ULTRAFAST RELAXATION DYNAMICS IN GRAPHENE OXIDE-DYE AND PEROVSKITES NANOCOMPOSITES

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Western Michigan University, 2019

Novel materials such as graphene oxide (GO), reduced graphene oxide (RGO), and Perovskites nanocomposites nanosheets have shown interesting electrical and optical properties. These materials have shown prominence in research regarding optical sensing applications. The interaction of different fluorescent molecules like dye molecules with GO, and RGO have been studied recently to develop novel optical sensors, photo-catalysts, and light-harvesting agents. In this study, we have monitored the excited state interactions of dyes covalently attached to GO and RGO nanosheets. Three amine derivatives of anthracene, pyrene, and coumarin were covalently bound to different systems via amide bonds and diazotization. Characterization of different systems via TEM, infrared spectroscopy, and optical absorption measurements have shown that the dyes changed upon binding. The fluorescence of the dyes was quenched upon binding to GO and RGO; suggesting efficient excited-state interactions. Time-resolved fluorescence and ultrafast transient absorption measurements suggested charge-transfer interactions for the dyes when they are bound the systems. Ultrafast transient absorption decay traces supported by transient absorption anisotropy data shed light on charge transfer and energy transfer interactions. The results show that there is an efficient electron transfer from Anthracene to RGO with time constants of 230 fs and 2.1 ps. However, the charge recombination was found to be equally faster with time constants of 23 ps and 1 ns. Contrarily, electron transfer from RGO to pyrene was observed with a time constant of 3.5 ps.

Regarding cesium lead halide perovskites (CsPbX₃), we have synthesized and characterized CsPbX₃ perovskites that can form nanosheets at room temperature synthesis conditions and
nanocrystals at high temperatures. The synthesis has yielded highly luminescent perovskite with their absorption and luminescence being adjustable in the entire visible region by changing the halide composition from chloride to iodide. The photoluminescence (PL) was narrow for crystals while it is broader for nanosheets suggesting the presence of more surface states in nanosheets. Ultrafast luminescence upconversion luminescence measurements carried out for sheets, and crystals have shown that the luminescence decay is faster for nanosheets compared to nanocrystals, suggesting efficient leakage of charge carriers to surface states. On the other hand, femtosecond transient absorption measurements have shown similar transient features for both sheet and crystals forms with dominant excited state absorption and stimulated emission. We have probed the two-photon absorption (2PA) cross-sections of CsPb-halide perovskites using a two-photon excited fluorescence technique. The 2PA cross-sections were found to be in the order of $10^6$ GM for perovskites, while normal organic dye molecules have cross-sections reaching only 100 GM. The fact that these nanoperovskites can be easily made into thin films and increase in photostability makes these perovskites nanoarchitectures ideal for broadband optical sensor protection systems.

Our results have shown interesting large cross-sections for both sheets and crystals. The larger optical nonlinearities can be ascribed to greater number of freely moving excitons in perovskites. Synthesis of cesium lead halide perovskite nanocrystals at different reaction conditions using different ligands to improve the water solubility of such systems for biophoton imaging and luminescent biosensors application. To investigate block copolymers as ligands and shown increase the water solubility for some provskites.
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CHAPTER 1

INTRODUCTION AND BACKGROUND

1.1 The World of Nanomaterials

The definition of the word "nano" is best described for phenomena associated with molecules that possess size from 1 to 100 nm. Novel synthetic methodologies, fabrication approaches, and the ability to characterize them are what make the realm of nanoscience exciting and has given rise to the emerging fields such as nanoscience and nanotechnology. Nanoscience can be defined as the science of objects that are in-between the largest molecules and the smallest structures (e.g., atoms). In chemistry, this nano-size-range has associated with small in size molecules, for instance, colloids, and micelles, phase-separated regions in block copolymers. Nanomaterials have received marvelous interest in a wide range of applications areas, including catalysis, energy conversion, energy storage, electronics, plasmonic, photonics, and biomedicine because of their unique optical, electronic, chemical, and magnetic properties.

Moreover, nanomaterials are versatile and well-studied that most of their properties are strongly dependent on their size, shapes, compositions, and architectures. The fact that nanoparticles exist in the same size domain as proteins make nanomaterials suitable for bio-imaging, drug delivery, labeling, and may sophisticated medical applications. However, size is just one of many characteristics of nanoparticles that itself is not enough if one is to use nanoparticles. For instance, nanoparticles often interact with biological systems to be targeted, biological or molecular coatings.

One of the foremost application of nanomaterials is catalytic applications. The use of catalysts in chemical technology is of great importance; using a small number of reactants with high activities is predominantly desirable for economic and environmental considerations.
Due to the defined microporous, a high shape selectivity and activity characterize crystalline structures of the nanomaterials.\textsuperscript{15,1} The applications of nanomaterials are vast, and the next revolution in nanoscience and nanotechnology is primarily focused on one aspect – which is nanomaterials, precisely the optical properties of planar nano-architectures and perovskites. Before introducing these materials, it is important to know the different kinds known of nanomaterials.\textsuperscript{17-19}

1.2 Different kinds of nanomaterials

Nanomaterials are the backbone of nanoscience and nanotechnology; recent technological advances have developed different synthetic and fabrication routes to make nanomaterials. Nanostructure science is a broad interdisciplinary area of research among research communities and great amount of development activity has been ongoing toward tremendous potential development of new applications for different areas and use with unique capabilities. Here we will briefly mention and describe mention some nanomaterials which are actively investigated.\textsuperscript{20,21}

1.2.1 Carbon-based Nanomaterials

Owing to their unique properties are due to its allotropic characteristics, carbon and carbene-based nanomaterials are widely studied for different applications. Carbon is one of the most abundant and versatile elements in the universe and the only element which can form different compounds that have completely different properties depending on the arrangement of the adjacent carbon atoms. Exceptional carbon-based nanomaterials are amongst the utmost promising in nanotechnology and its applications. Currently in use include fullerenes, carbon nanotubes, graphene oxide, reduced graphene oxide, and graphene. Carbon-based nanomaterials demonstrate unique physical and chemical properties such as high strength, excellent resistance to corrosion, exceptional electrical & thermal conduction, and excellent stability. Because of these unique qualities, nano-carbon materials are used in a wide range of fields, including biology, energy storage, and medicine. Spherical and ellipsoidal carbon nanomaterials are referred to as fullerenes.\textsuperscript{23-27}
1.2.2 Metal Nanomaterials

Plasmon metal nanoparticles like gold and silver are the most dominant in research among the research communities. Others like platinum, palladium, nickel, and bi-metallic metal nanoparticles are also and have been well invested in the field of nanotechnology. These elements are beneficial in many different filed of application because of their different excited phenomena like size-dependent electrical, optical, magnetic, and chemical properties. This progress has facilitated the capacity for manipulation of material properties to optimize their functional utility. Subsequently, nanomaterials have proven useful in diverse applications ranging from pharmaceutics and energetics to transportation and electronics. Also, they are actively studied for use in many other applications including catalysis, plasmonic, fuel cells, biotechnology and biosensors.30-33

1.2.3 Dendrimers

Dendrimers are known to be molecules that have a multivalent branched structure with nanometer size. The surface of dendrimer has numerous chain ends, that can easily be targeted for different chemical functionalization. These exciting materials possess three different domains; a central core and branches Their terminal functional groups present at the outer surface of the dendrimers are also known to increase in size with an increase of branching. They also have different applications. Examples include luminescent dendritic architectures, light-harvesting, catalytic and drug delivery.34-38

1.2.4 Composite Nanoparticles

Composites nanoparticles combine nanoparticles together to make bulk-type materials. Composite nanoparticles such as nanosized clays are already being used in many commercial products ranging from the automotive parts to packaging materials, Composites are used to enhance mechanical efficiency, and improve thermal retention, and flame-retardant properties. These unique properties give rise to novel electrical, catalytic, magnetic, mechanical, thermal, and imaging features that are highly desirable for applications in the commercial, medical, military, and environmental sectors. As new uses for materials are identified, the number of products containing such nanomaterials and their possible applications continues to grow.39,40
1.3 Planar Nanoarchitectures

1.3.1 Graphene Oxide

Graphene oxide is a unique carbon-based material; consists of a single layer of graphite oxide. It is usually produced by oxidation of graphite, dispersion, and exfoliation in water or polar organic solvents. It possesses a two-dimensional structure with a large surface area comprising single-layer sheets of sp²-hybridized carbon atoms, and sp³ carbon sites where there are oxygen hydrophilic functional groups. Projected structural of GO have shown a flat aromatic region with unoxidized benzene rings and wrinkled regions of acyclic six-membered rings bearing alkenes, and alcohols.⁴⁰

In recent years graphene oxide has attracted enormous research interest mainly for its wild use and applications. This material can be applied in several applications that include low-cost, large-area, flexible, and/or lightweight electronics. Other uses include electronic displays, polymer composites, catalysts, energy-related materials, sensors, and bio-derivatives⁴². GO contains both aromatic (sp²) and aliphatic (sp³) domains which further expand the types of interactions that can occur on the surface. RGO is easily reduced to reduced GO at high yields.⁴³ The quality of the produced graphene oxide is suitable for electronic applications or mechanical support of polymers. Even though the chemistry of graphene oxide has been well studied, the exact structure of GO is difficult to determine. GO has a unique structure – a contiguous aromatic lattice of graphene is interrupted by epoxides, alcohols, ketone carbonyls, and carboxylic groups⁴⁴,⁴⁵. The disruption of the lattice is reflected in an increase in interlayer spacing from 0.335 nm for graphite to more than 0.625 nm for GO. The covalent oxygen functional groups in GO give rise to extraordinary mechanical strength, along with molecular-level chemical sensing capability.⁴⁶,⁴⁷ The presence of functional groups also implies modification of the graphene electronic structure. Therefore, the chemical composition of GO, which can be chemically, thermally, synthesis, allows tunability of its optoelectronic properties⁴⁸. Graphene oxide can be a semiconductor or insulator, depending on the degree of oxidation, its electronic and optical properties can be different. Like, the controllable optical and electronic properties enable graphene oxide to be used in many fields.⁴⁹,⁵⁰ Relativistic charge-carrier transports and other physical properties have been observed in graphene and its moieties. GO is known to be easily synthesizable in large amounts through oxidation of natural graphene, ease of processing, and its versatile properties make it attractive for fundamental research as well as for applications.⁵¹ GO is a highly versatile material for several reasons. Firstly,
natural graphite is ubiquitous and an inexpensive resource. Secondly, the yield of a monolayer of GO is sufficiently high (>80%). This is due to efficient exfoliation so that a very small amount of bulk raw material translates into atomically thin films with large surface areas. Thirdly, the process is conducted in solution phase, allowing ease of thin-film deposition or fabrication of paper like structures. Fourthly, chemical processes simplify the integration of GO into composites with polymeric or ceramic hosts. Furthermore, a recent study shows that GO with its unique structure naturally has significant pore volume, high conductivity, rich surface chemistry, and high-density-aspect ratios which make it a favorable tool to use for adsorption and catalysis of organic pollutants from wastewater.

As mentioned earlier in this dissertation, the functional groups on GO, especially, the carboxylic groups are available as active sites for any functionalization. Recent research primarily focuses on different chemical functionalization on the surface of GO. Different reagents have been used to modify the functional groups on GO. For instance, coupling reagents like acyl chlorides using thionyl chloride (SOCl₂) to make different functionalities on the surface of GO.

Figure 1.1. Schematic illustration of GO-based electrodes for electrochemical applications.

Recent studies have shown the use of functionalized GO in different fields including biological and biomedical applications. For example, targeted drug delivery, bioimaging, and photodynamic therapy. These are possible because of large proportions of hydrophobic drugs, which can be adsorbed on the surface of GO by non-covalent interactions. When GO binds to hydrophobic drugs they are slowly released to specific regions in organisms according to their
specificity of their covalent functionalization. Furthermore, GO is an electronically hybrid material that features both conducting $\pi$-states from $sp^2$ carbon sites and a large energy gap (carrier transport gap) between the $\sigma$-states of its $sp^3$-bonded carbons. Those features are powerful tools in manipulating its band gap and therefore can transform GO from an insulator to a powerful semiconductor.

Another application of graphene-based materials is in optical power limiting. Optical limiting is an essential application of nonlinear optics; it is useful for the protection of human eyes from intense laser pulses. An optical limiter is a material that sharply reduces high-intensity light such as focused laser beams. Simultaneously it allows high transmission of ambient light. Optical limiting properties of graphene and graphene-like-materials have been well studied. The optical limiting responses of functionalized graphene and graphene-like-moieties have shown to be dominated by nonlinear scattering through nonlinear absorption mechanisms. They also exhibit significant solution-concentration-dependent optical limiting responses. Therefore, many efforts have been invested in the research of such organic and inorganic polymers. Much research has been done regarding GO’s practicality in a composite application. Overall GO has shown to be excellent in uses for optical limiting applications. Moreover, chromophores: functionalized GO has been widely investigated in order to facilitate photo absorptivity in the case of photochemical devices and for nonlinear optical materials applications. Studies shown chromophores functionalized GO increase the photoinduced electron or energy transfer from the chromophore to the GO sheets.

1.3.2 Reduced Graphene Oxide (RGO)

Reduced graphene oxide (RGO) is the form of GO that is processed by chemical, thermal and other methods to reduce the oxygen content, while graphene oxide is a material produced by oxidation of graphite which leads to increased interlayer spacing and functionalization of the basal planes of graphite. Reduced Graphene oxide is one of the most exciting materials, due to its exceptional physical properties, as the extremely high charge carrier mobility. It can be used to fabricate electronic devices such as; transparent electrodes, solar cells and since RGO can be made as a thin film from an aqueous dispersion in water and has moderate conductivity. It is attractive to use as the basis of electroanalytical sensors; visible light transparent electrodes. Polymer
composite materials, energy storage, biomedical applications catalysis, and as a surfactant with some overlaps between these fields.\textsuperscript{79-81}

Recently researchers are trying to develop ways to revolutionize the production of RGO sheets to the highest quality. Among these chemical methods, reduction of GO in a large scale and low-cost method that has been used to convert insulating GO to conducting graphene-like layers, the most promising ways to produce electrically conducting graphene-based platelets. The degree of reduction of graphene oxide will significantly influence the physical properties of chemically reduced graphene oxide materials and is dependent on reaction conditions and reduction agents. For example, it is known that the carbon to atomic oxygen ratio and electrical conductivity of reduced graphene oxide varies depending on the chemical of the reductants.\textsuperscript{82-84}

Hydrazine reduction of GO sheets is well established, which include ring-opening of epoxy groups, and the initial derivative produced by the epoxide opening reacts further to form an aziridine moiety, which then undergoes thermal elimination of di-imide to form a double bond.\textsuperscript{85}

Extensive research has focused on engineer graphene-based nanocomposites for different applications; because the composites not only combine the advantages of each component but offer the potential to introduce new properties that can potentially be used in a diverse range of applications. Indeed, considerable effort has been devoted to fabricating composites of reduced graphene oxide as a two-dimensional (2D) scaffold and metal nanoparticles, semiconductor nanoparticles, or photoactive molecules as a viable alternate to boost the efficiency of various catalytic and storage reactions in energy conversion applications.\textsuperscript{85-88}

\textbf{Figure 1.2}. Schematic representation of the application of reduced graphene oxide.
Also, recent research studies demonstrate new photocatalytic strategies toward RGO with the use of different organic dyes and or metal nanoparticles as an effective photocatalyst different chemical reactions or as an active layer for light-harvesting devices.\textsuperscript{89-91}

Graphene and graphene moieties have been used to enhance the Raman signal of target molecules. The ability of graphene to adsorb and concentrate target molecules makes it an attractive candidate for selective SERS sensing where molecule–graphene interaction controls the magnitude of SERS enhancement. This ability has prompted the design of graphene composites for sensing, electron transfer, and concentration of molecular species targeted for photocatalytic degradation. Selective SERS sensing through adsorption and complexation with target molecules is possible using graphene and graphene derivatives. Previous work has made use of functionalized graphene oxide for SERS sensing\textsuperscript{92-95}. A recent approach has used the advantage of the intrinsic ability of RGO to adsorb and complex with molecular species to enhanced SERS sensing.\textsuperscript{96}

Overall, GO and RGO nanocomposites have revolutionized the field of carbon-based materials and these 1D nanoarchitectures for their unique structure and versatile applications.

1.3.3 Perovskite Nanoarchitectures

Due to the increasing demand for energy due to the world's growing population and development. The need for new materials that can offer low cost and green energy has been the focus of scientific researches. It is essential to develop alternative clean energy sources that can fulfill the energy demand. One of these energy harvesting devices created with the intent of increasing energy efficiency is photovoltaic solar cells. Early photovoltaic cells and the most commercially available cells were all silicon-based single-crystal devices, which offer about 15% energy efficiency.\textsuperscript{97,98} The biggest collapse of these silicon-based devices is the high installation and manufacturing costs. Attempts at manufacturing cheaper photovoltaic cells with polycrystalline semiconductor thin films proved successful in decreasing the manufacturing price. However, the efficiency of such devices was too low to bring to the market.

Current studies aim to find photovoltaic devices that improve energy efficiency and engineering cost-effective materials. Among the forefront of these studies are nanomaterials\textsuperscript{99}. Semiconductor nanocrystals have been of increasing interest due to their applications in optics and electronics. These types of nanocrystals seem to be capable of low cost, scalable and robust power
generation. Due to this, much attention has been put into fine-tuning nanocrystals to give ideal power efficiency. Furthermore, all the properties determined as essential for improving the efficient design of electronic processes are (QD material, size, mode of attachment, and surface treatments). These properties allow for these nanocrystals to have other fascinating applications in many optoelectronic devices such as phototransistors, LEDs, Lasers, and more. A major problem with semiconducting NCs like SiNC, TiO$_2$, and CdSe is their trap states, which trap charge carriers between the electronic bands, decreasing the overall efficiency of optoelectronic processes. While these trap states are not able to be removed entirely, it is possible to shift energy levels, such that these trap states are in or near the valence band maximum or the conduction band minimum.$^{100,101}$

Recent years have seen multiple reports demonstrating outstanding optoelectronic characteristics of metal halide semiconductors with perovskite crystal structures, in the form of thin films, microcrystals, and bulk single-crystal Metal halide perovskites have fascinated the research community in short period of time. This is because of its strong optical absorption, light carrier masses, and consequence, high charge-carrier mobility, which then can be employed as absorber layers in highly efficient photovoltaic (PV) devices. Therefore, making them one of the best candidates for next-generation optoelectronic devices.$^{99-100}$ Other applications including light-emitting diodes, lasers, and photodetectors. This is a result of the unique combination of properties, including strong optical absorption, long diffusion lengths, and solution processability. Additionally, their broad, adjustable bandgap makes perovskites highly attractive for use in multijunction solar cells on top of the narrower-band gap, such as silicon, copper indium gallium selenide and Sn-containing perovskites$^{101-104}$. Perovskites typically adopt a 3D crystal structure composed of three primary ions with a stoichiometry of ABX$_3$. For the all-inorganic compounds, cesium is the A-cation, and either lead or tin is the B cation, with halides of chlorine, bromine or iodine as the X anion. The ‘hybrid’ perovskite compounds, which have shown most promise so far, have either methylammonium (MA) or formamidine (FA) as the A cation. Some of the most active and stable compounds even have multiple mixtures of ions at the A and X sites$^{105-107}$. 


Recent reports on the organometal halide-based perovskite for high-efficiency photovoltaics have demonstrated this class of materials to be excellent semiconductors for optoelectronic devices. Their primary advantages are based on the fact they can be solution-processed easily with no high-temperature treatment. They also possess an optical bandgap that is adjustable in visible infrared regions. This makes them very attractive materials for use in low-cost and large-scale optoelectronic applications.

Perovskites are known for their useful strong photoluminescent properties. This makes them great candidates for use in light-emitting devices. Previous attempts have been made to fabricate light-emitting devices using related perovskite materials. However, electroluminescence could only be achieved by using liquid-nitrogen cooling, rendering the devices impractical for common applications\textsuperscript{108-110}. Photoluminescence (PL) of CsPbX\textsubscript{3} NCs is characterized by narrow emission line widths of 12–42 nm, high quantum yields of 50–90%, and short radiative lifetimes of 1–29 ns\textsuperscript{111,112}. The electronic structure, optical, and magnetic properties of materials can be adjusted by varying the size of the crystal. Thus, leading to new useful findings, such as superparamagnetic of magnetic NCs, size-dependent bandgap of semiconductor NCs. These interesting new materials are new opportunities for device applications\textsuperscript{113}. Currently, synthetic protocols for colloidal CsPbX\textsubscript{3} NCs have demonstrated the ability to precisely control the size, shape, and compositions of the nanocrystals to adjust the size of their respective band gaps\textsuperscript{114-116}.

In general, the properties that make perovskites such remarkable semiconductors are not fully understood. By understanding these properties, we will be able to know how to control them in order to achieve long-term stability. A key principle to this control is understanding perovskite's strong optical absorption abilities. Extensive research has been done regarding
perovskite-based nanomaterials. Perovskite cells have shown to be applicable in other industries, here we will briefly explain their optical applications.

1.4 Optical Applications of Nanoarchitectures

1.4.1 Solar Cells, Optical Sensors, Light-emitting Diodes

Nanomaterials have unique properties and functionalities that differ substantially from their bulk counterparts. For instance, the quantum confinement effect of nanomaterials yields a significant change in the optical properties of semiconductor nanomaterials. This is largely due to the very large surface-to-volume (S/V) ratio of this nanomaterials\textsuperscript{121}. Also, parameters such as size, shape, and surface characteristics can be manipulated in order to yield products used in various practical applications\textsuperscript{122}.

Nanomaterial research in the field of energy conversion has been shown to greatly improve energy storage capacity in a short timeframe. Applications like solar-cells are the key to improving their overall efficiency and production of these materials. For example, nanomaterials are used in semiconductor nanostructures components, which include arrays of intermediate materials (e.g. semiconductor nanocrystals used in multiple exciton generation, antenna–rectifier cells, and effective optical frequency rectification). Nonetheless, nanomaterials application in optical technology has contributed to the development of novel renewable photoelectric conversion technologies and shows as a potential alternative to the traditional photovoltaic devices (e.g. dye-sensitized solar cells). This potential for the proliferation of nanomaterials is due the recent advancements in production efficiency\textsuperscript{123,124}.

The evolution of fluorescent nanomaterials with adjustable optical properties has given rise to the creation and proliferation of LEDs. This was only possible due to the use of semiconductor nanocrystals, colloidal quantum dots (QDs), carbon-based nanomaterials, silicon QDs, and organic-inorganic fluorescent nanocomposites\textsuperscript{125,126}.

Colloidal semiconductor nanocrystals (QDs) have unique characteristics such as narrow emission spectral bandwidth, high photoluminescence quantum yields (PL QYs), as well as size-adjustability of the bandgap for practical optical properties\textsuperscript{127,128}. Furthermore, colloidal semiconductor nanocrystals are promising luminophores for creating a new generation of electroluminescence devices. Advances include external quantum efficiency which has vastly improved in recent decades. When comparing to purely organic LEDs colloidal semiconductor
nanocrystals are more than an order of magnitude higher in luminesce than those of the purely organic LEDs. Advantages of nanocrystals, when compared to organic LEDs, include narrow emission peaks and adjustable bandgap. Other application-based uses include nanocrystal-based LEDs, which can improve material stability.\textsuperscript{129}

1.4.2 Biosensing and Biotechnology

Regarding the industry of biosensing and biotechnology, active research has shown the many practical uses of metal nanoparticles and nanomaterials. This is due to their notable properties which are gaining prominence in the areas of biosensing, biomedical sciences, the pharmaceutical industry, catalysis, and drug-gene delivery.\textsuperscript{130-132}

Other applications include medical imaging, nanocomposites, and uses in oncological treatments.\textsuperscript{132} Common nanocomposites include gold (AuNP) and silver bound (AgNP) nanocomposites. These nanocomposites can be manipulated as effective platforms for targeted drug delivery and imaging labels. In uses for in-vitro and ex-vivo applications, there are significant advantages for these nanodevices (e.g. nanosensors) over traditional methods\textsuperscript{133}. Recent research in the use of AuNPs in treating cancer has shown to be tremendously in mitigating the proliferation of cancer cells\textsuperscript{134-136}. This has shown to be much more effective as compared to traditional radiological treatments. Knowing the many uses of nanoparticles in bio-sensing applications other potential uses include bio-recognition systems. Nanoparticles have shown prominence in biosensing systems. Applications include bioprocesses, quality control of foodstuffs, and many healthcare applications. A great advantage of biosensing NPs is label-free detection of target molecules, this is achieved by their analogous size compared the organic molecules such as enzymes and proteins they are detecting.\textsuperscript{137}

1.4.3 Optical Sensors and Detectors

Nanoparticles have shown prominence in optical sensor applications. Research has shown uses in detecting the presence of pollutants, toxic materials, metal cations, and metal anions is often carried using semiconductor nanomaterials either by their electronic properties or optical properties. Notably, researchers have used the luminescent behavior of nanoparticles to develop specific optical sensors that can be used in different disciplines of science and engineering. Semiconductor nanoparticles or metal oxides (e.g. TiO\textsubscript{2}, SnO\textsubscript{2}, and ZnO) have been used for the detection of toxic pollutants and combustible gases due to their rapid response time and other
Another key aspect of nanoparticles is their use in optical detectors, especially in terms of high-frequency radiation; one reason for their use is their range of detectable wavelengths, because of their energy band gaps, along with the optoelectronic properties. The basics of optical detectors lie within classical analytical and optical spectroscopy.\textsuperscript{138-140}

### 1.5 The gap in the Field

With new nanoarchitectures being developed for many applications, recently significant research on GO, RGO, and perovskite nanomaterials have gained major prominence. GO, RGO, and perovskites offer excellent surface functionalization capabilities, electrical conductivity, optical sensing capabilities, optical limiting capabilities, and photocatalytic applications. However, not much effort has focused on synthesizing novel chromophore-functionalized architectures. A goal this research goal is to develop novel linear and nonlinear optically active GO and RGO architectures via covalent binding of organic chromophores by studying their excited state relaxation dynamics. Although perovskite nanomaterials have been used for optical applications, several questions remain to be understood regarding their exciton, biexciton dynamics, their interaction with metal nanoparticles, and so on. The work carried out in this dissertation is aimed at addressing these gaps in the field that can aid researchers in designing more efficient optoelectronic devices.

### 1.6 Aim and Objective of the Dissertation

The main goal of this dissertation is to study the excited state relaxation dynamics in novel 1D & 2D nanoarchitectures and 3D perovskite nanomaterials. Objectives include: (i) Synthesize, characterize the optical properties of chromophore-functionalized GO nanoarchitectures. (ii) Synthesize, characterize, and monitor the excited state relaxation dynamics in chromophore-functionalized RGO nanoarchitectures, (iii) Probing intrinsic exciton relaxation dynamics in perovskites and follow their interactions with metal nanoparticles. These studies can shed light on the fundamental excited state interactions.

### 1.7 Scope of the Dissertation

Chapter 1 introduces the realm of nanomaterials. The chapter briefly touches on several classes of nanomaterials including carbon-based nanomaterials and perovskites. Optical applications of
nanomaterials are also discussed that include applications in solar cells, light emitting diodes, and sensors.

Chapter 2 describes the experimental techniques used for monitoring the optical properties and charge carrier dynamics of functionalized graphene oxide, functionalized reduced graphene oxide and perovskites nanocrystals. A brief introduction to lasers and laser spectroscopic techniques is provided with an emphasis on time-resolved luminescence and transient absorption techniques that were used to monitor the excited state dynamics.

Chapter 3 is aimed at understanding the dynamics of charge carriers in their behavior between excited state relaxation in graphene oxide and chromophore-functionalized graphene oxide. The synthesis, characterization of graphene oxide, and dye-graphene oxide composites is presented. Steady-state absorption, fluorescence and time-resolved fluorescence decays of free dyes, and dye-functionalized graphene oxide is presented. Finally, the excited state relaxation dynamics of free dyes, and graphene oxide-dye composites is presented. The results point to ultrafast energy transfer from graphene oxide to attached dye molecules with infrequent partial electron transfer quenching.

Chapter 4 is focused on understanding the charge transfer and excited-state dynamics in chromophore-functionalized RGO. Here GO was reduced by hydrazine to form RGO and characterized using FTIR and TEM. Dye-functionalized RGO was also synthesized via the formation of C-C bond between the dye and RGO. Optical absorption and steady-state fluorescence measurements have shown that the dye was bound with significant changes to their ground state optical properties. Transient absorption studies have shown efficient electron transfer from RGO to Pyrene with electron transfer being observed from anthracene and coumarin to RGO. Interesting ultrafast electron transfer from the dyes to RGO was observed. However, faster charge recombination was seen in addition to some charge separation. The studies shed light on the fundamental electron transfer processes in dye-functionalized RGO nanocomposites.

Chapter 5 presents synthesis of perovskite-based nanocrystals and characterizing them using UV/Vis absorption, steady-state photoluminescence, time-resolved photoluminescence, and TEM measurements. Ultrafast charge carrier relaxation dynamics in these perovskite nanomaterials was studied with power-dependent transient absorption as well as transient absorption anisotropy. Interesting exciton thermalization, biexciton decay was observed in all cases. For the first time we are able to show transient absorption anisotropy can accurately monitor biexciton decay in cubic and elongated perovskite nanostructures. Two-photon absorption cross-sections of perovskite
nanostructures is also presented in this chapter. Here we also discuss efforts to increase the solubility of perovskite nanostructures.

Chapter 6 deals with the interaction of perovskite nanomaterials with plasmonic nanoparticles. The aim of the Chapter is to see if plasmon enhanced photoluminescence is possible from perovskite nanocomposites. Perovskite nanoparticles include gold and silver nanoparticles. These were synthesized using optical absorption spectroscopy. In addition optical absorption, steady-state and time-resolved photoluminescence measurements have shown interesting interactions of perovskites with gold and silver nanoparticles. Synthesis and characterization of metal-doped perovskites is also presented in this chapter.

1.8 References


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CHAPTER 2

EXPERIMENTAL TECHNIQUES

2.1. Introduction

The Analytical optical spectroscopy techniques were used to understand the optical properties of investigated systems; GO, RGO, and Perovskite nanostructures. These techniques include; optical absorption, steady-state fluorescence, time-resolved fluorescence, and time-resolved absorption techniques. Optical absorption and fluorescence measurement help understand the energy shifts as a function of particle size and can also probe the electronic transitions of semiconductors with adsorbates. Ultrafast Fluorescence measurements by means of laser spectroscopy are used to monitor complex charge carrier dynamics in semiconductor architectures.

2.2 Steady-State Methods

2.2.1 Optical Absorption Measurements

Optical absorption (electronic absorption spectroscopy, UV-Vis) spectroscopy can reveal information about the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) transitions in molecules as well as band edge absorptions. This is based on the structure and environment of the sample being analyzed\(^1\)-\(^3\). All absorbance measurements were recorded on a Shimadzu UV 2101 PC absorption spectrometer. The absorbance \(A\) of an absorbance species is related to the concentration \(C\) and molar extinction coefficient \(\varepsilon_\lambda\) a wavelength \(\lambda\) by the following equation:

\[
A = \log \left( \frac{I_0}{I} \right) = \varepsilon_\lambda C l 
\]  

(2.1)

where \(I_0\) (incident light) and \(I\) (the transmitted light). \(l\) is the path length of the light beam that is passing throughout the cuvette (quartz). All the measurements were carried out at \(l = 0.4\) cm.
2.2.2 One Photon Fluorescence Measurements

Fluorescence spectroscopy is a complimentary technique to UV-Vis absorption. Fluorescence spectroscopy is more sensitive and provides precision data regarding the identity of the molecule or semiconductor after photo-excitation\(^1\)\(^-\)\(^5\). Fluorescence or emission from semiconductor nanomaterials provides important information about the dynamics of charge carriers which is the main focus of this dissertation. Steady-state emission spectra were recorded on an Edinburgh F900 spectrofluorimeter comprising of a xenon lamp as the excitation source. Excitation and emission monochromators (M300) were used to avoid interference from the excitation and scattered radiation. A Hamamatsu R955P was used as the detector which enabled data acquisition through a photon counting scalar card (PCS900). Steady-state emission spectroscopy is used to record the band edge as well as trap state luminescence in semiconductor nanostructures. Molecules or materials absorb light energy leading to the excitation of an electron from a low energy state to a high energy state. States were seen to change either radiatively or non-radiatively\(^1\)\(^-\)\(^3\). The fluorescence of the compounds is quantified by the excitation and emission peaks; here the difference in the wavelength maxima of the two readings is the Stokes’ shift (\(\Delta \nu\), cm\(^{-1}\)) given by the following expression.

\[
\Delta \nu = \frac{1}{\lambda_{\text{abs(max)}}} - \frac{1}{\lambda_{\text{em(max)}}}
\]  

\(\lambda_{\text{abs}}\) (max) and \(\lambda_{\text{em}}\) (max) represent the maximum absorbance in cm\(^{-1}\).

2.3 Time-Resolved Measurements

Time-resolved optical characterization with femtosecond time resolution needs high-intensity laser light sources for excitation. Here a brief introduction to lasers and harmonic generation is provided here.

2.4 LASER

A laser is defined by (Light Amplification by Stimulated Emission Radiation) and can be created when the electrons emit radiation after excitation by a current. These redactions are all at the same wavelength and coherent. The ordinary visible light comprises multiple wavelengths and is not coherent, which makes a very intense light source with unique characteristics. This allows for use
in studying many things for various applications. One important application is its use to study nonlinear optical (NLO) properties of materials. The uniqueness of NLO materials lies within the attainability of the non-linear polarization from a laser source. Second-harmonic generation (SHG) is the generation of higher energy light from produced from a ruby laser source passing through a quartz crystal.\textsuperscript{4,16-18}

![LASAR Light Emission Process](image)

**Figure 2.1** LASAR Light Emission Process.

There are several components are essential and needed to create the laser. Which of those include an optical resonator which contains the gain medium (active medium) and the external pumping source to achieve population inversion. The main component of the laser is the gain medium where the lasing action occurs; it contains a collection of atoms and molecules which absorb and emit light\textsuperscript{4-18}

The emission is an essential component of lasing action where the emission of radiation is stimulated by another photon leading to two photons of the same wavelength, direction, and polarization. To achieve this stimulated emission, population inversion is very important to achieve by an external source of energy called the pumping mechanism to populate a specific energy level of the laser. The pumping source can be an electrical current or optical excitation\textsuperscript{4-18,23}. All the lasers used in this study have optical pump sources.
2.4.1 Monochromatic Light Source
In general, a light source achieves monochromaticity once it possesses one single wavelength with a narrow bandwidth. This property gives a laser beam sources its unique characteristics. However, no laser can be monochromatic due to the uncertainty of light but can produce pure wavelengths of narrow bandwidths. Monochromaticity is inversely proportional to the line, which depends on the nature of the source and the gain medium. Several laser sources produce an array of bandwidth ranges.\textsuperscript{20-22}

2.4.2 Coherence
One unique property of laser radiation is high coherence, which means the waves of light emitted have a constant relative phase. This occurs when stimulated emission that causes the emitted photons to be in phase as shown in Figure 2.2. This will allow lasers to possess a definite phase relationship to one another which can be in the form of temporal coherence and spatial coherence which are independent of each other.\textsuperscript{18-23}

![Figure 2.2 Emitted light having coherence after passing a wavelength filter](image)

2.4.3 Directionality
Laser light is highly directional, which implies laser light has a small divergence. The light beam divergence angle dictates the directionality. The brightness of the laser is dependent on its directionality. The active material is placed in a resonant cavity, and the emission wave, which
propagates along the cavity was sustained. This can be attributed to the partial coherence due to divergence being diffraction-limited, it allows the laser collimation properties to be credible. The brightness of the light is due to a given source of electromagnetic waves defining it as power emitted per unit surface area, per unit of solid angle.

2.4.4 Short Pulse Capability

One of the most useful properties of the laser radiation for time-resolved spectroscopy is the ultra-short capability of the laser pulses, which makes it a great candidate for interrogating phenomenon happening at fast time scales. A significant breakthrough in short-pulse lasers involves the mode-locking technique. This technique of lasers allows for beams of light to be produced in pico and femtoseconds, these lasers are often referred to as femtosecond lasers. These types of lasers can be used in various applications including the medical field and applications. Fast laser pulse or short time duration is an imperative component of a laser, which is made possible by other subcomponents of the laser such as the Q-switching and cavity dumping.

![Figure 2.3 Directionality of the beam displaying minor divergence of compact light waves](image)

![Figure 2.4 Schematic displaying locked signal of modes aligned in fixed position in three phase longitudinal modes](image)
If we consider 2n+1 equivalent modes with an amplitude $E_0$, the energy of a beam can be expressed as:

$$E(t) = \sum_{q=-n}^{n} E_q e^{i[(\omega_0 + q\Delta\omega)t + \varphi_q]}$$

(2.3)

where, $E_q$ is the amplitude of the $q^{th}$ mode, $\omega_0$ us the frequency of the central mode, $\Delta\omega$ is the angular frequency spacing in between the modes, and $\varphi_q$ is the phase of the $q^{th}$ mode. Essentially, this equation includes the summation of all modes, but with equal amplitudes, $E_0$, and constant successive modes, $\varphi_q - \varphi_{q-1} = \text{constant}$, then the present equation will reduce to

$$E(t) = E_0 e^{i\omega_0 t} \sum_{q=-n}^{n} E_q e^{iq\Delta\omega t}$$

(2.4)

It can be rearranged as

$$E(t) = A(t) e^{i\omega_0 t}$$

(2.5)

where $A(t)$ is given by:

$$A(t) = E_0 \sum_{q=-n}^{n} e^{iq\Delta\omega t}$$

(2.6)

$q$ has variation from $-n$ to $n$ and a geometrical progression lies within expression $e^{iq\Delta\omega t}$ allow us to express the term as:

$$I(t) \propto [A(t)]^2 = \frac{\sin^2[(2n+1)\Delta\omega t/2]}{\sin^2(\Delta\omega t/2)}$$

(2.7)

where the intensity is given as a function of time. Substantially the following equation corresponds to a periodic function where high signal peaks emerge equivalently with leaks of uneven peaks lying in between them. The period (T) is given by the function $2\pi/\Delta\omega$ and the pulse duration $\Delta t$ can be expressed as:

$$2\pi/(2n + 1) = 1/\Delta\nu$$

(2.8)
In which $\Delta v$ is the full width of the generation band. With varying amplitudes, the integration of the equation with infinite limits is given as:

$$A(t) = \int E_q e^{i q \Delta \omega t} dq$$  \hspace{1cm} (2.9)

This equation is representative of an integral from a Fourier transform function denoting the amplitude of a multi-mode output set by the transform of an amplitude distribution of modes in the frequency domain, all within the time domain. If the mode-locking of a continuum of oscillation modes with a Gaussian distribution of amplitudes will display Gaussian pulses represented by the equation:

$$I(t) = \alpha [A(t)]^2 \approx \exp \left[ -\ln 2 \left( \frac{2t}{\Delta \tau_p} \right)^2 \right]$$  \hspace{1cm} (2.10)

with the period ($\tau$) expressed as

$$\Delta \tau_p = \frac{2 \ln 2}{\pi \Delta v} = \frac{0.411}{\Delta v}$$  \hspace{1cm} (2.11)

$\Delta \tau_p$ and $\Delta v$ are relative and $\Delta v$ is composed of the equation:

$$\Delta v = \frac{\Delta \lambda c}{\lambda_0^2}$$  \hspace{1cm} (2.12)

Here $\lambda_0$ is the wavelength at maximum amplitude, $\Delta \lambda$ is the full width at half maximum and $c$ is the speed of light in nanometer per second. Thus, the short pulse duration is achieved from the superposition of several waves leading to constructive interference at one place which leads to short-pulse laser generation and frequency distribution of $\Delta v$ and short pulse duration would be achieved. Self-mode-locking is often seen with Ti: Sapphire laser which is used for all the investigations. This is obtained by the fact that there is an intensity-dependent change in the refractive index making the Ti: Sapphire crystal to act as a soft aperture creating mode locking to
generate 100 fs pulses. With the short pulses obtained from Ti:Sapphire laser, various time-resolved measurements were carried out.

2.5 Nonlinear Optical Properties and Time-resolved Spectroscopy

The nonlinear optical phenomenon is one of the important phenomena that make use of unique properties of laser radiation. In 1961 Peter Franken and his colleagues at the University of Michigan used laser radiation to produce harmonics. More importantly, nonlinear effects such as laser frequency conversion have been developed in using advanced applications that yielded technologies for generating varying wavelengths from a single frequency. This is especially important for the studies carried out here because different excitation wavelengths were derived from one specific UV region. Techniques which are used to generate different frequencies include: frequency mixing, optical parametric amplification (OPA), optical parametric oscillation (OPO), harmonic generation, and third harmonic generation that were used widely for the experiments carried out here.31-43

To fully understand NLO it is imperative to understand Maxwell’s equation of electromagnetism. Maxwell’s equation can be applied to all known materials. Maxwell equations relate the current density of the electric field by the conductivity, and the electric displacement to the electric field through the permittivity.

\[ D = \varepsilon \cdot E \]  
\[ (2.13) \]

Where \( \varepsilon \) is the permittivity tensor. Usually, one can factor \( \varepsilon \) into \( \varepsilon = \varepsilon_0 \varepsilon_r \) where the permittivity of free space \( \varepsilon_0 \), the relative permittivity \( \varepsilon_r \).

\[ D \equiv \varepsilon_0 E + P \]  
\[ (2.14) \]

where \( P \) is the polarization that is given by the electric dipole moment per unit volume (plus terms involving gradients of densities of higher electric multiple moments which seldom need to be considered and here disregarded. If we combine the equations, \( P \) can be reorganized as:

\[ P = \varepsilon_0 (\varepsilon_r - 1) \cdot E \equiv \varepsilon_0 \chi \cdot E \]  
\[ (2.15) \]
we can define the electric susceptibility tensor $\chi_n$. Within all linear materials, the response and stimulus are always proportional. For example, induced polarization is proportional to the field and the susceptibility is independent of the field (always the case in practice at sufficiently low fields.) In high fields the polarization no longer is proportional to the field, so then susceptibility will depend on the field. From this we can then have a nonlinear response, which can be given by:

$$P/\varepsilon_0 = \chi^{(1)}:E + \chi^{(2)}:EE + \chi^{(3)}$$

(2.16)

where $P$, induced by an electric field, is proportional to electric field $E$. $\chi^{(1)}$ is the susceptibility tensor, $\chi^{(2)}$ the quadratic susceptibility tensor and $\chi^{(3)}$ the cubic susceptibility tensor. However, in practice, terms beyond cubic are not normally required.\textsuperscript{23,31,32,33} The quadratic susceptibility $\chi^{(2)}$ gives rise to second harmonic generation (SHG) in non-centrosymmetric materials, the cubic susceptibility $\chi^{(3)}$ give rise to third-harmonic generation (THG) and following higher orders of nonlinear susceptibilities.\textsuperscript{23-33} For a harmonic generation, it is important for the angular momentum should be conserved.

2.6 Ultrafast Laser Spectroscopic Techniques

The analytical practices of ultrafast lifetime spectroscopic techniques have become an interdisciplinary area of research that incorporates the mechanistic and kinetic analyses associated with charge carrier dynamics of different chemical systems to be recorded using femtosecond, picosecond, and nanosecond time scales.\textsuperscript{34,35} Ultrafast spectroscopic techniques can be used in inorganic chemistry and solid-state physics. This allows for the probing of multi-excitation effects which measures the interaction of energies and the determination of relaxation dynamics of investigated materials. The idea behind these techniques is to excite the nanocomposite systems in a short time frame (e.g. nano, pico, and femo-seconds) with a light pulse and monitor the changes in their excited states with a second (delayed) laser pulse. Two main time-resolved laser techniques that are widely used are time-resolved fluorescence and time-resolved absorption. These can monitor the fluorescence and excited state absorption of different materials.
2.6.1 Femtosecond Fluorescence Spectroscopy

In this study, time-resolved fluorescence is monitored using time-correlated single-photon counting. Charge carrier dynamics in nanomaterials is high-speed; a technique that can measure these processes is necessary. One such time-resolved fluorescence technique is femtosecond fluorescence upconversion or a time-gated sum-frequency generation technique. The time resolution in fluorescence upconversion arises from the optical delay between the pump and the probe; this is not observed on the electronic response of the detectors. The pulse width of the laser limits Time-resolution. In the fluorescence upconversion set up, a gate pulse and a fluorescence signal is obtained from laser excitation and merged on a nonlinear crystal to generate an SFG signal (upconversion signal). This upconverted signal is monitored as a function of optical delay between the gate pulse and the fluorescence signal, monitoring the fluorescence decay process or emission decay processes23-37. Mathematically, the upconversion signal ($\omega_{sum}$) from the beta barium borate (BBO) crystals can be given by the following equation:

$$\omega_{sum} = \omega_{laser} + \omega_{fl}$$

(2.20)

where $\omega_{laser}$ and $\omega_{fl}$ are gate frequency and fluorescence frequency, respectively. This equation can be rewritten in terms of wavelengths as:

$$\frac{1}{\lambda_{sum}} = \frac{1}{\lambda_{laser}} + \frac{1}{\lambda_{fl}}$$

(2.21)

the function $\lambda_{sum}$ is the wavelength of the resulting sum-frequency signal, $\lambda_{laser}$, is the fundamental wavelength from the laser, and $\lambda_{fl}$ is the wavelength of the fluorescence signal. The radiated intensity of the up converted signal via sum-frequency signal is represented by the following equation:

$$I_{sum}(\tau) = \int_{-\infty}^{\infty} I_{fl}(t)I_{laser}(t-\tau)dt$$

(2.22)

The $\tau$ is the time delay between the fluorescence and the gating pulse and $t$ us the lifetime. The fluorescence upconversion system used in presented experiments was obtained from a CDP system. A schematic of the setup used for presented measurements is shown in Figure 2.5. Our system used both SHG and THG frequencies from a mode locked broadband Ti-Sapphire laser.
(Spectra Physics, Tsunami, 800 nm). The sample is continuously rotated with a rotating cell which is 1 mm thick to avoid the degradation of the sample. The fluorescence emitted from the sample was up converted in a nonlinear crystal of BBO with the pump beam at 800 nm, which first passed through a variable delay line. The instrument response was measured by the use of Raman scattering from water. A double monochromator with a photomultiplier tube was used to achieve the necessary resolution. Time-resolved fluorescence anisotropy measurements were carried out with parallel and perpendicular excitations whose polarization is changed with a Berek compensator. Fluorescence anisotropy ($r(t)$) is calculated from the traces obtained after parallel ($I_{\text{par}}$) and perpendicular ($I_{\text{per}}$) excitation with the following equation which is based on the ratio of the difference between parallel and perpendicular polarized emissions over magic angle fluorescence.

$$r(t) = \frac{I_{\text{par}}(t) - G I_{\text{per}}(t)}{I_{\text{par}}(t) + 2G I_{\text{per}}(t)}$$

(2.23)

where the G factor accounts for the differences in sensitivities for the detection of emission in the perpendicular and parallel polarized configurations. The G factor was obtained from the tail fitting of the anisotropy decays of perylene in methanol and Coumarin 485 in methanol.

![Second harmonic generation schematic of the fluorescence up conversion setup](image)

**Figure 2.5** Second harmonic generation schematic of the fluorescence up conversion setup that was used to carry out measurements presented in the dissertation. F1, F2, F3, F4 and F5 are filters. NC2 and NC3 are BBO crystals. ND is the neutral density filter. BS3 is the dichroic mirror. L3, L4, L5, L6 and L7 are lenses. PMT represents photomultiplier tube.
2.6.2 Ultrafast Transit Absorption Spectroscopy

To investigate the ultrafast phenomena and charge carrier dynamics in the investigated systems, transient absorption spectroscopy via pump-probe spectroscopy was done. Even in the pump-probe spectroscopy, time resolution is achieved via an optical delay between pump and the probe pulse. The pump beam excites the sample and probe beam monitors the excited state absorption. The change in absorbance ($\Delta A$) is monitored as a function of optical delay between the pump and probe beam as well as a function of wavelength. The given spectral readings may then be expressed in a three-dimensional view from which various data interpretations can be obtained. Figure 2.6

![Schematic diagram of transient absorption setup](image)

Figure 2.6 Schematic diagram of transient absorption setup. Spitfire generates amplified laser pulse at 800 nm. OPA is optical parametric amplifier. WLG is white light generation. CCD is the charge couple device.

Femtosecond transient absorption measurements were carried out at the Center for Nanoscale Materials, Argonne National Laboratory. A Spectra Physics Tsunami Ti:Sapphire set at 75 MHz was used to feed a 1.66 KHz Spectraphysics Spit-Fire Pro regenerative amplifier with a 100 fs pulsewidth. Ninety-five (95%) of the output from the amplifier is used to pump a TOPAS optical parametric amplifier. This is used to provide the pump beam in the Helios transient absorption setup (Ultrafast Systems). The remaining five percent (5%) of the amplifier is focused
onto a sapphire crystal to create a white light continuum that serves as the probe beam in our measurements (430 - 780 nm). The pump beam was depolarized and chopped at 833 Hz, and both pump and probe beams were overlapped in the sample.

Transient absorption spectral data includes three main features as shown in Figure 2.7. One is a positive feature which is called excited state absorption (ESA). ESA is positive as we are monitoring the excited states of molecules or materials that are created by photon excitation. The pump beam excites the sample and creates population in the excited state. The probe beam which produces a broad band of wavelengths can be absorbed by the excited state which reduces its intensity.

**Figure 2.7** Different processes present in the transient absorption spectra (A) Excited absorption (singlet-singlet), (B) Bleach and (C) stimulated emission.

The ESA of molecules or materials can be due to several reasons: it can be either due to singlet-singlet absorption or triplet-triplet absorption of charge carriers absorption; or cation/anion radical absorption. With time, the excited states or charge carriers relax and the change in absorption reduces thus monitoring the charge carrier dynamics\textsuperscript{38-42}. The secondary contribution to transient absorption signals is the stimulated emission which is a negative signal. Stimulated emission occurs from molecules or materials in which the emission is stimulated by the incoming probe photon. The light intensity is expected to be higher with the pump than without pump thus leading to negative change in absorption. Another contribution to transient absorption spectra is a negative signal is due to the bleach of the ground state. This is a negative signal because of the
following reasons: when the pump is not present, the probe beam would be absorbed significantly near the ground state absorption of the material. With the pump beam exciting the sample, a significant fraction of the ground state reaches the excited state. This is done when the probe beam monitoring the ground state absorption of the material. This leads to a negative change in absorbance. The way to differentiate the two negative absorptions, is by checking where the negative signal arises. If it arises at the absorption of the material, it is considered a bleach signal and if the negative signal’s wavelength matches that of emission spectrum it can be considered to be stimulated emission of the material.\textsuperscript{33-46}

2.7 References

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20. http://www.mrl.columbia.edu/ntm/level1/ch02/html/l1c02s02.html


3.1 Introduction

This dissertation is focused on understanding the excited state relaxation dynamics in 1D nanoarchitecture and at the interface of chromophores and 1D planar nanoarchitecture and 3D perovskite nanocomposites. One of the prominent 1D nanoarchitecture that has received enormous applications in recent years is based on Graphene Oxide (GO). This Chapter of the dissertation has focused on understanding the dynamics of excited-state relaxation in chromophore-functionalized GO nanoarchitectures.

Graphene-based materials hold strong potential for practical applications in nanoelectronics and are the most heavily studied materials. This single-atom-thick sheet of carbon atoms arrayed in a honeycomb pattern is the world’s thinnest, most active, and stiffest material, as well as being an excellent conductor of both heat and electricity. It is no wonder that this two-dimensional material is considered, from the application viewpoint, to be even more promising than other nanostructured carbon allotropes.\textsuperscript{1-4} A major focus of experimental research has been concentrated on the development of new synthetic routes for the fabrication of graphene-based nanomaterials. The major route towards the preparation of bulk quantities of graphene is via oxidation of the completely insoluble graphite to GO. It is the presence of numerous oxygenated species, carboxylic acids located at the peripheral edges as well as epoxy and hydroxy groups at the basal planes of GO sheets, which is responsible for the formation of stable aqueous dispersions of GO\textsuperscript{5,6}. GO has great nonlinear optical (NLO) properties that due to the significant absorption, ultrafast carrier dynamics.\textsuperscript{10-13}
To further improve processability and NLO performance, considerable efforts and significant progress have been made in the preparation of functionalized GO nanohybrids, as well as the exploration of their novel properties\textsuperscript{14,15}. One of the fascinating hybrid systems was a GO functionalized different nanoparticles and organic luminescent dyes, which has been elucidated to show photoelectrochemical behavior, photocatalytic activity, and dramatically enhanced NLO effects due to photoinduced electron/energy transfer process. Further, the promising applications of NLO are limiting optical materials or sensor protection and these are called optical limiters. Optical limiters are materials that strongly attenuate optical beams to the specific safe level intense irradiation while exhibiting linear transmittance at low laser energies. Since GO has noteworthy π-electron conjugation and several functional groups that make the material great for many applications, it is possible to attach dye molecules to make them active optical limiting materials. That can easily form a thin sheet. Also, these materials are also considered for applications in solar cells, LED and optical sensing. However, very few studies have focused on making chromophore-functionalized GO nanocomposites and in this study, we have synthesized chromophore-bound GO nanomaterials and studied the excited state relaxation dynamics. Three different luminescent organic dyes we wanted to investigate. Those dyes are for are shown in Figure 3.1. The carboxylic acid groups of GO can be bond to the amine group of the dye with the formation of an amide bond.\textsuperscript{16,17}

\begin{center}
\textbf{Figure 3.1.} Molecular structures of the dye molecules used in the study.
\end{center}
3.2 Experimental

3.2.1 Synthesis

3.2.1.1 Synthesis and Structural Characterization of GO

The synthesis procedure of GO was adopted from the synthetic methodology developed by Marcano et al.\textsuperscript{10}. For this synthesis, a concentrated \( \text{H}_2\text{SO}_4 \) (70 mL) was added to a mixture of graphite flakes (3.0 g) and \( \text{NaNO}_3 \) (1.5 g, 0.5 wt equiv), and the mixture was cooled using an ice bath to 0 °C. \( \text{KMnO}_4 \) (9.0 g) was added slowly in portions to keep the reaction temperature below 20 °C. The reaction was warmed to 35 °C and stirred for 7 h. Additional \( \text{KMnO}_4 \) (9.0 g, 3 wt equiv) was added in one portion, and the reaction was stirred for 12 h at 35 °C. The reaction mixture was cooled to room temperature and poured onto ice (∼400 mL) with 30% \( \text{H}_2\text{O}_2 \) (3 mL). The mixture was purified by vacuum filtration through filter paper of 0.45 Micron. The filtrate was washed three times with 200 mL of distilled water, and 200 mL of ethanol; for each wash. The material remaining after this extended, multiple- washing was vacuum-dried overnight at room temperature, obtaining 6.3 g of product.

3.2.1.2 Functionalization Graphene Oxide with Organic Dyes

We investigated three different dyes shown in Figure 3.1. The synthesis of dye-functionalized GO with amino dyes was adopted from the work of Bala Murali Krishna et al.\textsuperscript{11} and synthetic scheme in Figure 3.2. Briefly, Graphene Oxide (0.5 g) was suspended in \( \text{SOCl}_2 \) (30 mL) and 5 mL of DMF was added and refluxed at 70 °C for 24 h, under nitrogen atmosphere. The resultant solution was filtered and washed with anhydrous tetrahydrofuran (THF) and dried under vacuum, yielding acylated graphene oxide (GO–COCl) (0.495 g). Further a mixture of GO-COCI (30mg) and the Amino dye (1-Aminopyrene, 2-Aminoanthracene, and 7-Amino-4-(trifluoromethyl) coumarin 97% (60mg) were loaded into 100mL around bottom flask and (3mL) of Trimethylamine and (15mL) of DMF were added and the mixture was heated to 80 °C for 72 h under nitrogen atmosphere, and an additional 6 hrs of sonication to give a homogeneous black dispersion. After the reaction, the solution was cooled to room temperature, and then poured into diethyl ether (300 mL) to precipitate the product. The precipitate was collected by centrifuging at 8000 rpm for 0.5 hrs. The supernatant which contained dissolved Amino dye was discarded and the precipitate was washed thoroughly. After adding another 100 mL of diethyl ether, the mixture
was sonicated for 5 min and then centrifuged at 8000 rpm for 0.5 h to collect the Amino-dye–GO. Finally, the precipitate was washed with CHCl$_3$ five times following the above procedure.

Figure 3.2. Schematic representation of the synthetic for dye covalently attached to GO.
3.3 Methods

3.3.1 Optical Absorption and Steady-State Fluorescence

Optical absorption measurements were carried out in Shimadzu UV-2102PC spectrophotometer. An Edinburgh F900 spectrofluorometer, used to carry out steady-state luminescence measurements of GO-dye complexes.

3.3.2 Time-Resolved Fluorescence Upconversion

Time-resolved luminescence measurements of GO-dye complexes were studied using set femtosecond luminescence up-conversion spectroscopic technique. The upconversion system used in our experiments was obtained from CDP Instruments, Inc., Russia. Specifically, the system used third harmonic generation from the mode-locked broad band Ti-sapphire laser (Spectra Physics, Tsunami, 710 to 920 nm). The present measurements were carried out with 280 nm excitation (the fundamental of Ti:Sapphire was set at 840 nm). Polarization of the excitation beam for the magic angle luminescence and anisotropy measurements was controlled using a Berek compensator and the sample was continuously rotated with a rotating cell of 1 mm thickness. Horizontally polarized luminescence emitted from the sample was up-converted in a nonlinear crystal of $\beta$-barium borate using a pump beam at 800 nm, which first passed through a variable delay line. Instrument response function (IRF) was measured using the rise time of several dye molecules. Fitting the rise time of the luminescence traces gave a sigma value of $\sim$290 fs. Parallel and perpendicular decay traces were obtained from which the magic angle luminescence decay was calculated from these traces. Fitting of the luminescence decay traces were carried out with DecFit software. Spectral resolution was achieved using a double monochromator and photomultiplier tube. The excitation average power varied but was around 10 ± 0.3 mW. No degradation of the sample was observed as the traces overlapped after each repetition.

3.3.3 Transient Absorption Measurements

Transient absorption experiments were carried out at the Center for Nanoscale materials, Argonne National Laboratory.
3.3.4 FTIR and TEM measurements

The FTIR carried out using Thermo Science. Nicolet iS 5 FTIR Spectrometer at WMU, KBr pallet was used to measure the sample. TEM carried out at WMU imaging center using Joel 1400.

3.4 Results and Discussion

3.4.1 Characterization of GO and Dye-GO Architectures

TEM measurements were carried out to understand the sizes of the nanoarchitectures and corresponding data for GO and Dye-GO is shown in Figure 3.3. The left figure shows the TEM image of GO and a flaky 1D nanoarchitecture image can be seen. With Dye-functionalization, subtle variations are observed but overall structure remained same.

![Figure 3.3](image)

**Figure 3.3.** TEM images of GO and GO-dye. No significant changes in GO sheet structure was observed with binding of the dye.
Figure 3.4. FTIR spectra of GO and GO-Dye architectures. Absence of OH and new broad band emerge at 1620 cm$^{-1}$, which corresponding to the C=O characteristic band of amide group. The stretch band of amide C-N peak appears at 1290 cm$^{-1}$, indicating the successfully covalently bonded the two systems by an amide linkage. suggesting efficient excited state interactions.

Figure 3.4 shows the FTIR spectra of GO-dye and GO. In the spectrum of graphene oxide, the peak at 1730 cm$^{-1}$ was the characteristic C═O stretch of the carboxylic group on the GO. In the spectrum of GO-dye, the peak at 1730 cm$^{-1}$ almost disappeared and a new broadband emerged at 1620 cm$^{-1}$ corresponding to the characteristic stretching band of the amide group. The stretching band of amide C─N peak appeared at 1290 cm$^{-1}$. These results clearly indicated that the dye molecules are covalently bonded to the GO via the amide linkage. Figure 2 shows the FTIR spectra of GO.

### 3.4.2 Optical Absorption and Steady-state fluorescence Measurements

FTIR measurements have shown that dyes are covalently bound to GO. To understand the interaction of dyes with GO, optical absorption and steady-state luminescence measurements were carried out.
Figure 3.5. Optical absorption spectra of dye-NH$_2$, dye-GO and GO for (A) Anthracene, (B) Pyrene and (C) Coumarin. The excited state interaction in the binding systems suggesting efficient excited state interactions. Shown in parts A, B and C of Figure 3.5 are the optical absorption spectra of GO, free dye and Dye-GO for Anthracene, Pyrene and Coumarin dyes, respectively. Structured absorption is observed Anth-GO when compared to Anthracene suggesting a covalent binding of the dye with GO (Figure 3.5A). On the other hand, no significant changes in the absorption spectra were observed for Pyr-GO and Coum-GO suggesting that the binding of the dye to GO did not lead to any changes in the ground state interactions for these dye systems.
Figure 3.6. Comparative fluorescence spectra of Dye-NH$_2$, Dye-GO GO for (A) Anthracene, (B) Pyrene and (C) Coumarin. All dye molecules show significant fluorescence quenching when bound to GO indicating good complexation suggesting excited state interaction in the systems.

3.4.3 Fluorescence upconversion measurements

Steady-state fluorescence measurements have shown some quenching of fluorescence for the dyes when they are bound to GO. Fluorescence upconversion measurements were carried out to see if there is any change in decay kinetics. Figure 3.7A shows the decay kinetics at 500 nm for free anthracene amine and Anth-GO. It is quite evident that there is a faster decay when the dye is bound to GO. Two-exponential decay was observed for Anth-NH$_2$ in methanol with life times of 26 ps and 640 ps.
Figure 3.7. Fluorescence decay traces of dye and dye/GO in water at their respective fluorescence maxima for (A) Anthracene, (B) Pyrene and (C) Coumarin. Fluorescence of dye/GO has decayed much faster indicating electron or energy transfer from dye to GO.

Much faster decay was observed for Anth-GO with lifetimes of 6.5 ps, 90 ps and > 1 ns. (Figure 3.7A, Table 3.1) Faster decay time for Anth-GO suggest that there is an excited state interaction between Anthracene and GO. In contrast, a growth of fluorescence is observed for Pyr-NH$_2$ when monitored at 480 nm after excitation at 400 nm. (Figure 3.7B) The growth of emission is ascribed to the solvation of the emissive state wherein a growth is observed at red wavelengths and the dye decays with a single exponential decay after that. Interestingly, no growth of fluorescence was observed for GO-Pyr suggesting that Pyrene is strongly bound to GO and different photophysical properties are observed with the system. There is a faster decay component for Pyr-GO also
indicating excited state interaction. Much slower growth of fluorescence is observed for Coum-NH2 after excitation at 400 nm and emission monitored at 500 nm (Figure 3.4C). The growth is attributed to solvation component. However, the fluorescence decays much faster for Coum-GO again indicating efficient excited state interactions. However, fluorescence upconversion measurements cannot be able to differentiate whether it is energy transfer or electron transfer interactions that are giving rise to different fluorescence decay traces when the dyes are covalently bound to GO. To understand what is happening in these chromophore-functionalized GO, transient absorption measurements were carried out.

**Table 3.1. Fluorescence lifetimes of dyes alone and dyes bound to GO.**

<table>
<thead>
<tr>
<th>Lifetime</th>
<th>Free dye</th>
<th>GO-Dye</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coum-NH2</td>
<td>( \tau_{gr} = 45.0 \text{ ps, } \tau_d &gt; 1 \text{ ns} )</td>
<td>( \tau_1 = 65 \text{ ps (9.3%), } \tau_2 = 92 \text{ ps (38.5%), } \tau_3 &gt; 1 \text{ ns (25.6%)} )</td>
</tr>
<tr>
<td>Anth-NH2</td>
<td>( \tau_1 = 26.4 \text{ ps (9.3%), } \tau_2 = 640 \text{ ps (90.7%)} )</td>
<td>( \tau_1 = 6.5 \text{ ps (9.3%), } \tau_2 = 92 \text{ ps (38.5%), } \tau_3 &gt; 1 \text{ ns (25.6%)} )</td>
</tr>
<tr>
<td>Pyr-NH2</td>
<td>( \tau_g = 12.5 \text{ ps, } \tau_d = 370 \text{ ps} )</td>
<td>( \tau_g = 69.0 \text{ ps (47%), } \tau_2 = 520 \text{ ps (53%)} )</td>
</tr>
</tbody>
</table>

### 3.4.4 Transient Absorption Measurements

#### 3.4.4.1 Excited state dynamics in Pyr-GO

To understand the excited state interactions of Pyr-GO system, transient absorption measurements carried out. Time-resolved fluorescence measurements have already shown evidence for either electron or energy transfer happening in Pyr-GO. Before understanding the excited state dynamics in Pyr-GO, it is important to follow the dynamics of free Pyr-NH2 in solution. Shown in Figure 3.8A are the transient absorption spectra at different time delays for Pyr-NH2 in methanol after excitation at 370 nm. It shows an excited state absorption at 515 nm with a decay at lower energies and growth higher energies with increase in time delay. Species-associated spectra was obtained from global fit analysis and shown in Figure 3.8B. One fast component with a lifetime of 6.2 ps was obtained from the analysis that can be attributed to simple excited state
thermalization. The long-lived component is the excited state decay of Pyr-NH₂ and matched well with the fluorescence lifetime obtained for the free dye. Figure 3.8C shows the kinetic decay trace at 515 nm that shows a single exponential decay with a lifetime of 3.5 ns. The transient absorption analysis of free Pyr-NH₂ shows simple excited state decay for the free dye without any unusual relaxation pathways.

**Figure 3.8.** (A) Excited state absorption spectra at different time delays for free Pyr-NH₂ in methanol after excitation at 370 nm. (B) Species-associated spectra obtained from global fit analysis for Pyr-NH₂. (C) Kinetic decay trace of Pyr-NH₂ at 515 nm showing single exponential lifetime.

Excited state interactions between GO and Pyr were studied using time-resolved transient absorption measurements after excitation at 370 nm where Pyr as well as GO absorbs. Figure 3.9A shows the excited state absorption spectra at different time delays from 200 fs to 296 ps for GO-Pyr. At 200 fs time delay, a broad excited state absorption (ESA) was observed that decayed with
increase in time delay to give rise to an ESA with a maximum at 510 nm. This ESA is ascribed to singlet-singlet absorption of Pyr as it is similar to what was observed for free dye. However, no clear picture of excited state decay is observed from the spectra. Species-associated spectra were obtained after global fit analysis of all kinetic decay traces and shown in Figure 3.9B for GO-Pyr. Three main components were observed in global fit analysis. Firstly, 2.4 ps decay component with a maximum at 610 nm is observed and the spectral position of the ESA matches well with GO alone. With increase in time, GO decays and forms the singlet state of Pyr which decays back to ground state. The results suggest that there is an efficient energy transfer from GO to Pyr with a time constant of 2.4 ps. Such faster energy transfer can be envisioned when the dyes are covalently bound to GO. The kinetic decay trace at 525 nm shows the decay of the singlet state of Pyr with lifetimes of 72 ps and > 1 ns. The decay of 72 ps might have something to do with the quenching of fluorescence of Pyr when it is bound to GO, probably electron transfer quenching of Pyr fluorescence by GO.
Figure 3.9. (A) Excited state absorption spectra at different time delays for free GO-Pyr in methanol after excitation at 370 nm. (B) Species-associated spectra obtained from global fit analysis for GO-Pyr. (C) Kinetic decay trace of GO-Pyr at 525 showing faster decays.

3.4.4.2 Excited state interaction in GO-Coum

Transient absorption spectra at different time delays for Coum-NH$_2$ in methanol is shown in Figure 3.10A. Initially at 200 fs, a bleach at 460 nm is observed that grew with increase in time delay. Species-associated spectra obtained from global fit analysis (Figure 3.10B) shows an interesting scenario wherein there is a decay component with a maximum at 480 nm that decayed to give rise to the bleach that decays back to ground state. The 1.5 ps component is assigned to locally excited state that relaxes to give rise to intramolecular charge transfer state that decays back to ground state with its lifetime of > 1 ns. (Figure 3.10C)
Figure 3.10. (A) Excited state absorption spectra at different time delays for free Coum-NH$_2$ in methanol after excitation at 370 nm. (B) Species-associated spectra obtained from global fit analysis for Coum-NH$_2$. (C) Kinetic decay trace of Coum-NH$_2$ at 485 nm showing growth and single exponential decay lifetime.

Interesting excited state relaxation dynamics is observed for GO-Coum in water. For this system, we have excited at two different excitation wavelengths and followed the transients in visible region. Figure 3.11A shows the transient absorption spectra at different time delays for GO-Coum in water after excitation at 370 nm. The spectral features observed for GO-Coum are definitely different from what was observed for Coum-NH$_2$. In the case of free Coum-NH$_2$, we have observed locally excited state and bleach arising from the disappearance of the ground state of the molecule and no stimulated emission is observed. In contrast for GO-Coum, a negative absorption with a maximum at 480 nm is observed that can be ascribed to stimulated emission from Coumarin. With increase in time delay, the stimulated emission grows further to give rise to stimulated emission at 495 nm and this process can be attributed to the solvation of the ICT state. Global fit analysis of GO-Coum has yielded species-associated spectra (Figure 3.11 B) with three different components. Like in the case of free dye, a faster component with a lifetime of 5.6 ps was observed and this component is slower than what was observed for the free dye. 110 ps component can be a combination of the stimulated emission and a long-lived component is observed which is attributed to the singlet state decay.
Figure 3.11. (A) Excited state absorption spectra at different time delays for free GO-Coum in water after excitation at 370 nm. (B) Species-associated spectra obtained from global fit analysis for GO-Coum. (C) Kinetic decay trace of GO-Coum at 515 nm showing a growth of emission and long-lived decay.

The kinetics at 515 nm is shown in Figure 3.11C and the data shows similar response as that of the free dye. At 370 nm, excitation is mostly populating the Coumarin bound to GO and the dynamics observed at this excitation wavelength was unable to shed light on the role of GO on the excited state relaxation dynamics in GO-Coum. For a better understanding, transient absorption measurements after excitation at 440 nm were carried out where the contribution of GO would be higher. Transient absorption spectra at different time delays for GO-Coum after excitation at 440 nm is shown in Figure 3.12A. Interestingly, different excited state spectral features are observed at 440 nm excitation where the absorption is mostly by GO. With increase in time delay, the
transients of GO decays to give rise to a stimulated emission at 500 nm and broad excited state absorption at 220 ps.

Figure 3.12. (A) Excited state absorption spectra at different time delays for free GO-Coum in methanol after excitation at 440 nm. (B) Species-associated spectra obtained from global fit analysis for GO-Coum. (C) Kinetic of lifetime decay trace of GO-Coum at 640 nm.

Species-associated spectra obtained from global fit analysis has shown three main components, one with a lifetime of 700 fs whose spectrum matches well with the ESA of GO. Also another 25 ps decay component was observed that also resembles the excited state spectrum of GO (Figure 3.12 B). The long-lived transient resembles the stimulated emission of Coumarin. The results suggest an efficient energy transfer from GO to attached dye with lifetimes of 700 fs and 25 ps. The two different time constants suggest the inhomogeneity with which the Coumarin is
bound to GO. The kinetic decay trace of GO-Coum at 640 nm (Figure 3.12 C) accurately represents the 700 fs and 25 decay components of GO to give rise to the transient absorption of Coumarin.

3.4.4.3 Excited state interactions in GO-Anth

In the cases of both GO-Pyr and GO-Coum, it was observed that there is an energy transfer from GO to bound dyes and no evidence for charge-transfer was observed. It is interesting to see if GO-Anth would be any different. Firstly, the transient absorption dynamics of Anth-NH$_2$ in methanol after excitation at 370 nm. Shown in Figure 3.13A are the transient absorption spectra at different time delays for Anth-NH$_2$. At 150 fs time delay, a transient with a maximum at 500 nm was observed that quickly leads to rather broad absorption with a maximum at 530 nm and a shoulder at 580 nm. Figure 3.13B shows the species-associated spectra obtained from global fit analysis. The results show one ultrafast decay and growth component that gives rise to long-lived transient. The results are rationalized based on the fact there is a relaxation from locally excited state to give rise to the singlet state of Anth-NH$_2$. The kinetic decay trace at 500 nm represents the faster locally excited state to relaxed singlet state. (Figure 3.13C)
Figure 3.13. (A) Excited state absorption spectra at different time delays for free Anth-NH$_2$ in methanol after excitation at 370 nm. (B) Species-associated spectra obtained from global fit analysis for Anth-NH$_2$. (C) Kinetic of lifetime decay trace of Anth-NH$_2$ at 500 nm.

Transient absorption measurements were also carried out on GO-Anth at two different excitation wavelengths: 370 nm and 440 nm. Shown in Figure 3.14A are the transient absorption spectra at different time delays from 130 fs to 300 ps for GO-Anth after excitation at 370 nm. The data shows broad positive absorption with no distinctive features and all the transients decayed with increase in time delay. Figure 3.14B shows the species-associated spectrum obtained after global fit analysis that resulted in 3 different decay components. First two components of 3.2 ps and 55 ps are eerily like the ESA of GO alone. The long-lived transient has spectral features of Anthracene. Here again, the results show that there is an energy transfer from GO to Anthracene with time constants of 3.2 ps and 55 ps. Although energy transfer was observed in all cases from GO to attached dyes but the rate of energy transfer was found to be different for different systems. The kinetic decay trace at 630 nm fitted with two-time constants representing the energy transfer from GO to Anthracene. (Figure 3.14C).
Figure 3.14. (A) Excited state absorption spectra at different time delays for free GO-Anth in methanol after excitation at 370 nm. (B) Species-associated spectra obtained from global fit analysis for GO-Anth at different time delay. (C) Kinetic of lifetime decay trace of GO-Anth at 630 nm.

To understand if same energy transferred will be observed after excitation at 440 nm, transient absorption measurements were also carried out on GO-Anth. Figure 3.15A shows the transient absorption at different time delays from 130 fs to 300 ps. Species associated spectra obtained from global fit analysis (Figure 3.15B) also show three main components. Component 1 and 2 of 3.2 ps and 45 ps matched well with the energy transfer time constants obtained after 370 nm excitation. The kinetic decay trace at 620 nm also shows the same two time constants for energy transfer from GO to Anthracene.
Figure 3.15. (A) Excited state absorption spectra at different time delays for GO-Anth in water after excitation at 440 nm. (B) Species-associated spectra obtained from global fit analysis for GO-Anth. (C) Kinetic decay trace of GO-Anth at 620 nm.

3.5 Mechanism of Energy transfer from GO to attached dyes

TEM images have shown the formation of 1D GO nanoarchitectures and were able to show evidence for Dye-GO composite. FTIR measurements have shown the absence of carboxylic functional group and amide bond formation was observed confirming Dye-GO composite. Optical absorption and steady-state fluorescence measurements have shown excited state interaction between Dye and GO. Transient absorption measurements were carried out to understand the energy and electron transfer interactions between GO and dye. In the case of GO-Pyr, 370 nm excitation excited both GO and the dye and energy transfer from GO to Pyr was observed which happened with a time constant of 2.4 ps. However, there is a 72 ps decay component for Pyr singlet state which is attributed to electron transfer from Pyr to GO. Also, long-lived Pyrene was observed,
and the results have shown that Pyr is attached to GO at different environments with inhomogeneities. Both energy transfer from GO to Pyr as well as electron transfer from Pyr to GO was observed in this system and depicted in Figure 3.16.

![Diagram](image)

**Figure 3.16.** Cartoon diagram depicting both energy transfer from GO to Pyr and electron transfer from Pyr to GO in GO-Pyr.

Interesting relaxation dynamics was observed for GO-Coum. The relaxation in Coum-NH₂ was dominated by locally excited state to long-lived charge-transfer. The transient absorption measurements carried out on GO-Pyr at two different excitation wavelengths of 370 nm and 440 nm. Both excitation wavelengths have shown transients corresponding to GO followed by efficient energy transfer from GO to Pyr with lifetimes of 700 fs and 25 ps at both excitation wavelengths. Two different energy transfer rate constants again signify the inhomogeneities where the dye is bound to GO. The mechanism of excited state relaxation is presented in Figure 3.17.
Similarly, the relaxation dynamics in GO-Anth was also dominated by energy transfer from GO to Anth from the data obtained from two excitation wavelengths. The energy transfer rate constants of 3.2 ps and 50 ps at two different excitation wavelengths was observed. Slower energy transfer rate constants can be attributed to the spectral overlap as well as the orientation of the dye with GO. Anthracene can \( \square \)-stack with GO while such interaction is probably not possible with Coum. Schematic of energy transfer from GO to Anth is shown in Figure 3.18.
3.6 Conclusions

The main objective of this study is to understand the type on interactions between GO and covalently attached dye molecules. Dye-GO composites using Pyrene, Coumarin and Anthracene were synthesized with amide bond coupling reaction and characterized with FTIR. Optical absorption and steady-state fluorescence measurements did not show significant changes in the ground state optical properties. However, fluorescence quenching was observed for the dyes bound to GO. Fluorescence upconversion measurements have also shown faster decay for the dyes bound to GO suggesting excited state interactions and probable charge-transfer. However, transient absorption measurements carried out of GO-Pyr has shown efficient energy transfer from GO to Pyr with a time constant of 2.4 ps. Also, 72 ps decay component for Pyr was observed that can be attributed to electron transfer from Pyr to GO. In contrast, two energy transfer rates were observed in GO-Coum and GO-Anth. Ultrafast energy transfer of 700 fs and 25 ps energy transfer from GO to Coum was observed. However, the energy transfer time constants little slowed down in GO-Anth where 3.2 ps and 50 ps energy transfer rates were observed. The differences in energy transfer rates can be attributed to different orientations of dyes with GO. Overall, in the case of GO-dye
systems, energy transfer from GO to dyes dominated excited state interactions and the presence of charge-transfer interactions were not as dominant.

3.7 References


CHAPTER 4

EXCITED STATE DYNAMICS IN CHROMOPHORE-FUNCTIONALIZED REDUCED GRAPHENE OXIDE NANOARCHITECTURES

4.1 Introduction

In the previous chapter, we have investigated the interaction of dyes with GO. The results have shown minimal charge transfer interactions and mostly we observed energy transfer from GO to dye depending upon the dye where sub-picosecond and 10s of ps energy transfer rate constants were observed. It will be interesting to see if similar interactions or different things can be observed with reduced graphene oxide (RGO).

Graphene and GO show good linear and nonlinear optical properties and usually considered to be promising candidates for optical communication, optical limiting, optical storage, information processing.1-7 Also, the bandgap of GO is usually high but can be made smaller by reducing it to form RGO. Thus, RGO has also garnered good research attention for optical applications. Also, the electrical conductivity of RGO is better than GO and it was also considered good catalytic material when compared to GO. The reason for the lower bandgap and better optical properties is the partial restoration of sp² π-conjugated network in RGO. However, the low solubility and poor processability are some of the obstacles for the applications of RGO. However, it is possible to functionalize RGO and increase the solubility as well as enhance their linear and NLO properties. Very few studies have focused on understanding the excited state relaxation in dye-functionalized RGO composites. This formed the motivation for the work carried out in this Chapter. Three dyes, 1-Aminoanthracene (Anth-NH₂), 1-Aminopyrene (Py-NH₂) or 7-Amino-4-(trifluoromethyl) coumarin (Coum-NH₂) (Figure 4.1) were used to bind to RGO via the formation of C-C bond with RGO.
4.2 Experimental
4.2.1 Synthesis

4.2.1.1 Synthesis and Structural Characterization of GO and RGO

The synthesis procedure of GO was adopted from the synthetic methodology developed by Marcano et al.\textsuperscript{10} For this synthesis, a concentrated H\textsubscript{2}SO\textsubscript{4} (69 mL) was added to a mixture of graphite flakes (3.0 g, 1 wt equiv) and NaNO\textsubscript{3} (1.5 g, 0.5 wt equiv), and the mixture was cooled using an ice bath to 0 °C. KMnO\textsubscript{4} (9.0 g, 3 wt equiv) was added slowly in portions to keep the reaction temperature below 20 °C. The reaction was warmed to 35 °C and stirred for 7 h. Additional KMnO\textsubscript{4} (9.0 g, 3 wt equiv) was added in one portion, and the reaction was stirred for 12 h at 35 °C. The reaction mixture was cooled to room temperature and poured onto ice (~400 mL) with 30% H\textsubscript{2}O\textsubscript{2} (3 mL). The mixture was purified by vacuum filtration through filter paper of 0.45 Micron. The filtrate was washed three times with 200 mL of distilled water, and 200 mL of ethanol; for each wash. The material remaining after this extended, multiple- washing was vacuum-dried overnight at room temperature, obtaining 6.3 g of product. Synthetic scheme to make RGO is shown in Figure 4.2.
Figure 4.2 Scheme to synthesize RGO from GO.

4.2.2 Functionalization RGO with Organic dyes

The diazotization reaction to dye-functionalized RGO was performed based on a published procedure with some changes to accommodate the dyes we used and lab condition, as shown in Fig. 4.3 RGO (40 mg) was sonicated for 2hrs in THF (50 mL). The suspension was transferred to a 100 mL round-bottom flask. The solution was deoxygenated by sparging with nitrogen for 15 min, and then Dye-NH₂ (10 mg) and isoamyl nitrite (0.5 mL) was quickly added. The suspension was heated and stirred at reflux under N₂ for 72hrs. After the reaction was finished, sonication of the solution for 1hr. Then the solvent was removed by evaporation, and the resultant solid residue was homogenized with dichloromethane with the aid of an ultrasonic bath. The resultant suspension was filtered, and the collected solid was washed with dichloromethane and ethanol until the filtrate was colorless. The desired nanohybrid material RGO-dye was obtained as a black powder and was dried under vacuum overnight.
Figure 4.3. Covalently functionalization of reduced graphene oxide. Investigated dyes were then covalently grafted onto GO sheets. Isoamyl nitrite was used to oxidize the amino group on dye-NH$_2$ to an aryl diazo group, followed by transfer of a delocalized electron from RGO to the diazo group, forming an aryl radical after release of N$_2$. The resultant is a C-C bound dyes to RGO.

4.3 Methods

4.3.1 Optical Absorption and Steady-State Fluorescence

Optical absorption measurements were carried out in Shimadzu UV-2102PC spectrophotometer. An Edinburgh F900 spectrofluorometer, used to carry out steady-state luminescence measurements of RGO-dye complexes.

4.3.2 Time-Resolved Fluorescence Upconversion

Time-resolved luminescence measurements of GO-dye complexes were studied using set femtosecond luminescence up-conversion spectroscopic technique. The upconversion system used in our experiments was obtained from CDP Instruments, Inc., Russia. Specifically, the system used third harmonic generation from the mode-locked broad band Ti:sapphire laser (Spectra Physics, Tsunami, 710 to 920 nm). The present measurements were carried out with 280 nm excitation (the fundamental of Ti:Sapphire was set at 840 nm). Polarization of the excitation beam for the magic
angle luminescence and anisotropy measurements was controlled using a Berek compensator and the sample was continuously rotated with a rotating cell of 1 mm thickness. Horizontally polarized luminescence emitted from the sample was up-converted in a nonlinear crystal of β-barium borate using a pump beam at 800 nm, which first passed through a variable delay line. Instrument response function (IRF) was measured using the rise time of several dye molecules. Fitting the rise time of the luminescence traces gave a sigma value of ~290 fs. Parallel and perpendicular decay traces were obtained from which the magic angle luminescence decay was calculated from these traces. Fitting of the luminescence decay traces were carried out with DecFit software. The spectral resolution was achieved using a double monochromator and photomultiplier tube. The excitation average power varied but was around 10 ± 0.3 mW. No degradation of the sample was observed as the traces overlapped after each repetition.

4.3.3 Transient Absorption Measurements

Transient absorption experiments were carried out at the Center for Nanoscale materials, Argonne National Laboratory.

4.3.4 FTIR and TEM Measurements

The FTIR carried out using Thermo Science. Nicolet iS 5 FTIR Spectrometer at WMU, KBr pallet was used to measure the sample. TEM carried out at WMU imaging center using Joel.

4.4 Results

4.4.1 Characterization of RGO and RGO-Dye Complexes

Shown in Figure 4.4 TEM images of RGO and RGO-dye composites. RGO shows exfoliated structure like what was reported in literature. However, the dye modification altered the surface structure of RGO.
Figure 4.4. TEM image of RGO and RGO-dye.

FTIR spectra of GO and RGO are shown in Figure 4.5. Prominent OH stretch and C=O stretch were seen for GO. However, after reduction, both OH stretch and C=O stretches decreased suggesting the reduction of RGO.
Figure 4.5. FTIR comparison of GO and RGo. FTIR spectroscopy provides evidence for the reduction of the oxygen-containing groups, disappear the peak at 1735 $\text{cm}^{-1}$ in GO which corresponded to the (C=O) of the (COOH).

Dye-RGO composites were also characterized by FTIR and corresponding FTIR spectra of RGO and RGO-dye were shown in Figure 4.6. The C=O stretch at 1700 cm$^{-1}$ for RGO vanished giving rise to two peaks around 1600 cm$^{-1}$ that correspond to C=C stretching band of Dye-RGO complex. Also, aromatic C-H stretches were observed. However, no amine or amide bonds were observed indicating that the dye is covalently bound to RGO with the formation of C-C bond unlike Dye-GO composites.

4.4.2 Optical Absorption Measurements

Unlike what was observed in the case of dye-functionalized GO in Chapter 3, the chromophores covalently bound to RGO bound via C-C bond rather than an amide bond. It is

Figure 4.6. FTIR comparison of RGO and dye-functionalized RGO. New absorption bands are observed in the spectrum of RGO-dye, indicating covalent attachment of dye to the RGO.
expected that the interactions that are observed here can be different from previous case. Optical absorption measurements were carried out to see if there are any change in the ground states of dye molecules when they are bound to RGO. Parts A, B and C of Figure 4.7 show the optical absorption spectra of RGO, dye-NH₂, RGO-dye where dye is Pyrene, Coumarin and Anthracene, respectively. Pyr-NH₂ absorbs around 380 nm but it shifted to blue with a maximum around 350 nm and structured absorption resembling of free pyrene in RGO-Pyr. (Figure 4.7A) The conjugation is extended with NH₂ conjugation in Pyr-NH₂ and thus it is shifted till 390 nm. However, when it is bound the NH₂ is disrupted with the formation of a C-C bond and thereby the spectral features of Pyrene when bound to RGO resemble that of free pyrene. Optical absorption spectrum of RGO-Pyr confirms that Pyrene is bound to RGO via the formation of C-C bond.

**Figure 4.7.** Optical absorption spectra of Dye-NH₂, Dye-RGO and RGO for (A) Pyrene, (B) Coumarin and (C) Anthracene.
It can be observed from Figure 4.7B that the absorption spectrum of Coum-NH₂ is broad with a maximum around 400 nm. This absorption is normally assigned to the intramolecular charge-transfer state of the dye. In the case of RGO-Coum, the absorption is shifted to 360 nm and this can be attributed to the fact that when Coum-NH₂ is bound to RGO, the amine is replaced by C-C bond and there is no intramolecular charge transfer state for that system and thereby the absorption is similar to simple Coumarin and not 7-amino Coumarin. This result again confirms that Coumarin is covalently coupled to RGO via C-C bond and this dye is uniquely different from the Coumarin that was bound to GO. Figure 4.7C shows the absorption of Anth-NH₂, RGO-Anth and RGO. Anth-NH₂ shows absorption of the Anthracene transitions around 340 nm and a broad absorption band at 400 nm that can be attributed to charge transfer transition from amino group to anthracene. Similar absorption features are also seen for RGO-Anth where there is a charge-transfer from RGO to Anthracene.

4.4.3 Steady-State fluorescence Measurements

Normalized fluorescence spectra of dye-NH₂ and RGO-dye are presented in parts A, B and C of Figure 4.8 for Pyrene, Coumarin and Anthracene, respectively. Significant fluorescence quenching (100 times when compared to free dye) is observed for all dyes when they are bound to RGO suggesting strong excited state interaction. The normalized fluorescence spectra are presented here to show what dye binding to RGO did to the spectra of the dyes. There is a clear shift to higher energies for RGO-Pyr and RGO-Coum suggesting that replacing amino group with C-C bond to RGO altered the electronic absorption spectral properties of free dye molecules. However, the shift to higher energies is not that significant for RGO-Anthracene suggesting that the charge-transfer transition in Anth-NH₂ is replaced by another charge-transfer interaction between Anthracene and RGO. (Figure 4.8C) However, the fluorescence quantum yields of all the dyes have significantly reduced when they were bound to RGO indicating either energy or charge-transfer interactions.
### Figure 4.8

Comparative fluorescence spectra of dye-NH$_2$ and RGO-dye for (A) Pyrene, (B) Coumarin and (C) Anthracene.

#### 4.4.4 Time-Correlated Single-Photon Counting Measurements

Both optical absorption and steady-state fluorescence measurements have shown that the transitions in dye molecules are altered when they are bound to RGO. This is ascribed to the way the dyes are bound to RGO via formation of C-C bond. Also, fluorescence quenching is observed for all dyes bound to RGO. As a first start, fluorescence lifetime measurements were carried out for dye-NH$_2$ and RGO-dye systems using time-correlated single photon counting measurements with 370 nm diode laser excitation and monitoring the fluorescence at their respective fluorescence maxima. Shown in Figure 4.9 A are fluorescence decay traces of Coum-NH$_2$ and RGO-Coum. The fluorescence of Coum-NH$_2$ is fitted to a single exponential decay lifetime of 5.2 ns while that of RGO-Coum was fit to 1.1 ns and 3.9 ns with an average lifetime of 3.6 ns. The decrease in...
fluorescence lifetime for Coum when it is bound to RGO is ascribed to the lack of ICT character of Coum as 7-amino group is replaced by C-C bond.

Figure 4.9. Fluorescence decay traces of dye-NH$_2$ and RGO-dye for (A) Coumarin, (B) Pyrene and (C) Anthracene. Fluorescence lifetime is decreased for all dyes when they are bound to RGO.

Figure 4.9B shows the fluorescence decay traces of Pyr-NH$_2$ and RGO-Pyr. The fluorescence decay of Pyr-NH$_2$ is fit to a single exponential lifetime of 4.4 ns while the decay of RGO-Pyr was fitted to 1.5 ns (95.2%) and 3.1 ns (4.8%) suggesting different structure of Pyrene as well as excited state interaction between pyrene and RGO. Similar to Coumarin and Pyrene functionalized RGO, the fluorescence decay of RGO-Anth is also significantly smaller when compared to Anth-NH$_2$. (Figure 4.9C) Anth-NH$_2$ has a long lifetime of 15.8 ns and reduced to 3.5 ns (98.7%) and 13.6
(1.4%) for RGO-Anth. Again the change in fluorescence lifetime for dyes bound to RGO suggest that there is a change in electronic transitions. However, the decrease in fluorescence lifetimes cannot explain huge fluorescence quenching observed and probably things are happening much faster than the instrument response of time-correlated single photon counting technique.

4.4.5 Transient Absorption Measurements

4.4.5.1 Excited State Interactions in RGO-Pyr

The transient absorption spectral characteristics of Pyr-NH$_2$ were already discussed in Chapter 3. It shows a long-lived singlet state with excited state absorption maximum at 515 nm. Shown in Figure 4.10A are the excited state absorption spectra at different time delays for RGO-Pyr after excitation at 370 nm. Immediately after excitation, a broad absorption with a maximum at 500 nm was observed. With increase in time delay the broad absorption $> 550$ nm decays to give rise to the singlet state absorption at 515 nm. As the spectral profiles and kinetics are quite complex, global fit analysis was carried out corresponding species-associated spectra for RGO-pyr is shown in Figure 4.10B. Interesting transient spectral features were obtained from global fit analysis. The ESA maximum at 500 nm can be attributed to the anion radical of Pyrene as it matched well with the anion radical transient spectrum obtained from global fit analysis. Broad 3.5 ps is ascribed to the decay of RGO to form the anion radical of Pyrene. Then Pyr$^-$ recombines and a residual singlet state absorption at 515 nm is observed. Overall, the transient absorption spectral properties of RGO-Pyr have shown evidence for electron transfer from RGO to Pyr with a time constant of 3.5 ps and it recombines very fast with a time constant of 32 ps. However, there is residual Pyrene singlet state absorption suggesting that not all Pyrenes are in the same environment, some are involved in electron transfer while some not. This is arising from the fact that even in RGO, not everything is homogeneous. Figure 4.10C shows kinetic decay traces for RGO-Pyr at 670 nm and 515 nm where the decay kinetics is significantly faster at 670 nm when compared to 515 nm.
Figure 4.10. (A) Excited state absorption spectra at different time delays for free RGO-Pyr after excitation at 370 nm. (B) Species-associated spectra obtained from global fit analysis for RGO-Pyr. (C) Kinetic decay traces of RGO-Pyr at 515 nm and 670 nm.

4.4.5.2 Excited State Interactions in RGO-Coum

Free Coum-NH₂ shows interesting transient absorption spectral features with a strong bleach around 460 nm and small ESA >500 nm and its characteristics are discussed in Chapter 3. Different transient features were observed for RGO-Coum after excitation at 370 nm. Figure 4.11A shows the transient absorption spectra at different time delays from 150 fs to 850 ps for RGO-Coum. At 370 nm, the absorption has significant contribution from Coumarin. After excitation at 370 nm, first it populates the locally excited state which decays with time as observed in Figure 4.11A. For a better understanding, global fit analysis was carried out that yielded species-associate spectra as shown in Figure 4.11B. Faster 300 fs component is ascribed to the singlet state absorption of Coumarin which quickly decays to give rise to ESA with a maximum at 560 nm.
Previous studies of pulse radiolysis have shown the cation radical of coumarin absorbing in the region of 560 to 590 nm. Thus the 11 ps and 1.2 ns components observed in Figure 4.11B are ascribed to the cation radical of Coum that recombines with those time constants. Overall, the excited state dynamics of RGO-Coum can be explained by ultrafast electron transfer from Coum to RGO with a slower charge recombination times of 11 ps and 1.2 ns. Ultrafast electron transfer from Coum to RGO can be exploited for linear and nonlinear optical applications. The kinetic decay trace at 535 nm shows faster decay when compared to the kinetics at 650 nm. (Figure 4.11C)

![Figure 4.11](image)

*Figure 4.11* (A) Excited state absorption spectra at different time delays for RGO-Coum after excitation at 370 nm. (B) Species associated spectra obtained after global fit analysis. (C) Kinetic decay traces at 535 nm and 650 nm for RGO-Coum.

### 4.4.5.3 Excited State Interactions in RGO-Anth
Transient absorption spectral characteristics (presented in Chapter 3) of Anth-NH$_2$ has yielded two main components, one locally excited (LE) state with a decay lifetime of 400 fs and a long-lived charge-transfer (CT) state which arises from the transfer of electrons from amine donor group to Anthracene ring. To understand the characteristics of RGO-Anth, transient absorption measurements were carried out after excitation at 370 nm. Figure 4.12A shows transient absorption spectra at different time delays for RGO-Anth from 150 fs to 5 ps. One can observe ESA at 490 nm that decays fast with time while a concurrent growth is observed >600 nm.

Figure 4.12. (A) Excited state absorption spectra at different time delays for RGO-Anth after excitation at 370 nm at different time delay (B) Species associated spectra obtained after global fit analysis for different species such as Anthacene cation radical can be observed and charge recombination. (C) RGO-Anth, lifetime decay.
Figure 4.12B shows the transient absorption spectra from 5 ps to 700 ps that shows a decay of all transients. Species-associated spectra obtained from global fit analysis has yielded very interesting time constants with unique spectral characteristics. There is an ultrafast component of 400 fs that can be attributed to electron transfer from LE state to give rise to Anth\textsuperscript{+} at 700 nm. However, additional 2.1 ps decay component was observed that is assigned to charge transfer from CT state to form Anth\textsuperscript{+}. These assignments are done as the spectral profiles match the LE and CT state of Anth-NH\textsubscript{2}. However, faster charge recombination was observed with a time constant of 23 ps and > 1 ns. Overall, two different electron transfer rates were observed from LE and CT states of Anthracene to RGO. Good charge separation making these materials ideal for linear and nonlinear optical applications.

4.5 Discussion

Chemically reduced GO by hydrazine to synthesize RGO and was characterized by FTIR spectroscopy and TEM. FTIR has shown the disappearance of C=O stretching of GO at 1700 cm\textsuperscript{-1} with appearance of new stretching peaks at 1627 cm\textsuperscript{-1} and 1384 cm\textsuperscript{-1} for C=N, C-N respectively confirming the formation of RGO. The Dye-RGO was also successfully characterized by FTIR and TEM images have shown subtle change upon dye binding. Optical absorption and steady-state fluorescence measurements of dye-NH\textsubscript{2} and RGO-dye has shown significant shifts to absorption and fluorescence of the dyes when they are bound to RGO suggesting that dyes covalently bound to RGO via the formation of C-C bond with it. Fluorescence lifetimes have shown faster decays for the dye bound to RGO again confirming that the structure of the dye molecules was influenced with binding to RGO and the greater fluorescence quenching confirm that the dyes have strong excited state interactions with RGO. Different excited state interactions can be seen between RGO and attached dye molecules as shown in Figure 4.13.
Figure 4.13 Schematic illustration for the possible interaction of RGO with covalently attached dyes.

4.5.1 Mechanism of Excited State Deactivation in RGO-Dye Systems

Transient absorption measurements were carried out to understand the excited state interactions between RGO and dyes. Following results were observed. For RGO-Pyr, formation of Pyr\(^{-}\) was observed and a broad absorption >600 nm with a maximum at 700 nm. The broad absorption is attributed to the absorption of RGO which quickly decays to form the anion radical or Pyr\(^{-}\) with a time constant of 3.5 ps. Then the anion radical recombines with a time constant of 32 ps. However, at the end, we still observed the singlet states of Pyrene suggesting some of the Pyrenes did not participate in electron transfer reactions. The mechanism of excited state deactivation in RGO-Pyr can be summarized as shown in Figure 4.14.
Figure 4.14. Schematic illustration of excited state deactivation in RGO-Pyr.

Transient absorption measurements of RGO-Coumarin system has shown interesting excited state deactivation wherein we observed the formation of cation radical of Coumarin (Coum\(^{+}\)). As 7-amine group is replaced with a C-C bond, there is no CT state for Coumarin, and the excitation only populates the LE state. This state decays very fast with an electron transfer time of 300 fs to form Coum\(^{+}\). Then charge recombination happens with lifetimes of 11 ps and > 1 ns. Although there is ultrafast electron transfer, equally faster charge recombination was observed in RGO-Coum. A cartoon diagram depicting the electron transfer from Coum to RGO is shown in Figure 4.15.
Interesting excited state deactivation was observed for RGO-Anth. Free Anth-NH$_2$ has shown the presence of both LE and CT states in its excited state deactivation. When Anthracene was bound to RGO, there is an efficient electron transfer from both LE state as well as the CT state of Anthracene to RGO leading to the formation of Anth$^+$. With time charge recombination is complete with a time constant of 23 ps. Ultrafast electron transfer from two different states is clearly observed and this can be attributed to the covalent coupling of Anthracene with RGO where Anthracene is acting as a good electron donor. The mechanism of excited state deactivation in RGO-Anth is presented in Figure 4.16.

**Figure 4.15.** Schematic illustration of excited state deactivation in RGO-Coum.
4.6 Conclusions

In summary, GO was synthesized using modified Hummer’s method and reduced via hydrazine to make RGO. FTIR and absorption spectra show efficient reduction of GO. Investigated dye molecules were covalently coupled to RGO via C-C bond formation and characterized with absorption and FTIR measurements. Steady-state fluorescence measurements have shown blue shift as well as significant fluorescence quenching for dye-rGO samples suggesting excited state interactions. Time-resolved fluorescence measurements have shown decreased fluorescence lifetimes again point to excited state interactions. Transient absorption measurements carried out on RGO-Anth suggested ultrafast electron transfer and multi-exponential charge recombination. On the other hand, electron transfer from RGO to Pyrene was observed in RGO-Pyrene. If the electron transfer from RGO is altered by analyte, fluorescence of pyrene can be enhanced providing a pathway for making optical sensors. Similarly, ultrafast electron transfer from Coumarin to RGO was observed with a time constant of 300 fs. However equally faster recombination was observed with a time constant of 11 ps and also charge separation was observed. Efficient excited state interaction in chromophore-functionalized RGO suggest that these systems can be utilized for linear and nonlinear optical applications.
4.7 References


CHAPTER 5

LINEAR AND NONLINEAR OPTICAL PROPERTIES OF CESIUM LEAD HALID PEROVSKITE NANOCRYSTALS

5.1 Introduction

Chapters 3 and 4 have focused on excited-state relaxation in 1D planar nanoarchitectures and interesting energy and charge transfer interactions were observed. A new class of perovskite nanocrystals has arisen recently, and this Chapter describes the exciton relaxation in different CsPb-halide perovskite nanocomposites as well as the strategies to increase water solubility and to prepare metal-doped perovskite nanoparticles.

Renewable energy sources have been the topic of intense research interest among scientists for the last three decades and the growing concerns of climate change and environmental effects are promoting the need for efficient renewable energy sources and one among them is photovoltaic cells. In the early photovoltaic cells, and the most commercially available cells, were all silicon-based single-crystal devices, which offer about 15% energy efficiency.\textsuperscript{1} Recent solar cell systems of silicon-based devices big downfall is the high installation and manufacturing costs. Attempts to engineering cheaper photovoltaic cells. However, the efficiency of such devices was too low to bring to the market. Current studies are aimed to find photovoltaic devices with improved energy efficiency and manufacturing costs have been very active.\textsuperscript{2,3} Semiconductor nanocrystals have been of increasing interest due to their applications in optics and electronics. These types of nanocrystals seem to be capable of low cost, scalable and robust power generation.\textsuperscript{4} For this reason, much attention has been put into tuning nanocrystals to give ideal power efficiency. Several properties were investigated for improving the efficiency of solar cells that include: types of QD nanomaterials, size, mode of attachment and surface treatment. These properties can allow for
these nanocrystals to have applications in other optoelectronic devices such as phototransistors, LEDs, Lasers, and more.\textsuperscript{4,10,11} Beginning with the Protesescu group in 2015, much attention has been put into all-inorganic cesium lead halides perovskites for solar cells and optoelectronic devices. Perovskite is a naturally occurring mineral CaTiO\textsubscript{3} which lends its name to a class of compounds that follow the same crystal structure as CaTiO\textsubscript{3}. The compounds following this crystal structure are known as perovskites and are ternary compounds with a chemical composition of ABX\textsubscript{3}. This crystal structure exhibits a cubic close-packed arrangement with the B cation occupying the octahedral holes left by the X\textsubscript{3} anions and the A cations occupying the cuboctahedron holes (supplemental figure eventually).

Research on all-inorganic perovskites began with CsPbX\textsubscript{3} (X= Cl, Br, or I), first synthesized as a colloidal solution by the Protesescu group in 2015. These halide perovskites exhibit high photoluminescence quantum yield (PLQY), narrow PL band gaps and low lasing thresholds, making them viable for use as biological sensors as well as in optoelectronic devices such as LEDs, solar cells, and lasers (Figure 5.1).\textsuperscript{5,9} These qualities and others of perovskites and other QDs make these molecules beneficial for many different applications. These applications range from quantum computing, to photocatalysts, to photovoltaic devices. Here we turn our attention to the use of QDs like perovskites for optical applications and to understand their excitonic properties.
Figure 5.1. Schematic showing the structure of perovskites and varying luminescence spanning the visible region.

Although lot of work has focused on the optical properties of perovskite nanocomposites, several questions remain to be understood such as their exciton relaxation dynamics, nonlinear optical properties, solubility in water, effect of metal doping and main more. This research aims to understand linear and nonlinear optical properties of perovskites and find ways to make water soluble perovskites, which in turn, can be applied as fluorophores for optical microscopy in biological imaging.

5.2 Experimental
5.2.1 Synthesis
5.2.2 Preparation of Cesium lead Halides Nanocrystals

We follow a published procedure by Protesescu and his group, cesium lead halide nanocrystals were prepared via solution phase hot injection. (Figure 5.2) For single halide perovskites PbX₂ (0.376 mmol) and octadecene (10 mL) were added into a two or three-neck flask and dried under vacuum for 1 h at 120 °C. This initial step was performed identically for mixed halide perovskites, however for the major contributing halide PbX₂ (0.251 mmol) and the minor
contributing halide PbX₂ (0.125 mmol). Following reflux dried capping ligands oleylamine (1 mL) and oleic acid (1 mL) were injected into the mixture under N₂ gas. The lead salts were allowed to dissolve completely and the temperature was raised to 180 °C. Cesium oleate ( < 0.8 mL) was quickly added and the solution was immediately transferred to an ice water bath. The solution was allowed to sit in the water bath overnight. For perovskites containing chloride, trioctylphosphine (1 mL TOP, tech., 90%) is necessary for the complete solubilization of PbCl₂.³

### 5.2.3 Isolation and Purification of CsPbX₃ Nanocrystals

Immediately upon the addition of Cs-oleate, a precipitate is formed in the solution. Gradually, the solution fully precipitates and after a night in the water bath, solutions were transferred to 50 mL centrifuge tubes. The solutions were centrifuged at 23 °C and 9000 RPM for 10 min using a Sorvall Lynx 4000 centrifuge. The supernatant was discarded, and the nanocrystals were re-dispersed in toluene. To redisperse the nanocrystals the precipitate was sonicated for 1 h using a Branson 1510 sonicator. Following sonication, the solution was centrifuged for 5 min at 23 °C and 3000 RPM. The resulting supernatant was the purified colloidal solution of perovskite nanocrystals.³⁷

**Figure 5.2.** Synthesis scheme of CsPbX₃ nanocrystals
Synthesized perovskites are characterized with TEM measurements. TEM images were taken at Argonne National Laboratories and the data for three of perovskites is shown in parts A-D of Figure 5.3. Cubic structures for Cl and Br based perovskites is observed while hexagonal shape is seen for I₃ perovskite. Obtained TEM matched well with literature reports.

![TEM images](image)

**Figure 5.3** TEM for (A) CsPbBr₃ (B) CsPbCl₃ (C) CsPbI₃ and (D) CsPbBr₂I confirming the cubical shape for the nanocrystals. Hexagonal shape was observed for CsPbI₃. Average size of nanocrystals was around 10 nm.

5.3 Results and Discussion

5.3.1 Optical absorption and Steady-state Photoluminescence

Optical absorption spectra were run for each of the perovskites to characterize if they match with literature reports. The colloidal solutions were diluted in toluene and scanned from 800 nm to 300 nm. Parts A-D of Figure 5.4 shows the normalized absorbance and PL for CsPbCl₃, CsPbCl₂Br, CsPbClBr₂ and CsPbBr₃ nanocrystals. As the halide is changed from Cl to Br, both the PL maxima and absorption maxima shifted to longer wavelengths. The halide dependence of the optical properties is related to the charge-transfer transition that is influencing the bandgap of the semiconductors.
Figure 5.4. Normalized optical absorption (black) and steady state PL spectra (red) of the synthesized perovskite nanocrystals dissolved in toluene for (A) CsPbCl$_3$, (B) CsPbCl$_2$Br, (C) CsPbClBr$_2$ and (D) CsPbBr$_3$.

Parts A-C of Figure 5.5 shows the normalized absorption and PL spectra of CsPbBr$_2$I, CsPbBrI$_2$ and CsPbI$_3$ nanocrystals. Obtained absorption and PL maxima matched with literature reports. Here again, the PL maxima has shifted to red wavelengths with a change in halogen from Br to I.
Figure 5.5. Normalized optical absorption (black) and steady state PL spectra (red) of the synthesized perovskite nanocrystals dissolved in toluene for (A) CsPBr$_2$I, (B) CsPbBrI$_2$ and (C) CsPbI$_3$.

5.3.2 PL Lifetimes

PL lifetimes of perovskite nanocrystals were measured using time-correlated single-photon counting measurements. The PL decay traces for different perovskite nanocrystals is presented in Figure 5.6A-F. As the halide is changed from Cl to I, the PL lifetime increased matching what was reported for these perovskites. The PL lifetimes arise from band edge luminescence but they alone cannot give information about exciton relaxation dynamics in perovskite nanocomposites. So, we have carried out transient absorption measurements to understand the exciton relaxation dynamics.
Figure 5.6 Lifetime scans for different perovskites at their PL maxima for (A) CsPbI$_3$, (B) CsPbBrI$_2$, (C) CsPbBr$_2$I, (D) CsPbBr$_3$, (E) CsPbClBr$_2$ and (F) CsPbCl$_2$Br.
5.3.3 Ultrafast Optical Properties Perovskite Nanomaterials

Exciton dynamics in perovskite nanomaterials is fundamental to determine the optical response of this new class of materials. In this study, we are trying to understand the exciton interactions through ultrafast transient absorption spectroscopy. This work on exciton dynamics can be able to shed light on the use of perovskite nanomaterials for applications light-emitting devices, lasers, and solar cells\textsuperscript{26,27}. Excitation of perovskite NCs by photons with energies higher than the band-gap energy creates electrons and holes in higher excited states and these hot carriers relax to the band-edge through carrier–carrier and carrier–phonon interactions dissipating excess energy and reach the equilibrium temperature with the lattice. Overall, exciton thermalization, biexciton recombination through Auger recombination and exciton decay can be observed in perovskite nanocomposites. To understand the exciton dynamics in presently synthesized perovskite nanomaterials, transient absorption measurements after excitation at 370 nm were carried out. In addition, power-dependent transient absorption and transient anisotropy measurements were also carried out.

5.3.3.1 Transient Absorption Measurements

Shown in parts A and B of Figure 5.7 are the transient absorption spectra of CsPbBr\textsubscript{3} in toluene at short and long-time delays, respectively. Immediately after excitation, a negative absorption centered on 500 nm and a positive excited state absorption (ESA) at 520 nm is observed. As the time delay is increased, the negative signal is increased as well as the positive absorption decayed to give rise to negative absorption. (Figure 5.7A) The negative signal is ascribed to the bleach arising out of the disappearance of the ground state absorption of the perovskite after laser excitation. The growth in the bleach is assigned to exciton thermalization. Similar transient spectral characteristics were observed for CsPbBr\textsubscript{3}. With increase in further time delay, the bleach is recovered. Species-associated spectra were obtained after fitting all kinetics using global fit analysis and shown in Figure 5.7C. Four components were observed: 800 fs, 9 ps, 45 ps and > 1 ns component. The 800 fs component can be attributed to exciton thermalization. However, the observation of 9 ps, 45 ps time constants are unique at this pump power of 300 µW. Such
components were not observed for CsPbBr$_3$ at 12 $\mu$W pump power. This can be attributed to multi-excitons and corresponding recombination at higher pump powers.

![Figure 5.7](image)

**Figure 5.7.** Excited state absorption spectra of CsPbBr$_3$ at a pump power of 300 $\mu$W (A) at short time delays and (B) long time delays. (C) Species-associated spectrum obtained after global fit analysis.

As the observed transients are different with changing pump power, pump power dependent transient absorption measurements were carried out for CsPbBr$_3$ while changing the pump power from 12 $\mu$W to 1 mW. Shown in Figure 5.8 are transient absorption surfaces and corresponding transient spectra at representative time delay for CsPbBr$_3$ at pump powers of 12 $\mu$W, 100 $\mu$W and 600 $\mu$W. As can be observed from Figure 5.8, significantly increased bleach and broadened bleach were observed at higher pump powers.
Increased bleach is expected as more excitons are generated at higher pump powers and more ground state population reaches higher energy levels. The broadened bleach is surprising and can be attributed to generation of more than one exciton system, probably biexciton generation. Kinetic decay traces were monitored at 510 nm at all pump powers and plotted as a function of pump power in Figure 5.9. At low pump powers, the decay is mostly single exponential and however with increase in pump powers, one can observed faster bleach recovery in addition to long lived decay. The decay traces at different pump powers are fitted with three components, one growth component and two decay components. The growth component is independent of pump power while the first decay component increased with increase in pump power. The growth component is attributed to exciton thermalization, the decay component which is dependent on pump power is ascribed to biexciton decay via Auger recombination and the long lived decay is related to exciton decay.
Figure 5.9. Normalized kinetic decay traces for CsPbBr$_3$ at 510 nm at different pump powers from 12 $\mu$W to 1 mW.

Similar transient absorption spectral features were observed for all different perovskite nanocomposites. Pump power dependence is observed for all of them. Observed transient spectral features and corresponding decay components are similar to what was reported in literature. To avoid repetition, the data of other perovskite nanocomposites is not presented here. However, extracted exciton thermalization, biexciton decay and exciton recombination are presented in Table 5.1. Interesting aspects can be understood from the table. Exciton thermalization that is based on career-career or career-lattice phonon relaxation have increased when the halide is changed from Cl to I. Also, biexciton recombination time constants through Auger recombination have become longer when the halide composition changed from Cl to I, so does the exciton recombination. It is important to find a reason why such a trend is observed and additional theoretical explanation is needed. One probable explanation is the increase in ionic radius that alters the phonon energies and also changing the halide composition from Cl to I can increase the strength of charge-transfer interaction and thereby enhancing the radiative decay rates. These explanations are probable but additional measurements and theoretical explanation are needed to understand these observations.
Table 5.1. Table summarizing the exciton thermalization, Biexciton recombination and exciton decay of CsPbX₃ perovskite nanocomposites.

<table>
<thead>
<tr>
<th>System</th>
<th>Thermalization</th>
<th>Biexciton decay</th>
<th>Exciton decay</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsPbBr₂Cl</td>
<td>0.4 ± 0.1 ps</td>
<td>24 ± 4 ps</td>
<td>8.0 ± 0.8 ns</td>
</tr>
<tr>
<td>CsPbBr₃</td>
<td>0.9 ± 0.2 ps</td>
<td>44 ± 6 ps</td>
<td>11 ± 2 ns</td>
</tr>
<tr>
<td>CsPbBr₂I</td>
<td>0.6 ± 0.1 ps</td>
<td>51 ± 5 ps</td>
<td>21 ± 3 ns</td>
</tr>
<tr>
<td>CsPbBrI₂</td>
<td>1.1 ± 0.2 ps</td>
<td>70 ± 10 ps</td>
<td>40 ± 4 ns</td>
</tr>
<tr>
<td>CsPbI₃</td>
<td>1.3 ± 0.2 ps</td>
<td>120 ± 20 ps</td>
<td>56 ± 7 ns</td>
</tr>
<tr>
<td>CsPbBrCl₂</td>
<td>---</td>
<td>---</td>
<td>6.0 ± 0.5 ns</td>
</tr>
<tr>
<td>CsPbCl₃</td>
<td>---</td>
<td>---</td>
<td>5.8 ± 0.5 ns</td>
</tr>
</tbody>
</table>

5.3.3.2 Ultrafast Transient Absorption Anisotropy Measurements

The data obtained from transient absorption measurements were in line with what were reported in literature for exciton dynamics in perovskite nanocomposites with subtle trends that were observed here. Also, the nature of excitons and their orientation is difficult to obtain from conventional transient absorption measurements that were carried out at magic angle. Additional aspects can be obtained if we can monitor the transient absorption anisotropy that can shed light on the orientation of the excitons. Transient absorption anisotropy measurements were able to probe the intrinsic energy transfer in molecular systems, light harvesting antennae and among others. However, the use of these measurements for understanding the excitons in semiconductor quantum dots or perovskite nanocomposites is limited. In this study, we have attempted to use the power of transient absorption anisotropy measurements to monitor the excitons and especially that are related to bi-excitons. Anisotropy measurements are mostly aimed at molecules as the dipoles are aligned in one direction and if the dipole is parallel to excitation, one can expect an anisotropy of 0.4. In contrast, semiconductor quantum dots in principle should not show any anisotropy as they are spherical and the excitation is delocalized and one can expect anisotropy close to 0.0. That is probably the reason why anisotropy measurements were not normally used for nanomaterials.
However, the shape of perovskite nanomaterials that were observed here is cubical but there is small anisotropy there with long axis little bit longer than shorter axis. Transient absorption anisotropy measurements can be able to shed light on even such small differences. The transient absorption anisotropy is given by: \( r(t) = \frac{\Delta A_{||}(t) - \Delta A_{\perp}(t)}{\Delta A_{||}(t) + 2\Delta A_{\perp}(t)} \), where \( \Delta A_{||}(t) \), \( \Delta A_{\perp}(t) \) are change in absorbance signals when the pump and probe are parallel and perpendicular, respectively. The setup used for measuring anisotropy is shown in Figure 5.10.

![Figure 5.10](image.png)

**Figure 5.10.** Cartoon diagram showing the setup to measure transient absorption anisotropy.

Transient absorption anisotropy measurements were carried out at Argonne national laboratory and we thank Dr. Gary Wiederrecht for his help with measurements. The anisotropy data for couple of systems, CsPbBr\(_3\) and CsPbI\(_3\) is discussed here. As shown above from TEM measurements, CsPbBr\(_3\) has cubic structure while CsPbI\(_3\) has shown hexagonal structure and our idea is to see if the anisotropy measurements can be able to point out such subtle differences. Shown in parts A-D of Figure 5.11 are the transient absorption spectra at different time delays and at pump powers of 12 \( \mu \)W, 100 \( \mu \)W, 300 \( \mu \)W and 600 \( \mu \)W, respectively. It is interesting to note presence of anisotropy between 500 to 510 nm for CsPbBr\(_3\) and a value of 0.03 at 507 nm was observed. (Figure 5.11A) The low anisotropy initially after excitation suggests that the cluster is more symmetric, and the exciton is delocalized. However, the presence of small anisotropy indeed
supports the presence of polarization of the exciton. Even at 12 mW, there is a small growth of anisotropy till 1 ps indicating the exciton thermalization. However, the anisotropy remained steady and did not change after that. However, as the pump power is increased, the initial anisotropy at 200 fs was small and a growth of anisotropy is observed. It is surprising to see such subtle changes in anisotropy even though they are quite small.

![Image of transient absorption anisotropy spectra of CsPbBr$_3$ at different time delays and different pump powers: (A) 12 µW, (B) 100 µW, (C) 300 µW, and (D) 600 µW.](image)

**Figure 5.11.** Transient absorption anisotropy spectra of CsPbBr$_3$ at different time delays and different pump powers of (A) 12 µW, (B) 100 µW, (C) 300 µW, and (D) 600 µW.

Different transient absorption anisotropies were observed with varying pump powers, the anisotropy decay traces at 507 nm for CsPbBr$_3$ with varying pump powers are shown in Figure 5.12. At very low pump power of 12 µW, there is a very fast growth and did not change after that.
However, a consistent growth from smaller values to higher values was observed at higher pump powers. The anisotropy growth at higher pump powers was fitted to 45 ps decay constant that matched well with bi-exciton decay via Auger recombination. The results are rationalized in the following way. At low pump powers, there is exciton thermalization followed by exciton decay. The exciton in CsPbBr$_3$ has an anisotropy of 0.034 indicating that there is an inherent polarization in CsPbBr$_3$ nanocrystals even though they are cubic. At high pump powers, the initial anisotropy decreased from 0.025 to 0.02 to 0.01 and 0.005 at a pump power of 1 mW. With increase in pump powers, bi-excitons are formed and it is reasonable that bi-excitons have zero anisotropy as it is a superposition of two excitons. The growth of anisotropy suggests that the bi-excitons are decaying via Auger recombination to form single excitons. The bi-exciton recombination matched the anisotropy growth and this result is by far the first study where transient absorption anisotropy was able to show the bi-excitons and their decay via Auger recombination.

![Figure 5.12](image_url)

**Figure 5.12.** Transient absorption anisotropy kinetic decay traces for CsPbBr$_3$ at different pump powers, monitored at 507 nm.

Another nanocrystal that was studied using transient absorption anisotropy is CsPbI$_3$, which is hexagonal in shape. Figure 5.13 shows the transient anisotropy surface and transient anisotropy decay kinetics at 674 nm of CsPbI$_3$ at different pump powers of 12 µW, 100 µW and 500 µW. At a pump power of 12 mW, anisotropy of 0.007 ± 0.003 was observed. This is
significantly smaller when compared to CsPbBr$_3$. The smaller anisotropy is ascribed to the hexagonal shape of CsPbI$_3$ which is mostly close to spherical shape. Even with CsPbI$_3$, there is a small growth in anisotropy at a pump power of 500 µW indicating the bi-exciton recombination.

![Ultrafast transient absorption anisotropy of CsPbI$_3$ at different pump powers. As CsPbI$_3$ is hexagonal, smaller anisotropy in the system was observed.](image)

**Figure 5.13.** Ultrafast transient absorption anisotropy of CsPbI$_3$ at different pump powers. As CsPbI$_3$ is hexagonal, smaller anisotropy in the system was observed.

### 5.4 Two-Photon Optical Properties of Perovskite Nanomaterials

In recent years, Cesium lead halide perovskites (CsPbX$_3$) have gained enormous research attention for their applications solar cells and light emitting diodes. In addition, these perovskite structures can be made into stable nanosized architectures that can be easy to make stable thin films for optical applications. Colloidal nanostructures of perovskite semiconductors have
recently been synthesized to further promote their light-emitting performance by the aid of the quantum confinement effect\textsuperscript{25}. Further, the amplified spontaneous emission (ASE) and lasing from NCs of cesium lead halide (CsPbX\textsubscript{3}, X= Cl, Br, and I) have recently been studied with one-photon pumping\textsuperscript{26-28}. Although some of the nonlinear optical properties of perovskite nanocomposites were studied, the studies on two-photon absorption cross-sections were limited. Thus, we have probed the two-photon absorption (2PA) cross-sections of CsPb-halide perovskites using two-photon excited fluorescence technique. Shown in Figure 5.14A is the plot of log(PL) vs log(power) for a typical perovskite of CsPbBr\textsubscript{2}Cl and C515 and a slope of 2.00 was observed indicating it is two-photon excitation. 2PA cross-sections were determined for both perovskite nanocrystals and nanosheets and all of them have shown cross-sections reaching $10^6$ GM for perovskite nanocrystals, significantly larger than what one can observed for organic dye molecules. Large 2PA cross-sections of perovskite nanocomposites suggest that they can be used for nonlinear optical applications such as optical limiting.

![Figure 5.14](image_url)

**Figure 5.14.** (A) Plot of log(PL) versus log(power) for CsPbBr2Cl and C515, which is a standard. The slope of the curve is 2.00 indicating two-photon excitation. (B) Comparison of the two-photon cross section of perovskite nanocrystals, nanosheets and organic dye.

5.5 Block-Copolymers for Water Soluble Perovskite Nanocomposites

Now we understand the excitation dynamics in perovskite nanocrystals and 2PA properties of perovskites, it is important to increase the solubility of perovskite nanocrystals in water. One
drawback of perovskites is their lack of solubility in water. In this part of the work, we have attempted to make perovskites nanocrystals soluble in water. To achieve perovskite nanocrystals that are soluble in water, we have used block copolymers that can solubilize the nanocrystals in their hydrophobic region and make them soluble in water from its hydrophilicity. In this study block copolymers were used as surfactants to get this phase transfer to occur. The block copolymers form micelles around the perovskites which are then able to dissolve in polar solvents. An attempt at adding the block copolymer was done during the synthesis of the nanocrystals. The synthesized CsPbBr\(_3\) perovskite by adding block copolymer (L64) as capping agent was used. Figure 5.15 shows the chemical structure of L64.

![Figure 5.15 Block copolymer (L64) used in the synthesis](image)

Parts A and B of Figure 5.16 shows the absorption and PL spectra of CsPbBr\(_3\)–TOA and CsPbBr\(_3\)–L64 in H\(_2\)O, respectively. A small change in the absorption spectra was observed with L64 capping and also there is a shift of PL maximum to higher energies.
Figure 5.16. Absorption and emission spectra of free CsPbBr$_3$ (Red) and CsPbBr$_3$-L64 (blue). The free CsPbBr$_3$ nanocrystals were dissolved in toluene while the L64/CsPbBr$_3$ nanocrystals were dissolved in H$_2$O.

Figure 5.17 shows the PL decay of CsPbBr$_3$ and CsPbBr$_3$/L64. The PL decay of CsPbBr$_3$/L64 in water became faster suggesting change in the local environment around perovskite. From this study, it can be suggested that it is possible to increase the solubility of perovskites using block copolymers as a capping agent.

Figure 5.17 Lifetime scans of free CsPbBr$_3$ (Red) and CsPbBr$_3$-L64 (blue). The free CsPbBr$_3$ nanocrystals were dissolved in toluene while the L64/CsPbBr$_3$ nanocrystals were dissolved in H$_2$O.

5.6 Metal-Doped CsPbX$_3$ Nanocrystals

Recently, researchers have reported that optoelectronic properties of perovskite NCs can be efficiently tuned through metal doping with a low concentration of metal dopants or metal doping/alloying with a higher substitution ratio of metal elements in the perovskite crystal structure$^{30}$. Recently, post-synthesis doping of Mn$^{2+}$ ions in CsPbX$_3$ nanocrystals via simultaneous anion and cation exchange was demonstrated in several studies$^{31,32}$. Also, hot injection, one-pot synthesis of Mn-doped cesium lead halide (CsPbX$_3$) perovskite nanocrystals has been reported and efficient intraparticle energy transfer between the exciton and dopant ions resulting in intense
luminescence. To probe their optical properties, we synthesized metal-doped cesium lead halide perovskite nanocrystals through one pot-hot injection method because of the resulting doped perovskite more stable.

### 5.6.1 Synthesis of Cu$^{+2}$ and Co$^{+2}$ Doped CsPbBr$_3$ NCs

We modified a published method reported by Lee, E. and Sheldon$^{33}$. PbBr$_2$ (0.0541 g), CuBr$_2$ (0.00322 g), or CoBr$_2$ (0.0049 g), OAm (0.5 mL), OA (0.5 mL), and ODE (5 mL) were added to a 50-mL 3 neck round bottom flask and were evacuated and refilled with N$_2$ followed by heating the solution to 120 °C for 1 hr. The solution was then increased to 180 °C and after completely dissolved the materials in the flask, dried OAm (0.5 mL) and dried OA (0.5 mL) were subsequently injected to solubilize the solution. Then the Cs-oleate (0.4 mL) was quickly injected and after 10 seconds the solution was cooled with an ice bath. The NCs were precipitated with acetone and the centrifuged followed by dissolving in hexanes. Shown in parts A and B of absorption and PL of CsPbBr$_3$ and CsPbCuBr$_3$, respectively. There is a shift of absorption onset to higher energies with Cu doping. Also, there is a decrease in PL and a shift of PL to lower energies were observed. These changes suggested that Cu doping altered the inner crystal structure of the nanocrystal.

**Figure 5.18.** Comparison steady state measurements Cu-doped CsPbBr$_3$ and CsPbBr$_3$ both in hexanes.
Also, the PL decay became faster with Cu doping when compared to un-doped CsPbBr$_3$ nanocrystals. (Figure 5.19 left) It looks like copper doping made the crystal spherical. (Figure 5.19 right)

![Graph showing lifetime scan of CsPbBr$_3$ and CsPbCuBr$_3$](image)

**Figure 5.19** Lifetime scan of CsPbBr$_3$ and CsPbCuBr$_3$ (left) and TEM for Cu-doped CsPbBr$_3$ (right).

Along similar lines, Co$^{2+}$ doped CsPbBr$_3$ was synthesized and the optical absorption and PL spectra of CsPbBr$_3$ and Co-doped CsPbBr$_3$ is shown in parts A and B of Figure 5.20. A shift in the absorption to longer wavelengths and a shift in PL maximum was observed with Co$^{2+}$ doping. The PL decay trace (Figure 5.20C) of Co-doped CsPbBr$_3$ became faster when compare to undoped perovskite nanocrystal. The results point to the fact that Co-doping significantly alters the optical properties.
Figure 5.20 (A) Optical absorption, (B) PL and (C) time-resolved PL decay of CsPbBr$_3$ and Co-doped CsPbBr$_3$.

5.7 Summary

Cesium lead halide nanocrystals were prepared via solution phase hot injection and tip sonication methods and characterized by TEM, optical absorption spectra as well as steady state PL. The excitation and emission wavelengths for each compound were determined from their respective absorbance spectra, as the halide is changed from Cl to Br and to I, both the PL maxima and absorption maxima shifted to longer wavelengths and results matched well with literature reports. The halide dependence of the optical properties is related to the charge-transfer transition that is influencing the bandgap of the semiconductors. Time-resolved absorption and time-resolved PL measurements were carried out to understand the optical properties of perovskite...
nanocomposites. As the halide is changed from Cl to I, the PL lifetime increased matching what was reported. Excitation of the perovskite NCs by photons with energies higher than the band-gap energy creates electrons and holes in higher excited states. These hot carriers relax to the band-edge states through carrier–carrier and carrier–phonon interactions dissipating excess energy and reach the equilibrium temperature with the lattice. Power-dependent transient absorption measurements have shown exciton thermalization, biexciton recombination and exciton decay. The lifetimes of all these processes increased when the halide is changed from Cl to I. In addition, we have shown that ultrafast transient absorption anisotropy can be able to successfully monitor the biexciton recombination. To the best of our knowledge, this is one of the first study to show the same. Also, 2PA cross-sections of perovskite nanocomposites were determined and they were found to be around $10^6$ GM and have shown that perovskites can be used for nonlinear optical applications. A proof of the principle study has shown that with block copolymers, it is possible to make water soluble perovskite nanocomposites. Also, successful doping of Cu$^{2+}$ and Co$^{2+}$ into perovskites is demonstrated and they seem to influence the optical properties.

5.8 References


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CHAPTER 6

INTERACTION OF SILVER AND HOLD NANOPARTICULES WOTH PEROVSKITE - NANO COMPOSITE- TOWRD PLASMON ENHANCED PHOTOLUMINESCENCE

6.1. Introduction

Chapter 5 dealt with ultrafast exciton relaxation dynamics and two-photon absorption properties of perovskite nanocomposites, making them water-soluble and doping them with metal ions. As the objective of the dissertation is to understand the interactions between nanocomposites and adsorbates, we have investigated the interaction of perovskite nanocomposites with gold and silver nanoparticles. The hypothesis is that as gold and silver nanoparticles, it is possible to achieve plasmon-enhanced PL from them so that it can be used in plasmon-enhanced light-emitting diodes.

Perovskite nanocrystals are considered for many optical applications because the luminescence in the entire visible region can be obtained from changing the halide composition. Several strategies are used to achieve greater PL from perovskites. One such strategy is using plasmons of noble metal nanoparticles and achieves plasmon-enhanced PL from perovskites. Noble metal nanoparticles such as gold, silver, and copper give visible absorption arising from the collective oscillation of electrons called plasmons. The localized surface plasmon resonance (LSPR) in metal nanoparticles has attracted enormous research interest for both fundamental standpoints as well as for applications in interdisciplinary areas of sciences that include photothermal imaging and therapy, plasmon sensing and surface-enhanced Raman scattering (SERS). Strong contribution to SERS arises from electric field enhancement because of surface plasmons of gold and silver nanoparticles. Not only plasmons can enhance Raman signals, they can also be used to enhance the fluorescence of nearby molecules that is termed as metal enhanced fluorescence. To enhance the PL from perovskites, we propose to use the plasmons of gold and silver nanoparticles. However, one negative aspect of gold or silver nanoparticles is the non-radiative deactivation when the fluorophores are close to them either via energy or charge transfer quenching pathways.
CsPbX₃ perovskite nanocrystals synthesized using high temperature route is protected with oleylamine and is soluble in non-aqueous solvents. For studying interactions of plasmonic nanoparticles, it is important to synthesize gold or silver nanoparticles soluble in non-aqueous solvent so that it is possible to study their interactions. Plasmonic enhancement of light harvesting was observed with perovskite based solar cells. But, plasmonic PL enhancement was not well studied. This forms the main motivation behind the research carried out in this Chapter. Silver nanoparticle has strong absorption around 410 nm, therefore it can enhance the PL of CsPbCl₃ perovskite. On the other hand, the gold nanoparticle has an absorption peak around 530 nm which is close to CsPbBr₃ and CsPbI₃ perovskite absorption peak. These differences in the optical properties of gold and silver nanoparticles allow them to interact with certain perovskites that match the optical property of gold and silver nanoparticle.

With perovskite nanocrystals, it is possible to achieve enhanced PL via plasmon effect or energy transfer from metal nanoparticle to perovskites (figure1). However, at the same time, it is possible to have deleterious effects such as PL non-radiative quenching of the perovskite via the energy transfer or electron transfer from the perovskite to metal nanoparticles. The parameters such as the distance between the metal nanoparticle and perovskites, solvent and fabrications can be altered to achieve enhanced PL from perovskites.
6.2 Experimental

6.2.1 Silver Nanoparticle Synthesis

The synthesis procedure of Ag NPs was followed from a published procedure for Qian, D.-J and his group.\textsuperscript{37} Into 25 mL 3-necked flask, AgNO\textsubscript{3} (1.472 mmol, Alfa Aesar, 99.9\%) and 25 mL mixture of ODE and OLA (v/v 4:1) were added. The solution was left under N\textsubscript{2} for 20 minutes, and the solution was stirred to form a cloudy solution. The solution was then heated to 180\textdegree C at a speed of 4\textdegree C/min and left for 2 hours at 180\textdegree C. The precipitate formed as the color of the solution changed from transparent, yellow, dark brown, and finally black. After 2 hours, the temperature was lowered to 150\textdegree C and allowed to ripening for 6 hours. The solution was cooled to room temperature. The solution was transferred to a 50 mL centrifuge tube with absolute ethanol (solution: ethanol v/v 1:2, Alfa Aesar, 85.4\%). Then, the solution was centrifuged at 12000 rpm
for 10 minutes at 25°C. The supernatant was discarded, and the pellet was redispersed in ethanol and sonicated, and centrifuged at 9000 rpm for 10 minutes at 25°C. This washing with ethanol was repeated a total of three times. The final pellet was dispersed in an appropriate amount of hexane and saved as Ag nanoparticles.

6.2.2 Gold Nanoparticle Synthesis

We followed a published procedure for Polavarapu, L. et al.\textsuperscript{38} In 100 mL 3-necked flask, hydrogen tetrachloroaureate (III) hydrate (0.5 mmol, HAuCl\textsubscript{4}·3H\textsubscript{2}O, Sigma-Aldrich, 99.9%) and 40 mL mixture of the solvent of OLA and ODE (v/v 1:1) was added. The solution was sonicated for 10 minutes and stirred in room temperature under N\textsubscript{2} flow. The reducing solution was prepared in different 25 mL flask by dissolving t-butylamine-borane complex (0.5 mmol, tBAB, Sigma-Aldrich, 97%) in OLA (1 mL) and ODE (1 mL) solution. The reducing solution was also sonicated until tBAB was completely dissolved. The reducing solution was added to the precursor solution under vigorous stirring. The solution was allowed to react in N\textsubscript{2} atmosphere for 2 hours at room temperature. After 2 hours, 30 mL of acetone was added to the solution to quench the reaction. The solution was transferred to two 50 mL centrifuge tube, with a large amount of absolute ethanol so that Au nanoparticle can precipitate. The tubes were centrifuged at 9000 rpm at 25°C for 10 minutes. Same with the silver nanoparticle, gold nanoparticle pellet was washed with ethanol three times and dispersed in hexane.

6.2.3 Methods

6.3 Results and Discussion

6.3.1 Characterization of Silver Nanoparticles

The characterization of silver nanoparticles was done using optical absorption spectral measurements. The absorption spectrum of Ag nanoparticles was scanned from 800-300 nm and presented in Figure 6.2. An absorption maximum centered on 413 nm was observed, and it matched well with the plasmon absorption of Ag nanoparticles for a size of 10 nm.\textsuperscript{38}
**Figure 6.2.** The optical absorption spectrum of silver nanoparticles dissolved in hexane measured at room temperature.

### 6.3.2.4 Characterization of Gold Nanoparticles

Like silver nanoparticles, gold nanoparticles that can be made soluble in non-aqueous solvents were also synthesized with oleylamine as the capping agent. The characterization of gold nanoparticles was done using optical absorbance spectral measurement and shown in Figure 6.3. The presence of gold nanoparticle was determined based on plasmon absorption maximum at 523 nm. This spectrum matched well with the literature reports of oleylamine capped gold nanoparticles.

**Figure 6.3.** Optical absorption spectra of gold nanoparticles dissolved in hexane.
6.3.3 Interaction of Gold Nanoparticles and CsPbX₃ Perovskites

The interaction of CsPbX₃ perovskites with gold nanoparticles was investigated with optical absorption, steady-state PL, and PL lifetime measurements.

6.3.3.1 CsPbCl₃ with Gold Nanoparticles

Parts A and B of Figure 6.4 show the optical absorption and steady-state PL of CsPbCl₃ with an increase in Au Np concentration. Enhancement in the PL of the CsPbCl₃ with the increase of the concentration of AuNPs. Suggesting excited-state interaction between the two systems, Also, lifetimes were determined using time-correlated single-photon counting and an increase in a lifetime was observed. (Figure 6.4C).
Figure 6.4. A) UV-vis spectra of CsPbCl$_3$ perovskite with increase in concentration of gold nanoparticles. (B) PL spectra showed an increase in the PL intensity with increase the concentration of Au NPs. (C) PL lifetime of CsPbCl$_3$ with increase in concentration of Au Nps (D) Change in PL intensity and lifetimes as a function of Au Nps.

6.3.3.2 CsPbCl$_2$Br with Gold Nanoparticles

Figure 6.5A and 6.5B show the absorption and PL spectra of CsPbCl$_2$Br perovskite nanocrystals with increase in the concentration of gold nanoparticles. There was a little increase in the PL intensity, suggesting small interaction of perovskite with gold nanoparticles.
Figure 6.5. (A) UV-vis spectra of CsPbBrCl$_2$ with increase in Au Nps concentration. (B) PL spectrum of the system showing small change. (C) Lifetime spectrum of the system showing little change in lifetime.

6.3.3.3 CsPbClBr$_2$ with Gold Nanoparticles

Shown CsPbCl$_2$Br perovskite and Au NPs. The PL of the perovskite has shown a decrease in PL intensity probably arising from energy transfer of perovskite to Au Nps.
Figure 6.6. (A) UV spectrum of CsPbClBr$_2$ as Au NPs concentration increase. (B). PL spectrum for the system of CsPbBr$_2$Cl as the concentration of AuNPs showing quenching in the system as AuNPs increase with a slight peak shift from 478 nm to 472 nm observed. (C) Lifetime decay showing very small change as AuNPs increase. (D) Plot of PL intensity change and lifetime change as a function of Au Np concentration.

6.3.3.4 CsPbBr$_3$ with Gold Nanoparticles

Parts A, B and C of Figure 6.7 show changes in optical absorption, PL intensity and PL lifetimes for CsPbBr$_3$ as a function of Au Np concentration. CsPbBr$_3$ perovskite demonstrated small enhancement of PL intensity, with the increase in absorbance by increasing concentration of gold nanoparticles.
Figure 6.7. (A) UV-vis spectra for CsPbBr$_3$ as the concentration of AuNPs increase. (B) Change in the PL intensity as the concentration of AuNPs increase. (C) Lifetime decay of perovskite as a function of Au Np concentration.

6.3.3.5 CsPbBrI$_2$ with Gold Nanoparticles

Optical absorption, steady-state PL, PL lifetimes of CsPbBrI$_2$ as a function of Au Nps concentration increase is shown in parts A, B and C of Figure 6.8, respectively. CsPbBrI$_2$ perovskite demonstrated a quenching of PL intensity
Figure 6.8. (A) UV-vis spectra of CsPbBrI₂ perovskite as increase in AuNPs concentration. (B) PL spectra of CsPbBrI₂ with increasing AuNPs concentration steady quenching was observed in PL spectra with shift of the maximum emission peak from 640 nm to 610 nm. (C) Lifetime decay showing mostly decrease in the lifetime as the concentration of AuNPs increase. (D) The ratio of PL intensity and ratio of lifetime as a function of Au Nps concentration.

6.3.3.6 CsPbI₃ with Gold Nanoparticles

The interaction of CsPbI₃ nanocrystal with gold nanoparticles investigated. Figures 6.9 A, B and C show the changes in optical absorption, steady-state PL and PL lifetime as a function of Au Np concentration.
Figure 6.9. (A) UV-vis spectra of CsPbI\textsubscript{3} perovskite with gold nanoparticles. (B) PL spectra of CsPbI\textsubscript{3}, with increasing gold nanoparticles concentration. (C) PL lifetime of the system with Au Np concentration increase.

6.3.4 Interaction between Silver Nanoparticles with CsPbX\textsubscript{3} Perovskites

We wanted to investigate the interaction of Provskite with AgNPs.

6.3.4.1 CsPbCl\textsubscript{3} with Silver Nanoparticles

Parts A, B and C of Figure 6.10 show enhancement in PL intensity of provskites and its lifetime as a function of increase in Ag Np concentration.
6.3.4.2 CsPbCl$_2$Br with Silver Nanoparticles

Parts A-C of 6.11 shows CsPbCl$_2$Br perovskite nanocrystal as a function of AgNp concentration. CsPbCl$_2$Br perovskite demonstrated an enhancement of PL intensity.
Figure 6.11. (A) Absorption spectra of CsPbCl₂Br perovskite with increase in concentration of AgNPs. (B) PL Intensity change with increase in AgNPs. (C) PL decay traces at different AgNp concentrations.

6.3.4.3 CsPbBr₃ with Silver Nanoparticles

Figure 6.12A-C shows the absorption, steady-state PL and time-resolved PL decay traces of CsPbBr₃ as a function of Ag Np concentration. As the concentration of AgNps increase, the PL of CsPbBr₃ perovskite quenched, as well as the PL lifetime. The PL intensity quenching is greater than lifetime quenching (Figure 6.12D) indicating charge transfer interactions between CsPbBr₃ and Ag Nps.
Figure 6.12. (A) Absorption spectra of CsPbBr$_3$ with increase in Ag Np concentration. (B) PL intensity change. (C) PL decay traces at different AgNp concentration (D) Comparing the ratio of PL lifetime and PL intensity ratio.

6.3.4.4 CsPbBrI$_2$ with Silver Nanoparticles

The interaction of CsPbBrI$_2$ nanocrystals with silver nanoparticles is shown in Figure 6.13A-C. Silver nanoparticles interacted with CsPbBrI$_2$ perovskite, which resulted in quenching of PL intensity,
Figure 6.13. (A) Absorption absorption spectrum of CsPbBrI$_2$ as the AgNps concentration increase. (B) PL spectra of the system showing quenching the PL as the concentration of AgNPs increase. (C) PL decay traces with increasing AgNPs (D) Plot of PL intensity ratio vs PL lifetime ratio.

6.3.4.5 CsPbI$_3$ with Silver Nanoparticles

The interaction of CsPbI$_3$ at different Ag Np concentrations is shown in Figure 6.14A-C. the data show quenching of PL intensity. The decrease in PL lifetime. The decrease in PL intensity and PL lifetime suggest dynamic quenching and electron transfer interaction between perovskite and Ag Np. There is not plasmon enhancement of PL.
Figure 6.14. (A) Absorption spectrum of CsPbI$_3$ at different AgNp concentrations. (B) PL spectra of CsPbI$_3$ as the concentration of AgNps increase. (C) PL decay traces at different AgNp concentrations. (D) Ratio of PL lifetime and PL intensity as a function of AgNp concentration.

6.4 Discussion and conclusion

In order to investigate the interaction between CsPbX$_3$ perovskites and plasmon nanoparticles, we use the same ligand between CsPbX$_3$ and metallic nanoparticles. Therefore silver and gold nanoparticles were synthesized with Oleylamine which the same for the Perovskite nano crystals as a ligand for better interaction between both systems.$^{16}$ According to the literature, synthesized gold nanoparticle has a size of about 5 nm.$^{23}$ This small size metallic nanoparticle would make interaction with CsPbX$_3$ easy, and possibly give higher plasmon resonance effect.
Also, gold nanoparticles have an absorption peak at around 500-550 nm, which is similar to the absorption peak of CsPbBr$_3$ perovskites.

With other perovskites, gold nanoparticles quenched the PL of perovskites, especially with iodide, tend to prefer orthorhombic phase which losses its property of luminescence.[$^{24}$] Introducing metallic nanoparticles such as gold nanoparticles may have accelerated this property of mixed halide included CsPbX$_3$ perovskites. The perovskites that performed an emission peak shift or fluctuation may went through shape change or deformation. CsPbCl$_3$ perovskite with gold nanoparticles, showed a tremendous enhanced the perovskite PL and fluorescence lifetime. Since silver nanoparticles had an absorption peak at around 410 nm the expectation was formed that silver nanoparticles could enhance the optical properties of CsPbCl$_3$ and CsPbCl$_2$Br perovskites. The reported size of a silver nanoparticle according to the literature, was ~10 nm.[$^{22}$] This size is bigger than gold nanoparticles that were in size of ~4 nm. This bigger size might have caused the quenching of other perovskites.

In the case of the fluorescence quenching, two types of quenching possibilities; collisional or dynamic quenching, and static quenching. Collisional or dynamic quenching can happen by diffusion, when fluorophore and quencher collide during the excited state, the fluorophore can go back to the ground state without emission of a photon. In the case of static quenching, fluorophore and quencher form a complex, which is less fluorescent. Since dynamic and static quenching affects ground and excited state, lifetime measurement helps to determine what type of quenching is CsPbX$_3$ perovskites have with metallic nanoparticles. Dynamic quenching decreases lifetime since quencher depopulates excited state. However, static quenching does not decrease lifetime since quencher is already bound as a complex with a fluorophore. Therefore, if the lifetime is decreasing at the same rate as fluorescence is quenching, it is dynamic quenching, and if fluorescence is quenching faster than lifetime decrease, it is static quenching.[$^{25}$] In this research, CsPbClBr$_2$ with gold nanoparticles, CsPbBr$_3$ with silver nanoparticles, and CsPbI$_3$ with silver nanoparticles are static quenching since their fluorescence-quenching rate is faster than lifetime decrease rate. Therefore, there must be a complex formed in the mixture of perovskites with metallic nanoparticles. This understanding could help such that for future research, researchers can
use different ligands that have weaker intermolecular interaction to prevent them from forming a ground-state complex.

6.5 References


