to investigate the charge transfer between [TiO$_2$(e$_{CB}$)] and the Pd or Pt nanoparticles, sealed colloidal TiO$_2$ solution in ethanol was purged with nitrogen for 20 minutes and irradiated using the solar simulator for 20 minutes to obtain stable and measurable [TiO$_2$(e$_{CB}$)]. The UV-visible absorbance spectra were recorded before and after irradiation to confirm electron accumulation in the TiO$_2$ conduction band. Then known amounts (2 µL, [Pd] = 30.54 x 10$^{-10}$ moles) of deaerated (N$_2$ purged for 20 minutes) Pd nanoparticles were added into the sealed [TiO$_2$(e$_{CB}$)] solution. Titration of [TiO$_2$(e$_{CB}$)] with metal nanoparticles were continued until the disappearance of absorption band corresponding to [TiO$_2$(e$_{CB}$)] or blue color. Each reading was recorded after 2 minutes of Pd nanoparticle addition to allow for equilibration.
Figure 3.9: Schematic diagram for charge transfer and the expected Fermi level equilibration between TiO$_2$ and metal nanoparticles.

This procedure was repeated for all 3 sizes of Pd nanoparticles and one size of Pt nanoparticles. UV-visible absorbance measurements (Figure 3.10) showed that the absorbance intensity at 650 nm corresponding to TiO$_2$(e$_{CB}$) decreased with increase in Pd nanoparticle concentration, suggesting that electrons were transferred to and stored within the Pd nanoparticles. The Pd nanoparticles alone or with stored electrons do not show any characteristic absorbance peaks.
Figure 3.10: UV-visible absorption spectra of colloidal TiO$_2$, before and after UV irradiation, and addition of known amount of 1.9 nm Pd nanoparticles.

Figure 3.10 shows the changes the UV-visible absorbance peak of TiO$_2$(e$_{CB}$) with addition and increasing concentrations of the Pd nanoparticles. The final concentration of Pd nanoparticles that was added was 33.44 x 10$^{-6}$ M which was found to be sufficient to totally quench the blue color of the TiO$_2$(e$_{CB}$), indicating complete transfer of TiO$_2$(e$_{CB}$) to the Pd nanoparticles. The observation of charge transfer from TiO$_2$ to Pd nanoparticles is similar to the previously reported observations of excited TiO$_2$ and electron acceptors such as fullerene$^{30}$, gold nanoparticles,$^{51,7}$ and dye molecules$^{52}$. We further made an estimation of the transferred electrons from TiO$_2$(e$_{CB}$) to the Pd nanoparticles. The calculated initial concentration of trapped electrons was 7.487 x 10$^{-4}$ M (Table 3.2).
Table 3.2: Calculated amount of stored electrons for increased concentration of 1.9 nm Pd nanoparticles

<table>
<thead>
<tr>
<th>Number of moles of Pd/ ( x 10^{10} )</th>
<th>Absorbance at 650 nm</th>
<th>Concentration of ([\text{TiO}_2(e^-)]/ x 10^{-4} \text{ mol/L})</th>
<th>(\text{TiO}_2(e^-)/\mu \text{ mols})</th>
<th>Stored electrons in Pd NPs</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.5690</td>
<td>7.487</td>
<td>3.22</td>
<td>0</td>
</tr>
<tr>
<td>30.54</td>
<td>0.5146</td>
<td>6.771</td>
<td>2.91</td>
<td>0.31</td>
</tr>
<tr>
<td>61.08</td>
<td>0.4694</td>
<td>6.175</td>
<td>2.66</td>
<td>0.56</td>
</tr>
<tr>
<td>91.62</td>
<td>0.4229</td>
<td>5.564</td>
<td>2.39</td>
<td>0.83</td>
</tr>
<tr>
<td>122.16</td>
<td>0.3710</td>
<td>4.881</td>
<td>2.09</td>
<td>1.13</td>
</tr>
<tr>
<td>152.7</td>
<td>0.3318</td>
<td>4.265</td>
<td>1.88</td>
<td>1.34</td>
</tr>
<tr>
<td>183.24</td>
<td>0.3012</td>
<td>3.971</td>
<td>1.71</td>
<td>1.51</td>
</tr>
<tr>
<td>213.78</td>
<td>0.2600</td>
<td>3.421</td>
<td>1.47</td>
<td>1.75</td>
</tr>
<tr>
<td>244.32</td>
<td>0.2025</td>
<td>2.664</td>
<td>1.15</td>
<td>2.05</td>
</tr>
<tr>
<td>274.86</td>
<td>0.1771</td>
<td>2.331</td>
<td>1.00</td>
<td>2.22</td>
</tr>
<tr>
<td>305.4</td>
<td>0.1046</td>
<td>1.376</td>
<td>0.59</td>
<td>2.63</td>
</tr>
</tbody>
</table>

The molar absorptivity of \(\text{TiO}_2(e^-)\) is \(\varepsilon = 760 \text{ M}^{-1} \text{ cm}^{-1}\) which was used for this calculation. Table 3.2 shows the calculated amount of stored electrons for 1.9 nm Pd nanoparticles. Using the data in Table 3.2, the amount of stored electrons on the particles vs. moles of 1.9 nm Pd nanoparticles was plotted (Figure 3.11).
Figure 3.11 shows a plot of the number of moles of electrons stored in Pd nanoparticles as a function of number of moles of Pd nanoparticles present in the reaction. The plot was linear and the slope of the graph allowed for the calculation of the approximate number of moles of stored electrons per moles of Pd nanoparticles. The slope of the graph is a measure of the efficiency of electron storage capacity of Pd nanoparticles (Table 3.3). Same experimental procedure was carried out for the investigation of charge transfer between excited TiO$_2$ and two other sizes of Pd nanoparticles (2.3 nm and 2.5 nm) as shown in Figure 3.12.

Figure 3.12 shows that larger sizes of Pd nanoparticles also behave in a similar manner and are able to accept electrons when brought in close proximity to charged TiO$_2$ nanoparticles.
Figure 3.12: (a), (c) UV-visible absorbance spectra of TiO$_2$ nanoparticles before and after irradiation and with increasing moles of Pd nanoparticles. The arrow shows the decrease in absorbance intensity with increase in Pd nanoparticles (a is for 2.1 nm Pd and c is for 2.3 nm Pd). (b) and (d) show the corresponding plots of stored electrons in Pd nanoparticles.
Table 3.3: Electron storage efficiency for Pd nanoparticles of varying diameter

<table>
<thead>
<tr>
<th>Pd Nanoparticle diameter/nm</th>
<th>Moles of electrons stored per mole of Pd nanoparticles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9</td>
<td>96</td>
</tr>
<tr>
<td>2.3</td>
<td>115</td>
</tr>
<tr>
<td>2.5</td>
<td>129</td>
</tr>
</tbody>
</table>

The results as shown in Table 3.3 indicate that the electron storage ability increases with the increasing size of Pd nanoparticles. Thus, the larger the Pd nanoparticle the more electrons it is capable of storing. For larger particles, potential difference associated with one electron transfer is smaller than that of smaller particles. That means larger particles need more electrons to be transferred from TiO$_2$ to metal to achieve the charge equilibration or Fermi level equilibration.$^7$
3.3.4 Interaction of TiO$_2$($e_{CB}$) with Pt nanoparticles

**Figure 3.13:** (a) UV-visible absorbance spectra of TiO$_2$ nanoparticles before and after irradiation after irradiation with increasing moles of Pt nanoparticles. (b) shows the corresponding plots of stored electrons in Pt nanoparticles.

Electron storage in Pt nanoparticles (2.5 nm) was investigated following a similar procedure as described for Pd nanoparticles. Figure 3.13 shows (a) the quenching of TiO$_2$ conduction band electrons with increasing moles of Pt nanoparticles and (b) the linear relationship between the amounts of store electrons vs. amount of Pt nanoparticles. Only one size of Pt nanoparticles was investigated due to the inability to control Pt nanoparticle size using our methods. We found that based on the results, Pt nanoparticles store a smaller amount of charge relative to Pd nanoparticles of similar size, indicating that Pd nanoparticles are more efficient in charge storage relative to Pt nanoparticle.
Control experiments were conducted in which a deaerated solution of the stabilizer \( n \)-dodecyl sulfide alone or the solvent alone, with no metal nanoparticles were added to the \( \text{TiO}_2(\text{e}_{\text{CB}}) \) solution in ethanol. However, neither the stabilizer alone nor solvent alone affected the \( \text{TiO}_2(\text{e}_{\text{CB}}) \) UV-visible absorbance intensity significantly, suggesting that the metal nanoparticles are indeed storing the charge. In addition, a similar experiment was conducted in which Pd black was added to \( \text{TiO}_2(\text{e}_{\text{CB}}) \). However, the Pd black did not show a significant effect on the \( \text{TiO}_2(\text{e}_{\text{CB}}) \) UV-visible absorbance intensity either (Figure 3.14).

**Figure 3.14:** UV-visible absorbance spectrum of \( \text{TiO}_2(\text{e}_{\text{CB}}) \) titrated with Pd black particles.
3.3.5 Fermi level equilibration

The accumulated electrons in the conduction band within a semiconductor are a key factor for the Fermi level position of that semiconductor.

\[ E_F = E_{CB} + kT \ln \frac{n_e}{N_c} \]  

(3-9)

\( E_{CB} \) = Conduction band energy level vs. NHE, \( n_e \) = density of accumulated electrons, \( N_c \) = charge carrier density of the semiconductor.

The more accumulated electrons in the semiconductor (TiO\(_2\)) or semiconductor-metal (TiO\(_2\)-Pd or TiO\(_2\)-Pt) lead to shift in the Fermi level to more negative potentials. As a result, semiconductor-metal composite enhance the overall energetics and improve catalytic activity of the semiconductor.\(^7\) For example, Kamat’s group showed that for TiO\(_2\)-Au nanocomposites, the Fermi level shifted to negative potential.\(^7\) The negative shift of the Fermi level improves the semiconductor charge separation and consequently minimizes charge recombination.\(^7\) Figure 3.15 illustrates the Fermi level shift of semiconductor metal composite as a result of charge equilibration.
Figure 3.15: Equilibration of semiconductor-metal nanoparticles with the redox couple before and after UV irradiation. Taken with permission from reference [7].

According to Kamat’s group, larger particles would require more charge to achieve equilibration, which is in agreement with our observations.

3.3.6 On-demand discharge of electrons stored in metal nanoparticles

The observation of electron storage within Pd and Pt nanoparticles required confirmation and to accomplish this task methyl viologen, a well-known electron acceptor was selected for this study. Methyl viologen (MV$^{2+}$) dissolved in solution is capable of accepting one electron which leads to the formation of MV$^{+}$, which has an electrode potential of -0.45 V vs. normal hydrogen electrode (NHE) in an inert atmosphere (Scheme 3.1).$^{53-55}$ The reaction of MV$^{2+}$ $\rightarrow$ MV$^{+}•$ is accompanied by drastic color changes which are visible with the naked eye; MV$^{2+}$ forms a clear solution whereas
MV$^{+\bullet}$ forms a dark colored blue solution. These species are measureable by UV-visible absorbance spectroscopy (Figure 3.16).

![Scheme 3.1: Reaction for formation of MV$^{+\bullet}$ from MV$^{2+}$ by accepting an electron](image)

To study the electron discharging ability of Pd and Pt nanoparticles that had electrons stored in them, a deareated solution (0.1 M) of methyl viologen (MV$^{2+}$) was added to the charged colloidal metal nanoparticles. Upon addition of the colorless MV$^{2+}$ solution, the color changed to blue. The UV-visible absorbance spectrum showed the emergence of peaks at 397 nm and 607 nm, (Figure 3.16) indicating the formation of MV$^{+\bullet}$. The fact that MV$^{2+}$ is reduced to MV$^{+\bullet}$ provides substantial evidence that these metal particles are capable of storing charge and transferring the charge as needed.
Figure 3.16: UV-visible spectrum for the formation of MV$^{++}$ upon the acceptance of the electrons from the charged metal nanoparticles.

Figure 3.17: UV-visible spectra for TiO$_2$ nanoparticles (a) before irradiation, (b) after irradiation, (c) after addition of Pt nanoparticles [Pt] = 19.767 x 10$^{-6}$ M, and (d) after addition of methyl viologen.
Figure 3.17 shows the changes in the UV-visible spectrum for charging and discharging of Pt nanoparticles.

3.4 Conclusion

Pd and Pt nanoparticles brought in close proximity to charged TiO$_2$ nanoparticles were found to accept and store electrons. The Pd nanoparticles showed that the storage of electrons within metal nanoparticles is size-dependent and that larger nanoparticles are able to store more charge relative to smaller particles. Interestingly, exposure of Pd black to charged TiO$_2$ had no effect and electrons were not transferred from the TiO$_2$ conduction band to Pd, indicating that the ability of charge storage and transfer is a feature of metal particles in the 1-4 nm size range. When MV$^{2+}$ was used as a probe for monitoring the electron discharge from the charged metal nanoparticle, we observed that the electrons stored in the Pd and Pt nanoparticles were effective in the MV$^{2+}$ reduction process. This work is important as it demonstrates important features of catalytic metal nanoparticles and methods by which their efficiency can be enhanced.
3.5 References


CHAPTER IV

SIZE DEPENDENT INTERACTIONS BETWEEN SEMICONDUCTOR QUANTUM DOTS AND PALLADIUM NANOPARTICLES

4.1 Introduction

Semiconductor quantum dots (QDs) have been extensively studied in many interdisciplinary fields due to their unique optical properties such as tunable bandgap and photostability.\textsuperscript{1-3} The size dependent electronic structure and the ease of designing devices by altering the size of the QDs are key features toward their potential technological applications.\textsuperscript{4,5} Often QDs are coupled with the other materials to optimize their properties, for example, biomolecules have been functionalized onto QDs for imaging purposes,\textsuperscript{6-9} fluorophores have been linked to QDs for sensor design,\textsuperscript{9-13} and sensitizing molecules or semiconductors have been coupled to QDs to build next generation photovoltaics.\textsuperscript{14-17} Since QDs are often coupled to other molecules and materials, it is crucial to understand their electronic interactions. A few studies on the electronic interactions between organic molecules and QDs have been reported in the scientific literature.\textsuperscript{18-21} However, the electronic interactions between QDs and metallic materials are yet to be studied extensively as there is a major difference between the two systems. Metallic materials consist of a continuum of electronic states while organic molecules possess discrete electronic states which are crucial for the electron transfer or
energy transfer interactions.\textsuperscript{5} According to the reported studies, QDs are capable of donating or accepting electrons. The electron transfer or energy transfer reactions determine the efficiency of the device or system. Therefore, it is critical to have a better understanding of the interactions of nanoscale metallic particles and QDs.

A few studies have been reported on the interaction between CdSe QDs and metal oxide nanoparticles,\textsuperscript{5,22,23} and CdSe QDs with gold (Au) nanoparticles.\textsuperscript{24} Gold nanoparticles with different shapes were added to colloidal solutions of CdSe QDs and resulted in fluorescence quenching.\textsuperscript{24} The results suggested that the fluorescence quenching was a result of electron transfer rather than a Foster Resonance Energy Transfer (FRET) process. Studies have also been conducted to understand the interactions in general between semiconductor materials and metal particles deposited on their surface. The studies indicated that the metal is capable of improving the charge-separation process within the semiconductor which is vital for solar energy conversion processes.\textsuperscript{25–28} The interaction of other transition metal nanoparticles with QDs have not been reported and such an understanding is important for the development of future devices.

Here, we study the effect of bringing Pd nanoparticles in close proximity to CdSe QDs. We have investigated the changes in absorbance and fluorescence intensity of the CdSe QDs when interacted with three different sizes of Pd nanoparticles and compared the results to bulk Pd (Figure 4.1). Our results indicate that quantum size metal nanoparticles quench the emission of QDs and the quenching process depends on the size of the metal nanoparticles. These results are paramount toward developing a fundamental understanding of the nanoscale materials and for advancing their potential applications.
4.1.1 Semiconductor quantum dots

The history of studying ‘quantum structures’ dates back to the late 70s/early 80s when the concept of utilization of excited electrons via quantum confinement in different types of semiconductor materials was reported. Semiconductors can undergo ‘quantization’ when electrons and holes are confined to a small space less than the de Broglie wavelength of the charge carriers. If the electrons and holes of a semiconductor are confined by potential barriers in three spatial dimensions (x, y and z), then it is called a quantum dot.
Figure 4.2: Progressive generation of nanostructures and their density of states. Taken with permission from reference [30].

Figure 4.2 shows the progressive generation of quantized nanostructures and their density of states. Bulk materials have three dimensions and their density of states consists of continuous energy levels. The generation of two-dimensional quantum wells from bulk materials is a result of reducing one dimension while keeping the other two dimensions. Quantum wires or rods are one-dimensional and are a result of reducing two dimensions and leaving one dimension unchanged. Reducing the size of all three dimensions results in zero-dimensional quantum dots. The latter two cases have discrete density of states.\(^{31}\)

It is important to understand the quantum mechanical process of zero-dimensional QDs. When an electron in the valence band is excited to the conduction band, it leaves a positively charged hole in the valence band. The excited electron and the hole are attracted to each other by Columbic attraction and this electron-hole pair is called an exciton.
Figure 4.3: Electronic energy levels depending on the number of bound atoms. Taken with permission from reference [13].

\[
r = \frac{\varepsilon h^2}{\pi m_r e}
\]  \hspace{1cm} (4-1)

where

- \( r \) is the radius of the 3-D sphere electron – hole pair,
- \( \varepsilon \) is the dielectric constant of the semiconductor,
- \( m_r \) is the reduced mass of the electron-hole pair,
- \( h \) is Planck’s constant, and
- \( e \) is the charge on the electron.

The reported value for the mass of the electron-hole pair is in the range of 0.1-3 m\(_e\) where m\(_e\) is the mass of an electron\(^{13,30}\). The values for the separation of an electron-hole pair for several other semiconductors were reported to be in the range of 1-10 nm\(^{29}\).
Therefore, the electronic structure of QD fits in between that of molecules and bulk solid-state materials (Figure 4.3).

### 4.1.2 Quantum size effect

The properties of semiconductor nanoparticles vary as a function of their size.\(^{32,33}\) Since the diameter of the QD is smaller than that of the exciton, in most cases it can be considered as a “particle in a box”. Accordingly, the size of the particle is determined by the size of the box and the bandgap energy of the QD is estimated as:

\[ E_g(d) = E_g(bulk) + E_{well} + E_{Coul} \quad (4-2) \]

The minimum energy, \(E_g\), required for creating an exciton is a combination of the bandgap energy of the bulk [\(E_g(bulk)\)], the bandgap energy of the potential well [\(E_{well}\)] and the Coulombic interaction [\(E_{Coul}\)] (Equation 4-2). By substituting actual terms for Equation (4-2), the following Equation (4-3) is obtained.\(^{13,34–39}\)

\[ E_g(d) = E_g(bulk) + \frac{\hbar^2}{2d^2m^*} - \frac{1.8e^2}{2\pi\rho\varepsilon\varepsilon_0} \quad (4-3) \]

Where \(\hbar = \) Planck’s constant, \(d = \) the diameter of the QD, \(m^* = \) is the reduced mass of the exciton, \(\varepsilon = \) dielectric constant of the solid, and \(\varepsilon_0 = \) permittivity of the vacuum.

Equation (4-2) consists of two size dependent terms: a) confinement energy, \(1/d^2\) and b) the Coulombic attraction, \(1/d\). The confinement energy is always a positive term and is the predominant parameter for QDs. (Figure 4.3).\(^{34}\)
Figure 4.4: Calculated energy of lowest electronic state of the semiconductor quantum dots in relation to the bulk bandgap. Taken with permission from reference [37].

According to the above equation and Figure 4.4, the bandgap energy of QD is size dependent.\textsuperscript{1,30,40–44} The absorbance spectra of different QD sizes are shown in Figure 4.5 and shows that decrease in particle size results in a shift of the absorbance wavelength maxima to shift toward higher energy, corresponding to an increase in the bandgap energy. Semiconductor nanoparticles can be divided into two groups (strong confinement and weak confinement). Equation (4-2) only applies to ‘strong confinement’ semiconductors. The strong confinement semiconductors have dimensions that are smaller than that of the Bohr radius of the exciton while the opposite is valid for weak confinement materials. Another size dependent property of semiconductor QD is the oscillator strength of the lowest energy transition.\textsuperscript{40}
Figure 4.5: Room temperature spectra of CdSe quantum dots. (a) Absorbance and photoluminescence spectra as a function of size. (b) Quantum yield of photoluminescence as a function of size. Taken with permission from reference [13].

For weak confinement QDs, the oscillator strength of the lowest energy transition is proportional to the volume of the QD. However, for strong confinement QDs, the oscillator strength is size independent.\textsuperscript{40,41}

4.1.3 Synthesis of semiconductor quantum dots

Synthesis procedures for semiconductor QDs began to be developed in the late 1970s. The main motivation for synthesizing the materials at that time was to design crystalline materials that could be used as color staining of glass.\textsuperscript{29,35} Improvement in synthesis conditions to establish size-controlled QDs developed in the 1990s where the ability to control the size and shape and fabricate core-shell nanostructures were established.\textsuperscript{13,29,42,45}
Cadmium (Cd) based QDs are very common and synthetic procedures for their preparation are well established. The bandgap energy of bulk CdS and CdSe at room temperature are 4.4 eV and 1.7 eV (~520 nm and ~720 nm), respectively. There are two common methods to prepare semiconductor QDs: bottom-up method and top-down method. In the bottom-up method, molecular or ionic precursors react together in a solution to produce colloidal QDs while in the top-down method, semiconductor substrates are broken down to 1-10 nm sizes of QDs lithographically or electrochemically. There are five common bottom-up approaches for the preparation of II-VI nanocrystals: arrested precipitation, termination of particle growth by a capping agent, the use of organometallic-based precursors, utilization of nanoscale cavity, and biosynthesis. Among them, organometallic precursor method is the most cited method for making CdS, CdSe and CdTe QDs. In this method, Cd(CH$_3$)$_2$ is mixed with a chalcogenide in a coordinating solvent which is usually trioctyl-phosphine oxide at high temperature range 200-350 °C in an inert atmosphere. Peng et al. reported the use of CdO instead of Cd(CH$_3$)$_2$, which is a less toxic precursor.

4.1.4 Optical properties of quantum dots

Colloidal solutions of QDs show size dependent absorption bands. As the size of the QD decreases, the wavelength maximum shifts to a lower wavelength (blue-shift).

The fluorescence of QDs is a result of radiative combination of the electron-hole pair. After the excitation of an electron from the valence band of QD’s to the conduction band, the generated hole recombines with the electron which relaxes to the valence band
and releases energy equal to the bandgap. “Trap states” on the surface of QDs can trap the electrons and minimize the energy and consequently lower the QD quantum yield (Figure 4.6). Trap states result from various types of factors including structural defects, atomic vacancies, dangling bonds and adsorbates at the interface.

\[ \text{Figure 4.6: Energy level diagram showing exciting an electron from the valence band to the conduction band, leaving a hole behind. Taken with permission from reference [13].} \]

Trapping an excited electron is called “fall” and trapping a hole that is left behind is called “float”. To minimize trap states, QDs are surface passivated with a semiconductor with a large bandgap energy forming thus core-shell nanocomposites. Often, CdSe QDs are coated with ZnS to minimize trap states. The characterization of QDs is performed using UV-visible absorbance and fluorescence spectroscopies as
well as TEM and XRD methods. In this project, CdSe semiconductor QDs were used as energy donors to metal nanoparticle acceptors.

4.2 Experimental section

4.2.1 Chemicals: Selenium (powder-100 mesh, 99.99% trace metal basis), 1-octadecene (technical grade), trioctylphosphine (97%), oleic acid (technical grade, 90%), CdO (powder, 1 micro meter, 99.5%, trace metal basis), Pd black (40-60 m$^2$/g surface area), and CdSe (610 nm, core-type QD, 5 mg/l in toluene, FW=191.7 g/mol) were purchased from Sigma Aldrich and used as received. Toluene was HPLC grade and purchased from the Sigma Aldrich Company.

4.2.2 Synthesis of CdSe QDs: CdSe QDs were synthesized using CdO and elemental Se. A solution of elemental Se and a solution of CdO were prepared by following a reported procedure.

*Se solution:* 30 mg of Se was added to a round bottom flask containing 5 mL 1-octadecene while stirring. Safely measured 0.4 mL of trioctylphosphine was added to the reaction mixture and stirring was continued until all the Se was dissolved.

*CdO solution:* 50 mL of 1-octadecene, 3 mL of oleic acid and 65 g of CdO were added to a 250 mL round bottom flask. The resulting mixture was heated to 225 °C.

Once the temperature of the solution reached 225 °C, 5 mL aliquot of Se solution was added to the CdO solution. CdSe QD samples were collected at different time
intervals (30 seconds, 1 minute, 2 minutes and 3 minutes since the addition of Se solution) using a 10 mL glass pipette.

**4.2.3 Synthesis of Pd nanoparticles:** The procedures for the synthesis of 1.9 nm, 2.1 nm and 2.5 nm Pd nanoparticles were described in Chapter 2.

**4.2.4 Titration of CdSe QDs with Pd nanoparticles:** Two types of CdSe nanoparticles were used – commercial and those synthesized as described in section 4.2.2. A sample of CdSe QDs was purchased from Sigma Aldrich and the concentration was adjusted to 1.244 µM by diluting with toluene. For the synthesized QDs, 3 mL of QD was placed in a cuvette prior to titration with the metal nanoparticles. Palladium nanoparticles (0.1 µL) were then added to the QD solution (purchased or synthesized). The resulting solution was mixed and a fluorescence spectrum was recorded after 2 minutes by exciting at 550 nm.

**4.2.5 Control experiments:** Control experiments were performed using Pd black particles dispersed in toluene. A sample of CdSe (1.244 µM) was prepared and titrated with 0.1 µL of Pd black.

**4.2.6 Measurements:** UV-visible absorbance spectra were recorded using a Varian Cary 50 spectrophotometer. Fluorescence spectra were recorded using a Varian-Cary Eclipse fluorescence spectrophotometer. Fluorescence lifetime measurements were performed using an Edinburgh FL 900 fluorescence lifetime instrument.
4.3 Results and discussion

4.3.1 Optical characterization of synthesized CdSe QDs

Different sizes of CdSe QDs were synthesized and characterized using transmission electron microscopy, UV-visible absorbance spectroscopy and fluorescence spectroscopy.

Figure 4.7: Photograph representing the color of the different QD sizes prepared. The photograph was taken under a UV-lamp.

Figure 4.8: UV-visible absorbance spectra of different sizes of CdSe QDs [(2.1-2.3 nm), (2.4-2.6 nm), (3.0-3.5 nm), (3.5-4.0 nm)].
Figure 4.9: Fluorescence spectra of different sizes of CdSe QDs. [(2.1-2.3 nm), (2.4-2.6 nm), (3.0-3.5 nm), (3.5-4.0 nm)].

To study the size-dependent interactions between CdSe QDs and metal nanoparticles, it is very important to synthesize QDs that exhibit a relatively narrow size distribution. If the particles are monodisperse, absorption and emission spectra should show narrow peaks. The photograph in Figure 4.7 shows the color of the samples withdrawn from the reaction mixture. From left to right shows samples formed with increasing reaction time. Figure 4.8 shows UV-visible absorption spectra of CdSe QD samples while Figure 4.9 shows the size-dependent fluorescence of CdSe QDs.
Table 4.1: Absorption and emission maxima of QDs with different sizes

<table>
<thead>
<tr>
<th>Absorption maxima/nm</th>
<th>Emission maxima/nm</th>
<th>Size range/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>485</strong></td>
<td>492</td>
<td><strong>2.1-2.3</strong></td>
</tr>
<tr>
<td><strong>529</strong></td>
<td>542</td>
<td><strong>2.4-2.6</strong></td>
</tr>
<tr>
<td><strong>545</strong></td>
<td>563</td>
<td><strong>3.0-3.5</strong></td>
</tr>
<tr>
<td><strong>560</strong></td>
<td>581</td>
<td><strong>3.5-4.0</strong></td>
</tr>
</tbody>
</table>

Table 4.1 shows the wavelength at which the absorbance and fluorescence maxima occur based on the QD diameter.

4.3.2 Optical and electrical characterization of purchased CdSe QDs

UV-visible and fluorescence spectrum of commercially available QDs were also recorded. The absorbance maximum of the QDs was at 615 nm while the emission maximum was at 635 nm. The capping agent on the QD surface was reported to be hexyldecylamine/triocetylphosphene oxide and the QDs were dispersed in toluene. The narrow absorbance and emission bands also confirm the monodisperse nature of the QD.
Figure 4.10: (a) Emission (b) absorption spectra of commercially obtained CdSe QDs.

Fairly small Stoke shift indicated the well-passivated nature of the QDs (Figure 4.10). Figure 4.11 (a) shows monodisperse QDs with an average diameter of 6.5 nm.

Figure 4.11: TEM image of commercially available CdSe QDs (a) before and (b) after titration.
4.3.3 Titration of CdSe QDs with different sizes of Pd nanoparticles

4.3.3.1 CdSe QDs (6.5 nm) with Pd nanoparticles

Monodisperse CdSe QDs (1.244 µM) with a diameter of 6.5 nm were titrated with 1.9 nm, 2.3 nm, 2.5 nm Pd nanoparticles by adding 0.1 µL aliquots at a time to the QD solution. The resulting solution was mixed and the fluorescence spectra were recorded after 2 minutes by exciting at 550 nm (emission at 635 nm). Figure 4.13(a), (b) and (c) show the fluorescence quenching of CdSe QDs using Pd nanoparticles. When the colloidal Pd nanoparticles were brought in close proximity to CdSe QDs the QDs fluorescence intensity decreased. But, when Pd bulk metal (Pd black) was used, the fluorescence intensity of the QD remained unchanged (Figure 4.13(d)). The quenching of the QD fluorescence intensity can be quantified by a Stern-Volmer plot which describes the relationship between fluorescence intensity and concentration of the quencher. The UV-visible absorbance spectrum of CdSe QD was recorded before and after titration and during the titration (Figure 4.12). It did not show any changes such as aggregation and degradation of CdSe QDs as a result of addition of Pd nanoparticles. The TEM after titration (Figure 4.11 (b)) shows no aggregation.
Figure 4.12: UV-visible absorbance spectra of CdSe QDs upon addition of Pd nanoparticles.

Figure 4.13(a): Change in fluorescence intensity of CdSe QDs with increasing the concentration of 1.9 nm Pd nanoparticles.
Figure 4.13(b): Change in fluorescence intensity of CdSe QDs with increasing the concentration of 2.3 nm Pd nanoparticles.

Figure 4.13(c): Change in fluorescence intensity of CdSe QDs with increasing the concentration of 2.5 nm Pd nanoparticles.
Figure 4.13(d): Change in fluorescence intensity of CdSe QDs with increasing the concentration of Pd black particles.

4.3.3.2 Synthesized CdSe QDs with Pd nanoparticles

The synthesized CdSe QDs (Table 4.2) were titrated with Pd nanoparticles (1.9 nm, 2.3 nm, and 2.5 nm). The fluorescence intensity of all four QD sizes decreased with increase in the concentration of Pd nanoparticles (Figure 4.14).
Figure 4.14(a): Change in fluorescence intensity of CdSe QDs (3.0-3.5 nm) with increasing the concentration of 1.9 nm Pd nanoparticles.

Figure 4.14(b): Change in fluorescence intensity of CdSe QDs (3.0-3.5 nm) with increasing the concentration of 2.3 nm Pd nanoparticles.
Figure 4.14(c): Change in fluorescence intensity of CdSe QDs (3.0-3.5 nm) with increasing the concentration of 2.5 nm Pd nanoparticles.

4.3.4 Quenching constants from Stern-Volmer model

The fluorescence quenching the QDs by Pd nanoparticles can be quantified by the Stern-Volmer method which describes the relationship between fluorescence intensity and concentration of the quencher.\textsuperscript{52}

For linear relationship between the fluorescent intensity and the quencher concentration,

\[
\frac{F_0}{F} = 1 + K_D [Q] \quad (4-4)
\]

For non-linear form,

\[
\frac{F_0}{F} = 1 + (K_D + K_s) [Q] + K_D K_s [Q]^2 \quad (4-5)
\]

Where $F_0 = \text{emission intensity}$
F = emission intensity in the presence of the quencher

$K_D = \text{Stern-Volmer quenching constant for collisional deactivation}$

$[Q] = \text{Concentration of Quencher}$

$K_S = \text{association constant for binding of the quencher to the luminescent species when there is a static quenching process.}$

Equation (4-6) was used to analyze time resolved fluorescence quenching data, which attributes to dynamic quenching.

$$\frac{\tau_0}{\tau} = 1 + K_D [Q] \quad (4-6)$$

Where $\tau_0$ and $\tau$ are lifetime of the fluorophore in the absence and the presence of the quencher, respectively. In this case, the Stern-Volmer quenching constant is, $K_D = \tau_0 k_q$, Where $k_q$ is the bimolecular quenching constant.53

The linear behavior displayed by the Stern-Volmer plot suggests dynamic quenching mechanism which is a result of collision between the fluorescent species and quencher molecules. When both dynamic and static quenching occur, the Stern-Volmer plot shows an upward curvature. In addition, when $\frac{F_0}{F}$ and $\frac{\tau_0}{\tau}$ are similar, it is explained as an emitting state quenching.24
4.3.5 Stern-Volmer plot for 6.5 nm QDs

According to the Stern-Volmer plot (Figure 4.15 and Table 4.2), the relationship between $\frac{F_0}{F}$ and the quencher concentration shows a similar behavior for all three sizes of Pd nanoparticles. The data show a linear relationship between all three sizes of Pd nanoparticles, which is an indication of pure dynamic quenching or pure static quenching. To distinguish between dynamic and static quenching, UV-visible absorption measurements during the titration are required. Figure 4.12 shows no change in optical density of QDs upon addition of Pd nanoparticles, indicating static quenching is improbable. The slope of the plot indicates the fluorescence quenching constant to be $(3.36 \times 10^5 \text{ M}^{-1}$ (for 1.9 nm Pd), $2.30 \times 10^5 \text{ M}^{-1}$ (for 2.3 nm Pd) and $1.72 \times 10^5 \text{ M}^{-1}$ (for 2.5 nm Pd) showing a decrease in quenching constant with increase in QD size.

Figure 4.15: Stern-Volmer plot and best fit lines for quenching of CdSe QDs (emission max=640 nm).
Table 4.2: Calculated quenching constants of 6.5 nm QDs titrated with Pd nanoparticles obtained using the Stern-Volmer plot

<table>
<thead>
<tr>
<th>Pd nanoparticle size/ nm</th>
<th>Quenching constant, ( K_0 / M^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9</td>
<td>( 3.26 \times 10^5 )</td>
</tr>
<tr>
<td>2.3</td>
<td>( 2.30 \times 10^5 )</td>
</tr>
<tr>
<td>2.5</td>
<td>( 1.72 \times 10^5 )</td>
</tr>
</tbody>
</table>

4.3.6 Stern-Volmer plot for synthesized QDs

Figure 4.16: Stern-Volmer plot and best fit lines for quenching of CdSe QDs (3.0-3.5 nm).
Table 4.3: Quenching constants for all 4 sizes of QDs with all 3 sizes of Pd nanoparticles

<table>
<thead>
<tr>
<th>Pd NP size/nm</th>
<th>$K_{Q/QD}(2.1-2.3 \text{ nm})/\text{M}^{1}$</th>
<th>$K_{Q/QD}(2.4-2.6 \text{ nm})/\text{M}^{1}$</th>
<th>$K_{Q/QD}(3.0-3.5 \text{ nm})/\text{M}^{1}$</th>
<th>$K_{Q/QD}(3.5-4.0 \text{ nm})/\text{M}^{1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9</td>
<td>2313.2</td>
<td>2739.6</td>
<td>1823.3</td>
<td>7277.8</td>
</tr>
<tr>
<td>2.3</td>
<td>2118.1</td>
<td>2807.9</td>
<td>2556.7</td>
<td>5350.1</td>
</tr>
<tr>
<td>2.5</td>
<td>2095.9</td>
<td>1995.6</td>
<td>3954.2</td>
<td>3279.9</td>
</tr>
</tbody>
</table>

To observe the size-dependent interactions between QDs and Pd nanoparticles, quenching constants were calculated for each size category of QD with each size of Pd nanoparticles (Figure 4.16 and Table 4.3). Among them, the quenching constants of 3.0-3.5 nm QDs increase with increase in Pd NP size. These results are in agreement with studies reported in the literature based on Au NPs titrated with QDs.24,28,54 The quenching constants for the other three sizes of QDs [(2.1-2.3 nm), (2.4-2.6 nm), (3.5-4.0 nm)] were found to decrease with increasing Pd nanoparticle size as shown in Table 4.3. The latter results are similar to what was observed with the larger 6.5 nm CdSe QDs.

4.3.7 Lifetime measurements of CdSe QD and CdSe QD-Pd nanoparticles

Fluorescence lifetime ($\tau$) is the time that an excited species remains in the excited state before decaying to the ground state. The excited species relaxes via radiative as well as non-radiative pathways. Non-radiative decay involves dissipation of energy by
vibrational and collisional methods.\textsuperscript{55} If $r$ and $k$ are the radiative and non-radiative decay rates, $N$ is the fraction of fluorophores in the excited state and the temporal evolution of the excited fluorophores can be described as:

$$\frac{dN}{dt} = -(r + k)N \quad (4-7)$$

Where $N = N_0 e^{-(r+k)t} = N_0 e^{-t/\tau}$

The lifetime ($\tau$) measures the combined rate of radiative and non-radiative decays.

$$\tau = \frac{-1}{r+k} \quad (4-8)$$

When non-radiative decay is absent,

$$\tau = \frac{-1}{r}$$

Static quenching is a process that involves the formation of a non-fluorescent complex in the ground state. The lifetime of such a system remains unchanged due to the presence of un-complexed fluorophores. Therefore, lifetime of such a system remains the same regardless of the presence or absence of the quencher. In contrary, when dynamic quenching takes place, the excited species is brought to the ground state by non-radiative decay processes which reduce the lifetime of the species relative to the lifetime in the absence of a quencher.\textsuperscript{52,55}

Since the Stern-Volmer plot for all three sizes of Pd nanoparticles is completely linear, which represents pure dynamic quenching, lifetime measurements were performed
for the system consisting of CdSe QDs and 1.9 nm Pd nanoparticles to confirm the dynamic quenching process.

Figure 4.17: Nanosecond time resolved CdSe fluorescence and changes in the PL decays on adding Pd nanoparticles.

Lifetime measurements shown in Figure 4.17, shows a decrease in fluorescence lifetime with increase in Pd nanoparticle concentration. The average lifetime was calculated after each titration by Equation (4-9) (Table 4.4).

\[
\text{Average lifetime, } \tau_0 = \frac{\tau_1 a_1 + \tau_2 a_2 + \tau_3 a_3}{a_1 + a_2 + a_3} \quad (4-9)
\]
Where, \( \tau_1, \tau_2 \) and \( \tau_3 \) are lifetime component 1, component 2 and component 3 respectively while \( a_1, a_2 \) and \( a_3 \) are the percentage abundance of lifetime component 1, 2 and 3.

**Table 4.4:** Calculation of average lifetime and \( \frac{\tau_0}{\tau} \) after each titration

| [Pd]/M | \( \tau_1 \) | \( a_1 \) | \( \tau_2 \) | \( a_2 \) | \( \tau_3 \) | \( a_3 \) | \( |r| \) | \( \frac{\tau_0}{\tau} \) |
|--------|-------------|--------|-------------|--------|-------------|--------|--------|-----------------|
| 0      | 0.2771      | 2.85   | 4.266       | 12.3   | 19.4524     | 84.86  | 17.03822 | 1               |
| 4.02E-07 | 0.1083     | 4.03   | 4.5005      | 19.00  | 19.74       | 76.97  | 16.05334 | 1.061351        |
| 8.04E-07 | 0.4016     | 6.95   | 4.3734      | 23.44  | 19.181      | 69.61  | 14.40493 | 1.182805        |
| 1.21E-06 | 0.9168     | 10.42  | 5.1123      | 25.51  | 18.4937     | 64.07  | 13.24859 | 1.28604         |
| 1.61E-06 | 0.929      | 16.45  | 5.4949      | 32.31  | 18.827      | 51.25  | 11.5759  | 1.47187         |
| 2.01E-06 | 0.7996     | 19.13  | 4.3658      | 29.13  | 16.5769     | 51.18  | 9.96458  | 1.709878        |
| 2.41E-06 | 0.7948     | 27.72  | 5.0681      | 33.08  | 16.6224     | 39.19  | 8.412006 | 2.025464        |
Theoretically, if dynamic quenching takes place, the relationship between \( \frac{\tau_0}{\tau} \) and [Q] should be linear. Therefore, \( \frac{\tau_0}{\tau} \) was calculated and plotted vs. [Q] (Figure 4.18) showing a linear relationship with slight upward curvature. This deviation is likely due to competition between radiative recombination of electrons and holes with the dynamic quenching. Other studies have shown that dynamic quenching processes compete with the radiative recombination process.\(^{28}\) Therefore, lifetime measurements indicate that dynamic quenching is plausible and support the data obtained using the UV-visible absorbance measurements.

### 4.3.8 The quenching mechanism

There are two possible deactivation pathways - charge transfer (CT) and energy transfer (ET), for quenching excited states by metal nanoparticles.\(^{14,28}\) Both mechanisms
were reported as major deactivation pathways for quenching the fluorescence of CdSe QDs by monolayer protected Au nanoparticles (MPC).\(^{24,28}\) The charge transfer mechanism takes place through a mercaptopropionic acid link between QD and MPC.\(^{24}\) However, for this system, CdSe QDs were well protected by trioctylphosphine oxide whereas our Pd nanoparticles were protected using \(n\)-dodecyl sulfide. The passivating ligand used for the Pd nanoparticles does not provide the possibility of creating a chemical bond between the QD and Pd nanoparticles. Therefore, CT is not a possible mechanism that can describe the quenching behavior for this system. Since there is no surface plasmon resonance band for Pd nanoparticles, a spectral overlap between QDs and Pd nanoparticles is not expected. Therefore, Foster Resonance Energy Transfer (FRET) is not expected to occur. The efficiency of FRET is highly dependent on spectral overlap and distance between donor and acceptor molecules.\(^{54}\)

Persson’s theory describes a Nano metal Surface Energy Transfer (NSET)\(^{54,56–58}\) NSET mechanism, which is a possible mechanism for the observed quenching. The mechanism does not require resonant interaction between electrons, but it requires interaction of electromagnetic fields of donor-dipole with the free conduction electrons of the accepting metal.\(^{57}\) NSET describes the formation of dipole induced electron-hole pair in a metal nanoparticle.\(^{56,57}\) According to the NSET theory, metal nanoparticles that do not exhibit a surface plasmon resonance band can accept energy by formation of electron-hole pairs near the surface of metal nanoparticles.\(^{54}\) Therefore, NSET is a suggested mechanism for fluorescent quenching of CdSe QDs by different sizes of metal nanoparticles.
4.4 Conclusion

The studies conducted in this chapter indicate that the fluorescence quenching of CdSe QDs is size dependent. For the majority of QDs, smaller Pd nanoparticles are more efficient in fluorescence quenching compared to larger particles. Fluorescence lifetime measurements showed that the quenching mechanism was competing with electron-hole recombination. The UV-visible absorbance results showed the formation of a non-fluorescent complex is also improbable. The results rather indicated that the fluorescence quenching of the QDs by Pd is due to energy transfer between CdSe QDs and Pd nanoparticles and the results are consistent with NSET whereby the metal nanoparticles do not show surface plasmon resonance. Finally, this information is useful for fundamental science and increasing the understanding of electron and energy transfer between nanoscale particles. The work is also important as it provides insights that may be useful toward potential applications in light harvesting assemblies and sensors.
4.5 References


42. Murphy, C. J.; Coffer, J. L. Quantum Dots: A Primer. *Appl. Spectrosc.* **2002**, *56*, 16A.


CHAPTER V

SIZE DEPENDENT FLUORESCENCE QUENCHING OF MOLECULAR FLUOROPHORES AND GRAPHENE OXIDE BY PALLADIUM NANOPARTICLES

5.1 Introduction

The interactions of metals with molecules and with semiconductors have shown potential implications in several technological applications including chemical sensing, alternative energy, optoelectronics and photonics.\textsuperscript{1,2} Such interactions indicate the potential of metal/semiconductor and metal/molecules hybrid structures as efficient building blocks for next generation energy conversion devices.\textsuperscript{3,4} Developing donor-acceptor type systems using metal nanoparticles and photoactive molecules provide photoresponsive nanohybrid materials with optoelectronic properties. Coupling luminescent molecules to nanoscale metal particles offers a wide range of opportunities for the design of new photoresponsive devices for nanophotonics, sensing, switching and drug delivery.\textsuperscript{2,5,6} In this chapter, the size-dependent interactions between Pd nanoparticles and organic/inorganic luminescent dyes and graphene oxide is discussed.
5.1.1 Fluorescence quenching of fluorophores by metal nanoparticles

In 1974, Kuhn and co-workers observed that the luminescence of fluorescent and phosphorescent dyes was quenched when a thin layer of gold was placed precisely at an appropriate distance to the dye molecule. The mechanism was identified as energy transfer of the dye (donor) excited state to the thin layer of gold (acceptor). In 1999, Pagnot and his group demonstrated a near-field optical microscopy study which involved energy transfer quenching of luminescent europium dibenzolymethide chromophore by gold films. One of the major questions that arise following this work is how do transition metal nanoparticles influence the optical properties of dye molecules when brought in close proximity. The topic is not well studied especially for metal nanoparticles that are not plasmonic. An improved understanding of such processes is paramount toward enhancing our understanding of metal-molecule interactions.

There are three types of fluorescence quenching mechanisms that a fluorophore could undergo when brought in close contact to a metal surface: (1) If a chemical bond forms between the fluorophore and the metal surface static quenching is dominant and has been observed in a number of fluorophores: dansyl, florenyl, fullerene, fluorescein and porphyric dyes. In some cases the metal surface could result in fluorescence enhancement. (2) Electrostatic interactions between fluorophores and anionic ligands bound to gold surfaces lead to both static and dynamic quenching. Examples of this type of interaction has been reported for fluorophores such as inorganic dyes, [Ru(bpy)$_3$]$^{2+}$. (3) Quenching of fluorophores not bound to the gold surface. Only one study has been reported that matches this category and involves the quenching of the luminescence of rhodamine by 1-4 nm diameter gold nanoparticles.
The work described in this chapter is consistent with the third category. In the example mentioned above, the metal surface primarily consisted of Au nanoparticles, which are plasmonic. The interactions of non-plasmonic nanoparticles with fluorophores have not been reported. Here, the interaction between 1-3 nm Pd metal nanoparticles and organic/inorganic dye molecules and graphene oxide is discussed.

5.1.2 Fluorescence of excited molecules and deactivation

Photoactive molecules in the ground state can absorb ultraviolet or visible light and be promoted to electronic excited states. Upon excitation, molecules tend to return to the ground state by emitting the energy absorbed which is called relaxation.

Relaxation can occur through a series of deactivation pathways.\textsuperscript{18} The pathway which has the minimal lifetime is the most preferable pathway. Internal and external conversion deactivations are considered as non-radiative pathways. In internal conversion the absorbed energy is given off as heat, and then molecules relax to the vibrational energy levels. External conversion originates due to the collisional deactivation with solvent molecules or excited molecules. This non-radiative deactivation path is also called collisional quenching of photoluminescence. Intersystem crossing is another non-radiative pathway and occurs when a molecule is deactivated by going from a singlet to a triplet excited state.

The major radiative deactivation pathways are fluorescence and phosphorescence. Fluorescence takes place when a molecule at the singlet excited state returns to the singlet ground state by emitting the absorb energy as radiation. When the same process occurs
whereby an excited molecule is transferred from the singlet excited state to the triplet state, it is called phosphorescence. Since singlet to singlet relaxation is more favorable than singlet to triplet, fluorescence lifetimes \((10^{-5}-10^{-8} \text{ s})\) for most molecules is less than the lifetime of phosphorescence \((10^{-4} \text{ to } 10^{0} \text{ s})\).\(^{18}\)

If the emitted energy is exactly the same as the absorbed radiation, it is called resonance fluorescence. In non-resonance fluorescence, vibrational deactivation is involved and the absorption wavelength is larger than the emission wavelength, which is called Stokes shifts.\(^{18}\)

### 5.1.3 Fluorescence quenching and Stern-Volmer plot for quenching efficiency

Fluorescence quenching is defined as the decrease in intensity of the photoluminescence of a known material. There are number of fluorescence quenchers and oxygen is a well-known quencher for luminescent compounds.\(^{18}\) There are also a number of fluorescent quenching mechanisms, amongst which static quenching and collisional quenching are the most common pathways. Collisional or dynamic quenching is a result of collision between an excited fluorophore and a quencher in the medium to cause a non-radiative decay of the fluorescence (Figure 5.1).
Figure 5.1: Schematic diagram for collisional or dynamic quenching.

The Stern-Volmer equation is derived for a system containing a fluorescent material and a quencher. The fluorescence intensity of the fluorophore (F) is proportional to the fluorescence intensity of its excited state (F*). Also the number of excited fluorophores is constant during the excitation. Therefore, a differential equation is established (Equation (5-1)).

\[
\frac{d[F^*]}{dt} = 0 \quad (5-1)
\]

When there is no quencher for the fluorophore, the decay rate for the excited portion is given by the equation, \( \gamma = \tau_0^{-1} \). \( \tau_0 \) is the lifetime of the excited state fluorophore. Modification for that lifetime is possible via radiative as well as non-radiative pathways. There are two differential equations for the concentration of excited state fluorophore in the presence and absence of a quencher.

When there is no quencher, the rate of change of the concentration of the excited state fluorophore is given by Equation (5-2):

\[
\frac{d[F^*]}{dt} = f(t) - \gamma[F^*]_0 = 0 \quad (5-2)
\]
Where \( f(t) = \) constant, excitation function and \( \gamma[F^*_0] = \) decay rate.

When the quencher is available, the rate of change of the concentration of the excited state fluorophore is given by Equation (5-3):

\[
\frac{d[F^*]}{dt} = f(t) - \left( \gamma + k_q[Q] \right)[F^*] = 0 \quad (5 - 3)
\]

When a quencher is present, there is an additional decay rate, \( k_q[Q] \). By dividing above two equations, the Stern-Volmer equation yields (Equation (5-4)),

\[
\frac{F_0}{F} = \frac{\gamma + k_q[Q]}{\gamma} = 1 + k_q \tau_0[Q] = 1 + K_D[Q] \quad (5 - 4)
\]

where, \( F_0 \) and \( F \) are fluorescence intensity of fluorophore in the absence and presence of the quencher respectively. \( k_q \) is called bimolecular quenching constant. \( \tau_0 \) is the lifetime of the fluorophore in the absence of the quencher. \([Q]\) is the concentration of the quencher. In dynamic quenching, the Stern-Volmer constant, \( K_D = k_q \tau_0 \). If dynamic quenching in not dominant, the Stern-Volmer constant is explained as \( K_{sv} \). Values of \( \frac{F_0}{F} \) are plotted versus \([Q]\). Since, the Stern-Volmer equation corresponds to the equation of a straight line, i.e. \( Y = mX + C \), the plot of \( \frac{F_0}{F} \) should be linear. The intercept of the plot is 1 since the initial \( \frac{F_0}{F} = 1 \). The slope of the plotted line represents the Stern-Volmer constant, \( K_D \).

Static quenching occurs when the quencher is in contact with the fluorophore. In this case, quenching occurs by the formation of a non-fluorescent complex consisting of the fluorophore and the quencher. The complex absorbs light and is promoted to an
excited state where it returns to the ground state without emitting a radiation. The formula for deriving the quenching constant for static quenching is given by Equation (5-5),

\[ K_s = \frac{[F - Q]}{[F][Q]} \quad (5-5) \]

where \( K_s \) is the quenching constant which is similar to the association constant of the reaction of the formation of a fluorophore-quencher complex. \([F - Q]\) is the concentration of fluorophore-quencher complex, \([F]\) and \([Q]\) are concentrations of fluorophore and quencher before they are mixed, respectively. If the complex formed is not fluorescent, the fluorescent intensity of the sample is due to the fluorophores which are not part of the formed complexes. Therefore, the initial fluorescent intensity of the fluorophore \([F_0]\) is given by Equation (5-6),

\[ [F_0] = [F] + [F - Q] \quad (5-6) \]

By substitution of value for \([F - Q]\) to the equation,

\[ K_s = \frac{[F - Q]}{[F][Q]} = \frac{[F_0 - F]}{[F][Q]} = \left[ \frac{F_0}{F} - 1 \right] \frac{1}{[Q]} \quad (5-7) \]

\[ \frac{F_0}{F} = 1 + K_s[Q] \quad (5-8) \]

The above equation is identical to Equation (5-4), which is derived for dynamic quenching. The only difference is that instead of having the quenching constant, here we have an association constant. Both plots are linear. Therefore, by plotting the values of \( \frac{F_0}{F} \), we cannot distinguish the static and dynamic quenching. The most useful tool for the
differentiation of those two mechanisms is lifetime measurements of the samples. Since static quenching removes a fraction of fluorophores resulting in non-fluorescent complexes, the fluorescent intensity of the remaining fluorophores are constant. Therefore, the lifetime of the sample is the same as the lifetime of the initial sample. For static quenching, \( \frac{t_0}{\tau} = 1 \). However, for dynamic or collisional quenching, \( \frac{t_0}{\tau} = \frac{F_0}{F} \). Thus, lifetime measurements are very useful tools for identifying whether the quenching mechanism involves static or dynamic quenching.

In some quenching processes, both static and dynamic quenching occurs simultaneously. In this case, the resulting Stern–Volmer plot will have an upward curvature. For this incident, the Stern-Volmer equation is used as shown below.

\[
\frac{F_0}{F} = 1 + K_{app}[Q] \quad (5 - 9)
\]

Where \( K_{app} = (K_D + K_S) + (K_D K_S)[Q] \)

\( K_D \) is the dynamic constant and \( K_S \) is the static quenching constant.

### 5.1.4 Fluorescent dye molecules

In this study four fluorescent dyes were investigated as donors while Pd nanoparticles were used as acceptors. The chemical structures of the dyes are shown below: Figure 5.2 shows the structure of rhodamine B, Figure 5.3 shows the structure of Tris(2,2′-bipyridine)dichlororuthenium(II)hexahydrate (Ru(bpy)_3^{2+}), Figure 5.4 shows the structure of fluorescein and Figure 5.5 shows the structure of benzodipyrido[2,3-a: 2′,3′-
clphenanzine (BDPPZ). All the dyes were purchased commercially with the exception of BDPPZ.

**Figure 5.2:** Chemical structure of rhodamine B.

**Figure 5.3:** Chemical structure of Tris(2,2′-bipyridine)dichlororuthenium(II)hexahydrate (Ru(bpy)$_3$Cl$_2$).
Figure 5.4: Chemical structure of fluorescein.

Figure 5.5: Chemical structure of benzodipyrido[2,3-a: 2’,3’-c]phenazine (BDPPZ).
5.1.5 Graphene oxide

In 1859, Benjamin Brodie discovered that the exfoliation of graphite oxide produces an atomically thin sheet of graphene oxide (GO).\textsuperscript{19,20} Recently, the isolation of crystalline graphite and its characterization was recognized by the 2010 award of the Nobel Prize in Physics to Andre Geim and Konstantin Novoselov.\textsuperscript{21} Graphene oxide has single-atom thickness and consists of a 2-D sheet of hexagonally arranged carbon atoms.

5.1.5.1 Properties of GO

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{graphene_oxide.png}
\caption{Chemical structure of graphene oxide. Taken with permission from reference [22].}
\end{figure}

GO consists of epoxy, hydroxyl and carboxylic groups on the basal plane and the sheet edge (Figure 5.6) which are ideal for interactions with a wide range of organic and inorganic materials.\textsuperscript{23} In addition, the electronic structure of GO consists of both conducting $\pi$-states from $sp^2$ carbon sites and wide energy gap $\sigma$-states of $sp^3$ bonded
carbon sites. Due to the hybrid electronic structure of GO, the band gap of GO can be tuned by controlling the ratio of $sp^2$ and $sp^3$ fractions.\textsuperscript{24}

![Graph showing energy gap as a function of number of aromatic rings](image)

**Figure 5.7:** Calculated energy gap of $\pi-\pi^*$ transitions as a function of fused aromatic rings Taken with permission from reference \[25\].

Due to strong electron confinement the aromatic rings or the $sp^2$ domains have a large bandgap (Figure 5.7).\textsuperscript{25} The reduction of GO creates new $sp^2$ domains as a result of removal of oxygen as CO or CO\textsubscript{2}.\textsuperscript{20} Due to the tunable bandgap, GO shows near-infrared (NIR), visible and ultraviolet fluorescence.\textsuperscript{25,26} As GO consists of heterogeneic atomic and electronic structure, the fluorescence of GO is a result of recombination of electron-hole pairs in localized electronic states such as $sp^2$ and $sp^3$. Furthermore, the mechanism of photoluminescence of GO is not well studied.\textsuperscript{20}
Figure 5.8: Schematic band structure of GO; pink-conduction band, blue –valence band. Taken with permission from reference [25].

Figure 5.8 shows the band structure of GO. The generation of an electron-hole pair upon light absorption ($E_{\text{exc}}$ and red arrow) is followed by radiative or non-radiative recombination, which results in fluorescence ($E_{\text{PL}}$ and blue arrow). The black arrows in Figure 5.8 show the electron-hole transition. The size of the $sp^2$ domains determines the bandgap of GO and the wavelength of the emitted light. For example, $sp^2$ clusters less than 1 nm show fluorescence in the UV-visible region and larger $sp^2$ domains show fluorescence in the red-NIR region.\textsuperscript{20}

5.1.5.2 GO as a popular material in solar energy conversion, storage and sensing

Graphene based materials possess remarkable and tunable electronic and optical behavior as described above. In addition, these materials have very high surface area, mechanical strength and are naturally abundant.\textsuperscript{27} All these properties together make
graphene based materials ideal for designing multifunctional composite materials for energy conversion, storage and sensing.\textsuperscript{28–31} Recent studies have shown that GO sheets act as scaffolds for anchoring semiconductor and metal nanoparticles for increased charge separation.\textsuperscript{29,31} Also, Kamat’s group demonstrated that the excited TiO\textsubscript{2} and ZnO nanostructures are capable of transferring electrons to GO.\textsuperscript{29,32} In both cases, GO was found to accept electrons from semiconductors leading to the formation of reduced graphene oxide (rGO), which can store and transport electrons.

In this Chapter, the interaction between fluorescent GO and quantum sized metal nanoparticles were studied. The results indicate that GO-metal or GO-semiconductor hybrid systems have the potential to function as assemblies in next generation light harvesting, energy conversion and sensing systems.\textsuperscript{27}

\section*{5.2 Experimental section}

\subsection*{5.2.1 Chemicals:} Rhodamine B (95\%), ethanol (200 proof), fluorescein free acid (95\%), Pd black (40-60 m\textsuperscript{2}/g surface area), \textit{n}-dodecyl sulfide (93\%) were purchased from Sigma Aldrich and used as received. Ru(bpy)	extsubscript{3}Cl\textsubscript{2}, 98\% was purchased from Spectrum Chemicals. Single layer graphene oxide (99 \%) in solid form was purchased from ACS Material Advanced Chemical supplier. Toluene (99.5 \%), and acetonitrile (99.5\%) were purchased from Pharmco-AAPER.

\subsection*{5.2.2 Synthesis of different sizes of Pd nanoparticles:} The procedures for the synthesis of different sizes of Pd nanoparticles are described in Chapter II.
5.2.3 Preparation of fluorescent dye solutions: 2.1 µM of rhodamine B, 33.3 µM of Tris(2,2’-bipyridyl)ruthenium (II) chloride hexahydrate, 92.4 µg/mL of GO and 200 µM of fluorescein solutions were prepared in absolute ethanol. 0.26 mM of BDPPZ solution was prepared in acetonitrile.

5.2.4 Titration of dyes and GO with different sizes of metal nanoparticles: Dye samples were prepared and placed in a quartz cuvette. For each experiment, Pd nanoparticles were added to the dye and the mixture was allowed to equilibrate for two minutes then a fluorescent spectrum was recorded.

5.2.5 Control experiments: Control experiments for dyes were carried out with toluene, Pd black, n-dodecyl sulfide.

5.2.6 Instrumentation: UV-visible absorbance spectra were recorded using a Varian Cary 50 spectrophotometer. Fluorescence spectra were recorded using a Varian-Cary Eclipse fluorescence spectrophotometer.

5.3 Results and discussion

5.3.1 Interaction of rhodamine B with Pd nanoparticles: The UV-visible absorbance spectrum of rhodamine B was recorded before and after the titration with Pd nanoparticles as shown in Figure 5.9. The results show that the rhodamine B absorbance peak centered at 550 nm is slightly blue-shifted to 546 nm with increasing Pd nanoparticle concentration. The blue shift was consistent with all three sizes of Pd
nanoparticles. There is no significant change in the UV-visible absorbance spectrum after the titration.

![UV-visible absorbance spectrum of rhodamine B before and after titration.](image)

**Figure 5.9:** UV-visible absorbance spectrum of rhodamine B before and after titration.

The fluorescence spectrum of a dilute (2.1 µM) solution of rhodamine B ($\lambda_{\text{max}} = 572$ nm) along with the changes in the fluorescence after addition of Pd nanoparticles (1.9 ± 0.1 nm, 2.3 ± 0.1 nm, 2.5 ± 0.1 nm) is shown in Figure 5.10. When the first 10 µL (8.2 µM) of Pd nanoparticles were added, the fluorescence intensity of rhodamine B increased and the wavelength maximum shifted to a lower wavelength value (572 nm to 567 nm). Increase in Pd nanoparticle concentration then resulted in a decrease in the fluorescence intensity at 567 nm (Figure 5.10 a, b and c). The final concentration of Pd nanoparticles of all sizes for each titration was 82.0 µM.
Figure 5.10(a): Change in fluorescence intensity of rhodamine B with increasing the concentration of 1.9 nm Pd nanoparticles. (1-enhancement, 2-decreasing of fluorescence)

Figure 5.10(b): Change in fluorescence intensity of rhodamine B with increasing the concentration of 2.3 nm Pd nanoparticles. (1-enhancement, 2-decreasing of fluorescence)
Figure 5.10(c): Change in fluorescence intensity of rhodamine B with increasing the concentration of 2.5 nm Pd nanoparticles. (1-enhancement, 2-decreasing of fluorescence).

Figure 5.10(d): Change in fluorescence intensity of rhodamine B with increasing the concentration of Pd black particles.
Control experiments were performed where rhodamine B was titrated with toluene (the solvent in which Pd nanoparticles are dissolved in), Pd black (Figure 5.10(d)), and \( n \)-dodecyl sulfide. There was no change in the absorbance or the fluorescence spectra of rhodamine B exposed to any of the aforementioned substances.

The results obtained suggest the fluorescence quenching of rhodamine B by Pd nanoparticles is an effect of the nanoscale-size of the metal nanoparticles. The results further show that larger nanoparticles are more efficient quenchers relative to smaller nanoparticles. The fluorescence quenching of rhodamine B by Pd nanoparticles can be attributed to the Nano Surface Energy Transfer (NSET) mechanism. According to the NSET theory, metal nanoparticles that do not display a surface plasmon resonance bands can accept energy by formation of electron-hole pair near the surface of metal nanoparticles.\(^{33}\)

5.3.2 Interaction of Ru(bpy)\(_3\)\(^{2+}\) with Pd nanoparticles: Ru(bpy)\(_3\)\(^{2+}\) displays a UV-visible absorbance peak at 450 nm which is attributed to the metal to ligand charge transfer (MLCT) from Ru(d\(\pi\)) to \( \pi^* \).\(^{34}\) Figure 5.11 shows the UV-visible absorbance spectrum of Ru(bpy)\(_3\)\(^{2+}\) before and after addition of Pd nanoparticles. The results indicate that there was no change in the absorbance peak of Ru(bpy)\(_3\)\(^{2+}\). The fluorescence quenching of Ru(bpy)\(_3\)\(^{2+}\) solution (33.3 \( \mu \)M) was investigated by adding 3 sizes of Pd nanoparticles (Figure 5.12).
Figure 5.11: UV-visible absorbance spectrum of Ru(bpy)$_3^{2+}$ before and after titration.

Figure 5.12(a): Change in fluorescence intensity of Ru(bpy)$_3^{2+}$ with increasing the concentration of 1.9 nm Pd nanoparticles.
Figure 5.12(b): Change in fluorescence intensity of $\text{Ru(bpy)}_3^{2+}$ with increasing the concentration of 2.3 nm Pd nanoparticles.

Figure 5.12(c): Change in fluorescence intensity of $\text{Ru(bpy)}_3^{2+}$ with increasing the concentration of 2.5 nm Pd nanoparticles.
**Figure 5.12(d):** Change in fluorescence intensity of Ru(bpy)$_3^{2+}$ with increasing concentration of Pd black particles.

**Figure 5.13:** Stern-Volmer plot and best fit lines for quenching fluorescence of Ru(bpy)$_3^{2+}$. 

[y = 8597.8x + 1  
$R^2 = 0.992$  

$y = 4795.5x + 1$  
$R^2 = 0.981$  

$y = 2576.4x + 1$  
$R^2 = 0.9817$]
Table 5.1: Quenching constants for Ru(bpy)$_3^{2+}$ with Pd nanoparticles

<table>
<thead>
<tr>
<th>Diameter of Pd nanoparticles/nm</th>
<th>Quenching constants/M$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9</td>
<td>2.58 x $10^3$</td>
</tr>
<tr>
<td>2.3</td>
<td>4.80 x $10^3$</td>
</tr>
<tr>
<td>2.5</td>
<td>8.60 x $10^3$</td>
</tr>
</tbody>
</table>

All three sizes of Pd nanoparticles were effective in quenching the fluorescence of Ru(bpy)$_3^{2+}$. To observe the fluorescence quenching, Ru(bpy)$_3^{2+}$ was excited at 435 nm. The titration was done by adding 10 µL increments of Pd nanoparticles (Figure 5.12 a, b, and c). As a control experiment, a Ru(bpy)$_3^{2+}$ solution was titrated with Pd black particles and no fluorescence quenching was observed (Figure 5.12(d)). The Stern-Volmer plot (Figure 5.13) shows size-dependent fluorescence quenching; the quenching efficiency increased with increase in Pd nanoparticle size. The final concentration of Pd nanoparticles of all sizes in each titration was 82.0 µM. The quenching constant was calculated based on the Stern-Volmer plot (Table 5.1). According to a published article by Cheng et al$^{17}$, fluorescence quenching of Ru(bpy)$_3^{2+}$ by troponin-stabilized Au nanoparticles was due to a static quenching mechanism. The explanation is valid because tiopronin is a negatively charged ligand while Ru(bpy)$_3^{2+}$ is positively charged indicating the possibility of the formation of a chemical bond between tiopronin ligand and the dye molecule resulting in static quenching. However, in our work, we have used the n-dodecyl sulfide, a neutral ligand, as a stabilizer for the Pd nanoparticles. Therefore, it is
not expected that a chemical bond would form between the dye and the stabilizer at the nanoparticle interface. Thus, the NSET is the most plausible mechanism for the data acquired.

5.3.3 Interaction of fluorescein with Pd nanoparticles: Fluorescein is a commonly used molecular probe due to its high molar absorptivity, large quantum yield and high photostability.\textsuperscript{35–37} Fluorescein and its derivatives exist in different structural forms in different media and give different absorption peaks, emission peaks, quantum yields and lifetime. The optical properties of fluorescein and its derivatives depend highly on the pH, hydrogen bonding power and the polarity of the medium that they are dissolved in.\textsuperscript{38,39} To investigate the interaction between fluorescein and Pd nanoparticles, fluorescein free acid was used (Figure 5.4).

![UV-visible absorbance spectrum of fluorescein before and after titration with 1.9 nm Pd NPs](image)

**Figure 5.14:** UV-visible absorbance spectrum of fluorescein before and after titration with 1.9 nm Pd nanoparticles.
The fluorescence free acid has a carboxylic functionalized phenyl group that lays perpendicular to the xanthene ring. This structural feature is an advantage because it prevents conjugation from occurring between xanthene and the carboxylic phenyl ring. Therefore, ionization or alkylation of carboxylic group is not expected to affect the UV-visible absorbance spectrum of fluorescein.\textsuperscript{37} Fluorescein free acid shows a strong absorption peak at 445 nm and a weak absorbance peak at 488 nm (Figure 5.14). These spectral data are consistent with previously reported data for the neutral form of fluorescein.\textsuperscript{35} After titration of fluorescein with 1.9 nm Pd nanoparticles, it was observed that the UV-visible absorbance peak shifted from 445 nm to 455 nm, while the peak at 488 nm remained unchanged. Literature reports indicated that the spectrum of fluorescein obtained after addition of Pd nanoparticles is similar to that of fluorescein that has undergone ring opening resulting in anionic fluorescein (Figure 5.15). According to the literature, fluorescein ring opening occurs only in the presence of metal ions or when the medium acidity changes.\textsuperscript{40} The Pd nanoparticles that were added to fluorescein contained no metal ions; however, as metal they have acidic character. Comparative studies with Pd black did not affect the fluorescein peaks, thus the effect observed is due to the nanoscale size of the Pd nanoparticles.

![Fluorescein and anionic fluorescein](image)

**Figure 5.15:** Fluorescein and anionic fluorescein.
Changes in the fluorescence spectra of fluorescein titrated with Pd nanoparticles were measured as shown in Figure 5.16. The results show that the size of the Pd nanoparticles plays an important role in the overall interactions. The initial fluorescence spectrum of fluorescein shows two emission peaks at 475 nm (low intensity) and at 520 nm (high intensity).

**Figure 5.16:** Change in fluorescence intensity of fluorescein with increasing the concentration of (a) 1.9 nm, (b) 2.3 nm, (c) 2.5 nm Pd nanoparticles and (d) Pd black particles.
During the addition of the first 6 µL of Pd nanoparticles, the fluorescence intensity of both fluorescein peaks decreased in intensity, and the peak at 475 nm disappeared. Increasing the Pd nanoparticle concentration increased the intensity of the peak at 520 nm (Figure 5.16). In addition a new peak centered at 570 nm appeared. The final concentration of Pd nanoparticles of all sizes for each titration was 16.4 µM. It was found that the smaller the size of the Pd nanoparticle the higher the fluorescence intensity. Control experiments were performed with n-dodecyl sulfide, toluene and Pd black (Figure 5.16(d)). All reagents were found to quench the fluorescence intensity but none resulted in fluorescent enhancement.

The results suggest that Pd nanoparticles are capable of enhancing the fluorescein fluorescence. The enhancement is a result of either a structural change of fluorescein or due to the concept of metal enhanced fluorescence (MEF). Metal enhanced fluorescence of fluorophores due to metal nanoparticles has been investigated by a few researchers.\textsuperscript{41–43} Geddes et al. studied the interaction of fluorophores with plasmonic metal nanoparticles including silver\textsuperscript{44}, gold\textsuperscript{45} and copper\textsuperscript{46}, as well as with chromium, zinc\textsuperscript{47}, tin and nickel\textsuperscript{48}.

**5.3.4 Metal enhanced fluorescence (MEF)**

Studies involving MEF date back to the 1960s where Drexhage noticed that when a luminescent molecule was brought close to a metal film, its lifetime decay was affected.\textsuperscript{49,50} Recently, Lakowicz and Geddes extensively investigated MEF for several metal nanoparticles.\textsuperscript{41,44,47,48,50} MEF is defined as a physical phenomenon which occurs at
nanometer distances between metal and fluorophore.\textsuperscript{42} In addition, for many of the fluorophores investigated, their absorption/emission bands overlap with the absorption (plasmonic) band of the metal nanostructures.\textsuperscript{42,51} In the case of MEF, metallic surface can act as an antenna and concentrates the electromagnetic field of the fluorophores leading to enhancement of the fluorescence\textsuperscript{50}

In the work conducted in this chapter, it is plausible that the results obtained are a result of MEF caused due to increased electromagnetic field via the antennas of the Pd nanoparticles, or may be due to a structural change from fluorescein free acid to anionic fluorescein.

5.3.5 Interaction BDPPZ and Pd nanoparticles: BDPPZ is a highly conjugated derivative of the well-known 1,10-phenanthroline molecule.\textsuperscript{52} The UV-visible absorbance spectrum of BDPPZ dissolved in acetonitrile shows two peaks at 390 nm and 410 nm (Figure 5.17). Following the titration of BDPPZ with Pd nanoparticles, there was no significant change in the UV-visible spectrum peak position. To obtain the emission spectrum, BDPPZ was excited at 385 nm leading to an emission maximum at a wavelength of 560 nm.
Figure 5.17: UV-Visible absorbance spectrum of BDPPZ before and after titration.

A 0.26 mM of BDPPZ solution was titrated with 1.9, 2.3 and 2.5 nm of Pd nanoparticles. Fluorescence quenching of BDPPZ was observed for all three sizes of metal nanoparticles (Figure 5.18 a, b and c). For all three sizes of Pd nanoparticles, after the addition of the first 10 µL, the emission maximum at 560 nm was red-shifted to 585 nm while the fluorescence was quenched. The final concentration of Pd nanoparticles of all sizes for each titration was 82.0 µM. Pd black particles did not quench the fluorescence of BDPPZ (Figure 5.18 (d)). Stern-Volmer for all three sizes was plotted and quenching constants were calculated (Figure 5.19 and Table 5.2).
Figure 5.18(a): Change in fluorescence intensity of BDPPZ with increasing the concentration of 1.9 nm Pd nanoparticles.

Figure 5.18(b): Change in fluorescence intensity of BDPPZ with increasing the concentration of 2.3 nm Pd nanoparticles.
Figure 5.18(c): Change in fluorescence intensity of BDPPZ with increasing the concentration of 2.5 nm Pd nanoparticles.

Figure 5.18(d): Change in fluorescence intensity of BDPPZ with increasing the concentration of Pd black particles.
Figure 5.19: Stern–Volmer plot and best fit lines for quenching of BDPPZ titrated with Pd Nanoparticles.

Table 5.2: Quenching constants of BDPPZ titrated with Pd nanoparticles

<table>
<thead>
<tr>
<th>Diameter of Pd nanoparticle/nm</th>
<th>Quenching constants/M⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9</td>
<td>3.48 x 10⁴</td>
</tr>
<tr>
<td>2.3</td>
<td>7.27 x 10⁴</td>
</tr>
<tr>
<td>2.5</td>
<td>1.65 x 10⁵</td>
</tr>
</tbody>
</table>

The quenching constants increased with increase in the Pd nanoparticle diameter and the results indicate that NSET is the most suitable energy transfer mechanism for this interaction.

5.3.6 Interaction of graphene oxide (GO) and Pd nanoparticles: Diameter and thickness of GO are 1–5 µm and 0.8-1.2 nm, respectively. Both single layer ratio and
purity of GO is 99%. The elemental composition of GO is C = 51.26 %, O = 40.78 % and C/O = 1.67. The UV-visible absorbance spectrum of GO (92.4 µg/mL) was recorded as shown in Figure 5.20 and showed two distinct peaks. The fluorescence spectrum of GO (Figure 5.21) was taken at an excitation wavelength of 265 nm and showed three peaks at 305 nm, 425 nm and 485 nm which confirm that the $sp^2$ cluster sizes are less than 1 nm amounting to roughly 20 aromatic rings.$^{20}$

**Figure 5.20:** UV-visible absorbance spectrum of GO.

**Figure 5.21:** Fluorescence spectrum of GO.
A solution of GO (92.4 µg/mL) was prepared and 4 mL of the solution were placed in a quartz cuvette. Pd nanoparticles (10 µl) were added to the GO solution and the fluorescence spectrum of the sample was recorded after each titration. The GO fluorescence was quenched by all three Pd nanoparticle sizes (Figure 5.22 a, b and c). We note that control experiments were performed in which Pd black (Figure 5.22(d)), n-dodecyl sulfide and toluene were added to GO while monitoring the fluorescence. In all cases, there was no quenching observed. The final concentration of Pd nanoparticles of all sizes for each titration was 16.4 µM. The fluorescence quenching data allowed us to, analyze the data using Stern-Volmer plots, $F_0/F$ vs. concentration of Pd nanoparticles (Figure 5.23).

Figure 5.22(a): Change in fluorescence intensity of GO with increasing the concentration of 1.9 nm Pd nanoparticles.
Figure 5.22(b): Change in fluorescence intensity of GO with increasing the concentration of 2.3 nm Pd nanoparticles.

Figure 5.22(c): Change in fluorescence intensity of GO with increasing the concentration of 2.5 nm Pd nanoparticles.
**Figure 5.22(d):** Change in fluorescence intensity of GO with increasing the concentration of Pd black particles.

**Figure 5.23:** Stern-Volmer plot and best fit lines for quenching of GO with Pd nanoparticles.
Table 5.3: Quenching constants quenching GO with Pd nanoparticles

<table>
<thead>
<tr>
<th>Size of the Pd nanoparticles/nm</th>
<th>Quenching constant/M⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9</td>
<td>3.78 x 10⁵</td>
</tr>
<tr>
<td>2.3</td>
<td>7.10 x 10⁴</td>
</tr>
<tr>
<td>2.5</td>
<td>1.06 x 10⁵</td>
</tr>
</tbody>
</table>

Fluorescence quenching constants were calculated for all three sizes of Pd nanoparticles using the Stern-Volmer equation (Table 5.3). The calculated quenching constants show that an increase in nanoparticle size results in an increased quenching efficiency. This observation is in agreement with previous observations of quenching efficiency of Pd nanoparticles. NSET is the most suitable energy transfer mechanism for this system as Pd nanoparticles do not display a surface plasmon resonance band.
Table 5.4: Excitation, emission wavelengths, concentration and solvents of dyes and GO

<table>
<thead>
<tr>
<th>Dye</th>
<th>$\lambda_{\text{Excitation}}$ (nm)</th>
<th>$\lambda_{\text{Emission}}$ (nm)</th>
<th>Dye Concentration</th>
<th>Solvent</th>
<th>([Pd])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhodamine B</td>
<td>510</td>
<td>572</td>
<td>2.1 µM</td>
<td>Ethanol</td>
<td>(82.0 µM)</td>
</tr>
<tr>
<td>Ru(bpy)$_3^{2+}$</td>
<td>435</td>
<td>560</td>
<td>33.3 µM</td>
<td>Ethanol</td>
<td>(82.0 µM)</td>
</tr>
<tr>
<td>Fluorescein</td>
<td>425</td>
<td>475, 520</td>
<td>200 µM</td>
<td>Ethanol</td>
<td>(16.4 µM)</td>
</tr>
<tr>
<td>BDPPZ</td>
<td>385</td>
<td>560</td>
<td>0.26 mM</td>
<td>Acetonitrile</td>
<td>(82.0 µM)</td>
</tr>
<tr>
<td>GO</td>
<td>260</td>
<td>425, 485</td>
<td>92.4 µg/mL</td>
<td>ethanol</td>
<td>(16.4 µM)</td>
</tr>
</tbody>
</table>

Table 5.4 shows a summary including emission, excitation wavelengths, concentration of compounds, solvents and total concentration of Pd nanoparticles used in titrations.

5.4 Conclusion

The work described in this chapter focused on elucidating the interactions between Pd nanoparticles and fluorophores. For all the fluorophores investigated, i.e. rhodamine, Ru(bpy)$_3^{2+}$ and BDPPZ, the fluorescence was quenched by Pd
nanoparticles. At low concentrations of Pd nanoparticles, rhodamine B showed a fluorescence enhancement and the emission maximum was shifted to higher energy. Increasing the Pd nanoparticle concentration resulted in fluorescence quenching of rhodamine B. The fluorescence intensity of Ru(bpy)$_3^{2+}$ and BDPPZ were quenched by all three Pd nanoparticle sizes. GO also displayed fluorescence quenching upon interacting with Pd nanoparticles. Interestingly, for all three dyes, and GO the 2.5 nm Pd nanoparticles were the most efficient quenchers. Depending on the optical characteristics and the small size of Pd nanoparticles, NSET is the suggested mechanism for the energy transfer process. Electron transfer is less favorable for Pd nanoparticles due to their thick neutral ligand coating.
5.5 References


CHAPTER VI

CONCLUSION AND FUTURE PERSPECTIVES

Metallic nanoparticles exhibit unique chemical and physical properties due to their high surface to volume ratio as well as their electronic band structure.\textsuperscript{1,2} Metal nanoparticles consist of discrete energy levels and as a consequence, exhibit unique properties relative to their bulk counterparts. For example, the melting point of a 1.5 nm of gold nanoparticle is 500 °C while that of a 2.2 nm gold nanoparticles is 700 °C.\textsuperscript{3} Despite the small difference in particle diameter a drastic difference in the melting point is observed indicating the size-dependent properties of these materials. Therefore, one of the important goals in nanoscale science is to establish procedures that produce well-defined nanoparticle samples that have a precise size which will allow and understand of their properties and their structure-function relationship.

6.1 Synthesis of monodisperse metal nanoparticles

One of the main goals of the work described in this dissertation was to establish synthetic procedures for monodisperse Pd and Pt nanoparticles. Thioether ligands were used to stabilize the Pd and Pt nanoparticles. Thioethers are sulfur based soft ligands that interact strongly with soft metals such as Pd and Pt. TEM images of Pd and Pt
nanoparticles showed that the developed procedure showed the formation of spherical particles with a narrow size distribution. HRTEM, XRD and SAED were used to further characterize the nanoparticles and confirmed their crystalline structure.

6.2 Evaluation of catalytic activity of Pd nanoparticles

Sulfur is well known to act as a poison to metal catalysts due to its strong interaction with the surface. While a few sulfur-based stabilizers have been found to not affect the overall catalytic activity of nanoparticles it is still important to evaluate the catalytic activity of thioether ligand stabilized Pd nanoparticles. The catalytic activity of thioether stabilized Pd nanoparticles (Pd nanoparticles supported on silica) were tested in a hydrogenation reaction. The results obtained from hydrogenation of cinnamaldehyde and citral (Scheme 6.1 and 6.2) showed that Pd nanoparticles are catalytically active and more effective relative to bulk Pd.

Scheme 6.1: Hydrogenation of cinnamaldehyde using Pd nanoparticles supported on silica
Scheme 6.2: Hydrogenation of citral using Pd nanoparticles supported on silica

The results obtained indicate that thioether ligands do not have an adverse effect on the catalytic activity of Pd nanoparticles.

6.3 Interaction of metal nanoparticles with fluorescent molecules and semiconductor nanomaterials

One of the important features of the Pd and Pt nanoparticles we developed in this dissertation is that they exhibited quantized double layer charging at a size less than 5 nm. This feature allowed for further investigation of their ability to transfer energy and electrons. We investigated the interaction of the Pd nanoparticles when brought in close proximity to fluorescent molecules where energy transfer could occur, and to semiconductors where electron transfer could take place.

6.3.1 Interaction with semiconductor nanoparticles

We studied the effect of Pd and Pt nanoparticles brought in close contact to colloidal TiO$_2$ nanoparticles. The colloidal TiO$_2$ nanoparticles were synthesized using a previously reported method.$^7$ When the Pd or Pt nanoparticles were brought in contact with the colloidal TiO$_2$ nanoparticles, no change occurred. To study electron transfer, the charge was separated within the TiO$_2$ nanoparticles, so that electrons were promoted to
the semiconductor conduction band leaving holes in the valence band, the colloidal TiO$_2$ nanoparticles changed color from a clear solution to a dark blue solution. As Pd or Pt nanoparticles were brought in close contact to charged TiO$_2$, the blue color began to fade away indicating loss of electrons from the TiO$_2$ conduction band (Figure 6.1).

![Figure 6.1: UV-visible absorbance spectra of colloidal TiO$_2$, before and after UV irradiation, and addition of a known amount of 1.9 nm Pd nanoparticles.](image)

The amounts of electrons that could be stored in the nanoparticles varied for each of the three Pd nanoparticles examined (1.9 nm, 2.3 nm and 2.5 nm) as shown in Table 6.1. It was found that the larger sized nanoparticles were more efficient and were able to accept and store more electrons relative to the smaller sized particles.
Table 6.1: Efficiency of electron storage ability of Pd nanoparticles

<table>
<thead>
<tr>
<th>Pd nanoparticle size</th>
<th>Moles of electrons stored per mole of palladium nanoparticles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9 nm</td>
<td>96</td>
</tr>
<tr>
<td>2.3 nm</td>
<td>115</td>
</tr>
<tr>
<td>2.5 nm</td>
<td>129</td>
</tr>
</tbody>
</table>

To investigate whether the electrons were stored within the Pd or Pt nanoparticles, we exposed them to methyl viologen (MV$^{2+}$), a molecule that is clear in solution when oxidized but exhibits blue coloration when in its reduced form (MV$^{+}$). As soon as methyl viologen was exposed to the Pd and Pt nanoparticles, the color of the methyl viologen changed from clear to blue indicating that the Pd and Pt nanoparticles had stored electrons from the TiO$_2$ nanoparticles and were able to transfer these electrons to methyl viologen (Figure 6.2). The ability of the Pd and Pt nanoparticles to store electrons is an important feature of these catalytic nanoparticles because it indicates that their reducing ability can be further enhanced by their electron-storing ability. This work will be the subject of future investigations.
Figure 6.2: UV-visible absorbance spectra for TiO$_2$ nanoparticles (a) before irradiation, (b) after irradiation, (c) after addition of Pt nanoparticles [Pt] = 19.767 x 10$^{-6}$ M, and (d) after addition of methyl viologen.

6.3.2 Interaction with fluorescent molecules

We further investigated the interaction of four fluorescent dyes when brought in close proximity to Pd nanoparticles: rhodamine B, fluorescein, tris(bipyridine)ruthenium(II) dichloride [(Ru(bpy)$_3$Cl$_2$] and benzodipyrido[3,2-a:2′,3′-c]phenazine (BDPPZ) (Table 6.2). The fluorescence of each dye was measured and then each dye molecule was titrated with Pd nanoparticles. It was found that the increase in Pd nanoparticle concentration resulted in a decrease in fluorescence intensity of, [(Ru(bpy)$_3$Cl$_2$] and BDPPZ. Fluorescence of Ru(bpy)$_3$$^{2+}$ and BDPPZ quenched readily with all three sizes of Pd nanoparticles and quenching was size dependent. Quenching constants which determine quenching efficiency were calculated using Stern-Volmer
plot. The higher the quenching constant the more efficient was the quenching. Table 6.3 and 6.4 show quenching constants for fluorescence quenching of Ru(bpy)$_3^{2+}$ and BDPPZ, respectively. 2.5 nm Pd nanoparticles was the most efficient quencher. The control experiments were done using Pd black particles, which did not show any quenching of fluorescence of either dye molecule.

At low concentrations (8.2 µM) of Pd nanoparticles, the fluorescence intensity of rhodamine B was enhanced and the emission wavelength shifted to higher energy. When the concentration of nanoparticles increased (more than 8.2 µM), the fluorescence intensity of rhodamine B decreased. The largest Pd nanoparticles were found to be the most efficient quenchers. In the case of fluorescein, the fluorescence intensity decreased with increasing Pd nanoparticle concentration up to a certain point ([Pd] = 9.84 µM), then the fluorescence intensity of fluorescein was enhanced with increasing Pd nanoparticle concentration. The trend was found to be dependent on the Pd nanoparticle size. The results obtained from both the fluorescence data and the UV-visible absorbance spectra suggest that a structural change occurs from fluorescein free acid to anionic fluorescein or may be an effect of metal enhanced fluorescence.
**Table 6.2:** Fluorescent dye molecules used to investigate the effect of energy transfer to Pd nanoparticles

<table>
<thead>
<tr>
<th>Rhodamine B</th>
<th>Fluorescein</th>
<th>Ru(bpy)$_3$Cl$_2$</th>
<th>BDPPZ</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Rhodamine B" /></td>
<td><img src="image" alt="Fluorescein" /></td>
<td><img src="image" alt="Ru(bpy)$_3$Cl$_2$" /></td>
<td><img src="image" alt="BDPPZ" /></td>
</tr>
</tbody>
</table>

**Table 6.3:** Quenching constants for Ru(bpy)$_3^{2+}$ with Pd nanoparticles

<table>
<thead>
<tr>
<th>Size of the Pd nanoparticles/nm</th>
<th>Quenching constants/M$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9</td>
<td>$2.58 \times 10^3$</td>
</tr>
<tr>
<td>2.3</td>
<td>$4.80 \times 10^3$</td>
</tr>
<tr>
<td>2.5</td>
<td>$8.60 \times 10^3$</td>
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**Table 6.4:** Quenching constants for BDPPZ with Pd nanoparticles

<table>
<thead>
<tr>
<th>Size of the nanoparticle/nm</th>
<th>Quenching constants/M$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9</td>
<td>$3.48 \times 10^4$</td>
</tr>
<tr>
<td>2.3</td>
<td>$7.27 \times 10^4$</td>
</tr>
<tr>
<td>2.5</td>
<td>$1.65 \times 10^3$</td>
</tr>
</tbody>
</table>
6.3.2.1 Interaction with graphene oxide

GO is considered to be an insulator. However, its band gap energy is tunable depending on the ratio of $sp^2$ and $sp^3$ clouds present within the structure. The fluorescence of GO is a result of recombination of electron-hole pairs in localized electronic states such as $sp^2$ and $sp^3$. Therefore, the fluorescence of GO arises from phenomena different from that of typical semiconductors where a fluorescence originates from band-edge transitions. However, the mechanism of photoluminescence of GO is not well studied.\textsuperscript{11}

In our work, GO was titrated with all three sizes (1.9 nm, 2.3 nm and 2.5 nm) of Pd nanoparticles. The fluorescence intensity of GO was quenched by all three sizes of Pd nanoparticles. GO titrated with Pd black did not show significant quenching. To measure the quenching efficiency, Stern-Vomer plots were constructed. Table 6.5 summarizes the quenching constants calculated from Stern-Volmer plots for each Pd nanoparticle.

<table>
<thead>
<tr>
<th>Size of the Pd nanoparticles/nm</th>
<th>Quenching constants/M$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9</td>
<td>$3.78 \times 10^3$</td>
</tr>
<tr>
<td>2.3</td>
<td>$7.10 \times 10^4$</td>
</tr>
<tr>
<td>2.5</td>
<td>$1.06 \times 10^5$</td>
</tr>
</tbody>
</table>

2.5 nm Pd nanoparticles shows the highest quenching constant.
6.3.3 Interaction of Pd nanoparticles with CdSe QDs

To study the interaction between Pd nanoparticles and semiconductor quantum dots (QDs), different sizes of QDs [(2.1-2.3 nm), (2.4-2.6 nm), (3.0-3.5 nm), (3.5-4.0 nm)] were synthesized (Figure 6.3) and one large size of QD (6.5 nm) was purchased from the Sigma Aldrich Company.

Figure 6.3: Fluorescence of synthesized QDs as a function of size Blue to red, size of the QD increases.

These five sizes of QDs were titrated with three sizes of Pd nanoparticles. All three sizes of Pd nanoparticles were able to quench the fluorescence of all five sizes of CdSe QDs. The fluorescence quenching of CdSe QDs was found to be size-dependent for both commercially available and synthesized QDs (Table 6.6). K_Q is the quenching constant.
Table 6.6: Quenching constants for fluorescence quenching of QDs with all 3 sizes of Pd nanoparticles

<table>
<thead>
<tr>
<th>Size of the Pd NP</th>
<th>$K_{Q/QD(2.1-2.3 \text{ nm})}/\text{M}^{-1}$</th>
<th>$K_{Q/QD(2.4-2.6 \text{ nm})}/\text{M}^{-1}$</th>
<th>$K_{Q/QD(3.0-3.5 \text{ nm})}/\text{M}^{-1}$</th>
<th>$K_{Q/QD(3.5-4.0 \text{ nm})}/\text{M}^{-1}$</th>
<th>$K_{Q/QD(6.2-7.7 \text{ nm})}/\text{M}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9 nm</td>
<td>2313.2</td>
<td>2739.6</td>
<td>2560.8</td>
<td>7277.8</td>
<td>326000</td>
</tr>
<tr>
<td>2.3 nm</td>
<td>2118.1</td>
<td>2807.9</td>
<td>3295.4</td>
<td>5350.1</td>
<td>230000</td>
</tr>
<tr>
<td>2.5 nm</td>
<td>2095.9</td>
<td>1995.6</td>
<td>3602.4</td>
<td>3279.9</td>
<td>172000</td>
</tr>
</tbody>
</table>

The results showed that smaller Pd nanoparticles were more efficient in quenching the fluorescence of a majority of CdSe QDs compared to larger particles. The fluorescence lifetime measurements showed upward curvature due to competition between radiative recombination of electrons and holes with the dynamic quenching. The UV-visible absorbance results showed that the formation of a non-fluorescent complex is also improbable. The results rather indicated that the fluorescence quenching of the QDs by Pd is due to energy transfer between CdSe QDs and Pd nanoparticles and the results are consistent with an NSET mechanism.

6.4 Fluorescent quenching mechanisms

The fluorescence quenching of fluorophores caused by Pd nanoparticles can be considered to be due to an energy transfer mechanism rather than an electron transfer
mechanism, because well-passivated Pd nanoparticles have a high barrier for electron transfer between the dye molecule and the nanoparticle. The most suitable energy transfer mechanism is nano surface energy transfer (NSET) which does not require a spectral overlap between the donor and the accepter. NSET does not need a resonant electronic transition as the fundamental process because it originates from the interaction between an electromagnetic field of a donor molecule (which is a dipole) and the free electrons in the discrete electronic levels of the metal nanoparticle. Both fluorescent quenching and enhancement by Pd nanoparticles in the size range 1-3 nm is paramount for developing assemblies for next-generation materials, energy sensors and biological imaging.

6.5 Future work

The studies conducted and described in this dissertation have shown the luminescent quenching ability of Pd nanoparticles and that the interactions are dependent on the nanoparticle size. More mechanistic studies need to be conducted for confirmation of NSET as the literature is limited to only one type of nanoparticles, i.e. gold nanoparticles. It has been shown that the catalytic efficiency of semiconductor nanoparticles is greatly enhanced when coupled to metal nanoparticles such as Au and Pt. Therefore, charged Pd and Pt nanoparticles are potentially useful for many reactions such as the degradation of chemical pollutants, organic catalyzed reactions and water splitting for hydrogen production. These concepts will be the basis of future studies in our group.
6.6 References


Appendix

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