EXCITED STATE INTERACTIONS IN GRAPHENE OXIDE-SEMICONDUCTOR/METAL
NANOPARTICLE ARCHITECTURES FOR SENSING AND ENERGY CONVERSION

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by

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Abstract

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The recent emergence of graphene, along with its unique and impressive set of properties, has resulted in a concerted effort to incorporate the material into electronic devices and composite materials. Graphene oxide, a chemically modified form of graphene which can be produced economically and in large scale, is one of the most common starting materials for making graphene composite materials with improved conductivity, photovoltaic performance, and photocatalytic activity, to name a few examples. This dissertation describes progress made in understanding and quantifying the electronic properties of graphene oxide as they relate to electron storage and shuttling in composite materials.

A more complete understanding of the nature of electronic interactions in graphene composites was achieved through two processes: 1) A dual electron-titration showing storage and shuttling of electrons in reduced graphene oxide. 2) A method
developed to isolate the energy and electron transfer pathways involved in the deactivation of excited CdSe quantum dots by RGO. The results obtained from these two processes provide insight into the electronic interactions between graphene, semiconductors, and metals.

Additionally, composite films were constructed to demonstrate the electron transfer properties of reduced graphene oxide. TiO$_2$-reduced graphene oxide films were made via a simple drop-cast technique. The films show enhanced photovoltaic and photocatalytic characteristics when compared to TiO$_2$-only films. A stacked architecture incorporating single-layer reduced graphene oxide on thin TiO$_2$ nanoparticle films was developed as a method for illumination-controlled deposition of metal nanoparticles. Films of metal nanoparticles made using this technique were employed as Surface Enhanced Resonance Raman (SERRS) sensors and show nano-molar sensitivity. Finally, quantum dot-reduced graphene oxide composites were made via an electrophoretic deposition process. The resulting films were used as photoanodes in photoelectrochemical cells and show improvements in photocurrent generation of up to ~150% over CdSe-only photoanodes.

On account of the advantageous electronic properties and improved device performance, the work described in this dissertation provides a basis for further exploration in the field of reduced graphene composite materials. The versatility of the material along with the methods designed for customizable film construction makes it an ideal material for next-generation sensors and catalyst materials.
to my wife, Joy
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1.1 The 2-D Discovery

Andre Geim stood grinning on a stage in front of a prestigious crowd of dignitaries and Nobel laureates as he received his own Nobel Prize. Only a few years prior, he and Konstantin Novoselov had busied themselves pulling scotch tape from chunks of graphite. After successfully isolating a single layer of graphite, called graphene, the two-dimensional sheet of sp²-bonded carbon atoms arranged in the shape of a honeycomb lattice was fully probed and measured. The results were surprising to say the least, and represent a set of distinctly unique properties. One of the most peculiar of these is the room-temperature observation of the Quantum Hall Effect.¹ ² Graphene was also the first stable, two-dimensional solid state material reported. Its existence contradicted the prevailing notion that 2-D materials would be too thermodynamically unstable to exist.³ Graphene also claims preeminence as the world’s strongest material with mechanical stiffness of 1,060 GPa, and one of the fastest and most thermally conductive with ambient electron mobilities of 15,000 cm² V⁻¹ s⁻¹
and 3,000 W m⁻¹ K⁻¹, respectively.²⁻⁴⁻⁶ It is also the thinnest at an atomic thickness of 4.2 Angstroms, and highest surface area, with a theoretical surface area of 2,630 m²/g and experimentally observed values up to 2,400 m²/g in activated graphene films.⁷⁻¹³ These high surface area films are achieved through careful control of KOH:GO ratios, and later, annealing conditions which finalize the surface roughening of the RGO sheets.¹³

The 2010 Nobel Prize in Physics, given to Geim and Novoselov for their work with graphene, was awarded based upon the gravity of these findings and the broad implications on the potential of graphene to transform a number of fields. The last few years has indeed produced considerable advancements in both the understanding of the material and its performance-enhancing application in devices ranging from the use of pristine graphene in 100 GHz transistors to the incorporation of reduced graphene oxide in next-generation catalyst substrates.¹⁴⁻¹⁶

1.2 Practical Graphene: Graphene Oxide and Its Reduction

Mass production of graphene is a challenge for those seeking to incorporate it into next-generation devices. Some common routes to pristine graphene include single-layer exfoliation, chemical vapor deposition on carefully prepared transition metal substrates, thermal decomposition of SiC, and surfactant-assisted exfoliation.¹⁷⁻²⁰
One of the most versatile methods of forming single to few-layer graphene on a number of substrates in ambient pressure conditions was reported by Kong and coworkers.\textsuperscript{21} By modifying the deposition surface, typically e-beam deposited and thermally annealed polycrystalline Ni, a low concentration H\textsubscript{2}-CH\textsubscript{4} gas mixture is passed over the Ni during surface cooling. The proposed growth mechanism requires the existence of a solid mixture of Ni and C atoms at high temperatures. When the temperature drops, the carbon atoms’ solubility decreases and they precipitate as graphene on the Ni surface. The crystallite size of graphene therefore mirrors that of the polycrystalline transition metal substrate. Graphene films can then be transferred to another substrate by wet-etching the Ni with HCl.

Figure 1.1 TEM micrographs of CVD graphene grown under ambient pressure on polycrystalline Ni. (a) Graphene suspended over a lacey carbon film along with its electron diffraction pattern. (b) Color contrast shows the existence of single and multi-layer graphene. (Reprinted with permission from ref 21. Copyright 2010 American Chemical Society)
While it is possible to attain single sheets of graphene using these methods, they are not convenient for producing large, possibly even commercial-scale, quantities in a reasonable time-frame. Due to these limitations, oxidation of graphite, or chemical exfoliation, is widely used as a bench-top, water-based technique for achieving considerable amounts of single-layer graphene. Oxidation of graphite is accomplished using strong acids and oxidants, and as such, is a process that is undertaken with care. The process is not new, as earliest records show the first oxidation of graphite in the 19th century, when Brodie mixed graphite with KClO₄ in the presence of fuming HNO₃. He termed the material “graphon”, a name which did not stick. A modified approach on the reported oxidation of graphite by Hummers and Offeman using KMnO₄ and H₂SO₄ is the method that is widely practiced today. In this oxidation process, Mn₂O₇, which detonates when heated above 55 °C, is the most reactive species.

\[
\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow \text{K}^+ + \text{MnO}_3^+ + \text{H}_3\text{O}^+ + 3\text{HSO}_4^- \quad \text{Reaction 1.1}
\]

\[
\text{MnO}_3^+ + \text{MnO}_4^- \rightarrow \text{Mn}_2\text{O}_7 \quad \text{Reaction 1.2}
\]
After oxidation of graphite powder is complete, the material, now referred to as graphene oxide (GO), is easily dispersed in polar solvents, typically water or ethanol. Epoxy and hydroxide groups are imparted to the basal layer of graphene during the oxidation process, while carboxylic groups are found at edge locations. Together, the functional groups are responsible for maintaining exfoliation of single layers of GO by hindering the realignment and restacking of the pi-pi network between sheets.\textsuperscript{24}

Figure 1.2 Oxidation of graphene results in the formation of 1,2 epoxide and hydroxyl groups on its basal plane with carboxylic groups at edge sites. Voids resulting from oxidation also segment GO’s sp\textsuperscript{2} network. (Reprinted with permission from ref 24. Copyright 2010 American Chemical Society)

As convenient as oxidation of graphite is, the chemical exfoliation of graphene does present some drawbacks. Graphene’s superior properties are largely the result of its unique band structure and long-range sp\textsuperscript{2} network, which facilitates the high electron mobility desirable for many composite applications.\textsuperscript{2,25} Functionalization and oxidation of graphene imparts significant changes to its electronic properties, altering the band
gap, interrupting the conjugated network, and inducing surface defects. The properties of GO have been thoroughly characterized and are detailed later in this chapter. While GO maintains high surface area, its conductivity is sharply reduced, depending on degree of oxidation.

The negative impact suffered by GO due to its substantially reduced electron conducting properties can be mitigated by reducing GO in order to partially restore its sp$^2$ network. Reduction of GO to form reduced graphene oxide (RGO) is accomplished via chemical treatments, annealing in vacuum, microwave and laser irradiation, or by photochemical methods. Following reduction, RGO exhibits good conductivity, typically on the order of 1-100 S cm$^{-1}$, high surface area, and is a water-dispersible material useful for a wide range of applications.

A series of studies by Chhowalla and co-workers tracked the recovery of the sp$^2$ network necessary for percolation of the material as a function of annealing temperature. The connection between sp$^2$ regions slowly improves with annealing temperature. However, during reduction of GO, persistent carbonyl and ether groups are formed. Successful removal of these groups could result in conductivities approaching that of polycrystalline graphite, near 1500 S cm$^{-1}$. 

6
While chemical methods efficiently reduce GO, they often leave unwanted chemical residues behind, as observed in C1s XPS signals resulting from C-N bonds following hydrazine reduction, and can result in the restacking of graphene sheets if reduction conditions are too harsh. Photochemical reduction of GO typically involves the assistance of semiconductor nanoparticles, which have the added benefit of keeping RGO sheets from restacking. For example, when ZnO semiconductor nanoparticles are deposited on GO and subjected to band gap illumination, photogenerated electrons from the ZnO conduction band are transferred to GO, inducing reduction. This particular method allows for control of the reduction process, which proceeds with illumination-time.

Figure 1.3 Depictions of sp\(^2\) (dark grey) and sp\(^3\) (light grey) regions in GO as a function of annealing temperature. (a) room temperature; (b) ~100 °C; (c) ~220 °C; (d) ~500 °C. Percolation between sp\(^2\) cluster begins at ~220 °C, with a 0.6 sp\(^2\) fraction. (Reprinted with permission from ref 37. Copyright 2010 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.)
1.3 Spectroscopic Characterization of GO and RGO

The reduction of GO to RGO can be monitored using a variety of spectroscopic techniques. UV-visible absorption spectroscopy of dispersed GO reveals the $\pi$- $\pi^*$ transition which absorbs at $\sim230$ nm. Upon reduction, a red-shift to $\sim260$ nm occurs as a result of the restoration of sp$^2$ conjugation. The completion of this shift in the UV region of the spectrum occurs over a period of 6 hours when GO is thermally reduced at $180 \degree C$.\textsuperscript{40} Across the visible spectrum, a single sheet of graphene absorbs $\sim2\%$ of incident light.\textsuperscript{41} Qualitative assessment of unknown (R)GO concentrations can be estimated by matching the optical density of (R)GO dispersions with those from known concentrations. Concentrations can be determined by drying a known volume of (R)GO suspension and weighing the solid material.

Raman spectroscopy is a rich source of information for determining (R)GO characteristics such as doping, defect density, temperature effects, and the number of graphene layers in a sample.\textsuperscript{10,42-45} Four main bands exist in a typical Raman trace of GO: the G-band near 1560 cm$^{-1}$ resulting from zone-center optical phonons, the doubly resonant, disorder-induced D band near 1350 cm$^{-1}$, and the 2D band at 2600 cm$^{-1}$. In GO with a high concentration of defects, a $D'$-band emerges at $\sim1620$ cm$^{-1}$.\textsuperscript{26}
The ratio of the G:D intensities can be used to examine crystallite size. Additionally, the 2D band is used as an indicator of how many layers of graphene are present in the sample. The frequency of the 2D broadens and blue-shifts when multiple layers are present, and splits into a doublet when the material approaches graphite-like stacking.

Figure 1.4 Raman spectra of forms of graphite. Left: Characteristic Raman spectra of graphite, GO, and graphene. Graphene does not exhibit the defect-induced D-band. Right: The broad 2D band near 2700 cm\(^{-1}\) indicates the presence of few to multi-layer GO. (Reprinted with permission from ref 28. Copyright 2010 American Chemical Society)

X-ray diffraction, or XRD, is used to check the spacing of stacked graphene layers in films made from (R)GO. Pristine graphene exhibits 3.4 Å layering, corresponding to a 2theta value of 26.7°. Upon oxidation, these layers expand to accommodate functional groups. This is evidenced by a shift in the 2theta value from 26.7 ° to ~11°, which
corresponds to an increased layering to about 8.14 Å. Reduction of GO results in a decrease in the layering, but typically does not exhibit long-range stacking of similar heights, so a very broad, weak peak above 11° 2theta results.

X-ray photoelectron spectroscopy is another strong tool for determining the nature of (R)GO, specifically the degree of oxidation in the material. The C1s peak in GO is examined for the relative intensities of C-C, C=O, C-O, and C(O)O environments. XPS spectra taken prior to and following the reduction of GO can confirm the effectiveness of the reduction process.

![Figure 1.5 XPS spectra with peak fits for each C-O bond environment. (a) XPS spectrum for GO, and (b) XPS spectrum for RGO showing a reduced C-O bonding. (Reprinted with permission from Elsevier, ref 47.)](image)
Finally, transmission electron microscopy (TEM) of (R)GO is utilized to determine degree of exfoliation, size, crystallinity, and surface feature characteristics. While most methods of characterization indirectly provide information concerning the size and layered nature of a GO sample, TEM allows one to “look” at the material and determine the (R)GO’s size or degree of exfoliation.

Typically, the (R)GO sample is placed on a holey carbon grid in order to provide sufficient contrast to locate single sheets of graphene. Operating the TEM in a defocused mode also assists in maximizing the contrast of these atomically thin sheets of carbon. Normal TEM grids have an amorphous carbon backing that individual sheets of graphene blend into, making them virtually invisible. Contrast and selected area diffraction patterns are used to determine the number of graphene layers in a particular sample. TEM is also an excellent system for analyzing the interaction and loading of graphene and deposited nanoparticles in composite materials. For atomic resolution of surface features, low accelerating voltages (60 kV) are used in combination with an aberration-corrected TEM system to provide detailed surface resolution of graphene, GO, and RGO.48
The usefulness of (R)GO as a composite material is evidenced by the large number of applications that have taken advantage of RGO’s high surface area, thinness, and conductivity. The favorable properties of (R)GO, in addition to its natural abundance, make it very attractive as a starting point for composite materials. Promising results have been reported using RGO in plastic composites to create stronger, conducting plastics, and it has been employed as a transparent conducting material in all-organic LEDs. Additionally, RGO is used as a delivery medium for cancer-fighting drugs, and is united with polyaniline nanofibers to make flexible...
supercapacitor materials. An especially promising area for RGO composites is in the field of sensing and energy conversion. RGO paired with metal and semiconducting nanoparticles have found numerous applications, ranging from simple catalyst mats for metal nanoparticle deposition to more complex tertiary structures designed for solar energy conversion.

The usefulness of RGO for composite application is demonstrated in polystyrene-graphene composites reported in which the electrical conductivity percolation threshold was achieved at 0.1 vol. % of filler. Conductivity levels approaching 1 S m\(^{-1}\) were recorded at 2.5 vol. %. These levels are very similar to those achieved in carbon nanotube-polystyrene composites, albeit with a more economical filler.

1.4.1 RGO-Metal Nanoparticle Composites.

RGO serves as an excellent substrate for the dispersion and deposition of metal nanoparticles for photocatalysis applications. A number of deposition techniques have been reported with the aim of selective size control of catalytically-active metals such as Ag, Au, Pt, and Pd. Sonication of a metal ion-GO dispersion in the reducing presence of polyethylene glycol results in high-coverage, metal nanoparticle-RGO sheets. An additional benefit of sonication-induced reduction is the exfoliation of individual RGO sheets induced by sonication. This increases the likelihood of metal nanoparticle deposition on single-layer RGO sheets. Other methods for inducing metal nanoparticle deposition on graphene include co-reduction of GO and metal ions using microwave irradiation, or gentle heating in the presence of ethylene glycol.
For microwave reduction of GO and metal nanoparticles, water-dispersed GO, at a concentration of 1 mg/mL, is combined with a reducing agent, typically hydrazine hydrate, and a metal precursor. This mixture is placed in a conventional microwave oven and irradiated at 1000 W for 10 seconds followed by mixing. This cycle is repeated twice, and results in to co-reduction of GO and metal precursor. Further, metal deposits with good dispersion onto the RGO surface. This method was used to form Pd, Cu, Pd/Cu, Au, Ag, and Cu metal nanoparticle composites on RGO.29

**Figure 1.7** Palladium nanoparticles on RGO shown at different magnification levels. (a)-(c) Pre-made Pd nanoparticles mixed with RGO. (d)-(f) Pd and RGO co-reduced with microwaves show excellent loading and smaller Pd nanoparticles on RGO. (Reprinted with permission by The Royal Society of Chemistry from ref 64.)
Additionally, metal nanoparticle-RGO composites have been employed in a number of sensing and catalytic applications with encouraging results.\textsuperscript{19,66,67} In one instance, Pt nanoparticles were solvothermally reduced in the presence of GO. The resulting composite material exhibited enhanced methanol oxidation performance when compared to a Pt/carbon black catalyst.\textsuperscript{66} The success of these initial efforts provides increased motivation for further manipulation of RGO-metal composite designs to optimize sensing and catalytic efficiencies.

1.4.2 RGO-Semiconductor Nanoparticle Composites

Semiconductor nanoparticle films used in fuel cell, photovoltaic and photocatalytic devices have shown improved performance in designs incorporating RGO.\textsuperscript{68-70} In one instance, RGO-Cu\textsubscript{2}S composites were developed as high-performance counter electrodes for quantum dot solar cells employing a polysulfide/sulfide electrolyte.\textsuperscript{71} In these systems, Cu\textsubscript{2}S participates in reduction of the polysulfide species while graphene serves as a high surface area, conducting substrate. Improved performance of semiconductor-RGO composites further solidifies RGO’s role as an electron mediator.

Semiconductor-RGO architectures have also been employed as Li-ion battery anodes, catalyst materials for hydrogen production, and substrates for dye-sensitized solar cells.\textsuperscript{70,72,73} Lithium ion battery anode composites made with RGO-Mn\textsubscript{3}O\textsubscript{4}, TiO\textsubscript{2}, and Co\textsubscript{3}O\textsubscript{4} have recorded high specific capacities, fast charging rates, and good cycling stability.\textsuperscript{74-76}
In a final example, TiO$_2$ nanoparticles were grown directly onto RGO for use in dye-sensitized solar cells. Such a configuration allows for intimate contact between the semiconductor and RGO, which is vitally important in systems that rely on interfacial electron transfer. Results show a nearly three-fold increase in photocurrent production from dye-sensitized solar cells made with RGO-TiO$_2$ composites versus TiO$_2$–only cells.

![Figure 1.8](image)

**Figure 1.8** (a) SEM image of TiO$_2$ grown on RGO, scale bar 10 micron. (b) High resolution TEM with diffraction pattern characteristic of TiO$_2$, scale bar 50 nm. (Reprinted from ref. 76. Copyright 2010 Springer.)

1.4.3 RGO-Quantum Dot Composites

The field of (R)GO-quantum dot composites has only recently emerged. Much of the initial work in this area has focused on the development of synthetic techniques for these composites, including chemical vapor deposition of quantum dots onto RGO, solution-based and electrochemical in-situ growth of CdS on RGO, and ligand exchange
of long-chained organics with pyridine to form water-soluble RGO-CdTe quantum dot composites.\textsuperscript{78-82} The pyridine in such systems serves to link quantum dots with RGO, providing improved electron transfer.

Current applications for the quantum dot-RGO composites include biomolecule sensing, bioimaging, LEDs, and flexible and transparent photoconductors.\textsuperscript{83-85} Forster Resonant Energy Transfer (FRET) between CdSe and graphene has been confirmed in a study involving pristine, single-layer graphene with deposited CdSe quantum dots.\textsuperscript{86} Fluorescence quenching through energy transfer can be used to detect target analytes which are capable of increasing the physical distance between the GO and quantum dot. In one study, CdTe quantum dots were functionalized with oligonucleotide molecular beacons.\textsuperscript{83} Upon introduction of a complimentary strand as a target molecule, the fluorescence of CdTe recovers as energy transfer to GO is greatly reduced due to an increase in the distance between CdTe and GO surface.

1.4.4 RGO Composites Utilizing Molecular Species

The versatility of RGO as an electron shuttle has demonstrated increased versatility due to the elucidation of charge transfer events between molecular species and RGO. The photogenerated radical species of methyl viologen, MV$^{+*}$ transfers electrons to GO in a manner similar to photoexcited TiO$_2$ nanoparticles.\textsuperscript{87} Strong interactions between RGO and 5, 10, 15, 20 tetrakis (1-methyl-4-pyridinio) porphyrin tetra (p-toluenesulfonate), or TMPyP, is evidenced by a red-shift in porphyrin absorbance, fluorescence quenching, diminishing singlet excited lifetimes, and the
creation of a porphyrin radical cation species, which directly implicates electron transfer in such composites.\textsuperscript{88} Several applications, including biosensing, nonlinear optics, and the creation of conducting films, take advantage of the electronic interactions observed in RGO-porphyrin composites.\textsuperscript{89-91}

1.4.5 Future Advancements in RGO Composite Designs

The promising results achieved in composites utilizing the high surface area and exceptional electronic properties of RGO serve as a foundation on which the next-generation of energy conversion and sensor materials can be erected. Specific areas requiring further research advancements include a more detailed and quantitative description of the electronic interactions in graphene composites, the development of techniques designed to increase the tailorability of graphene composites with specific loadings and inclusion of diverse active materials, and lastly, improvements in film-making processes designed to maximize graphene dispersion leading to optimum device performance at low graphene loadings.

One can imagine the possibility of utilizing semiconductor-graphene-metal nanoparticle composites as stand-alone, transferable films to accomplish selected photochemical catalytic reactions. It also is conceivable to engineer RGO composite films which separate different catalyst nanoparticles and functions on opposing sheet surfaces. This configuration could be exploited to separate half-reactions or enable a multi-catalytic response from a single sheet of RGO. Additionally, the combination of
conductivity and near-transparency in graphene places it in a unique position to boost performance in photovoltaic materials.
CHAPTER 2:

STORAGE AND SHUTTLING OF ELECTRONS IN REDUCED GRAPHENE OXIDE

A more complete description of electron transport in graphene composite systems is required to effectively design (R)GO composite systems for specific sensing and energy conversion processes. Promising results have already been achieved using the excellent electronic properties of graphene-based systems for nanoelectronics, polymer composites, intercalation materials, catalysis and photovoltaics. Many of these composite materials rely on RGO’s ability to store and shuttle electrons throughout its conjugated network. In an attempt to understand and quantify this process, a step-wise electron transfer system was developed to monitor electron shuttling to and from the RGO.54

2.1 Detailing Electronic Properties of GO Through Electron Titration

The solution-based electron transfer system developed exploits the electronic interactions between colloidal TiO₂ nanoparticles, graphene oxide, and silver. UV-visible spectroscopy was used to track the movement of electrons through this system. The photographs in Figure 2.1 provide a color map for each step of the process. Conditions were carefully controlled to ensure transfer of electrons proceeded in one direction,
from the TiO$_2$ nanoparticles, to the GO, then to the Ag nanoparticles. This process is described in Reactions 2.1-2.3.

$$\text{TiO}_2 + \text{hv} \rightarrow \text{TiO}_2(\text{e} + \text{h}) \quad \text{Reaction 2.1}$$

$$\text{TiO}_2(\text{e}) + \text{GO} \rightarrow \text{RGO} \quad \text{Reaction 2.2}$$

$$\text{RGO}(\text{e}) + \text{Ag}^+ \rightarrow \text{RGO} + \text{Ag} \quad \text{Reaction 2.3}$$

**Figure 2.1** Photographs showing the color changes observed during stepwise transfer of electrons. (1) Storing electrons in TiO$_2$ by irradiating the deaerated ethanol suspension with UV light ($\lambda > 300$ nm) for 30 minutes. (2) Addition of deaerated ethanol suspension of GO until no blue color remains. Gray-colored solution results due to the formation of RGO. (3) Reduction of Ag$^+$ to Ag nanoparticles (red color) by stored electrons in RGO following the addition of deaerated AgNO$_3$ solution. (Reprinted with permission from ref 54. Copyright 2010 American Chemical Society.)
2.1.1 Generating Titratable Electrons in TiO$_2$

The controlled electron transfer process begins by exposing an N$_2$-purged, colloidal TiO$_2$ solution to UV-illumination in order to generate a finite bank of electrons. Under these conditions, it is possible to store and quantify electrons in surface defect trap sites on the TiO$_2$. The colloidal titanium dioxide suspension (6.5 mM, degassed) was prepared by the hydrolysis of titanium (IV) isopropoxide in 200-proof ethanol. Under UV-illumination ($\lambda <$380 nm), colloidal TiO$_2$ nanoparticles suspended in ethanol undergo charge separation, forming electron-hole pairs. While the vast majority of these charge carriers recombine, a fraction of holes are scavenged by ethanol. The excess electrons become trapped at surface defect Ti$^{4+}$ sites.$^{100}$ The stored surface electrons remain stable for many days if the system is kept free from electron-scavenging species such as O$_2$. These trapped electrons absorb broadly in the red regime of the visible spectrum, and thus their concentration can be monitored using UV-visible spectrophotometry. The absorption reflects the energy associated with the electronic transition from the TiO$_2$ trapped state to the conduction band. The number of trapped electrons can be quantified from the absorption spectrum using an extinction coefficient of 760 M$^{-1}$cm$^{-1}$ (at 650 nm).$^{101}$ This peak can be seen in Figure 2.2 (A), trace (a).
2.1.2 Electron Transfer from TiO$_2$ to GO

Electrons are titrated from TiO$_2$ by simple addition of an N$_2$-purged GO dispersion. GO serves as the electron accepting material, and is consequently reduced by the electron transfer. The absorbance spectrum of the solution was recorded following each incremental addition of the GO dispersion to the blue-colored TiO$_2$ suspension. The maximum absorption peak appearing at ~700 nm in the absorption spectrum (trace a in Figure 2.2 (A)) represents the trapped electrons resulting from

![Absorbance](image)

**Figure 2.2** (A) Absorption profiles of (a) photoexcited TiO$_2$ suspension after UV irradiation (b) TiO$_2$-RGO suspension after addition of GO to photoexcited TiO$_2$ (c) TiO$_2$, 7.5 mM in deaerated ethanol and (d) GO, 0.5 mg/mL in ethanol. (B) Titration of trapped electrons from photoexcited TiO$_2$ by GO. Changes in the 650 nm absorption following incremental addition of GO are used to determine the number of electrons transferred from TiO$_2$ to GO. Electrons consumed levels off near 7 µmol electrons at additions of GO greater than 165 µg. (Reprinted with permission from ref 54. Copyright 2010 American Chemical Society.)
photoexcitation of TiO$_2$. A decrease in absorption is seen following the addition of GO suspension (spectrum b in Figure 2.2 (A)). This decrease in absorption occurs as electrons are transferred from TiO$_2$ to GO, where they are used in its reduction. A previous study describes the GO reduction by photoexcited TiO$_2$. The GO suspension is sequentially added until the broad absorption peak ~700 nm is fully bleached, indicating a complete transfer of stored TiO$_2$ electrons to GO.

The decrease in absorption at 650 nm is used to estimate the number of electrons transferred to GO. Figure 2.2 (B) shows the moles of electrons (6.7 µmol total) consumed with increasing addition of GO (0.5 mg/mL). At low GO concentrations (<10 µg/mL), the electron transfer from TiO$_2$ to GO is more efficient and occurs at a rate of ~0.10 moles of electrons per gram of GO. At higher GO concentrations, electron transfer occurs at a slower rate of 0.033 moles of electrons per gram of GO.

A fraction of the electrons transferred from the TiO$_2$ nanoparticles into GO are consumed in the reduction of GO while some are stored in the RGO network. The reduction step is associated with the partial restoration of the π-π network. The double layer charging usually facilitates stabilization of stored electrons in carbon nanostructures. As shown in a previous study, electron transfer from excited TiO$_2$ into single wall carbon nanotubes continues until the two systems attain charge equilibration. Because the conduction band of TiO$_2$ is -0.5 V vs NHE and the Fermi level of RGO is ~0 V vs NHE, a quick and efficient electron transfer occurs during initial
addition of GO. As the Fermi level equilibrates, a drop is duly observed in the rate of electron transfer from 0.10 moles/g GO to 0.033 moles/g GO.

2.1.3 Transfer of Stored Electrons from RGO to Ag⁺ Ions

Because the total disappearance of the 650 nm absorption peak is associated with the reduction of GO as well as storage of electrons, the quantity of stored electrons can be determined by titrating them with another electron acceptor. In order to estimate the number of stored electrons in RGO, a known concentration of deaerated AgNO₃ in ethanol (12.5 mM) is added in small increments to the RGO dispersion. With the incremental addition of AgNO₃ solution, a new absorption band emerges having a maximum around ~410 nm. This absorption band is characteristic of the surface plasmon resonance of Ag nanoparticles (Figure 2.3 (A)). Once all of the stored electrons are scavenged, further addition of AgNO₃ does not result in changes to the Ag nanoparticle absorption band.

Figure 2.3 (B) shows the quantitative transfer of stored RGO electrons (0.91 µmol) to Ag⁺, as measured from the increase in the absorption at 410 nm. The breakpoint at which no further increase is seen in the 410 nm absorbance corresponds to the titratable electrons that were previously stored in RGO. Using the ratio of electrons transferred to Ag⁺ to total electrons transferred to GO by photoexcited TiO₂, it is estimated that ~16 ± 4 % of electrons are stored in RGO while the rest are utilized in the reduction of GO to RGO.
Thus, a simple titration method was executed to distinguish stored electrons in RGO from those used in the reduction of GO, as well as establish the electron storage and shuttling properties of (R)GO.

2.2 Resulting Semiconductor-RGO-Metal Composites

This method of electron titration has an additional advantage of resulting in the formation of semiconductor-graphene-metal nanoparticle composites. Deposition of semiconductor and metal nanoparticles occurs concurrently with their respective electron transfer events. Further, the size of metal nanoparticles can be controlled via

Figure 2.3 (A) Traces (b)-(m) were recorded following incremental (10µL) addition of 12.5 mM AgNO₃ to RGO (~165 µg in 4.0 mL ethanol). The increase in the 410 nm absorbance peak is due to the sequential reduction of Ag⁺ by stored electrons in RGO. (B) The total amount of Ag⁺ required to extract the stored electrons in RGO is determined to be 0.91 µmoles. (Reprinted with permission from ref 54. Copyright 2010 American Chemical Society.)
illuminated time of TiO₂. Longer irradiation times correspond with more electrons for metal ion reduction and therefore larger particles.

2.2.1 Scanning Electron Microscopy: Surface Morphology of Composite Films

Films of the composite material were created to study metal nanoparticle size, film structure, and surface morphology. SEM images of the TiO₂-RGO-Ag composites at two different magnifications are shown in Figure 2.4. Several layers of stacked RGO composite sheets are observed (Figure 2.4 (A)). The stratified layers exhibit particle loading on all RGO surfaces. Despite the layering of RGO sheets due to solvent evaporation, the presence of TiO₂ and Ag nanoparticles keep these layers sufficiently exfoliated. Such a configuration helps to retain the characteristics of individual RGO sheets. Elemental analyses confirm the presence of both Ag and TiO₂ on RGO surfaces (Figure 2.4 (B)). These results further provide credence to the stepwise electron transfer process resulting in semiconductor and metal nanoparticle deposition on RGO.
2.2.2 Transmission Electron Microscopy: Shuttling Electrons Across the π–π Network

While the absorption changes and SEM images confirm the transfer of electrons from TiO$_2$ to GO and then RGO to Ag$^+$ to form Ag nanoparticles, it is important to confirm the placement of these Ag nanoparticles. If TiO$_2$ nanoparticles were directly involved in the reduction of Ag$^+$, deposition of Ag nanoparticles would occur directly on the TiO$_2$ surface. Depositing metal nanoparticles on the surface of UV-irradiated TiO$_2$ has been reported in earlier studies.$^{104-106}$ If indeed RGO is responsible for shuttling electrons from TiO$_2$ to Ag$^+$, the particles should be deposited at separate sites on the

![Figure 2.4](image)

**Figure 2.4** (A) SEM image of RGO-TiO$_2$-Ag composite showing stacked layers of RGO, each covered with TiO$_2$ and Ag nanoparticles. (B) EDS confirms the presence of Ag and Ti in the composite film. (C) Lower resolution image of composite. (Reprinted with permission from ref 54. Copyright 2010 American Chemical Society.)
same graphene sheet. Figure 2.5 shows the TEM images of the GO-TiO$_2$-AgNO$_3$ system before reduction (Figure 2.5 (A)) and RGO-TiO$_2$-Ag after Ag$^+$ reduction (Figure 2.5 (B)).

The micrograph of a physically mixed GO-TiO$_2$-AgNO$_3$ system (Figure 2.5 (A)) shows at least 3-4 stacked GO sheets. The TiO$_2$ in this system was not photoexcited; therefore, no step-wise reduction process occurred and no significant particle loading is observed on RGO sheets. The TEM image in Figure 2.5 (B) shows similar stacked sheets, albeit with deposited nanoparticles. In this system, TiO$_2$ was subject to initial photoexcitation, providing electrons available for transfer from TiO$_2$ to GO to Ag$^+$. Analysis of the lattice spacings resolved from the graphene composite shown in Figure 2.5 (B) reveal periodicities of 2.12 Å (Figure 2.5 (C)) and 2.35 Å (Figure 2.5 (D)) from separates sites on the composite. The lattice spacings correspond to the (0-110) plane of graphene and the (111) Ag face, respectively. Both TiO$_2$ and Ag nanoparticles are well-dispersed on most RGO sheets.

TEM analysis of the composite material without metal nanoparticles was conducted using a holey carbon grid to further ascertain the nature of TiO$_2$ on RGO. A dilute sample containing only TiO$_2$ on RGO was drop-cast on a holey carbon grid and TEM images were compared to a sample containing both TiO$_2$ and Ag particles on RGO sheets.
Figure 2.5 (A) The TEM micrograph of the TiO$_2$-GO-AgNO$_3$ composite system with no initial TiO$_2$ photoexcitation and no significant nanoparticle loading on GO sheets. (B) The RGO-TiO$_2$-Ag composite shown was subject to initial photoexcitation of TiO$_2$. This system shows significant nanoparticle loading, indicating the storage and shuttling of electrons across RGO sheets. Inset displays EDS data confirming presence of Ag and Ti. (C) HRTEM-resolved lattice image taken from composite shown in Figure 5B. The 0.212 nm lattice spacing corresponds to (0-110) graphene plane spacing. (D) Observed lattice spacing of 0.235 nm for the Ag (111) face. (Reprinted with permission from ref 54. Copyright 2010 American Chemical Society.)
Figure 2.6 (A) presents a TEM image of a TiO$_2$-RGO composite without Ag nanoparticles. The TiO$_2$ particles are not easily discernible at low magnifications due to their small size. Higher magnification of this composite reveals that most TiO$_2$ nanoparticles have diameters of ~3 nm, and are well-dispersed throughout the sheet (Figure 2.6 (B)). These images can be compared directly to the RGO-TiO$_2$-Ag composites shown in Figures 2.6 (C) and 2.6 (D). The composites including Ag exhibit larger, high-contrast particles.

Elemental analysis of two separate regions on the composite was performed to confirm the location of TiO$_2$ and Ag nanoparticles (Figure 2.6 (D)). Scanning transmission electron microscopy (STEM) was employed to analyze the energy dispersive x-ray spectra (EDS) at different locations within the composite. EDS spot #1 was taken from a high contrast particle and shows a strong peak indicating the presence of silver. EDS spot #2 was taken in the middle of the RGO sheet, away from any high contrast, silver nanoparticles. Spot #2 shows a clear titanium peak and the absence of a silver peak, indicating the presence of TiO$_2$ at locations on the RGO sheet separate from Ag.
Figure 2.6 (A) TEM micrograph of RGO-TiO$_2$ composite on holey carbon (prepared without AgNO$_3$) (B) A higher magnification image of the composite from Figure 2.6 (A) reveals TiO$_2$ nanoparticles with diameters of ~3 nm. (C) TEM micrograph of the RGO-TiO$_2$-Ag composite on holey carbon. (D) STEM image confirms Ag and TiO$_2$ nanoparticles at distinct sites on a RGO. (Reprinted with permission from ref 54. Copyright 2010 American Chemical Society.)
2.3 Atomic Force Microscopy (AFM) of Composites

The RGO composite with TiO$_2$ and Ag nanoparticles was further analyzed using AFM. Figure 2.7 compares the surface morphology of the three samples deposited on mica sheet, (A) neat GO before modification (B) TiO$_2$ + GO + AgNO$_3$ system before subjection to the reduction process, and (C) the photoexcited TiO$_2$ + GO + AgNO$_3$ system after completion of the electron transfer process.

The first two samples serve as blanks (Figures 2.7 (A & B)), and the third sample is the final composite product demonstrating the presence of TiO$_2$ and Ag nanoparticles on RGO. The neat GO shown in Figure 2.7 (A) displays a smooth surface with a height of 1.45 nm. This height is slightly greater than the pure graphene sheet and is attributed to the functionalization of GO and surface adsorption of ambient water. The height value observed for the GO sheet is within the range of previously reported GO thicknesses.$^{65,107-109}$ A curled edge is also observed, corresponding to a height profile that is approximately doubled. The sample of GO with TiO$_2$ and AgNO$_3$ that has not undergone the reduction process (Figure 2.7 (B)) exhibits a rougher surface than neat GO, with particles as large as 3 nm (diameter) on the GO surface. This increase in surface roughness is likely to arise from the binding of ~3 nm TiO$_2$ nanoparticles and adsorption of ions as the solvent evaporates during sample preparation. The final sample (Figure 2.7 (C)) of GO, having undergone electron transfer from photoexcited TiO$_2$ to GO and then RGO to Ag, displays a much higher surface roughness, with particles heights on the order of 5-15 nm significantly covering the RGO surface. The presence of
larger-sized particles confirms the simultaneous reduction of Ag\(^+\) ions by stored electrons within RGO and their deposition as Ag nanoparticles.

**Figure 2.7** AFM images and surface profiles comparing surface characteristics of three samples. (A) Neat GO with layer height of \(~1.45\) nm (B) TiO\(_2\)-GO-AgNO\(_3\) mixed system with no UV-illumination of TiO\(_2\) and therefore no electron transfer or Ag nanoparticle deposition (C) TiO\(_2\)-RGO-Ag system after completion of electron transfer, showing nanoparticle deposition on RGO. (Reprinted with permission from ref 54. Copyright 2010 American Chemical Society.)

This chapter highlights the quantitative electron transfer process devised to demonstrate storage and shuttling of electrons within (R)GO. The resulting description of the electronic interactions in (R)GO composites should serve to assist in the design of new RGO composite materials utilizing RGO’s excellent electronic properties. Also described is the semiconductor-graphene composite created as a result of the electron
transfer process. The illustration in Figure 2.8 summarizes the stepwise electron transfer processes involved in the making of a 2-dimensional semiconductor-metal nanoparticle mat. Photogenerated electrons in TiO\textsubscript{2} are first transferred to GO. A fraction of these electrons are used in the reduction of GO and the rest (~16\%) are stored in the RGO sheet. After the introduction of AgNO\textsubscript{3}, the stored electrons are used to reduce Ag\textsuperscript{+} to Ag\textsuperscript{0} nanocrystals, which then serve as seeds for additional silver growth.

This technique provides a convenient way to achieve a fairly uniform distribution of semiconductor and metal nanoparticles on RGO with spatial distinction. This approach can be conceivably extended to fabricate tailored semiconductor-metal catalyst or sensor systems on a 2-D, RGO substrate. Furthermore, by controlling the magnitude of electron storage in TiO\textsubscript{2} and the amount of AgNO\textsubscript{3} addition, it should also be possible to control the size of metal nanoparticles. In order to evaluate the potential of these composites for sensing or energy conversion, a successful transition from this solution-based technique to a film-based model must also be achieved.
Figure 2.8 Illustration depicting the 3 step electron titration process utilized to quantify storage and shuttling of electrons in (R)GO. The resulting composite materials should serve as customizable semiconductor-graphene-metal sensors or catalyst mats.
CHAPTER 3:
SOLUTION TO FILM TRANSITIONS: CREATION OF FILMS FOR NEXT-GENERATION PHOTOVOLTAIC, PHOTOCATLYTIC, AND SENSING COMPOSITES

The preeminence of graphene’s electronic properties has been well-described.\textsuperscript{1,2,5,9,10,110} A description of the electron storage and shuttling capabilities of (R)GO is presented in the previous chapter. Recent work has begun to leverage those excellent properties, specifically graphene oxide’s ability to function as an electron shuttle, into devices such as catalysts, batteries, and photovoltaics with enhanced performance.\textsuperscript{15,67,68,111,112} In order to realize the full potential of graphene composite materials, advancements in film assembly techniques must be developed which will enable tailoring of the composite film to meet the requirements of specific applications.

3.1 Improved Photovoltaic and Photocatalytic Response of Titanium Dioxide-RGO Composites

With the aim of successfully completing the transition from solution-based composites to practical films, a preliminary approach was adopted to discover the effectiveness of RGO as an electron shuttle in TiO\textsubscript{2} films for photovoltaic and photocatalytic applications. Films were constructed via mixing of P25 TiO\textsubscript{2} and GO. The
resulting composite mixture was deposited onto a defined area with gentle heating. Different amounts of RGO were incorporated into the composite films to monitor the balance between gains made by RGO conductivity and any possible losses due to light scavenging. Employed as a scaffold for TiO$_2$ nanoparticles, RGO should create a 2-D conductive support path for charge transport and collection at the electrode surface.

Surface morphology of films was examined using electron microscopy to determine the extent of TiO$_2$-RGO interaction as well as RGO dispersion throughout the TiO$_2$ network. Photocurrent and photocatalytic performance of films were also evaluated, and a description of RGO’s role in the performance of the composite films is included.


The morphology of RGO-TiO$_2$ nanocomposites was examined using both TEM and SEM. Diluted samples of the RGO-TiO$_2$ nanocomposite were placed on Toray carbon paper for SEM characterization. Images of the nanocomposite reveal the entwined nature of graphene sheets in TiO$_2$ nanoparticle networks.

Figure 3.1 (A) shows a SEM image of the RGO-TiO$_2$ nanocomposite with some graphene edges marked by dotted lines to assist the reader. The SEM image in Figure 3.1 (B) depicts a larger graphene sheet emerging from the TiO$_2$ assembly. The juxtaposition of the sheet with the TiO$_2$ nanoparticles provides excellent interfacial contact and should correspond to improved electron transfer through the film.
TEM was performed on composite films in order to determine the nature of TiO$_2$ adsorption on graphene sheets. Diluted samples of RGO-TiO$_2$ nanocomposites were placed on holey carbon grids under N$_2$ flow.

A TEM micrograph of a graphene sheet obtained from the RGO-TiO$_2$ nanocomposite can be seen in Figure 3.2 (A). The selected area diffraction pattern (SADP) exhibits reciprocal lattice spacings characteristic of anatase TiO$_2$ and graphene (inset). A high resolution micrograph of individual TiO$_2$ nanoparticles on graphene is shown in Figure 3.2 (B) along with elemental analysis verifying the presence of titanium.
3.1.2 Photoelectrochemical Behavior of Graphene-TiO₂ Films

Suspensions of known amounts of TiO₂ and graphene were deposited onto areas of ~2 cm² of the OTE by drop cast method. To maximize the homogeneity of composite films, gentle heating conditions of ~30-50 °C were used to ensure even solvent evaporation. Similar methods have been utilized to achieve consistent films.¹¹³,¹¹⁴ This careful deposition of the suspension results in the formation of homogeneous RGO-TiO₂ thin films as shown in Figure 3.3.

Figure 3.2 (A) TEM micrograph showing TiO₂ nanoparticles adsorbed onto a graphene sheet. Inset shows the diffraction pattern taken from sheet with spacings corresponding to graphene and anatase TiO₂. (B) High resolution image of TiO₂ nanoparticles on graphene. Insets show EDS (upper left) confirming presence of TiO₂ and magnification of TiO₂ lattice image (lower left). (Reprinted with permission from ref 68. Copyright 2010 American Chemical Society.)
While the pure TiO$_2$ thin film displays a uniform white color, the increasing addition of small amounts of graphene gradually darkens the film color. The concentration of TiO$_2$ was held constant at 2 mg/cm$^2$ for all films while the amount of graphene was varied. The composite film containing a 2:1 ratio of GO to TiO$_2$ is nearly black, and is expected to strongly interfere with the absorption of light by TiO$_2$ to produce photocurrent.

**Figure 3.3** Photographs of TiO$_2$ thin films with different graphene loadings. (Reprinted with permission from ref 68. Copyright 2010 American Chemical Society.)
In order to test the effect of RGO incorporated into TiO$_2$ films, the photocurrent generation of the composite films was evaluated by employing them as photoanodes in photoelectrochemical cells. The photocurrent response of RGO-TiO$_2$ films at different graphene loadings is shown in Figure 3.4 (A).

A photocurrent of \( \sim 20 \ \mu\text{A/cm}^2 \) was obtained using pristine TiO$_2$ films. The photocurrent response was prompt and reproducible during repeated on/off cycles of illumination. At concentrations below 0.05 mg/cm$^2$ we see an increase in photocurrent with increasing RGO content. A significant increase (\( \sim 90\% \)) in photocurrent generation up to \( \sim 38 \ \mu\text{A/cm}^2 \) was observed with 0.05 mg/cm$^2$ RGO RGO-TiO$_2$ nanocomposite films.

![Figure 3.4](image-url)  

**Figure 3.4** Photoelectrochemical measurements of RGO-TiO$_2$ composite films. (A) Photocurrent response vs. time profiles and (B) I-V characteristics of OTE/Graphene-TiO$_2$ with different amount of graphene. Results show an increased photoelectrochemical performance in composite films with a peak enhancement ratio followed by a decrease in performance when additional RGO is added. (Reprinted with permission from ref 68. Copyright 2010 American Chemical
The observed enhancement in the photocurrent represents improved charge transportation from the TiO$_2$ through the RGO-TiO$_2$ nanocomposites to the collecting electrode surface. At higher graphene loadings (>0.05 mg/cm$^2$), light absorption by RGO adversely affects the excitation of TiO$_2$ nanoparticles. This effect is also observed in the I-V curves of RGO-TiO$_2$ nanocomposite films in Figure 3.4 (B), where cell performance begins to decrease beyond an optimum graphene loading.

To further examine the photoelectrochemical properties of the nanocomposites, the incident photon-to-photocurrent efficiency (IPCE) of the films was performed. The RGO-TiO$_2$ films reduced by photocatalytic and chemical reduction (hydrazine) were compared with pristine TiO$_2$ films. The IPCE spectra were obtained using a monochromatic excitation source and calculated by normalizing the photocurrent to the incident light energy and intensity using Reaction 3.1.

\[
\text{IPCE} \, (\%) = 100 \times \frac{1240 \times I_{sc}}{P \times \lambda}
\]

*Reaction 3.1*

In Reaction 3.1, $I_{sc}$ is the short-circuit photocurrent (A/cm$^2$), $P$ is the incident light intensity (W/cm$^2$), and $\lambda$ is the wavelength (nm). All films (TiO$_2$ and composite films photocatalytic and hydrazine reduction) exhibit similar photoresponse patterns in the UV region, obtaining a maximum IPCE value at a wavelength of ~ 350 nm (Figure 3.5).
Films composed of TiO₂ without graphene yield a maximum IPCE value of 7.4%. The RGO-TiO₂ nanocomposite films yield maximum IPCE values of 13.9% for the in-situ reduced GO (photocatalytic reduction) and 11.4% for the hydrazine reduced GO (chemical reduction). As shown earlier, the majority (>90%) of the charge carriers generated following UV-excitation of TiO₂ undergo recombination. Quick capture followed by transport of electrons is an important aspect in enhancing the overall photoconversion efficiency. The higher IPCE values for the RGO-TiO₂ films confirm graphene’s role as electron collector, suppressing charge recombination in photoexcited TiO₂.

Figure 3.5 IPCE spectra comparing TiO₂ film with composite films. RGO-TiO₂ composite films show increased current contribution from TiO₂ nanoparticles due to the electron shuttling effect of the RGO incorporated into the film. (Reprinted with permission from ref 68. Copyright 2010 American Chemical Society.)
3.1.3 Photocatalytic Performance of RGO-TiO₂ Composite Films

In addition to photocurrent characteristics, the RGO-TiO₂ composite films were tested for their photocatalytic performance. The enhancements seen in the photocurrent production of composite films should carry over to improvements in the photocatalytic activity of TiO₂. A common photocatalytic application of TiO₂ is the remediation of contaminated water containing unwanted organics.¹¹⁵,¹¹⁶ Oxidative processes catalyzed by TiO₂ are often useful in degrading herbicides such as 2,4 dichlorophenoxyacetic acid (2,4-D).¹¹⁷

The merits of TiO₂-assisted photocatalytic degradation of 2,4-D compared to other oxidation processes like radiolysis and sonolysis has been discussed in detail earlier.¹¹⁷-¹¹⁹ The TiO₂ and RGO-TiO₂ films were placed in photolysis cells and irradiated with UV-light filtered through a CuSO₄ filter. Upon excitation by UV light, electron-hole pairs are generated within TiO₂. As the electrons are scavenged by dissolved oxygen, the holes participate in the generation of OH⁻ radicals that oxidize 2,4-D. The holes can either directly oxidize the organic substrate or can transfer to adsorbed water to form hydroxyl radicals.

\[
\text{TiO}_2 + \text{hv} \rightarrow \text{TiO}_2 \ (e + h) \quad \text{Reaction 3.2}
\]

\[
\text{TiO}_2 (e) + \text{O}_2 + \text{graphene} \rightarrow \text{TiO}_2 + \text{O}_2^- + \text{graphene(e)} \quad \text{Reaction 3.3}
\]

\[
\text{TiO}_2 (h) + \text{OH}^- \rightarrow \text{TiO}_2 + \cdot \text{OH} \quad \text{Reaction 3.4}
\]
TiO$_2$ (h) + •OH + 2,4-D $\rightarrow$ degradation products  \hspace{1cm} \textbf{Reaction 3.5}

As confirmed in previous mechanistic studies,$^{117-119}$ the herbicide is initially oxidized by hydroxyl radical to form the intermediate 2,4-dichlorophenol (2,4-DCP). The oxidation process further transforms the intermediates into quinones and ultimately to carboxylic acids. Figure 3.6 (A) shows UV-Vis absorption spectra recorded during the photocatalytic decomposition of 2,4-D solution (aqueous, O$_2$ saturated) at the UV-irradiated RGO-TiO$_2$ composite film. Since the herbicide absorbs only at wavelengths $<$300 nm (an intense and sharp peak at 230 nm and a broad peak at 285 nm), selective excitation was carried out of TiO$_2$ in the 300-350 nm region. Furthermore, the absorbance at 230 nm can be monitored to obtain the remaining concentration of 2,4-D in solution. With continued irradiation of the RGO-TiO$_2$ film with UV light, we see a decrease in the 2,4-D absorption bands indicating the photocatalytic degradation of the herbicide in about 80 min.
Figure 3.6 (B) shows the decrease in 2,4-D concentration with irradiation time in the absence and presence of TiO₂ and RGO-TiO₂ nanocomposite films. The blank experiments recorded in the absence of photocatalyst are also shown. Inset shows the pseudo first order fit of 2,4-D decay during initial 30 min. of UV excitation. (Reprinted with permission from ref 68. Copyright 2010 American Chemical Society.)

Figure 3.6 (B) shows the decrease in 2,4-D concentration with irradiation time in the absence and presence of TiO₂ and RGO-TiO₂ nanocomposite films. The blank experiment carried out in the absence of the catalyst film confirms that photolysis of 2,4-D occurs due to the photocatalytic properties of TiO₂. While both TiO₂ and RGO-TiO₂ are effective in degrading 2,4-D, the rate of 2,4-D decomposition is faster in the composite films. The degradation half-lives observed for these two sets of experiments were 147 min and 38 min for pristine TiO₂ and RGO-TiO₂ films, respectively. The decay of 2,4-D during the initial period of UV excitation was fitted to pseudo first order kinetics (inset Figure 3.6 (B)). The rate constants for 2,4-D degradation were 0.002 min⁻¹ and
0.008 min\(^{-1}\) for TiO\(_2\) and RGO-TiO\(_2\) films, respectively. The four-fold increase in the rate of photocatalytic degradation parallels the improvement in the photoelectrochemical behavior of RGO-TiO\(_2\) films.

A comparison of the improved photoelectrochemical and photocatalytic performance of the RGO-TiO\(_2\) films reveals a two-fold enhancement in the photocurrent response while the increase in the photocatalytic degradation rate is four-fold. In addition to the improved charge separation, the graphene sheets can assist in overcoming mass transfer limitations by increasing the availability of 2,4-D near the photocatalyst surface. As mentioned in previous sections, graphitic based materials have already been employed in the removal of organic pollutants.\(^{120}\) These studies have shown that TiO\(_2\) deposited on adsorbent supports like activated carbon and silica can have significant influence in concentrating pollutant from low solution-phase concentration.\(^{121,122}\) A similar 2,4-D rich environment is expected at the RGO-TiO\(_2\) interface to be an important contributing factor for achieving a high degradation rate.

Overall, SEM images of the composite films made via a drop cast method show good distribution of RGO in the TiO\(_2\) network. The experimental results for RGO-TiO\(_2\) composite films highlight the dual role graphene plays in improving the photoelectrochemical and photocatalytic performance of semiconductor nanoparticles. The improved photocurrent generation is attributed to the ability of dispersed graphene sheets to capture and transport charge to the collecting electrodes. Finally, the faster
rate of 2,4-D degradation observed with RGO-TiO₂ points out the additional benefit of concentrating organics near the photocatalyst surface.

3.2 The Solution to Film Transition Using Single Layer Graphene as an Ideal SERS Substrate

Detailed in chapter two, the method used to track electron transfer to and from (R)GO has the added benefit of extending the versatility of graphene by pairing the 2-D material with titanium dioxide nanoparticles. The coupling of GO with a semiconductor creates a photo-active graphene substrate which can be utilized for selective deposition of metal nanoparticles. Another advantage of this particular configuration is the implicit control over metal nanoparticle sizing by illumination.

In order to take advantage of the illumination-controlled metal nanoparticle deposition, practical films must be designed which maximize the unique electronic interactions in a semiconductor-graphene-metal structure. When TiO₂-assisted reduction of Ag⁺ is carried out in GO suspensions, there is no selectivity with respect to deposition location. However, the deposition of a GO film, ideally single layer, on a photocatalytically active substrate such as TiO₂ should provide the appropriate architecture enabling transportation of photogenerated electrons across the RGO sp² network. An illustration depicting a film with an ideal configuration in which single layer RGO is positioned on the surface of TiO₂ is presented in Figure 3.9. Illumination of TiO₂ would result in photogenerated electron transfer to the RGO sitting on its surface. This
configuration would enable an illumination-controlled deposition of metal nanoparticles on the side of RGO opposite the semiconductor nanoparticles.

Such a design does pose the question as to whether electrons in GO/RGO are able to hop from one side of RGO to the other with the aim of mediating side-selective reduction of metal ions. Such control over metal nanoparticle deposition and sizing on an RGO substrate would allow for the creation of customizable catalysts and sensors. Surface enhanced Raman spectroscopy (SERS) sensors fashioned in such a manner would also provide a convenient route for correlating SERS enhancement with metal

Figure 3.7 An ideal composite film architecture. Electrons photogenerated in TiO$_2$ are injected into single-layer RGO. Following a RGO side-hopping event, the electrons are then used to reduce Ag$^+$ ions on the opposing side of the RGO sheet.
nanoparticle size. Another incentive for using this method to create SERS sensors is that graphene possesses a number of qualities that make it well-suited for application as a SERS substrate.

In addition to serving as an electron mediating substrate, graphene itself has exhibited SERS-enhancing effects.\textsuperscript{123,124} Graphene may also assist in clarifying SERS signals by quenching background fluorescence, and could serve to concentrate target molecules near the SRES-active metal nanoparticles. In this role, graphene has displayed strong interactions with organic species through van der Waals forces, increasing local molecule concentrations near active surfaces.\textsuperscript{88,125} This behavior is analogous to the concentrating effect observed between organic material and activated carbon.\textsuperscript{121} Additionally, the epoxy, hydroxy, and carboxylic functional groups found on GO have been shown to enhance interactions with target molecules due to dipole/dipole attractions.\textsuperscript{126}

3.2.1 Deposition of Single-Layer GO on TiO\textsubscript{2}

While several methods exist for creating mono-to-few-layer films of graphene, most of these methods involve the use of finely-tuned temperature and pressure conditions for chemical vapor deposition of pristine graphene sheets on carefully prepared substrates.\textsuperscript{17,20,127,128} As described in chapter one, chemical exfoliation of graphite offers a convenient alternative to produce single graphene oxide sheets.\textsuperscript{22} These sheets can be dispersed on a variety of substrates through such deposition techniques as spin coating or electrophoretic deposition (EPD).\textsuperscript{129,130} To date, such
methods have not resulted in consistent, long-range deposition of single-layer GO. Films composed of multiple layers of graphene will impede the shuttling of electrons from the TiO$_2$ surface to the opposite, exposed side of GO.\textsuperscript{131}

Because of the importance of limiting GO to a single, electron-mediating layer between TiO$_2$ and the metal nanoparticles, an EPD-based method was developed that creates large-area (\textasciitilde 2 cm$^2$), single layer GO on TiO$_2$ nanoparticle films. The success of single-layer GO film formation obtained by this method is predicated upon proper EPD conditions and a high degree of GO exfoliation in the EPD medium.

First, a thin film of TiO$_2$ is prepared on an optically transparent electrode (OTE) via doctor blade method. The SEM image of neat TiO$_2$ is shown in Figure 3.11 (A). In order to deposit single sheets of GO, the TiO$_2$ films were submersed in a dispersion of

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3.8}
\caption{Electrophoretic deposition is used to deposit single sheets of GO on TiO$_2$. When a voltage is applied between two electrodes, negatively charged GO is driven through the resultant electric field and deposits on the positively charged electrode, where TiO$_2$ is been positioned.}
\end{figure}
highly exfoliated GO in ethanol. A graphic representing the EPD process is shown in Figure 3.10. The OTE/TiO$_2$ film was held ~4 mm apart from another OTE and a 30 V dc voltage was applied between the two electrodes.

Under the application of electric field, the negatively charged GO sheets are driven to the positive electrode where the TiO$_2$ film is positioned. This EPD process also enables the reduction of GO to RGO.$^{130}$ While this deposition process may result in partial reduction, further reduction of GO is achieved when the TiO$_2$ film is UV-illuminated. The reduction of GO by TiO$_2$ under illumination has been detailed in a previous report.$^{31}$ The reduction of GO under these conditions confirms photogenerated electron transfer from TiO$_2$ to the GO.

![Image](image_url)

**Figure 3.9** (A) SEM image of TiO$_2$ nanoparticle film. (B) Single layer GO electrophoretically deposited over a TiO$_2$ nanoparticle film. Wrinkles in the GO sheet and the shadowing of TiO$_2$ nanoparticles by GO is observed. (C) GO surface features are accentuated when lower accelerating voltages are used.
Deposition of single-to few layers of GO can be controlled by using appropriate concentration of GO, voltage, and deposition time. The optimum conditions for achieving single-layer GO on TiO$_2$ films were found to be 0.5 mg/mL GO in ethanol, 30 V dc, and a 1 minute deposition time. The SEM image of single-layer GO stretched over a nanostructured TiO$_2$ surface is shown in Figure 3.9 (B). The characteristic wrinkles of graphene are clearly seen, and it is also possible to see the details of the TiO$_2$ layer sitting just beneath the graphene sheet. While incoming beam electrons from the SEM penetrate through the graphene, secondary electrons with lower energies are screened when passing back through the graphene, producing the shadowy appearance of TiO$_2$. When SEM is utilized with lower accelerating voltages, for example 1 kV instead of 20 kV, incident electrons are unable to penetrate the graphene sufficiently to image the TiO$_2$ sub-layer. Under these conditions, it is possible to resolve the finer surface details of GO (Figure 3.9 (C)).

3.2.2 Activation of Graphene for Metal Nanoparticle Nucleation and Growth

TiO$_2$-GO films are activated for metal nanoparticle deposition by UV-illumination. The films are placed in an N$_2$-purged, $2.0 \times 10^{-4}$ M AgNO$_3$ solution in ethanol prior to back-side illumination. Equations 3.6-3.9 describe the electron transfer process in the semiconductor-graphene-metal (SGM) nanoparticle films. Upon UV-illumination, electrons are photogenerated in TiO$_2$ and transferred to GO, while holes are scavenged by ethanol. The electrons are then shuttled to the opposite side of GO where they are readily available for the reduction of metal ions to metal nanoparticles.
\[
\text{TiO}_2 + \text{hv (UV)} \rightarrow \text{TiO}_2 \text{ (e+h)} \quad \text{Reaction 3.6}
\]
\[
\text{TiO}_2 \text{ (e)} + \text{GO} \rightarrow \text{TiO}_2 + \text{(R)GO (e)} \quad \text{Reaction 3.7}
\]
\[
\text{TiO}_2 \text{ (h)} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{TiO}_2 + \cdot\text{C}_2\text{H}_4\text{OH} \quad \text{Reaction 3.8}
\]
\[
\text{(R)GO (e)} + \text{M}^+ \rightarrow \text{(R)GO} + \text{M} \quad \text{Reaction 3.9}
\]

This sequential electron transfer process allows for the tuning of metal nanoparticle size by regulation of illumination exposure time in TiO\textsubscript{2} films. Additionally, the RGO substrate should serve to disperse metal nanoparticles due to delocalization of electrons within its extended sp\textsuperscript{2} network. The binding of metal ions at defects such as epoxide sites further aids nucleation of Ag nanoparticles\textsuperscript{132}.

Morphologies of Ag nanoparticles deposited on TiO\textsubscript{2}-RGO and TiO\textsubscript{2}-only films were evaluated by SEM. Both substrates were subjected to identical conditions and illuminated for 10 minutes to induce Ag nanoparticle growth. As seen in the Figure 3.10 (A) SEM image, Ag particles reduced directly onto TiO\textsubscript{2} are larger (100-500 nm across) and less spherically symmetric than those found on RGO. Larger Ag nanoparticles on TiO\textsubscript{2} most likely result from the uneven growth and coalescence of smaller nanoparticles. The Ag nanoparticles formed on the TiO\textsubscript{2}-RGO shown in Figure 3.10 (B) are well-dispersed, the majority of which are considerably smaller (5-30 nm) than Ag nanoparticles on TiO\textsubscript{2}. The high-resolution image provided in Figure 3.10 (C) depicts the smallest Ag nanoparticles (~5 nm diameter) found covering the surface of RGO between larger particles (~50 nm diameters). This effect provides evidence that RGO’s sp\textsuperscript{2}
network, in addition to its wrinkles and surface defects, make it an excellent substrate for metal nanoparticle nucleation and dispersion.

Figure 3.10 SEM images show surface morphology of Ag nanoparticles created via irradiation of TiO$_2$ or TiO$_2$-GO films for 10 minutes in the presence of AgNO$_3$. (A) SEM image of Ag nanoparticles reduced directly onto TiO$_2$. (B) Ag nanoparticle deposition on RGO produces smaller particles with high surface loading. (C) A high resolution image of the SGM film from part (B) shows full coverage of small (~5 nm diameter) Ag nanoparticles on RGO.

Growth of Ag nanoparticles in SGM films was also examined using a systematic study of Ag nanoparticle morphology as a function of irradiation time. Figure 3.11 displays SEM images taken following illumination times of 1, 2, and 3 minutes. During UV-illumination of TiO$_2$-RGO film, electrons originating in the TiO$_2$ layer are transferred to and through the RGO sheet and then used to reduce Ag$^+$ ions.
After only one minute of illumination, Ag nanoparticles nucleate evenly onto the RGO surface opposite the TiO\textsubscript{2} with an average diameter of $\sim 25$ nm (Figure 3.11 (A)). Closer examination of the image reveals favorable Ag nanoparticle deposition on RGO surface features. As illumination continues, the average nanoparticle diameter grows to $\sim 50$ nm at 2 minutes (Figure 3.11 (B)), and then to a maximum diameter of $\sim 100$ nm at 3 minutes (Figure 3.11 (C)). Further irradiation results in increased loading of Ag nanoparticles on RGO in which smaller metal nanoparticles (5-20 nm diameters) coat the remaining available surfaces (Figure 3.10 (C)). Loading of smaller metal nanoparticles on RGO surface is important for increased activity in selected catalysis and sensing applications, which have shown improved performance with decreasing particle size.$^{133-135}$

**Figure 3.11** SEM images show Ag nanoparticle size distribution as a function of irradiation time. (A) After 1 minute, Ag nanoparticles diameters are 10-42 nm. (B) After 2 minutes, Ag nanoparticle diameters are 30-110 nm (C) After 3 minutes, Ag nanoparticle diameters are 15-150 nm.
Growth of Ag nanoparticles in SGM films was further elucidated through the use of UV-visible absorption spectrophotometry. Figure 3.12 (A) presents the absorption profiles for neat TiO\textsubscript{2} on OTE, TiO\textsubscript{2}-GO, and SGM films following 1, 2, 3, and 10 minutes of UV-irradiation. Because single layers of graphene absorb \textasciitilde2\% of incident light across the visible spectrum, the slight increase in absorption of TiO\textsubscript{2}-GO over TiO\textsubscript{2}-only films is expected (traces (a) and (b)). A sharp rise in absorption across the visible spectrum is seen after only one minute of irradiation. This increase in absorption is due to formation of Ag nanoparticles and is also influenced by the reduction of GO. The absorption changes resulting from the reduction of GO by photogenerated electrons from TiO\textsubscript{2} were isolated and can be seen in Figure 3.12 (B). Traces taken following 2 and 3 minutes irradiation of SGM films results in further broad-band absorption increases across the visible spectrum. After 10 minutes of irradiation, increased loading of Ag nanoparticles on the RGO surface results in a soft peak, emerging at \textasciitilde500 nm. This peak is attributed to the surface plasmon resonance signal of Ag nanoparticles.
An image of a SGM film with Ag nanoparticle growth following 20 minutes of irradiation time is shown in Figure 3.13 (A). With increasing irradiation time, the metal nanoparticles preferentially complete the coverage of RGO as opposed to forming larging nanoparticles. Deposition of Au nanoparticles was also accomplished using this method. Figure 3.13 (B) shows Au nanoparticles formed following a 10 minute irradiation period. These results are included to show the versatility of SGM films for different or additional metal nanoparticle deposition.
3.2.3 Utilization of Semiconductor-Graphene-Metal Nanoparticle Films as SERRS Sensors

Surface enhanced resonance Raman spectroscopy (SERRS) is a valuable tool for the detection of trace molecules.\textsuperscript{136-138} SERRS devices utilize the interaction between target molecule and the local surface plasmon resonance (LSPR) of noble metal nanoparticles as means to amplify the target Raman signal. The SGM films developed in this study are excellent candidates for custom SERRS sensors due to the ability to tune metal nanoparticle size and coverage with illumination. Additionally, the graphene in SGM films should serve as an ideal SERRS substrate due to fluorescence quenching and its Raman enhancing properties, as detailed previously.\textsuperscript{139,140}

\textbf{Figure 3.13} SEM images showing the versatility of SGM films. (A) Loading control of Ag nanoparticles through illumination time. (B) Different metal nanoparticles can be deposited with this method. Au nanoparticles following a 10 minute irradiation time.
To explore the potential of these films as sensors, SGM films were placed in 3 and 10 µM solutions of 5,10,15,20-Tetrakis(4-aminophenyl)-21H,23H-porphyrin (TAPP) in ethanol. The SERRS enhancement for TAPP in the presence of SGM films was compared to the response of the target molecule in the presence of a blank OTE. SERRS spectra shown in Figure 3.16 (A) display a strongly enhanced TAPP response in the presence of the SGM film. Enhancement of TAPP Raman bands is confirmed by the position of peaks in observed SERRS spectra which agree with previous literature reports.\textsuperscript{141,142} The SERRS enhancement factor is nearly 3 orders of magnitude larger than the response of TAPP in the presence of a blank OTE alone. Optimization of SERRS enhancement for TAPP was achieved following a 20 minute growth of Ag nanoparticles on RGO. As seen in Figure 3.13 (C) and Figure 3.15 (A), a high coverage of Ag nanoparticles exists on the RGO sheet for 10 and 20 minute illumination times. The high coverage should result in increased interactions between TAPP and the LSPR of Ag nanoparticles.

Of additional benefit to the efficacy of these composites as SERRS sensors is graphene’s ability to interact with target molecules. Improved interaction should result in augmented concentrations of TAPP near the RGO surface, which is covered with Ag nanoparticles. If this scenario is accurate, it should be possible to observe improved SERRS enhancements as a function of interaction time between SGM films and TAPP.
A time-dependent study of the interaction between SGM films and TAPP was conducted to investigate this expected effect. Briefly, the SERRS enhancement of TAPP was monitored as a function of soaking time, where the TAPP solution was introduced to the SGM film and allowed to soak prior to SERRS testing. Results shown in Figure 3.16 (B) confirm the role RGO plays as a concentrating agent in SGM films. As the 500 nM TAPP solution is allowed to soak in the presence of the SGM film for 1.5 hours prior to testing, the SERRS enhancement is improved by a factor of ~2 over SGM films tested immediately upon exposure to the target molecule (Figure 3.16 (B)).

Figure 3.14 SERRS spectra for the target molecule, TAPP. (A) A signal enhancement of nearly 3 orders of magnitude is seen for TAPP molecules in the presence of SGM films over the signal observed in the presence of a blank OTE. (B) Strong SERRS signal is obtained using SGM films to detect nano-molar concentrations of TAPP. Soaking of SGM films in TAPP produces enhanced SERRS response, demonstrating the concentrating effects of RGO.
3.3 Summary for Practical Device Film-Making

This chapter presents film-making techniques developed which enable the construction of practical films for photovoltaic, photocatalytic, and sensing applications. Enhanced performance in these devices is a consequence of the electronic, organic-concentrating, and surface area-related benefits of RGO. Films made from RGO-TiO$_2$ composites by a simple drop cast technique showed increased photovoltaic and photocatalytic performance. Tertiary porphyrin-semiconductor-RGO composites employing a more complex film-making strategy showed RGO’s ability to create a synergistic electron transfer cascade from molecular and semiconductor nanoparticles to a current-collecting electrode. Finally, construction of single to few-layer GO on thin films of TiO$_2$ nanoparticles was achieved through electrophoretic deposition. Illumination-controlled deposition of metal nanoparticles on these films results in solid-state semiconductor-graphene-metal composites. The realization of these structures also demonstrates the ability of RGO to shuttle electrons from face to face in order to deposit metal nanoparticles on the side opposite TiO$_2$. The aptitude of RGO as a SERRS substrate, as well as the application of SGM films as nanomolar-sensitive SERRS sensors was also presented.
While semiconductor and metal-RGO composites have been utilized in a wide range of applications (detailed in previous chapter), the field of quantum dot-(R)GO composites is still emerging. Because of the successes achieved in semiconductor-RGO photovoltaic devices, there exists a drive to realize similar performance boosts in quantum dot solar cells (QDSCs) by incorporating RGO. To date, reported gains have been modest and few, as improvements in device performance depend strongly on intimate quantum dot-RGO contact, and by extension, film preparation techniques. In order to maximize the potential of RGO in QDSCs, a more detailed description of the excited state interactions between the two is required. A better understanding of the electronic properties will allow for the adoption of a more rational approach to design and construction of quantum dot-RGO composites.

Quantum dot solar cells are an attractive option for solar energy conversion due to the ability to tune semiconductor bandgaps, high extinction coefficients, large molecular dipoles, and the potential for multi-layer sensitization. Another alluring property is the potential in QDSCs for multiple electron generation and hot electron
utilization, phenomena that boost the theoretical power conversion efficiency beyond the 32% Shockley-Queisser limit in silicon-based solar cells.\textsuperscript{150} In spite of these advantages, power conversion efficiencies of ~5\% in QDSCs still lag behind their more developed counterpart, the dye-sensitized solar cell. Recent optimization efforts have focused on working electrode surface modifications (e.g. treatment with dipole molecules and ZnS overcoating) and the use of Cu\textsubscript{2}S-based counter electrodes.\textsuperscript{151-155}

4.1 Isolating Energy and Electron Transfer in Quantum Dot-RGO Composites

Performance in QDSCs is stunted by limitations in sensitizer loading arising from losses inherent to the nature of electron transport throughout quantum dot networks. Electron conductance within quantum dot films proceeds via electron hopping between orbitals on adjacent quantum dots, a process termed random walk.\textsuperscript{156,157} To arrive at the current-collecting electrode, photogenerated electrons in quantum dots situated further from the wide bandgap semiconductor (e.g. TiO\textsubscript{2}, ZnO or SnO\textsubscript{2}) must successfully complete a greater number electron transfer hopping events without undergoing recombination or trapped-state termination, a process illustrated in Figure 4.1. In addition to poor electron transfer in thicker quantum dot films, increased quantum dot-layering inhibits electrolyte access to quantum dots closest to the TiO\textsubscript{2} surface, hindering quantum dot regeneration.\textsuperscript{153} Because of these kinetic limitations, most QDSCs utilize near-monolayer loading of the sensitizing semiconductor through linker-assisted deposition of pre-made colloidal quantum dots, or by in-situ formation of
quantum dots on TiO$_2$ via chemical bath deposition or successive ionic layer adsorption and reaction (SILAR).$^{158-160}$

While nanocrystal-graphene composites have demonstrated enhanced photocurrent and photocatalysis, very little has been done to interrogate the excited state interactions between CdSe quantum dots and graphene. Brus and coworkers concluded that excited state decay from photogenerated electrons in CdSe nanocrystals on pristine graphene decay via Forster Resonant Energy Transfer (FRET).$^{161}$ Decay via this pathway does not involve electron transfer and is therefore counterproductive to a quantum dot-graphene composite system designed for improved electron transfer. The aforementioned study was conducted by examination of CdSe quantum dots anchored to pristine graphene. However, when graphene-quantum dot composites are located
within the environment of a photovoltaic device under illumination, the presence of an electrolyte or other hole transporting material serves to regenerate CdSe quantum dots, enabling continuous charge transfer.

With the aim of determining the relative contributions of energy and electron transfer in quantum dot-RGO composites, it is desirable to manipulate the electron transfer from CdSe to RGO. One potential path toward this goal is to adjust the level of oxidation in graphene. Another strategy to control electron transfer is to create charging in RGO through prolonged photoexcitation of CdSe. Control of charging in RGO would allow for one to effectively “turn off” the electron transfer pathway from the quantum dot. Such control of electron transfer from quantum dots to RGO would enable isolation of the energy transfer process between the two. Using this method, comparison of the photoluminescence decay rates before and after charging should provide insight into the actual rates of both energy and electron transfer in the composites.

4.1.1 CdSe-GO and CdSe-RGO composites.

In order to test the excited state interactions in such a system, a small amount of GO was physically mixed with colloidal CdSe quantum dots. The quantum dots were prepared via a modified Peng approach. The absorbance spectra of pure CdSe colloidal quantum dots, pure GO and RGO dispersions, as well as CdSe-GO and CdSe-RGO composite dispersions are shown in Figure 4.2. As expected due to the addition of graphene, a slight increase in absorbance is observed in
composite dispersions versus CdSe quantum dots alone. Also, both the CdSe-RGO composite and RGO dispersions show increased absorbance over CdSe-GO and GO dispersions. The increased absorbance of RGO over GO was discussed in chapter three.\textsuperscript{31} This effect is clearly observed by the darker appearance of RGO dispersions (inset Figure 4.2).

![Absorbance profiles of CdSe and CdSe-(R)GO composites. Traces for RGO and GO in ethanol (dotted traces (d) and (e)) also included. Solutions (a-c) contain 9% ethanol.](image)

\textbf{Figure 4.2} Absorbance profiles of CdSe and CdSe-(R)GO composites. Traces for RGO and GO in ethanol (dotted traces (d) and (e)) also included. Solutions (a-c) contain 9% ethanol.

Transmission electron microscopy (TEM) was used to observe the extent of CdSe quantum dot physisorption to individual graphene sheets. Figure 4.3 (A) shows apparent sub-monolayer loading of quantum dots on RGO while (B) confirms the presence of deposited CdSe quantum dots.
4.1.2 CdSe-RGO Excited State Interactions.

Two methods were developed to differentiate energy and electron transfer processes in the quantum dot-RGO composites. First, the degree of oxidation within graphene was used to isolate the contribution of the electron transfer pathway during excited state deactivation of CdSe quantum dots by GO in CdSe-GO composite dispersions. Both GO and RGO are good electron acceptors, however, GO has a higher capacity to consume electrons due to its oxidation state. This allows for CdSe fluorescence-quenching to serve as a probe to distinguish the extent of excited state electron transfer to GO and RGO.\textsuperscript{163,164} While initial electron transfer results in partial

\textbf{Figure 4.3} (A) TEM micrograph of GO (on holey carbon grid) after illumination (>420 nm) of CdSe-GO dispersion. Inset shows a selected area diffraction pattern exhibiting the characteristic reciprocal lattice spacings of 1.23 and 2.13 Å. (B) High resolution image of CdSe quantum dots on graphene. Inset is the energy dispersive x-ray spectrum confirming the presence of CdSe.
reduction of GO, additional electron transfer leads to storage of electrons, as detailed in
the chapter two.\textsuperscript{54} However, continued irradiation makes further transfer of electrons
increasingly difficult as a consequence of the GO reduction and subsequent charging.
Charging of GO due to prolonged photoexcited electron transfer from CdSe quantum
dots is used as the second method to isolate energy and electron transfer in quantum
dot-RGO composites. Charge transfer events between photoexcited CdSe and GO (and
RGO) are summarized in Reactions (4.1-4.4).

\begin{align*}
\text{CdSe} + h\nu &\rightarrow \text{CdSe (e + h)} \quad \text{Reaction 4.1} \\
\text{CdSe (e)} + \text{GO} &\rightarrow \text{CdSe + RGO} \quad \text{Reaction 4.2} \\
\text{CdSe (e)} + \text{RGO} &\rightarrow \text{CdSe + RGO (e)} \quad \text{Reaction 4.3} \\
\text{CdSe (h)} + \text{C}_2\text{H}_5\text{OH} &\rightarrow \text{CdSe} + ^*\text{C}_2\text{H}_4\text{OH} \quad \text{Reaction 4.4}
\end{align*}

4.1.3 Concentration Dependent Quenching of CdSe Emission and Emission Lifetime

Photoluminescence quenching spectra displayed in Figure 4.4 reveal that both
RGO and GO serve as effective quenchers of excited CdSe. Both reduction and electron
storage (Reactions (2) and (3)) govern the quenching by GO while only Reaction (3)
dominates the quenching by RGO. This is seen in the quenching efficiency. GO
quenches more efficiently than RGO at all concentrations, confirming its greater
electron-accepting capacity (inset, Figure 4.4). The highly interactive nature of GO is also
evidenced by the strong quenching response which occurs even at the smallest GO
concentrations (9 µg/mL), in which nearly 95% of CdSe photoluminescence (PL) is effectively quenched.

![Figure 4.4 Quenching of CdSe quantum dot photoluminescence by GO and RGO. Inset shows effective quenching even at low graphene concentrations (excitation wavelength 373 nm, 420 nm long pass filter).](image)

Excited state electron transfer and energy transfer are responsible for the quenching of CdSe emission. The extent of energy transfer between donor (CdSe) and acceptor species (GO or RGO) is dependent on the proximity and spectral overlap between the two. If the excited state relaxation pathway occurs primarily via energy transfer, then increased optical density of RGO over GO should enable improved overlap with CdSe quantum dot fluorescence, resulting in larger quenching efficiencies with
respect to GO. In all cases, GO is instead shown to be the more effective quenching agent. This result provides further evidence that, in addition to energy transfer, an electron transfer pathway serves to control the excited state deactivation from CdSe to GO and RGO.

Figure 4.5 compares CdSe emission decay traces as a function of increasing GO concentration. Consistent with PL quenching results, increasing concentrations of GO successively decrease the PL lifetime of CdSe quantum dots. With increasing GO concentration, the fast time decay component ($\tau_1$) shows a slight decrease, from 3.24 to 0.93 ns over the range of GO concentrations of 9-45 µg/mL, while its contribution to the overall PL lifetime increases from 78.9% to 94.5% (Table 4.1). This increased contribution from the fast decay component is attributed to quenching of CdSe PL by GO through energy and electron transfer, and suggests considerable interaction between the two. Using Equation 4.1, the apparent rate of non-radiative excited state decay, $k_{NRD}$, is calculated to be $8.8x10^9$ s$^{-1}$.

\[
k_{NRD} = \frac{1}{\tau_{1(CdSe-GO)}} - \frac{1}{\tau_{1(CdSe)}}
\]

Equation 4.1
The lifetime of the slow decay component ($\tau_2$), which mainly arises from the free CdSe quantum dots in the suspension, shows a variance of 44-23.3 ns as we increase the concentration of GO from 0 to 45 $\mu$g/mL. Interestingly, the contribution of the slow component decreases to only about 5.5% at the highest GO concentration. As GO concentrations increase, the number of free CdSe quantum dots diminish, resulting in a smaller pre-exponential contribution ($a_2/(a_1+a_2)$) from the long decay component, $\tau_2$. These results confirm the strong interactive nature of GO towards CdSe quantum dots.

**Figure 4.5** As the GO concentration increases, CdSe photoluminescence lifetimes become successively shorter. Excitation wavelength = 453 nm; long pass filter = 500 nm; fluorescence monitored at 508 nm.
4.1.4 Excited State Dynamics Following Prolonged Illumination

It is evident from the GO and RGO emission quenching studies that electron transfer from CdSe to (R)GO plays a role in fluorescence quenching. Unfortunately, both electron and energy transfer processes are implicated in the observed fluorescence quenching. In order to further isolate the two excited CdSe deactivation routes, the fluorescence lifetimes of the RGO-CdSe composite are compared at different illumination times. Because illumination times correspond to different levels of charging in RGO, it is possible to correlate illumination time to different rates of electron transfer from excited CdSe to RGO.

<table>
<thead>
<tr>
<th>GO, µg/mL</th>
<th>$\tau_1$, ns</th>
<th>$\tau_2$, ns</th>
<th>$a_1/(a_1+a_2)$, %</th>
<th>$a_2/(a_1+a_2)$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.13</td>
<td>44.0</td>
<td>66.1</td>
<td>33.9</td>
</tr>
<tr>
<td>9</td>
<td>3.24</td>
<td>35.3</td>
<td>78.9</td>
<td>21.1</td>
</tr>
<tr>
<td>18</td>
<td>2.39</td>
<td>32.7</td>
<td>83.9</td>
<td>16.1</td>
</tr>
<tr>
<td>27</td>
<td>1.71</td>
<td>29.6</td>
<td>89.1</td>
<td>10.9</td>
</tr>
<tr>
<td>36</td>
<td>1.49</td>
<td>26.9</td>
<td>89.4</td>
<td>10.6</td>
</tr>
<tr>
<td>45</td>
<td>0.93</td>
<td>23.3</td>
<td>94.5</td>
<td>5.5</td>
</tr>
</tbody>
</table>

TABLE 4.1

CDSE-RGO FLUORESCENCE LIFETIME DECAY PARAMETERS FROM FIGURE 4.5
As indicated in Reactions 4.2 and 4.3, electron transfer from photo-excited CdSe quantum dots to GO results in the formation of RGO, and electron transfer to RGO leads to electron storage. The process of GO reduction and electron storage resulting from photoexcited electron transfer from a colloidal semiconductor was detailed in chapter two. Storage of electrons in RGO should result in diminished electron transfer rates from CdSe quantum dots to GO following prolonged illumination. As electron storage within the graphene network saturates, the electron transfer process slows. Thus, following prolonged irradiation, it should be possible to shut off the electron transfer pathway (right panel in Figure 4.6). In the absence of an electron transfer pathway, the emission decay is expected to be dominated solely by energy transfer.

\[
k_{\text{NRD}} = k_{\text{energy}} + k_{\text{electron}}
\]

\[
k_{\text{energy}} \gg k_{\text{electron}}
\]

\[
k_{\text{NRD}} \cong k_{\text{energy}}
\]

**Figure 4.6** Left: Initial illumination of CdSe-GO composite results in electron transfer from the CdSe conduction band to GO. Right: Continued illumination of the system results in the reduction of GO and eventual storage of electrons resulting in a decrease in electron transfer rate.
In order to test this method of isolating the energy transfer process, the emission lifetime of the composites were analyzed at the beginning of CdSe illumination (t=0 minutes) and also following 95 minutes of illumination time (t=95 minutes). Emission decay traces of CdSe-RGO composites shown in Figure 4.7 (A) highlight the effect of prolonged illumination on the deactivation of excited CdSe. During early illumination times (0-15 min), the CdSe PL lifetimes remain nearly constant as excited state electron transfer from CdSe results in the reduction of GO.

Under these conditions both energy and electron transfer contribute to fluorescence quenching. At longer illumination times (15-95 min), electron transfer from CdSe quantum dots to the now-reduced GO (or RGO) results in charging of the graphene network, causing further electron transfer to become increasingly difficult. With the electron transfer pathway unavailable, PL lifetimes necessarily increase as energy transfer becomes the only available route for conduction band electrons undergoing non-radiative excited state decay.

This effect is confirmed by the increasing PL lifetimes observed in CdSe-GO composites with prolonged visible light irradiation. As expected, CdSe-RGO composites show similar, but less pronounced, changes in its PL lifetime under similar conditions. The lifetime of CdSe quantum dots alone during visible irradiation remains unchanged (Figure 4.7 (A) inset).
The effect of visible irradiation on the PL lifetimes of CdSe-GO composites can also be visualized by observation of fluorescence recovery. Both CdSe-GO and CdSe-RGO composites show partial recovery of emission following prolonged visible illumination (Figure 4.7 (B)). Once again, this is a consequence of terminating the electron transfer pathway which results in a reduction of the quenching efficiency.

Through comparison of CdSe-GO PL lifetimes before and after illumination, it is possible to estimate the relative rates of electron and energy transfer. Prior to illumination ($h\nu_{t=0 \text{ min}}$), both electron and energy transfer processes dictate the fast PL

Figure 4.7 (A) CdSe-GO composites show increased photoluminescence lifetimes upon visible light irradiation (>420 nm). Inset: The effect of visible light illumination (>420 nm) on CdSe photoluminescence lifetimes in the presence of GO and RGO is shown. (B) Emission recovery of CdSe-RGO solution upon illumination with visible light (>420 nm), relative to CdSe-only emission. Inset compares the fluorescence recovery of CdSe in GO or RGO.
lifetime component, $\tau_1$ (Equation 4.2). After extended illumination ($h\nu_{t=95 \text{ min}}$) and subsequent charging of graphene sheets, the fast component of the excited state relaxation in CdSe quantum dots proceeds primarily through energy transfer, as electron transfer to charged graphene is shunted. This allows for estimation of the rate of energy transfer in these composites, $k_{\text{energy}} = 5.5 \times 10^8 \text{ s}^{-1}$ (Equation 4.3). Finally, by comparing the difference in the non-radiative decay rates at illumination times $t=0 \text{ min}$ and $t=95 \text{ min}$, it is possible to estimate the rate of electron transfer in CdSe-GO composites, prior to illumination, to be $6.7 \times 10^8 \text{ s}^{-1}$ (Equation 4.5).

\[
\begin{align*}
\text{at } h\nu_{t=0 \text{ min}}, \quad k_{\text{NRD}} &= k_{\text{energy}} + k_{\text{electron}} = \frac{1}{\tau_1(\text{CdSe-GO, } h\nu_{t=0 \text{ min}})} - \frac{1}{\tau_1(\text{CdSe})} \\
\text{at } h\nu_{t=95 \text{ min}}, \quad k_{\text{NRD}} &\approx k_{\text{energy}} \approx \frac{1}{\tau_1(\text{CdSe-GO, } h\nu_{t=95 \text{ min}})} - \frac{1}{\tau_1(\text{CdSe})} \\
\text{at } h\nu_{t=0 \text{ min}}, \quad k_{\text{electron}} &= k_{\text{NRD}} - k_{\text{energy}} \\
\text{at } h\nu_{t=0 \text{ min}}, \quad k_{\text{electron}} &= \left(\frac{1}{\tau_1(\text{CdSe-GO, } h\nu_{t=0 \text{ min}})} - \frac{1}{\tau_1(\text{CdSe})}\right) - \\
&\quad \left(\frac{1}{\tau_1(\text{CdSe-GO, } h\nu_{t=95 \text{ min}})} - \frac{1}{\tau_1(\text{CdSe})}\right) \\
\end{align*}
\]

Equation 4.2

Equation 4.3

Equation 4.4

Equation 4.5

The isolation of energy and electron transfer rates provides a more complete understanding of how deactivation of excited CdSe quantum dots proceeds through (R)GO. While the energy and electron rates calculated using this approach are quite similar, the existence of electron transfer from CdSe quantum dots to RGO provides a route to improved charge separation and transportation in quantum dot films. The
remaining sections in chapter 4 discuss the method used to create CdSe-RGO composite photoanodes and their resulting photoelectrochemical characteristics.

4.2 Electrophoretic Deposition of CdSe and CdSe-(R)GO Composites as Photoanodes

As alluded to in the beginning of the chapter, preliminary studies of SILAR-synthesized CdSe-graphene, as well as the in-situ growth of colloidal quantum dot-graphene composites, have demonstrated modest increases in photocurrent when compared to nanocrystal-only films.\cite{ref1, ref2} While these methods ensure good quantum dot-graphene contact, the effective loading of quantum dot sensitizer is limited to a few monolayers.

Careful control of graphene loading is required to extend quantum dot films into the third dimension, where an essential balance must exist between maximizing contact with quantum dots while minimizing incident light absorption by graphene, which absorbs \(\sim2\%\) of incident light per monolayer.\cite{ref3} Augmentation of quantum dot loading should enhance QDSC performance, provided that sufficient graphene is present to overcome electron transport limitations resulting from increasing quantum dot film thickness. Incorporating graphene in colloidal quantum dot solutions may prove successful in achieving this aim so long as the graphene maintains a high degree of dispersion during the transition from solution to film.

In order to leverage the benefits of electron transfer observed in CdSe-(R)GO composites, films created from the composites also must contain primarily single sheet
graphene in addition to having a high degree of dispersion. Film deposition of solution-based CdSe-(R)GO composites by means of a drop-cast method typically results in a loss of dispersion between the two species, variations in film thickness, and some degree of film inhomogeneity. Finally, it is essential for films to achieve a balance between the sufficient supply of graphene for ample quantum dot interfacial contact while also limiting graphene’s detrimental filtering of incident light.

4.2.1 Electrophoretic Deposition of CdSe-(R)GO Composites

The use of electrophoretic deposition (EPD) in composite film preparation has been shown to produce films with a good degree of composite homogeneity between CdSe quantum dots and C$_{60}$. Because of the generally well-dispersed, homogenous nature of films created with this method, EPD was chosen as the method to create high quality films of CdSe-(R)GO.

The deposition of CdSe quantum dots was monitored by UV-Vis absorbance spectroscopy. Absorption spectra of the EPD solution were taken following each cycle and show successively decreasing CdSe concentrations in the EPD solution until deposition of CdSe onto the photoanode is complete (Figure 4.8 (A)). The difference in initial and final quantum dot concentrations within the EPD suspension corresponds to the amount of quantum dots deposited on the TiO$_2$ film.
4.2.2 Photoelectrochemical Response of CdSe-RGO Composite Photoanodes

The CdSe and CdSe-(R)GO composite films created via EPD were then employed as photoanodes in photoelectrochemical cells. The cells were completed using a Cu$_2$S/GO counter electrode$^{71}$ and a $S^{2-}/S_n^{2-}$ redox couple as electrolyte. Photocurrent generated following visible excitation of CdSe-(R)GO films with different loadings of quantum dots and RGO are shown in Figure 4.8 (B). CdSe-(R)GO photoanodes show a significant enhancement in the photocurrent response over CdSe-only films. The maximum photocurrent was recorded at a loading of $\sim1.4\times10^{15}$ QDs/cm$^2$ and $\sim20$ µg/cm$^2$ RGO.
The incident photon to current efficiencies (IPCE) of CdSe-(R)GO films were examined to assess the photocurrent response as well as the role RGO plays in improving the efficiency of photocurrent generation. IPCE measurements show the presence of RGO in the CdSe enhances the photocurrent generation efficiency (Figure 4.9 (A)). IPCE contribution from the CdSe absorption peak at 530 nm increases from 3.8% in CdSe-only films to 13.8% in CdSe-RGO composites. CdSe loadings were kept constant in all films. The observed enhancement in the IPCE of composite films is
attributed to the mediating role RGO plays in accepting electrons and shuttling them to the collecting electrode surface.

![Image](image.png)

**Figure 4.9** (A) Incident Photon to Current Efficiency (IPCE) of CdSe and CdSe-(R)GO films. Contribution of CdSe QDs (~530 nm) to current generation is markedly improved in CdSe-RGO films. (B) The photocurrent response of CdSe and CdSe-(R)GO composite films to ON-OFF illumination cycles.

Preparation of CdSe-(R)GO films by EPD technique allows for increased stacking of quantum dots. When excited with visible light, charge separation occurs throughout the stack of CdSe particles. However, not all charges can be collected for photocurrent generation. In the absence of RGO, photogenerated electrons in CdSe quantum dot layers farthest from the TiO₂ network are likely to undergo recombination before reaching the collecting electrode surface. The loss of these electrons is evidenced by the low IPCE values of CdSe-only films at 530 nm. Thus, the charge recombination at the grain boundaries limits the overall collection efficiency at the electrode surface.
interface. Collection of photogenerated electrons through the RGO network in CdSe-(R)GO composite films is expected to minimize charge recombination losses. The higher IPCE values obtained with RGO further validate its important role in interacting with excited CdSe to facilitate electron transport within the film.

Figure 4.9 (B) shows the photocurrent-time profiles during on-off cycles of illumination. The observed higher current in CdSe-RGO films follows the trend established by the IPCE spectra. During the first cycle of illumination, we observe a slow rise in the photocurrent of CdSe-GO films. This rise in photocurrent reflects the reduction of GO within CdSe-GO composites during the initial illumination period. As discussed in preceding sections, the photogenerated electrons are first consumed in the reduction of GO, thus enabling the recovery of conductivity within graphene sheets. The rise in the photocurrent is much less pronounced during 3\textsuperscript{rd} cycle of illumination. In fact, under extended illumination (t >30 min), films made from CdSe-GO composites achieve photocurrent levels within ~15\% of CdSe-RGO composites.

The enhanced photoresponse of EPD-created films of highly dispersed graphene-CdSe quantum dot composites demonstrate the beneficial nature of electron transfer through graphene sheets in quantum dot films. Incorporation of graphene in quantum dot films represents a significant step towards overcoming conductivity problems inherent to quantum dot films, and as such, opens a new avenue towards improved sensitizer loading and performance in QDSCs.
CHAPTER 5:
SUMMARY AND FUTURE DIRECTIONS IN GRAPHENE-NANOPARTICLE ASSEMBLIES FOR
SENSING AND ENERGY CONVERSION

5.1 Summary

As described in chapter two, a two-step electron titration process was designed to interrogate the electron storage and shuttling properties of (R)GO. Briefly, a finite bank of electrons is photogenerated and stored in TiO_2 colloidal nanoparticles. These electrons are fully transferred to GO by incremental addition of nitrogen-purged GO to TiO_2. Electrons not consumed in reduction of GO are stored and then titrated from RGO by the incremental addition of Ag^+ ions. The step-wise electron accepting, storage, and transfer is quantifiable and demonstrates the aptitude of (R)GO materials to store and shuttle electrons. This electronic property, along with other remarkable properties such as high surface area, organic-concentrating interactions, and low cost of production, make graphene an ideal candidate for a host of composite material applications.

In this role, (R)GO has demonstrated its versatility and effectiveness as a substrate and framework in semiconductor, metal, and/or molecular composites where electronic communication between (R)GO and the active material is essential to performance. Chapter three details the construction of RGO-TiO_2 composite films which
demonstrate how RGO can be employed to enhance the photovoltaic and photocatalytic properties of TiO$_2$ films. In another RGO composite system detailed in chapter three, a method for depositing single-layer RGO onto TiO$_2$ films was created. This configuration allows for an illumination-controlled deposition of metal nanoparticles on the graphene surface opposite the TiO$_2$. SERRS sensors constructed using this technique showed nanomolar sensitivity.

In chapter four, excited state interactions in CdSe quantum dot-RGO composites were examined. Two methods were used to isolate the energy and electron transfer processes responsible for the deactivation of excited CdSe quantum dots. In the first, the quenching efficiency of CdSe-(R)GO composites were compared using composites with different levels of oxidation in graphene. In the second, prolonged illumination of CdSe-RGO composites was used to induce charging in RGO. Comparing the photoluminescence lifetimes of composites before and after prolonged illumination allows for the isolation and estimation of energy and electron transfer rates. Quantum dot-RGO composites were then employed as photoanodes in photoelectrochemical cells. Composite anodes produced up to $\sim$150% of the photocurrent observed in CdSe-only cells.

Future designs to tailor-make RGO-semiconductor-metal composites have the potential to advance current state-of-the-art catalyst and sensing materials. In order to realize this role, new methods must be developed to refine how more complex systems are deposited onto RGO sheets with greater site and side selectivity. Such control
should allow for multi-function composites with the ability to carry out complementary processes on single RGO sheets.

5.2 Future Directions: Metal Nanoparticle Sequential and Co-Deposition and Core-Shell Deposition

Sequential and co-deposition of metal nanoparticles, utilizing the TiO$_2$-single layer RGO-metal nanoparticle configuration detailed in chapter three, may be a promising route to achieve heterogeneous catalyst systems. Selection of proper illumination time and precursor concentrations would allow for relatively simple control over final metal nanoparticle size and loading. RGO with different metal nanoparticles adjacent to each other on the same surface would assist in multi-step reactions requiring catalysis of consecutive intermediate reactions. This process has been used in a heterogeneous catalyst system designed to form gasoline-like iso-paraffins. In this system, a co-catalyst design is used to convert syngas to linear hydrocarbons with a Fischer-Tropsch catalyst. These hydrocarbons subsequently undergo cracking and branching at neighboring catalytic sites.$^{168}$

The ability to add multiple metal nanoparticles on RGO along with respective size and loading control will allow for further versatility in these systems. For example, illumination driven deposition of multi-component systems provides the ability to modify SPR characteristics of films, or could provide enhanced selectivity in catalytic reactions. Sequential deposition of metal nanoparticles on RGO, under controlled
conditions, may enable creation of quasi core-shell nanoparticle arrays. Core-shell catalyst nanoparticles have seen application in a number of catalytic processes.\textsuperscript{169-171} The main reason given for core-shell catalyst success in these systems is the modification of surface binding properties between the catalyst and reaction intermediates. Additionally, the method of illumination control of particle sizing may serve as a straight-forward process to create not only a wide range of core-shell nanoparticles using different metals, but may also provide a simple route for the control of core and shell thicknesses.

5.3 Three-Dimensional RGO Composite Architectures

The majority of progress seen in RGO composites to date involves the study of fundamental electronic interactions at composite interfaces. Additional work in this area should focus on the nature and potential benefits of transitioning single layer RGO composites into stacked, three-dimensional architectures. Assuming individual RGO composites layers are sufficiently exfoliated to allow uninhibited diffusion of gaseous or solution-based molecules, stacking of the composites in a 3D arrangement should increase the turn over frequency of catalytic processes, or may serve to provide additional concentrating and local electric field enhancing interactions between target molecules and metal nanoparticles loaded onto RGO in a SERRS sensing film.
To date, few graphene composites have utilized a stacking arrangement to increase performance. The arrangement has been used for improved lithium loading lithium-ion batteries and for higher loading of semiconductor quantum dots for solar energy conversion.\textsuperscript{79,172}

![SEM image of stacked graphene nanosheets used for lithium ion storage.](image)

**Figure 5.1** SEM image of stacked graphene nanosheets used for lithium ion storage.

5.4 Improving Solar Paint with RGO

With the intent of creating an energy source that is both renewable and accessible, a first generation solar paint was developed.\textsuperscript{173} The paint can be applied in a one-step approach to make the photoanode portion of a quantum dot solar cell. Power conversion efficiencies just above 1% have been achieved using the solar paint as a photoanode material. In order to create a economically and commercially-viable solar
paint, efficiencies must be improved. Due to the positive photocurrent effects seen in semiconductor and quantum dot composites, RGO should be an excellent candidate to improve charge separation and transport to the current collecting electrode when added to solar paint. Additionally, RGO, with its residual oxygen-containing functionalities might serve as a stabilizing substance in solar paints, possibly linking TiO$_2$ and the active material within the water/tertiary-butanol solvent. This effect has been observed in an all-organic solar cell using GO as a stabilizing material.$^{174}$

5.5 Acknowledgements

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APPENDIX A:
LIST OF PUBLICATIONS


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