Assembly of Nanoparticles and Small Molecules on Graphene and Their Nonlinear Optical Limiting Properties

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Abstract

Graphene, as a two dimensional macromolecule, can be non-covalently functionalized by organic small molecules as well as inorganic nanoparticles to form graphene hybrids. However, due to the relatively weak interactions between graphene and other molecules, the functionalization of graphene is usually problematic which significantly limits its applications. Therefore, we carefully chose two conjugated planar organic molecules which can strongly interact with graphene as probes to investigate the synergetic effects between them. In another case, we devised a novel, two-phase strategy to deposit nanoparticles onto graphene which successfully led to high coverage. In all these cases, due to the properly aligned molecular orbitals which facilitate the electron or energy transfer between the two components in the hybrids, the electronic and electrochemical properties of graphene have been tailored. In addition, interesting nonlinear optical limiting properties could also arise from this hybridization which render them potential applications in protection of sensitive optical devices.
Acknowledgement

Firstly, I would like express my sincere gratitude to my supervisor, Professor Loh Kian Ping, for his in-depth and insightful teachings on doing scientific researches. Prof. Loh is an all-rounder with enormous energy and remarkable knowledge. But what impresses me most is his careful consideration for his students. He provides all the resources available in the world to help each of his students. He also has very high standard and expectations for his students which constantly motivate us to excel. He is the pivotal figure behind all the great results our group has achieved today. Apart from the academic front, he is a talkative and eloquent man. It is a pleasant process of enriching and enlightening just by listening to him. His words and deeds will continue to influence me in the future endeavours.

Secondly, I would like to pay tribute to my mentors: Dr. Yang Jiaxiang, Dr. Wang Junzhong, Dr. Wang Shuai, Dr. Guo Zhengang, and Dr. Deng Suzi for the instructions and helps that they gave me both professionally and personally. Also, I would like to thank my laboratory mates. They made my two-year journey at NUS fun and memorable.

Thirdly, I would like to thank my former classmates and friends for their constant concerns and support. Though living in different places, we keep each other updated with stories happened around and we share our views on every issue that concerning us. It is so good to have them as friends and I am sure that our friendship will sustain through life’s ups and downs.

Lastly, I want to say a huge thank you to my parents. My debt to them is beyond imagination. Being their son is so good, so warm, and probably a feeling no word can actually express
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<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
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<tr>
<td>CV</td>
<td>Cyclic Voltammetry</td>
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<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
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<tr>
<td>G</td>
<td>Graphene</td>
</tr>
<tr>
<td>GO</td>
<td>Graphene Oxide</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
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<tr>
<td>HRTEM</td>
<td>High Resolution Transmission Electron Microscopy</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium Tin Oxide</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multi Wall Carbon Nanotubes</td>
</tr>
<tr>
<td>NLO</td>
<td>Nonlinear Optical</td>
</tr>
<tr>
<td>ODCB</td>
<td>ortho-Dichloro Benzene</td>
</tr>
<tr>
<td>OL</td>
<td>Optical Limiting</td>
</tr>
<tr>
<td>P3OT</td>
<td>Poly (3-octylthiophene)</td>
</tr>
<tr>
<td>PDI</td>
<td>Perylene Diimide</td>
</tr>
<tr>
<td>PEDOT</td>
<td>Poly (3,4-ethylenedioxythiophene)</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>PSS</td>
<td>Poly (styrenesulfonate)</td>
</tr>
<tr>
<td>PyFc</td>
<td>Pyrene Ferrocene</td>
</tr>
<tr>
<td>PyS</td>
<td>Pyrene-1-Sulfonic Acid Sodium Salt</td>
</tr>
<tr>
<td>rGO</td>
<td>Reduced Graphene Oxide</td>
</tr>
<tr>
<td>TACO</td>
<td>Thiophene-Acrylonitrile-Carbazole Oligomer</td>
</tr>
<tr>
<td>TCNE</td>
<td>Tetracyanoethylene</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>UV-vis</td>
<td>Ultraviolet-Visible</td>
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<tr>
<td>WE</td>
<td>Working Electrode</td>
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Chapter 1

Background Introduction

1.1 Introduction

In 2004, Geim, Novoselov and coworkers at the University of Manchester in England intended to use the Scotch-tape approach to make even thinner samples of graphite. They simply stuck a flake of graphite debris onto plastic adhesive tape, folded the sticky side of the tape over the flake and then pulled the tape apart, cleaving the flake in two. As the experimenters repeated the process, the resulting fragments grew thinner. The as-prepared thin fragments were meticulously examined, and they were astonished to find that some were only one atom thick. This is the story of the discovery of graphene – one-atom thick planar sheet of sp$^2$-bonded carbon atoms and this mechanical exfoliation method is known as Scotch tape method.[1]

The experimental discovery of graphene led to a deluge of international research interest. Not only is it the thinnest of all possible materials, it is also extremely strong and stiff. Moreover, in its pure form it conducts electrons faster at room temperature than any other substance due to its massless dirac electrons and unique honeycomb structure.

The structure of graphene is shown in Figure 1.1. The charge carrier in graphene are Dirac fermions and the charge transport is ballistic[2]. Ballistic transport means the transport of electrons in a medium with minimal scattering. When incorporated into a composite material, graphene enhances the electronic and mechanical properties of the composite material by spreading out in the matrix as a conductive filler and structural reinforcement agent[3]
The Scotch tape method is not industrially scalable and more pragmatic approaches have to be sought. To date there are three general approaches: chemical efforts to exfoliate and stabilize individual sheets in solution\cite{4}, bottom-up methods to grow graphene directly from organic precursors\cite{5}, and attempts to catalyze growth in situ on a substrate\cite{6}. Each of these approaches has its drawbacks. For chemically derived graphene, complete exfoliation in solution so far requires extensive modification of the 2D crystal lattice, which degrades device performance. Bottom-up techniques have yet to produce large and uniform single layers. Total organic synthesis of graphene is challenging because macromolecules become insoluble and the occurrence of side reactions increases with molecular weight\cite{7}. Substrate-based growth of single layers by chemical vapor deposition (CVD) or the reduction of silicon carbide relies on the ability to walk a narrow thermodynamic tightrope. After nucleating a single layer, conditions must be carefully controlled to promote crystal growth without seeding additional second layers or forming grain boundaries.

Despite progress in various methods of producing graphene, mechanical exfoliation using the Scotch tape method still produces the highest quality graphene flakes available. This fact should not, however, dampen any interest from chemists. On the contrary, the recent transition from the consideration of graphene as a “physics toy” to its treatment as a large carbon macromolecule offers new promise. Years of carbon nanotube, fullerene, and graphite research have produced a myriad of chemical pathways for modifying sp$^2$ carbon structures, both covalently and non-covalently, which will undoubtedly be adapted to functionalize both the basal plane of graphene
and its reactive edges. This not only promises to exploit graphene’s intrinsic properties but also lead to the discovery of new properties.

One challenge for performing chemistry with graphene is its poor solubility or processibility due to its huge aromatic plane. The chemists work around this by using the oxygenated form of graphene, known as graphene Oxide (GO). GO is a water soluble nano-material prepared through chemical oxidation of graphite crystals to introduce oxygen-containing defects in the graphite stack, followed by complete exfoliation of the solid into sheets of atomic thickness by mechanical sonication. GO can be converted to G by either thermal or mechanical treatments[8]. GO sheets are composed of planar, graphene-like aromatic domains of random sizes interconnected by a network of cyclohexane-like units in chair configuration which are decorated by hydroxyl, epoxy, ether, diol, and ketone groups[9]. It has an overall planar structure as seen in Figure 1.2.

![Figure 1.2.](image)

These functional groups give GO solubility in water. This is significant because solution processibility is an advantage that GO has over pristine graphene. Because the conjugated plane of GO has been largely damaged through the preparative process, many fascinating properties intrinsic to pristine graphene have also been largely destroyed. However, some of the properties of graphene can be partially recovered by reductive methods. GO can be reduced in the hydrazine atmosphere or annealing in vacuum or nitrogen atmosphere at 500°C. Reduction removes the oxygenated groups chemically while annealing involves pyrolysis of the oxygenated carbon and removing it as carbon dioxide or carbon monoxide[10]. Therefore, the properties of G can be partially recovered. For example, the conductivity of the reduced graphene
oxide (rGO) can reach as high as $2.02 \times 10^4$ S/m while GO is an insulator. However, comparing to G, rGO inevitably will have hole defects as the oxide functional groups are removed as either carbon dioxide or water molecules.

Dispersion of graphene enables processing of this material by solvent-assisted techniques, such as layer-by-layer (LBL) assembly[4], spin-coating[11], and filtration[12]. Soluble or dispersible graphene sheets are usually prepared by chemical modifications (covalent) or non-covalent functionalizations. In the cases of chemical modifications, for example, rGO modified by alkylamine produced stable dispersions of graphene sheets in organic solvents[13], and water-soluble graphenes were obtainable by inducing carboxylic or sulfonate groups onto their basal planes[10,14].

Noncovalent functionalization, which has successfully been carried out in the case of carbon nanotubes[15], is also of interest for the solubilization of graphene because it enables the attachment of molecules through $\pi-\pi$ stacking and hydrophobic interactions while still preserving the intrinsic properties of graphene. Recently, interaction of electron-donor and -acceptor molecules with graphene has been exploited to control the electronic properties of graphene through molecular charge-transfer interactions[16]. For example, Su and coworkers have demonstrated that graphene can be functionalized with large aromatic donor and acceptor molecules, resulting in a novel combination of graphene and nano-graphene building blocks as shown in Figure 1.3[17]. By this means, one can effectively stabilize the aqueous dispersion of graphene sheets and hence yield monolayer and double-layer graphene sheets on substrates in large quantities. Moreover, they found that the different electronic characteristics of large donor and acceptor molecules enable a rational modification of both the electronic structure and conductivity of graphene sheets accompanied by additional thermal reaction of nano-graphene units lead to a dramatic increase of the conductivity. As a consequence, the power efficiency is greatly improved using graphene composite film as electrodes in heterojunction solar cells.
Figure 1.3. Schematic illustration and images of aqueous dispersions of graphene sheets (0.25 mg/mL) and composites on the surface: a) rGO aqueous dispersion, black precipitate after reduction; b) rGO-PDI aqueous dispersion, without precipitate after centrifugation (5000 rps/30 min); c) rGO-PyS aqueous dispersion, without precipitate after centrifugation (5000 rps/30 min). (Reproduced from [18])

Due to so many fascinating properties that graphene possesses, it becomes the hero of my entire Master study. This thesis focuses on the functionalization of graphene with organic molecules and nanoparticles. All the as-prepared nano-hybrids exhibit interesting nonlinear optical limiting mainly due energy or charge transfer between the organic molecules or nanoparticles and graphene.

1.2 References


Chapter 2

Graphene Induced Fluorescence Changes and Nonlinear Optical Limiting Properties of the Hybrid System

2.1 Introduction

As stated in the previous chapter that compared with exfoliation of graphite[1] and epitaxial growth on silicon carbide[2] the chemical reduction of exfoliated graphite oxide (GO) appears to be a more feasible fabrication technique in that it enables mass production of reduced graphene oxide (rGO) sheets. Nevertheless, two central challenges remain in the practical applications of rGO in electronics and composite materials: how to improve the dispersibility of rGO in solution[3] and how to tailor its electronic properties at the solid state.[4] To overcome the first obstacle, noncovalent functionalization, as introduced in carbon nanotubes (CNTs), is particularly attractive, since it can attach chemical handles through van der Waals forces or π-π interactions without destroying the electronic π-system.[5] As for the second and more critical issue of electronic properties, great efforts have been made to improve the electrical conductivities of rGO sheets by optimizing the reductive conditions.[6]

One of the well-known organic hole-and-electron semiconducting materials, namely pyrene with nanographene units, has large planar aromatic structures that strongly anchor it onto the hydrophobic surface of graphene sheets via π-π interactions without disruption of the electronic conjugation of graphene.[5] Therefore, pyrene derivatives are ideal for non-covalently functionalization of graphene. Moreover, pyrene derivatives are also valuable molecular probes via fluorescence spectroscopy due to
their high quantum yields and lifetimes. Their fluorescence emission spectra are very sensitive micro-environment which enables us to investigate the electronic status of other aromatic systems in a very feasible manner.

In this chapter, we will explore the non-covalent functionalization of graphene by making use of charge-transfer interactions with two aromatic pyrene ferrocene molecules which can be used as probes. In order to investigate the interactions between graphene and the aromatic molecules, cyclic voltammetry is utilized to monitor the change of the electronic status of the aromatic molecules. The structures of these aromatic pyrene ferrocene molecules are shown in Figure 2.1. Moreover, due to the existence of charge transfer, their optical limiting properties were also investigated.

![Figure 2.1. Structures of PyFc1 and PyFc2.](image)

### 2.2 Experimental

#### 2.2.1 Synthesis of GO

A conical flask equipped with a magnetic stirring bar was charged with 69 mL of H$_2$SO$_4$ and cooled to 0–5 °C by immersion in an ice bath. Graphite (1.5 g) was added slowly with vigorous stirring while maintaining the reaction mixture at 0–5 °C. After the added graphite flakes formed a well-dispersed black slurry, 1.5 g of NaNO$_3$ was added slowly over 15 min at 0–5 °C. The mixture was allowed to warm to room
temperature (RT) and stirred for 1 h. Water (120 mL) was added next, and the solution was stirred for 30 min while the temperature was raised to 90 °C. The mixture was poured into 300 mL of water, after which 10 mL of H₂O₂ was slowly added. The color of the solution changed from dark-brown to yellow. Next the solution was filtered. The material was redispersed in water and washed with water until the pH of the filtrate was neutral. The resultant GO material was dried in a vacuum desiccator overnight at RT and stored in the ambient environment.

2.2.2 Synthesis of rGO

A colloidal suspension of GO in purified water (4 mL, 3 mg/ml) was prepared in 2-L batches with 2 h of sonication. 36 mL of DMF was added into the aqueous GO suspensions, producing a homogeneous suspension of the GO sheets. Hydrazine monohydrate (1 μl for 3 mg of GO) was subsequently added to the suspension. After stirring at 80 °C for 12 h, a black suspension of rGO sheets was obtained. After cooling to room temperature, rGO paper was made by filtration of the colloidal suspension through a membrane filter (47 mm in diameter, 0.2-μm pore size), after which the deposit was dried in air and peeled off.

2.2.3 Synthesis of PyFc2

428 mg of ferrocenealdehyde and 434 mg of aminopyrene were added into a round bottom flask followed by addition of 10 mL of ethanol and 1 drop of acetic acid. The mixture was stirred at RT for 5 h. The as-obtained mixture was filtered and the solid phase was washed 3 times using ethanol. Yield: 86%.

2.2.4 Synthesis of PyFc1

230 mg of the as-prepared PyFc2 and excess NaBH₄ (350 mg) were added into a round bottom flask followed by addition of a mixture solvent of 10 mL of THF and 5
mL of methanol. The mixture was stirred overnight. After the reaction was finished, the mixture was poured into water, followed by filtration and washing with water. The as-obtained solid was recrystallized using THF and water. Yield: 79%.

2.3 Results and Discussions

First of all, we measured the UV-vis absorption and fluorescence spectra of these two pyrene ferrocene molecules with and without graphene. Figure 2.2 shows the UV-vis absorption spectra and fluorescence spectra of PyFc1 (left) and PyFc2 (right) in DMF at two different concentrations.

![Figure 2.2](image-url)

**Figure 2.2.** UV-vis absorption and fluorescence spectra of PyFc1 (left) and PyFc2 (right) in DMF. Excitation wavelength of fluorescence measurements is 290 nm.

PyFc1 solution in DMF is yellow, exhibiting two absorption peaks at 290 nm (sharp) and 416 nm which can be ascribable to the pyrenyl chromophore and a broad band centered at 393 nm. A solution of PyFc2 in DMF is reddish brown, exhibiting 2 absorption peaks at 279 nm (sharp) and 344 nm-400 nm (broad). PyFc1 and PyFc2 shared a common absorption band at 290 nm in the UV region. In the visible region, the absorption of PyFc1 is red-shifted with respect to PyFc2.

Graphene samples adsorbed with pyrene ferrocene (PyFc) molecules were prepared
by refluxing a DMF solution of PyFc together with G, followed by repeated centrifugation and washing. The UV-vis absorption spectra of G adsorbed with PyFc1 and PyFc2 are shown in Figure 2.3(left) and 2.3(right), respectively. Due to the increased scattering caused by the G sheets; the absorbance value is apparently high. The absorption maximum at 283 nm is mainly due to G while the absorption edge at 410 nm is due to the PyFc adsorbed on G. The emission spectra display typical monomer emission bands at 386, 435 nm ($\lambda_{ex} = 290$ nm) for both molecules. In order to obtain a comparison of the fluorescence emission for PyFc and G-PyFc, the emission of (G)PyFc is normalized by the value of absorbance at 290 nm (or 280nm for GPyFc) as shown in Figure 2.4. After normalization, we observed an interesting change that the intensity of the fluorescent peak in the case of G-PyFc1 is greatly enhanced comparing to pure PyFc1, while in the case of G-PyFc2, the intensity of the fluorescent peak is largely quenched comparing to pure PyFc2.

The quantum yield (QY) of PyFc1 is lower than that of PyFc2 which is similar to those exhibited by pyrene derivatives[7]. However, the addition of G to the solution of PyFc1 yields a remarkable enhancement of fluorescence emission. The fluorescence enhancement factor (FEF) was 47 for G-PyFc1 relative to PyFc1. However for PyFc2 the fluorescence is diminished by a factor of ~2.5.
Figure 2.4. Fluorescence spectra of the PyFc and GPyFc after normalizing the absorbance of the excitation wavelength to the same value.

As we know, the change of the intensity of the fluorescent peak is closely related to fluorescent QY. Therefore, given the above-mentioned phenomena, the QY of PyFc1 is very much enhanced with the presence of G, while the QY of PyFc2 is very much decreased with the presence of G. To display this in a clearer fashion, the integrated fluorescence peak intensity was plotted against the absorbance for (a) PyFc1 and PyFc2 (Figure 2.5 (left)) and (b) GPyFc1 and GPyFc2 (Figure 2.5 (right)). The slope of QY plot indicates the change in PL efficiency for PyFc1 and PyFc2 after binding to G. As we can see in Figure 2.5 (left), the slope of QY plot of PyFc1 is very flat, while the slope of QY plot of PyFc2 is very steep. However, after forming hybrid on G, the slope of QY plot of PyFc1 becomes much steeper, while the slope of QY plot of PyFc2 becomes flatter. Therefore, the slopes indicate that only for PyFc1 the PL is significantly enhanced after adsorption on G.

The difference in chemical structures of PyFc1 and PyFc2 may be the cause of this observation. Figure 2.6 and Figure 2.7 show the possible ways of interactions between G and PyFc1, G and PyFc2, respectively. In the case of PyFc1, there are two possible ways of interactions between G and PyFc1. In PyFc1, the pyrene moiety and the ferrocene moiety are not coplanar, therefore only one moiety of PyFc1 can π-π stack
onto G which leads to two different interaction models. It is thought that the tethered moiety (pointing away from substrate) will have redox characteristics similar to that in solution while the flat-lying moiety will have its properties changed. However, PyFc2 is a coplanar molecule. Therefore, both the pyrene moiety and ferrocene moiety can stack onto G which will lead to the change of the electronic properties of both moieties.

In order to verify the aforementioned interaction models, cyclic voltammetry (CV) was utilized to investigate the electronic properties of the pyrene and ferrocene moieties adsorbed. For each PyFc molecule, it has two electrochemically reactive groups. Therefore, we used aminopyrene and ferrocene alone to determine the
position of the redox peak of each group. Figure 2.8 shows the CV of the two reference molecules. As we can see, the redox peak of aminopyrene (+0.658 V (vs. Ag/AgCl)) is at higher voltage than that of ferrocene (+0.562 V (vs. Ag/AgCl)). Moreover, it has no reduction peak as can be seen from the red curve which means the oxidation of pyrene is irreversible.

Figure 2.9 shows the CV of PyFc1 in solution at different scan rates with different scan ranges. The peaks between -0.6 V to -1.0 V are the redox peaks of TBA adsorbed on the glassy carbon working electrode (WE). As we can see from Figure 2.9 (left), only one peak (+0.42 V (vs. Ag/AgCl)) is observed in the narrow scan which can be assigned to pyrene because of its irreversibility. However, we could observe three peaks in the wide scan. Two of these can be assigned to ferrocene (+0.717 V and +0.60 V (vs. Ag/AgCl)) and the other one can be assigned to pyrene (+0.42 V (vs. Ag/AgCl)). The electrochemical properties of each component are largely retained. The absence of quenching of redox properties is due to the lack of direct electronic coupling between these moieties and the glassy carbon electrode.

However, comparing the CV of PyFc1, the CV of PyFc2 is very different as shown in Figure 2.10. We could only observe one peak (+0.694 V (vs. Ag/AgCl)) assignable to pyrene even after scanning to higher voltage. This irreversibility of PyFc2 resembles the redox of aminopyrene. PyFc2 is a conjugated molecule. Therefore there is
electronic communication between pyrene and ferrocene moieties. Specifically, the ferrocene moiety donates electron to the pyrene moiety which makes the ferrocene moiety less susceptible to redox reactions.

To prepare the G-pyrene ferrocene hybrid system where pyrene ferrocene molecules adsorbed on G, PyFc is dissolved in DMF containing G and refluxed at 80 °C for 24 h. The solution is then centrifuged at a speed of 9000 rpm and washed with DMF. The precipitate is collected for further characterization. Figure 2.11 shows the CV of GPyFc1 and GPyFc2 in DMF solution. To our disappointment, we could not observe any obvious peaks in both cases except some tiny peaks. One possible reason is that
because after binding together, both PyFc1 and PyFc2 are wrapped up by G and becomes less sensitive to electrochemical reactions.

If that is true, it is reasonable that PyFc2 has lower peaks comparing to PyFc1 because PyFc2 has stronger interactions with G. Indeed, from Figure 2.11 we can see some small peaks in the case of GPyFc1 while peaks of GPyFc2 are unobservable. Therefore, we believe that passivation by G may be the origin of the electrochemical inactivity. In order to verify this, we added tetracyanoethylene (TCNE) into the system and at the same time we did not add TBA in order to minimize interference. TCNE is a strong electron acceptor or oxidizer which can oxidize ferrocene easily.
After oxidation, ferrocene will undergo a molecular rearrangement which decreases the binding affinity of the molecule with G. Therefore, the pyrene moiety will to some extent, be released from the wrapped-up state to the free molecular state and exhibits its intrinsic electrochemical properties. Figure 2.12 shows the CV of GPyFc2 after TCNE treatment at two different scan ranges. Indeed, after the TCNE treatment, the peak of pyrene re-appears. Thus, it can be proven that the PyFc2 binds very strongly with G which leads to a quenching of its electrochemical properties. However, in the case of PyFc1, we did not observe any obvious changes after TCNE treatment. Therefore, we believe that in GPyFc1, the pyrene moiety π-π stacks onto the G sheets while leaving the ferrocene moiety pointing away from G.

![Figure 2.12. CV of GPyFc2 after TCNE treatment at two different scan ranges.](image)

In order to get more insight into the interactions between G and the pyrene ferrocene molecules, we measured the CVs with different working electrode (WE). Figure 2.13 shows the CV of PyFc1 in DMF with graphene (prepared as epitaxial G), glassy carbon, and gold as WE. As we can see, the redox peaks of PyFc1 appear at different positions when different WE is used. Specifically, the potential is lowest when using G WE while the potential is highest when using gold WE. This trend indicates that the affinity is the strongest between G and PyFc1 and the lowest between gold and PyFc1. This is reasonable because PyFc1 can stack onto G strongly and to a less extent, glassy carbon. PyFc1 has no π-π interactions with gold at all; hence their interaction is the lowest. In the case of PyFc2, the same trend also exists. However, the gap of the two peaks in PyFc2 is much larger than that in PyFc1; this again indicates stronger
interactions between PyFc2 and G as shown in Figure 2.14.

![Figure 2.13. CVs of PyFc1 by using G, glassy carbon and gold WE.](image)

From the above discussions, we can infer that there is strong non-covalent binding interactions between G and PyFc molecules. However, the aforementioned explanations do not account for the observed fluorescence changes. Computer simulations were performed to explain it. Figure 2.15 shows the simulated HOMO and LUMO of PyFc1 and PyFc2 and their subunits. As we can see, conjugated PyFc2 has a smaller band gap value than unconjugated PyFc1. Despite this, the wavelengths of fluorescence emission from PyFc remain similar to pyrene.

![Figure 2.14. CVs of PyFc1 by using G, glassy carbon WE.](image)
From this energy level alignment, we can judge that in both PyFc1 and PyFc2, the electron flow between the two subunits is from ferrocene to pyrene. Therefore, quenching by the ferrocene subunit may occur via either energy or charge transfer from the ferrocenyl group that acts as an electron donor, to the excited state of the pyrenyl group, acting as an electron acceptor unit. After interfacing PyFc to G, electron transfer occurs from ferrocene to G because the HOMO of ferrocene is higher than G conduction band (-4.5 eV). As a result, the electron-donating ability of the ferrocene subunit to pyrene is reduced, leading to a fluorescence enhancement. It had been reported that the stronger donor ability of moieties like pentamethylferrocene compared to ferrocene, assists in the quenching of the photo-excited state of dimethyldihydropyrene, a conjugated structure similar to pyrene.[8] The conduction band of G is higher than HOMO of PyFc2, and only slightly higher than PyFc1. This means that electron transfer from HOMO of PyFc to G is more likely in the case of PyFc1. Experimentally, we observe a prominent increase in fluorescence for G-PyFc1 (relative to PyFc1) and reduced fluorescence in G-PyFc2 (relative to PyFc2).

![Figure 2.15. Simulated HOMO and LUMO of aminopyrene, ferrocene, PyFc1 and PyFc2 (eV).](image)

2.4 Application
Due to the existence of energy or charge transfer in the GPyFc systems, the nonlinear optical limiting (NLO) properties (a thorough introduction will be done in Chapter 2) of these hybrids were studied. The nonlinear optical properties of these materials were measured by Z-scan technique in the femtosecond regime. Figure 2.16 shows open aperture Z-scan results of G-PyFc2 at 800 nm with different input fluences 5-ns pulses. The open aperture Z-scan measures the transmittance of the sample as it translates through the focal plane of a tightly focused beam. As the sample is brought closer to focus, the beam intensity increases and the nonlinear effect increases, which leads to a decreasing transmittance due to reverse saturable absorption (RSA), two-photon absorption (TPA), or nonlinear scattering (NLS). At the focal point where the input fluence is maximum, the transmittances of G-PyFc2 drop down to 80%, at a laser fluence of 190nW. Graphene by itself does not exhibit a valley at low P, and at high P the transmittance exhibits a peak. Therefore, G-PyFc2 demonstrated much better nonlinear optical properties that is absent in the graphene sample alone.

![Figure 2.16. Laser fluence dependent NLO properties of GPyFc2.](image)

The NLO properties of molecules come from the conjugative effect of molecules, according to reverse saturable absorption mechanism, i.e., their first singlet and triplet states have larger absorption cross sections than the ground state. It is reasonable to expect that both a nonlinear absorption and a nonlinear light scattering mechanism
may play a role in the hybrid’s enhanced NLO performance. Figure 2.17 shows the change of valley value with the intensity at the square relation, meaning the existence of TPA. Therefore, indeed, nonlinear absorption plays an important role in the enhancement of the NLO properties.

![Figure 2.17. Relations between valley value and the incident fluence.](image)

Furthermore, another possible reason for this enhanced NLO performance may be attributed to the possible photo-induced energy or charge transfer mechanism between G and PyFc2. In the hybrid system, PyFc2 is a favorable electron donor and G is an electron acceptor when the two moieties $\pi$-$\pi$ stack together. Therefore, the intra-molecular donor-acceptor interaction between the two moieties of PyFc2 and G may have a charge transfer from the photo-excited singlet PyFc2 to G, and this results in the fluorescence quenching and energy releasing.$^{[9]}$

It is known that the photo-induced charge transfer can result in an enhanced NLO performance, as observed in the PVK modified SWCNTs system$^{[10]}$ and the SWNT-porphyrin system.$^{[11]}$ Therefore, the greatly enhanced NLO performance of GPyFc2 should arise from a combination of photo-induced energy or charge transfer, TPA, and nonlinear scattering mechanisms. Similar results have been observed in
hybrid materials of carbon nanotubes with porphyrins. However, due to the relatively weak interactions between G and PyFc1, we only observed much weaker NLO signals. This is in accordance with our predictions.

2.5 Summary

In summary, we have synthesized two pyrene ferrocene molecules which have strong interactions with graphene, leading to an interesting change of the fluorescent and electrochemical properties of the molecules. The differences in electrochemical and fluorescent properties were correlated to the different binding modes of the molecules on graphene. The electron or energy transfer between graphene and the molecules also gives rise to interesting non-linear optical limiting properties.

2.6 References


**2008**, *20*, 511.

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Chapter 3

Graphene Oxide Induced Aggregation of
Thiophene-Acrylonitrile-Carbazole Oligomer and Their
Nonlinear Optical Limiting Properties

3.1 Introduction

Nonlinear Optical limiting (NLO) materials have potential applications in protection of eyes and sensitive optical devices from laser-induced damage. Three main factors are believed to contribute to the optical limiting performance: scattering[1], multiphoton absorption[2] and energy/charge transfer[3,4]. Many carbon-based materials have been reported to exhibit strong optical limiting properties, such as carbon nanotubes (CNTs)[1,5,6], carbon-black suspensions[7] and graphene[8]. Covalent and non-covalent combinations of OL materials are commonly used approaches to improve OL performances[8]. Among those carbon-based materials, graphene - a two dimensional sheet of sp$^2$ hybridized carbon atoms - has attracted huge attentions recently due to the extraordinary thermal, electrical and mechanical properties.

In nonlinear optical limiting measurement, a Z-scan measurement is used to measure the non-linear index $n_2$ (Kerr nonlinearity) and the non-linear absorption coefficient $\Delta\alpha$ via the “open” and “closed” methods, respectively. As non-linear absorption can affect the measurement of the non-linear index, the open method is typically used in conjunction with the closed method to correct the calculated value. Figure 3.1 shows the typical closed aperture Z-scan measurement set-up. In the closed aperture Z-scan set-up, an aperture is placed to prevent some of the light from reaching the detector. A
Figure 3.1. Closed aperture Z-scan measurement set-up.

lens focuses a laser to a certain point, and after this point the beam naturally defocuses. After a further distance an aperture is placed with a detector behind it. The aperture causes only the central region of the cone of light to reach the detector. Typically, values of the normalized transmittance are between $0.1 < S < 0.5$. The detector is now sensitive to any focusing or defocusing that a sample may induce. The sample is typically placed at the focus point of the lens, and then moved along the $z$ axis a distance of $\pm z_0$ which is given by the Rayleigh length $z_0$:

$$z_0 = \frac{\pi W_0^2}{\lambda}$$

The thin sample approximation states that the thickness of the sample $L$ must be less than the Rayleigh length $L < z_0$. The open aperture Z-scan method is similar to the closed aperture one. However, the aperture is removed or enlarged to allow all the light to reach the detector. This in effect sets the normalized transmittance to $S = 1$. It is used in order to measure the non-linear absorption coefficient $\Delta \alpha$.

Different mechanisms exist for NLO properties, such as nonlinear absorption (multiphoton absorption, reverse saturable absorption (RSA)), nonlinear refraction (electronic or thermal effects), and nonlinear light scattering (NLS).

Multiphoton absorption process offers the possibility of maintaining high transparency in ambient light and achieving efficient and instantaneous protection against the high intensity delivered by high power lasers. Key ingredients for such purpose are a high transmission at low intensity (i.e., weak linear absorption) and high
multiphoton absorption cross-section (i.e., high nonlinear responses).

Some materials' absorption is weak at low incident light energy but becomes extremely strong under intense light radiation. Such nonlinear absorptive behavior is referred as reverse saturable absorption (RSA), in contrast to saturable absorption found in most materials. Physically, RSA occurs as a consequence of the absorption cross section of an excited molecular state being greater than that of the ground state. As the optical excitation intensity increases, more molecules are promoted to the excited state, thus giving rise to higher absorption at intense light excitation. Because the RSA process involves electronic transitions, materials that exhibit RSA generally have an extremely fast response. Many examples of the RSA process involve a long-lived triplet state. This is certainly true when the samples are illuminated by light pulses of a few nanoseconds or longer. The involvement of a long-lived triplet state ensures that the optical limiting response is relatively pulse-width independent over a wide range of pulse durations. Furthermore, many of these molecules have a broad linear absorption, resulting in a broadband limiting response. These advantages make RSA extremely attractive for use in broadband optical limiting of laser pulses.

Conceptually, refraction is a measure of how a medium can alter the propagation of light rays because of different propagation velocities of light in various media. Nonlinear refraction occurs when a material's refractive index is altered in the presence of an optical electric field. This means that the refractive index \( n \) coefficient depends on the irradiance of light impinging on the medium. Generally, the higher the irradiance, the stronger the effect. Nonlinear refraction is an important component of the area of nonlinear optics.

Nonlinear light scattering is observed in a multitude of photorefractive materials: illumination with an unexpanded laser beam leads to the build-up of scattered light into a wide apex angle around the directly transmitted laser beam. Hereby, the pump beam intensity is decreased, which can be as effective as 99% with respect to the
incoming laser light power, i.e. the incoming pump beam is nearly completely scattered. The NLS process can be understood in the frame of the interference of the pump beam with initial scattered waves: if a coherent laser beam propagates through a photorefractive material, it is scattered at inhomogeneities, such as defects or imperfections.

There have been a lot of researches on the graphene-based hybrid materials on their NLO properties, for example, Liu et al. have investigated the nonlinear optical properties of two novel GO nanohybrid materials covalently functionalized with porphyrin and fullerene using Z-scan technique at 532 nm in the nanosecond and picosecond time scale[8]. Results show that covalently functionalizing GO with the reverse saturable absorption (RSA) chromospheres like porphyrin and fullerene can enhance the nonlinear optical performance in the nanosecond regime. The covalently linked GO nanohybrids offer performance superior to that of the individual G, porphyrin, and fullerene by combination of a nonlinear mechanism and the photo-induced electron or energy transfer between porphyrin or fullerene moiety and GO. Scheme 3.1 shows the synthesis of the two hybrid materials. Because of the carboxylic groups in GO, these reactions are easy to realize.

The nonlinear optical limiting properties of these materials were measured by Z-scan technique in nanosecond and picoseconds regime. Figure 3.2a shows open-aperture Z-scan results of GO-porphyrin, porphyrin-NH\textsubscript{2}, graphene oxide, and a controlled blend sample of porphyrin-NH\textsubscript{2} with GO (1:1 w/w) at 532 nm with 5-ns pulses. As the sample is brought closer to focus, the beam intensity increases and the nonlinear effect increases, which leads to a decreased transmittance because of effects like reverse saturable absorption (RSA), two-photon absorption (TPA), and nonlinear scattering (NLS). As shown in Figure 3.2a, the GO-porphyrin has the largest dip among the transmittance curves of the studied materials. Therefore, GO-porphyrin demonstrated much better NLO properties compared with those of the controlled sample and the individual components of the hybrid.
Under the same experimental conditions, they also carried out the nanosecond open-aperture Z-scan experiments to study the NLO performance of GO, GO-C₆₀, GO/pyrrolidine fullerene blend, and pyrrolidine fullerene, as shown in Figure 3.2b. These results demonstrate that although excellent nonlinear optical properties were observed for all of the samples, the largest dip for the GO-C₆₀ hybrid among the transmittance curves indicates that it is the best one.

The NLO properties of fullerene and porphyrin come from the conjugative effect of molecules, according to RSA mechanism, i.e., their first singlet and triplet states have larger absorption cross sections than the ground state. For GO, studies have shown that TPA is the dominating nonlinear absorption mechanism in the picoseconds regime and a large excited state absorption in the nanosecond regime[9]. In addition, CNTs, another allotropic carbon nanostructure, have also been reported to have strong optical limiting effects, which arise from strong nonlinear light scatterings due to the creation of new scattering centers consisting of ionized carbon microplasmas and solvent microbubbles[10].
Figure 3.2. (a) Open-aperture Z-scan curves of graphene-porphyrin, porphyrin-NH$_2$, graphene oxide, and a controlled blend sample of porphyrin-NH$_2$ with graphene oxide (1:1 w/w). (b) Open-aperture Z-scan curved of graphene-C60, pyrroldine fullerene, graphene oxide, and a controlled blend sample of pyrroldine fullerene with graphene oxide (1:1 w/w) at 532 nm with 5-ns plses. (Reproduced from [8])

The reason that GO-C$_{60}$ and graphene-porphyrin hybrids exhibit the good NLO performance is not yet understood. However, from the similar electronic structures of C$_{60}$, graphene, and CNTs, it is reasonable to expect that both a nonlinear absorption and a NLS mechanism may play a role in the hybrid’s enhanced NLO performance.

Dual fluorescence is an anomalous emission behavior because it contradicts the well-established Kasha’s rule[11], which states that the fluorescence spectrum is dominated by a single S1 emission band arising from the first excited singlet state. Dual emission was first observed form the emission spectrum of 4-(dimethyl)aminobenzonitrile (DMABN) in 1959 by Lippert[12], and also discovered later in some less common molecules[13]. Dual fluorescent molecules can be sensitive probes of the molecular environment because the relative intensities of the two emission bands are influenced by parameters such as solvent polarity, viscosity and temperature[14]. For example, it is possible for the molecules to interact with solvent to form a molecule-polar solvent complex which can exhibit two
radiative pathways. The ability of a molecule to exhibit two-color emission is potentially useful in applications such as solvatochromic probe and biosensor. The different radiative pathways in such molecules for example can be either quenched or enhanced depending on coupling to the solvent bath or covalent bonding to a biomolecule[15].

For organic molecules, aggregation is a common phenomenon that occurs in solution of high concentrations. Molecules exhibiting emission behavior which depends on its aggregated state are of particular interest because the aggregation-dependent luminescence can find applications in the fields of sensors or OLED. However, one deleterious side effect of aggregation is the problem of emission quenching due to strong electronic interactions, hydrogen bonding or $\pi-\pi$ stacking[16]. Our group has previously reported that thiophene-acrylonitrile-carbazole oligomer (T1) (Figure 3.3. right) can exhibit dual emissions in solvent and solid[17]. Figure 3.3 (left) shows the UV-vis absorption, excitation and emission spectra of T1 in THF solution. The high-energy emission at 316 nm is assigned as a S2 peak because its wavelength is shorter than the lowest absorbance of 365 nm. The high energy S2 emission is most likely related to local emission from the carbazole moiety in the molecule, because modification of the carbazole with phenothiazine, a closely related structure with one extra S atom, resulted in only S1 emission. Similar to other rare molecules exhibiting anomalous emission, the S2-S0 emission is from fluorescence localized to specific functional moieties in the molecule, while the S1-S0 emission arises from delocalized molecular states. The S1 emission at the blue region (about 440-460 nm) is very weak in solution but greatly enhanced in the solid (aggregated) state, whereas the S2 emission shows the opposite behavior. To the best of our knowledge, this is the first example of a molecule exhibiting S1 and S2 dual emissions that depend on its aggregation behavior.

The change in the intensities of the dual emission intensities in different aggregation states of the molecules is illustrated in Figure 3.4. The anomalous S2 emission is
Figure 3.3. (left) UV-vis absorption (black curve), excitation and emission spectra of thiophene-acrylonitrile-carbazole oligomer in THF ($1 \times 10^{-5}$ M). The excitation spectrum was taken using the S2 emission peak at 316 nm, and the emission spectrum was obtained by 289 nm excitation. (right) Structure of the thiophene-acrylonitrile-carbazole oligomer (T1). (Reproduced from [17])

dominating in dilute solution. In the aggregated state (nanoparticle), the S2 and S1 dual emissions are peaked at 365 and 490 nm, with some red-shifts. However, the relative peak intensities of S2 compared to S1 are now reduced greatly. This trend is more pronounced for emission from the solid film (prepared by spin-coating).

Figure 3.4. Comparison of S2 and S1 emission intensities: solution (curve a), nanoparticles (curve b), solid film (curve c). (Reproduced from [17])

As the dual emission can be switched by intermolecular interactions, it should be influenced by different packing modes like H or J aggregation, or by H-bonding or electrostatic interaction with the carbazole moiety. It is expected that this kind of molecules would have some distinctive GO-induced emissions due to π-π interactions.
3.2 Results and Discussions

For this project, we have chosen the thiophene-acrylonitrile-carbazole oligomer (A) with a long alkyl chain as the non-covalent functionalization molecule of GO. A was prepared via the condensation of 9-dodecyl-3-carbazolecarboxaldehyde with 2-thiopheneacetonitrile using t-BuOK as the catalyst. A has three main absorption bands with two main peaks at 288 nm and 370 nm in THF which can be assigned to the S0-S2 and S0-S1 transition respectively as shown in Figure 3.5 (black curve). A exhibits dual emissions (excited at 288 nm) in THF with one dominant peak at 340 nm and one weak shoulder at about 430 nm (Figure 3.5 (red curve)). The high energy emission at 340 nm is assigned as a S2-S0 peak because its wavelength is longer than 288 nm but shorter than 370 nm; accordingly the low-energy emission at 437 nm is assigned as a S1-S0 peak. A similar molecule with phenothiazine replacing thiophene moiety results in only S2-S0 emission, therefore this is closely related to the local emission of carbazole[18]. The S1-S0 emission is thought to arise from the delocalized molecular states according to other rare molecules exhibiting the same property. In principle, the S2-S0 transition would appear if the S2-S1 radiationless internal conversion process is sufficiently slow. This depends on two factors: the energy gap between S2 and S1 levels and the density of states in these two electronic states. It is reasonable if the energy gap between S2 and S1 states is large enough ($\Delta E > 3000 \text{ cm}^{-1}$) which will reduce the vibronic coupling between these states and slow down the rate of 2-S1 internal conversion process. It has been calculated that in a similar molecule that the energy gap is 7519 cm$^{-1}$, this value is sufficiently large for the observation of S2-S0 emission. However, when A is in film state, the S2-S0 emission is largely quenched while the S1-S0 emission is enhanced (Figure 3.6 (black curve)) because the S2-S1 transition is fastened due to aggregation.

A is soluble in THF but insoluble in water, quite to the contrary, GO is soluble in water but not soluble in THF. In order to investigate the interactions between A and GO, THF/water (v:v, 1:1) was initially applied. As can be seen from Figure 3.6, there
Figure 3.5. UV-vis and PL spectra of A (10^{-5} M) in THF, the excitation wavelength of the PL spectrum is 288 nm.

Figure 3.6. PL of A and the mixtures.

is no obvious emission at around 425 nm for A in THF/water (red line). However, after the addition of GO, a new peak at around 425 nm emerges. We also observed that it takes some time for this new peak to appear. This is probably because the coupling of the two components needs some time to complete. Nevertheless, as can be seen from Figure 3.6, it is clear that the height of the new peak increases with the concentration of GO in the solution. As the concentration of GO increases from 0.005 mg/mL to 0.015 mg/mL, the intensity of the new peak increases accordingly. This is very interesting because GO is believed to quench the emissions of fluorescent
molecules after interactions (in most cases, $\pi-\pi$ interactions). However, we did observe that when GO was excess, both the main peaks tended to quench slightly as can be seen from Figure 3.7. As the concentration of GO increases from 0.015 mg/mL to 0.025 mg/mL, the PL intensity decreases slightly. This is in agreement with the fact that GO can quench the fluorescence of aromatic molecules[19].

To understand this phenomenon on an energy level basis, we drew all the energy levels of A as shown in Figure 3.8. Figure 3.8 (left) shows the transitions in the UV-vis absorption process. The electron in the ground state (S0) is excited to two separate excited states (S1 and S2). Therefore, we can see two absorption peaks in the UV-vis spectrum. When measuring the PL spectra, the excitation wavelength is set at 288 nm which corresponds to the S0-S2 transition. Due to the large band gap between S1 and S2, the intersystem crossing between S1 and S2 is largely prohibited. Therefore, we can only see one peak (corresponding to S2-S0 transition) and one small shoulder in the PL spectra (corresponding to S1-S0) (Figure 3.8 (middle)). When GO is added into the system, due to the GO induced aggregation of A, the transition between S1 and S2 is enhanced. Therefore, we can see both S2-S0 and S1-S0 transition peaks (Figure 8 (right)).
It is noted that the wavelength of the new peak is the same as that of the long wavelength shoulder as shown in Figure 3.4. Therefore, it is thought that this new peak is originated from the S1-S0 transition. Moreover, it is believed that the emergence of the new peak is due to the GO induced aggregation of A. To verify this hypothesis, we prepared GO on the SiO2 substrates via spin-coating, and dipped the substrate into the A solutions ($10^5$ mol/L in THF/water 1:1) for 3 hours and dried under nitrogen gas flow. Figure 3.9 shows two representative AFM images of the as-processed GO sheets on SiO2 substrate. As can be seen from the two images, a lot of small particles have grown on the GO sheets. These particles are A aggregates. The heights of most of the particles range from 5 nm to 30 nm. Moreover, most of the particles are located at the edges or creases of the GO sheets. It is probably because that the edge and creases can act as the aggregation centers which are similar to the crystallization centers. Therefore, the results unambiguously demonstrate that GO can induce the aggregation of A in THF/water (1:1) solution and result in the appearance of the new fluorescent peak.

Figure 3.8. Energy levels of A and the transition between levels under different circumstances.

Figure 3.9. Typical AFM images of A aggregates on GO sheets.
The change in relative intensity of the S2-S0/S1-S0 peak as a function of GO concentration is shown in Figure 3.10. As can be seen from Figure 3.10 that it is clear that the relative intensity of S2-S0/S1-S0 decreases as concentration of GO in the solution increases. The aggregation of A enhances the S2-S1 radiationless internal conversion process. Therefore, the S1-S0 peak increases and the S2-S0 peak decreases spontaneously. Due to the differences in solubility, it is expected that solvent compositions would render changes in fluorescent emissions. As shown in Figure 3.11, the peak intensity of S1-S0 increases significantly as the content of THF in the mixture solvent decreases. A is not soluble in water, therefore the higher the proportion of water in the mixture solvent, the easier the aggregation of A on GO sheets.

Figure 3.10. Relative intensity of the two peaks as a function of the concentration of GO.

Figure 3.11. Intensity changes of the new peak as a function of the composition of the solvents.
3.3 Application

The OL properties of the blend were measured by Z-scan technique in femtosecond regime. Figure 3.12 shows the open-aperture Z-scan results of A and GO solution after different mixing times at 780 nm with a laser pulse width of 300 fs. For better elucidation, we also checked the two individual components, but no signals were detected. This time-dependence is in accordance with the previous observation that when measuring the fluorescence of the mixture, the new peak also needs some time to emerge. As can be seen from Figure 3.12, after approximate 1 hour, the normalized transmittance reaches its lowest. That means it takes about 1 hour for GO and A to reach the equilibrium under that condition. After 56 min of mixing, the transmittance of the mixture drops down to 22%. Therefore, it proved that the optical limiting behavior is caused by the binding between A and GO.

It was also found that this binding is concentration-dependant as can be seen from Figure 3.13. Quite different results were obtained from three solutions with different concentrations while the ratio of A and GO was kept constant which was the same as that used in the sample which exhibited the strongest fluorescent emission. As the concentration increases, the signal increases dramatically. When the concentration is

![Figure 3.12. Time dependent fs OL performances of the mixtures of GO and A.](image)
one third of the maximum concentration measured, there is no transmittance drop at all. When the concentration reaches the maximum measured, the signal drops down to 28%. This phenomenon is probably due to that when the concentration is low; there is little GO induced aggregation of A on the GO sheets due to the low binding constant between A and GO.

![Figure 3.13. OL performances of the mixtures as a function of concentration.](image)

We also measured the OL properties of the mixture in the nanosecond regime using 532 nm laser as shown in Figure 3.14. As we can see from Figure 3.14 that there is only tiny difference between the transmittance curves of GO and the mixture. Thus, we conclude that the mixture exhibits remarkable OL properties only in the femtosecond regime.

![Figure 3.14. OL properties of the mixture and individual components in the nanosecond regime using 532 nm laser.](image)
Two factors are considered to render the mixture of A and GO good OL performance in femtosecond regime. As in most cases, nonlinear scattering is believed to be the first factor. As can be seen from Figure 3.15, the mixture exhibits obvious femtosecond nonlinear scattering signals. The scattering signal also increases drastically with the concentration. The aggregates formed on GO sheets can scatter the incident laser beam which leads to decreased transmittance. Another factor may arise from the energy transfer between the A and GO. The aggregates absorb the laser energy; the energy is transferred to the GO which results in the enhancement of the OL performance. Moreover, we believe the charge transfer rate between GO and TACO is in the femtosecond time scale. Charge transfer occurs only when the pulse of the laser source matches the charge transfer rate. The possibility of RSA can be excluded, because in most cases, RSA occurs when much longer laser pulses are applied. Multiphoton absorption can be ruled out too, because the energy level structures of TACO that it possesses no ability to absorb multiphoton at one time.

![Figure 3.15](image)

Figure 3.15. Scattering experimental results obtained by placing a detector at an angle of 30° to the laser beam.

### 3.4 Summary

In summary, thiophene-acrylonitrile-carbazole oligomer (TACO) exhibits aggregation-dependent dual emissions property due to the large band gap between its
two excited states. It was found that GO can induce the aggregation of TACO onto the GO sheets in THF/water mixture solvent which results in the emergence of a new fluorescent peak. Moreover, the GO and TACO blend exhibits remarkable nonlinear optical limiting performances in the femtosecond time scale. The femtosecond scattering centers and femtosecond charge transfer are thought to play the crucial roles in this nonlinear optical limiting observation.

3.5 References


Chapter 4

Nonlinear Optical Limiting Properties of Graphene and Copper (I) Sulfide Nanoparticles Hybrid Material

4.1 Introduction

Semiconductor nanostructures have various applications in photovoltaic devices, such as solar cells including dye-sensitized solar cells[1] and hybrid solar cells[2], light-emitting devices[3]. Chalcocite copper(I) sulfide is a p-type semiconductor with a bulk band gap of 1.21 eV[4], its synthesis and applications have been widely studied.

From the synthetic perspective, many methods have been devised to synthesize Cu$_2$S nanoparticles with different morphologies[5-7]. For example, Zhuang et al. demonstrated that different shaped and highly uniform Cu$_2$S nanocrystals can be synthesized through a simple water-oil interface confined reaction by introducing different ligands of copper like Cl$^-$ and Ac$^-$ and using dodecanethiol ($C_{12}H_{25}SH$) as capping reagent[8]. Moreover, the nanocrystals readily self-assemble into highly ordered multilayer superlattices as shown in Figure 4.1 and Figure 4.2. By controlling the size and shape of the building block nanocrystals, it is possible to adjust the packing symmetry of the superlattice and further to tailor the structures and performances of the assemblies. Figure 4.3 shows the detailed schemes and descriptions of the packing symmetry of nanocrystals.

Most recently, Talapin and co-workers found that various molecular metal chalcogenide complexes (MCCs), such as [Sn$_2$S$_6$]$^{4-}$ and [Sn$_2$Se$_6$]$^{4-}$, could serve as
Figure 4.1. TEM images of Cu$_2$S nanocrystals: TEM image (a), size distribution (b), and HRTEM image (c) of circular Cu$_2$S nanocrystals; TEM image (d), size distribution (e), and HRTEM image (f) of elongated Cu$_2$S nanocrystals; TEM image (g), size distribution (h), and HRTEM image (i, j) of Cu$_2$S hexagonal nanoplates. (Reproduced from [8])

Figure 4.2. TEM images of Cu$_2$S nanocrystal assemblies: (a) fcc packed circular nanocrystals; (b) hcp packed circular nanocrystals; (c) two layers of close-packed elongated nanocrystals; (d) multilayers of elongated nanocrystals. The top insets are the corresponding FFT patterns, and the bottom insets are the schemes of the stacking of nanocrystals. (Reproduced from [8])

convenient capping reagents or ligands for colloidal nanocrystals and nanowires[9]. The MCC capping agents act as electronically transparent “glue” for nanocrystals. With various special properties, inorganic ligands may open an innovative way to device-level manipulation of MCC-nanocrystals and benefit many nanocrystal-related
potential applications. Furthermore, they may also influence the self-assembly ability and morphology of nanocrystals as organic ligands do. Inspired by this discovery, Li and coworkers prepared columnar self-assembled Cu$_2$S hexagonal nanoplates induced by a Sn-X complex for the first time and demonstrated that the Sn-X complex can affect not only the morphology of the nanocrystals (as traditional organic ligands do) but also the self-assembly ability of the nanocrystals.[10] Figure 4.4A shows upright and tilted hexagonal nanoplates as marked by blue and red rectangles, respectively. It clearly reveals that the 1D superstructures of Cu$_2$S nanocrystals are composed of hexagonal nanoplates stacking face-to-face. Upon adjusting the experimental parameters, the as-synthesized Cu$_2$S hexagonal nanoplates can self-assembled into large-scale 1D and 3D columns as shown in Figure 4.5.

**Figure 4.3.** Schemes of the stacking of Cu$_2$S nanocrystals: (a) circular nanocrystal as building blocks; (b) elongated nanocrystal as building blocks. (Reproduced from [8])

**Figure 4.4.** (A) TEM images of typical Cu$_2$S nanoplates with columnar self-assembly. Blue and red rectangles indicate the upright and tilted hexagonal nanoplates, respectively. (B, C) High-magnification TEM images and (D, E) illustration of the upright and tilted hexagonal nanoplates. (Reproduced from [10])
Further experiments revealed that the size of the 1D-superstructured hexagonal Cu$_2$S nanoplates could be tuned simply by changing the reaction time. Although the particle size grew larger with prolonged reaction time, the distance between two adjacent face-to-face stacked nanoplates was kept constant (~1.0 nm). This value was much smaller than that of DDT-capped circular Cu$_2$S nanospheres, whose average spacing was ~2 nm which consistent with the theoretical values (1.9 nm $< d < 3.8$ nm)[11]. In comparison with the interparticle spacing of DDT-capped circular Cu$_2$S nanospheres, the ligands capping the hexagonal nanoplates should be shorter ligands related to the Sn-X complex which was confirmed by FTIR, XPS, and UV-vis spectra. The electric transport properties of Cu$_2$S nanocrystals with and without the participation of Sn-X complex were also studied. The as-synthesized DDT-capped nanocrystals showed low conductivity as a result of the large interparticle spacing connected by insulating DDT molecules. The conductivity of the self-assembled nanoplates, however, was improved nearly 1 order of magnitude because of the short interparticle spacing (~1.0 nm) linked by the Sn-X complex. This reported methodology of constructing self-assembled nanostructures may turn over a new leaf in device-level manipulation of nanocrystals and many nanocrystal-related potential applications.

From the applicative perspective, Cu$_2$S has been used in solar cells[12], cold
cathodes[13] and nanoscale switches[14], etc. For example, Lee and coworkers have grown single-crystalline hexagonal-phase Cu$_2$S nanocrystals (NCs) \textit{in situ} on acid-functionalized MWCNTs by solvothermal method.[15] The photovoltaic device fabricated from the blends of Cu$_2$S-MWCNTs (multi-wall carbon nanotubes) and P3OT responds sensitively to solar light. The maximum power conversion efficiency was found to be $\eta = 0.08\%$. Specifically, efficient electron transport from the

![Figure 4.6. TEM and HRTEM images of the Cu2S-MWCNT. (a) Triangularly shaped Cu2S NCs are grown on the MWCNTs. (b) One face of the triangular NC is bound to the wall of the MWCNTs. The inset corresponds to the FFT ED pattern. (c) A detached triangular NC from the MWCNTs shows flat side edges with a thickness of 2 nm. Its corresponding FFT ED pattern is shown in the inset. (d) A schematic diagram showing the crystal structure of the triangular nanoplates attached to the MWCNTs. (Reproduced from [15])](image)

photo-excited Cu$_2$S NCs to the MWCNTs would enhance their photocurrents. Figure 4.6a shows the Cu$_2$S-MWCNT hybrid nanostructures. It can be seen that triangularly shaped Cu$_2$S NCs grew on the MWCNTs. One face of these triangular Cu$_2$S NCs is usually bound to the wall of the MWCNTs.

Figure 4.7a shows incident photon-to-current conversion efficiencies (IPCE) of the P3OT and Cu$_2$S-MWCNT/P3OT devices. The active layers contain 10 wt % Cu$_2$S-MWCNT in the polymer blends. The presence of Cu$_2$S-MWCNT nanostructures results in an enhancement of the IPCE over the whole wavelength range of 400-800
nm. The UV-vis absorption spectrum of the composites was also measured to show the enhancement of absorbance due to the Cu$_2$S NCs. The power conversion efficiency (0.08%) is higher than that of SWCNTs/P3OT photovoltaic devices (0.04%), so these hybrid nanostructures are potentially useful in optoelectronic applications.

Figure 4.7. (a) IPCE of the solar cell devices using P3OT and Cu$_2$S-MWCNT/P3OT as active layers. (b) Current density (mA/cm$^2$) vs applied voltage ($V$) for the ITO/PEDOT/PSS/Cu$_2$S-MWCNT/P3OT/Al solar cell operated under AM 1.5 illumination, with a solar power conversion efficiency of 0.08%. (c) Energy diagram of the valence- and conduction-band levels showing the charge-transfer junction formed in this solar cell device. (Reproduced from [15])

In another example, Chen and coworkers have fabricated a bilayer cell Cu/Cu$_2$S/Cu-Pc/Pt, the structure is shown in Figure 4.8a and a controlled device (single layer) is shown in Figure 4.8b.[16] Figure 4.9 shows the typical $I$-$V$ characteristics of the Cu/Cu$_2$S/Cu-Pc/Pt structure. When the voltage sweeps between 3 and -3 V, the devices are switched on. The threshold voltage is 0.85 V and the devices preserve this on state until a reverse voltage is applied to switch the devices to its off state. The resistance ratio of the off/on states is about $10^7$. Although, the devices of the single layer Cu-Pc film also exhibit a switching behavior with a lower on/off states ($10^3$-$10^4$), the threshold voltage is higher than that of the bilayer structure device with the same cell size.

Cu electrode acts as a source of Cu$^+$, which migrates in copper sulfide film in the form of an ionic stream. When a positive voltage larger than the threshold one is
Figure 4.8. Schematic view cross section of the memory devices: (a) Cu/Cu$_2$S/Cu-Pc/Pt and (b) Cu/Cu-Pc/Pt. (reproduced from [16])

Figure 4.9. Current-voltage characteristics of the Cu/Cu$_2$S/Cu-Pc/Pt devices. Voltage sweep is 0-3 V. The switch voltage is about 0.85 V. (reproduced from [16])

applied, Cu atoms in the top Cu electrode will be dissolved into Cu$_2$S films by electro-chemical reaction, just like the anode of a plating bath. At the same time, the Cu ions in the Cu$_2$S film will drift into the organic layer and further toward the Pt cathode under the direct current electric filed. When Cu ions get electrons from cathode district or trapped in the two layers, they will congregate and form some metallic nanoparticles or filaments, distributed randomly in the two layers. The applied positive voltage is suggested to be responsible for the formation of metallic nanostructure in the solid electrolyte. The $I$-$V$ characteristic in the on state of the bilayer devices show the same metallic conductivity, as observed in other inorganic memory cells[17]. With the formation and connection of the metallic filaments in the bilayer system, the two electrodes can be connected with some of these metallic filaments. When the negative voltage is applied to the devices, the Cu atoms of the metallic filaments will be ionized and diffused back to the bilayer matrix. Once the filaments are broken, the device will be switched to the off state. In the single layer device, Cu electrode, directly contacts with Cu-Pc films, cannot offer enough
quantities of metallic ions to form filaments to bridge the two electrodes.

As have been discussed above, the synthesis and electronic applications of the Cu$_2$S nanoparticles have been extensively studied. However, its nonlinear optical limiting (NLO) properties remain largely unexplored. In this chapter, we devised a novel method to deposit Cu$_2$S nanoparticles onto the G and GO sheets. Figure 4.10 schematically shows the reaction mechanism of the design.

![Figure 4.10. Simplified illustration of the reaction system.](image)

This design was based on some reported findings. Recently, our group have found a new way to synthesize few-layer G flakes through electrochemical expansion of graphite in propylene carbonate electrolyte in a high-yield fashion[18]. We demonstrate a solution route inspired by the lithium rechargeable battery for the high-yield (>70%) exfoliation of graphite into highly conductive few-layer G flakes (average thickness <5 layers). A negative graphite electrode can be electrochemically charged and expanded in an electrolyte of Li salts and organic solvents under high current density and exfoliated efficiently into few-layer G sheets with the aid of sonication. As illustrated in Figure 4.11, graphite was used as the negative electrode in an electrochemical cell. Unlike the low-voltage (<1 V) and low-current electrochemical charging conditions typically used in graphite intercalation compounds (GICs), here we applied a high potential (-15±5 V) in order to activate Li/PC co-intercalation in graphite. The expanded graphite was sonicated in concentrated LiCl dissolved in propylene carbonate (PC) and DMF using high-intensity ultrasound. Ultrasonic cavitation injects thermal shock and results in both exfoliation and cutting of the G sheets. Removal of the intercalated Li$^+$/PC was
achieved by washing with acid and water. Figure 4.12 (left) shows the typical SEM images of the G sheets. On the basis of statistical sampling of the G flakes using AFM (Figure 4.12 middle), it was estimated that 50% of the G sheets comprised 2-3 layers of G (see the size histogram in Figure 4.12 right).

**Figure 4.11.** Exfoliation of graphite into few-layer G flakes via intercalation of Li\(^+\) complexes. (Reproduced from [18])

Kim and coworkers have demonstrated that GO is an amphiphile with hydrophilic edges and a more hydrophobic basal plane.[19] Despite its excellent dispersibility in water, GO is an amphiphile that can be adsorbed onto interfaces and lower surface and interfacial tension. Its amphiphilicity can be tuned by changing pH as it shuttles between water and the oil-water interface. GO is essentially a single atomic sheet, while its lateral dimension extends to the size of colloidal particles, which renders it a unique material exhibiting molecule-colloid duality. It creates highly stable emulsions

**Figure 4.12.** (left) Low magnification SEM image; (middle) AFM image of G spin-coated onto a Si substrate. The thickness was ~1.5 nm, corresponding to a bilayer; (right) Thickness and size distribution histograms of the G produced, as estimated from AFM analysis of the G flakes. (Reproduced from [18])
of organic solvents like molecular surfactants. After we successfully prepared relatively pristine G using electrochemical method, we also observed that the G sheets would segregate to the interface of the organic solvent and water after we mixed the water and organic solvent which contained G together.

In our design, Cu$_2$S nanoparticles were synthesized at the interface between the organic solvent dodecanethiol (DDT) and water; G sheets were also introduced at the interface at the same time. Thus, there is a high chance that the nanoparticles will deposit onto the G sheets using the air-water interface as a template for interfacial binding. In comparison, we also employed GO to replace G, hoping to achieve the deposition of Cu$_2$S on GO sheets.

4.2 Experimental

4.2.1 Synthesis of G and Spherical Cu$_2$S Nanoparticles Hybrid Material

CuSO$_4$ • 5H$_2$O (250 mg) was dissolved in H$_2$O (20 mL), followed by the addition of sodium acetate (82 mg) and acetic acid (0.60 mL). Next the solution was sonicated to mix well. Graphene (3 mg) was dispersed in DDT (10 mL) by sonication. 5 mL of the as-prepared CuSO$_4$ solution was added into an autoclave, followed by slow addition of 10 mL of the G solution. The autoclave was sealed and put in an oven and was heated at 200 °C for 6 hours. At the end, the autoclave was cooled to room temperature, the water in the product solution was discarded and excess ethanol was added. Next the solution was centrifuged at 6000 rpm for 5 min and the supernatant was discarded. The precipitate was redispersed in 10 mL of CHCl$_3$. A small amount of ethanol was added into the CHCl$_3$ solution and solution was centrifuged at a low speed (about 1000 rpm) for 5 min and the precipitate was collected. This process was repeated several times until the supernatant was colorless and the final precipitate was collected for characterization.
4.2.2 Synthesis of GO and Spherical \( \text{Cu}_2\text{S} \) Nanoparticles Hybrid Material

\( \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \) (250 mg) and 8 mL of GO solution (1.5 mg/mL) were dissolved in \( \text{H}_2\text{O} \) (12 mL) in a flask, followed by addition of sodium acetate (82 mg) and acetic acid (0.60 mL). The solution was sonicated to mix well. 5 mL of the as-prepared \( \text{CuSO}_4 \) solution was added into an autoclave, followed by slow addition of 10 mL of DDT. The autoclave was sealed and put in an oven and was heated at 200 °C for 6 hours. After the autoclave was cooled to room temperature, the water in the product solution was discarded and excess ethanol was added. Next the solution was centrifuged at 6000 rpm for 5 min and the supernatant was discarded. The precipitate was redispersed in 10 mL of \( \text{CHCl}_3 \). A small amount of ethanol was added into the \( \text{CHCl}_3 \) solution and solution was centrifuged at a low speed (about 1000 rpm) for 5 min and the precipitate was collected. This process was repeated several times until the supernatant was colorless and the final precipitate was collected for characterization.

4.2.3 Synthesis of Pure Spherical \( \text{Cu}_2\text{S} \) Nanoparticles

The pure spherical \( \text{Cu}_2\text{S} \) nanoparticles was synthesized as above, with no G added. The separation of spherical \( \text{Cu}_2\text{S} \) nanoparticles was done by adding excess ethanol followed by centrifugation. Next the precipitate was dispersed in \( \text{CHCl}_3 \) as the final product.

4.2.4 Synthesis of Tin (IV) Bis(acetylacetonate) Bichloride [\( \text{Sn(acac)}_2\text{Cl}_2 \)]

20 mmol \( \text{SnCl}_4 \) was dissolved in 10 mL deionized water. Under magnetic stirring, 2,4-pentanedione (5 mL, 50 mmol) was added and kept stirring for 15 minutes. \( \text{Sn(acac)}_2\text{Cl}_2 \) was precipitated after appropriate amount of triethylamine was added in the solution. Next precipitate was filtered and washed several times by ethanol and water. \( \text{Sn(acac)}_2\text{Cl}_2 \) was dried in vacuum at 50 °C for further use.
4.2.5 Synthesis of G and Hexagonal Cu$_2$S Nanoparticles Hybrid Material

CuSO$_4$ \cdot 5$H$$_2$O (250 mg) was dissolved in $H$$_2$O (20 mL) in a flask, followed by addition of sodium acetate (82 mg) and acetic acid (0.60 mL). Next the solution was sonicated to mix well. Graphene (3 mg) was dispersed in DDT (10 mL) by sonication followed by addition of Su(acac)$_2$Cl$_2$ (38.8 mg). 5 mL of the as-prepared CuSO$_4$ solution was added into an autoclave, followed by slow addition of 10 mL of the G solution. The autoclave was sealed and put in an oven and was heated at 200 °C for 6 hours. After the autoclave was cooled to room temperature, the water in the product solution was discarded and excess ethanol was added. Next the solution was centrifuged at 6000 rpm for 5 min and the supernatant was discarded. The precipitate was redispersed in 10 mL of CHCl$_3$. A small amount of ethanol was added into the CHCl$_3$ solution and solution was centrifuged at a low speed (about 1000 rpm) for 5 min and the precipitate was collected. This process was repeated several times until the supernatant was colorless and the final precipitate was collected.

4.3 Results and Discussions

4.3.1 Graphene and spherical Cu$_2$S nanoparticles hybrid

![Figure 4.13. UV-vis absorption spectra of G and spherical Cu$_2$S nanoparticles hybrid material and individual components.](image)
The G and Cu\textsubscript{2}S nanoparticles hybrid material and individual components were characterized by UV-Visible (UV-vis) spectroscopy. Figure 4.13 shows the UV-vis spectra of the hybrid material as well as individual components. As we can see, the pure Cu\textsubscript{2}S nanoparticles have an absorption peak at about 375 nm, while G has broad and flat absorption in a wide range. In the hybrid, the absorption peak of Cu\textsubscript{2}S is present, while in the long wavelength area, the broad and flat absorption is also present. Therefore, it is evident that the coupling of G and Cu\textsubscript{2}S nanoparticles is successful.

To provide visual evidence of the deposition of the spherical Cu\textsubscript{2}S nanoparticles onto the G sheets, SEM and TEM were utilized. Figure 4.14 shows the typical SEM images of the hybrid. The as-prepared hybrid was drop-cast onto the aluminum foil. As can be seen, the G sheets are almost fully covered with spherical Cu\textsubscript{2}S nanoparticles and with few free-standing Cu\textsubscript{2}S nanoparticles can be found outside the G sheets. In addition, the size of the nanoparticles is very uniform.

![Figure 4.14. Typical SEM images of the G and spherical Cu\textsubscript{2}S nanoparticles.](image)

Figure 4.15(left and middle) shows the typical TEM images of the as-prepared G and spherical Cu\textsubscript{2}S nanoparticles hybrid. Once again, these images prove that the G sheets are almost fully covered by the nanoparticles. From these images, we determined the coverage of the Cu\textsubscript{2}S nanoparticles on the G sheets is around 90%. Figure 4.15(right) shows the size distribution of the Cu\textsubscript{2}S nanoparticles. The average size of the
Figure 4.15. (left and right) Typical TEM images of the as-prepared G and spherical Cu$_2$S nanoparticles; (right) size distribution of the Cu$_2$S nanoparticles.

nanoparticles is around 50 nm which is much larger than its Bohr Radius (about 10 nm).

Cu$_2$S spherical nanoparticles are easy to self-assemble together and form superlattice structure under specific conditions as mentioned previously. But to our disappointment, we did not observe any superlattice structures on the G sheets in this case.

4.3.2 Application

Figure 4.16. Fluence-dependent transmittance of the hybrid and individual components at 532 nm(left) and 1064 nm(right) in chloroform.

The NLO properties of the G and spherical Cu$_2$S hybrid material at 532 nm was investigated using CNT as the reference. The NLO properties of CNT have been
studied extensively because of its excellent NLO responses, so it is generally taken as a benchmark in research of the NLO effect[20]. Figure 4.16(left) shows the OL properties of the hybrid in chloroform at 532 nm at the linear transparency of 70%. Compared to individual components, the hybrid has enhanced performance. As the light fluence increases, the transmittance of the hybrid decreases significantly. From this figure, the limiting threshold which is defined as the input fluence at which the transmittance falls to 50% of the linear transmittance, can be determined. The threshold of the hybrid is about 2.11 J/cm$^2$ which is lower than that of the CNT which is about 3.65 J/cm$^2$. That means the limiting effect of the as-synthesized hybrid is better than that of CNT. When the incident fluence is increased to 15 J/cm$^2$, the transmittance drops to 19% of the normalized transmittance.

![Figure 4.16](image-url)

**Figure 4.16.** (left) Optical limiting properties of the hybrid in chloroform using 532 nm laser source. (right) Scattering results of the hybrid at an angle of 20°.

We also investigated the NLO properties in o-dichlorobenzene (ODCB) as shown in Figure 4.17 (left). The hybrid in chloroform was prepared by centrifugation at 5000 rpm for 10 min, and the supernatant was discarded, followed by addition of ODCB. As can be seen, the normalized transmittance drops down to 67% at the focal point. Therefore, this hybrid exhibits NLO properties regardless of the medium. By comparing the limiting threshold alone, we found that the NLO performance is comparable to carbon analogues, for example graphene-TPP, rGO, and even CNT as shown in Table 4.1.

Scattering, multiphoton absorption and energy/charge transfer are known to be the
three main factors which contribute to the NLO properties. To elucidate the mechanism of the NLO enhancement of this hybrid, we measured the scattering effect of the samples at 532 nm. Figure 4.18 shows the fluence-dependent scattering results of the hybrid and individual components at 532 nm. As can be seen, it can be concluded that scattering plays a role in the NLO properties at 532 nm. Generally, in the two components system, the effect of charge/energy transfer cannot be excluded in the NLO effect. Williams and coworkers have demonstrated that the electron transfer from excited ZnO nanoparticles to GO is effective in carrying out reduction and decreasing the resistivity of chemically functionalized graphene films as shown in Figure 4.19. On the basis of the luminescence decay measurements, they estimated the apparent electron-transfer rate constant to be $1.2 \times 10^9 \text{ s}^{-1}$. Therefore, the properties of the graphene sheets like conductivity, catalytic and photocatalytic activities can be finely tuned in this way. Although we did not carry out charge or energy transfer study in detail, we believe the enhanced NLO properties arise from a combination of nonlinear scattering and energy/charge transfer.

![Figure 4.18](image)

**Figure 4.18.** Fluence-dependent scattering of the hybrid and individual components at 532 nm.

As seen from Figure 4.13, the hybrid has strong absorption at 532 nm which is due to the presence of the Cu$_2$S nanoparticles. Therefore, the Cu$_2$S nanoparticles absorb the incident light and transfer the energy to the graphene sheets which lead to the NLO properties. In order to verify it, we also measured the NLO properties at 1064 nm. Figure 4.16 (right) shows the NLO properties of the hybrid at 1064 nm. As can be seen, the hybrid only shows trivial NLO properties. That is because the nanoparticles
have virtually no absorption at 1064 nm. Therefore, there is no charge transfer between the nanoparticles and the G sheets which results in little NLO performance. As discussed above, in this G and Cu$_2$S nanoparticles hybrid system, energy/charge transfer and scattering are the major factors which contribute to the NLO properties.

### Table 4.1. Comparison of our results with reported results.

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<th>Reference</th>
<th>Sample</th>
<th>Wavelength</th>
<th>Pulse Width</th>
<th>Focal length</th>
<th>Beam Waist $w_0$</th>
<th>Solvent</th>
<th>Linear Trans. $T_0$</th>
<th>Path Length $L$</th>
<th>Limiting Threshold $F_{th}$ ($\text{W/cm}^2$)</th>
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<td>30 cm</td>
<td>DI Water</td>
<td>70%</td>
<td>5 mm</td>
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<td>1.4</td>
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Our Sample

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<th>Pulse Width</th>
<th>Focal length</th>
<th>Beam Waist $w_0$</th>
<th>Solvent</th>
<th>Linear Trans. $T_0$</th>
<th>Path Length $L$</th>
<th>Limiting Threshold $F_{th}$ ($\text{W/cm}^2$)</th>
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<td>70%</td>
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**Figure 4.19.** Excited-state interaction between ZnO and Graphene Oxide. (Reproduced from [21])
4.4 Other Hybrid Systems

4.4.1 Reduced Graphene Oxide and Cu₂S Nanoparticles Hybrid

For comparison, we also successfully deposit Cu₂S nanoparticles onto the reduced GO (rGO) sheets. The experimental setup is similar to that of using G except that GO is dissolved in the water phase. Similar to the case before, GO will go to the interface between DDT and water in order to lower the surface and interfacial tension. During the reaction process, due to the high temperature (200 °C) and the existence of DDT which is a reducing reagent, GO is partially reduced. However, one problem of rGO is its poor solubility, because after reduction the conjugated structure of G is partially restored which drastically decreases its solubility. This present a problem when we want to test its applications which require good dispersibility in some organic solvents. Therefore, in this part, we will only demonstrate that Cu₂S nanoparticles can be deposited onto the rGO sheets.

Figure 4.20 shows the typical SEM images of the as-synthesized rGO and Cu₂S nanoparticles hybrid material. As can be seen from these images, the rGO sheets are almost 100% covered with Cu₂S nanoparticles. As compared to Figure 4.14, we can conclude that the coverage of rGO is higher than that of using G. This is because there are still many residual functional groups existing in the rGO structure, specifically oxygen atom-containing groups like hydroxyl (-OH) groups and carbonyl (=O) groups. These groups have strong interactions with Cu₂S nanoparticles due to the strong coordinating and electrostatic interactions between the copper atoms and oxygen atoms. Another significant advantage of using rGO is that the uniformity of the Cu₂S nanoparticles has been greatly improved comparing that of using G. However, we could not observe any superstructures on the rGO sheets and these Cu₂S nanoparticles are randomly decorated on the rGO sheets.
To observe this hybrid material with greater detail, TEM analysis of the material was carried out. Figure 4.21 shows some typical TEM images of the rGO and Cu$_2$S nanoparticles hybrid. For TEM results, we can only see those unstacked rGO sheets, because if the rGO sheets form aggregates, we could not observe the real structure of the hybrid material due to the poor transmission ability. So we only observed those thin areas which most likely are monolayer graphene. As we can see, the nanoparticles are spherical and the creases of the rGO can be clearly observed which is consistent with the property of rGO.

4.4.2 Hexagonal Cu$_2$S Nanoparticles

The capping reagent is crucial for the control of the morphology and self-assembling ability of the nanoparticles. Therefore, by employing specific capping reagents,
different shaped Cu$_2$S nanoparticles with superstructure can be synthesized.

Similar to the way that atoms bond to form molecules and crystalline structures, colloidal nanoparticles can be combined together to form larger assemblies. The properties of these structures are determined by the properties of individual nanoparticles and by their interactions. The insulating nature of organic ligands typically used in nanocrystal synthesis like DDT used in the previous synthesis results in very poor interparticle coupling. Various molecular metal chalcogenide complexes (eg. Sn$_2$S$_6^{4-}$) and charged organic molecules can serve as convenient capping reagents or ligands for colloidal nanoparticles and nanowires.

In order to demonstrate that hexagonal Cu$_2$S nanoparticles with superstructures can be prepared on G or rGO sheets, we utilized MCCs as the capping reagent. Specifically, we utilized Sn(acac)$_2$Cl$_2$ which under the reaction conditions can decompose into Sn$_2$S$_6^{4-}$. Figure 4.22 shows some typical TEM images of the as-synthesized Cu$_2$S and G hybrid material. We can clearly see numerous hexagonal Cu$_2$S nanoparticles on the G sheets. More importantly, two dimensional superstructures could be observed due to the overlayer stacking of the Cu$_2$S nanoparticles on itself.

We also prepared hexagonal Cu$_2$S nanoparticles on the rGO sheets. Figure 4.23 shows the typical SEM (left) and TEM (right) images of the as-prepared hexagonal Cu$_2$S nanoparticles on the rGO sheets. From the SEM image (Figure 4.23. left), we can see that the rGO sheets are also densely covered with Cu$_2$S nanoparticles. From the TEM image (Figure 4.23, right), we can clearly see the hexagonal morphology of the nanoparticles. The Cu$_2$S nanoplates either stack onto the rGO sheets or stack onto each other to form superstructure.

We can conclude that the use of MCCs can truly improve the self-assembling ability of the Cu$_2$S nanoparticles. In order to further know whether superstructures on the G sheets can be achieved or not, we utilize charged capping reagents.
4.4.3 Charge Capping Reagents

Over the last decade, self-assembled monolayers (SAMs) of thiols and disulfides on
gold [22] and to a lesser degree on Ag [23], Cu[24], etc. have emerged as one of the most important classes of surface coatings. Long-chain alkanethiols adsorb onto the surface of nanoparticles and form densely-packed, well-ordered monolayer films. The synthesis of thin films using this method permits atomic-level control over the structure and composition of the exposed interface. In particular, alkyl thiols (as used in our previous experiment, dodecanethiol) and disulfides are widely used to prepare highly ordered monolayers whose properties can be adjusted by changing the chemical nature of the terminal groups [25]. SAMs of alkyl thiols and disulfides are used in modern micro- and nano-fabrication [26], in biomaterials and biological assays [27], in molecular electronics [28], in analytical [29] and sensory applications [30], and as molecular lubricants [31], protective coatings [32], or templates for crystal nucleation and growth [33].

As shown above, the use of DDT could not help with the formation of the 2-D superlattice of Cu$_2$S nanoparticles on the G and rGO sheets. In this section, we wanted to employ polarized or even charged alkyl thiols to see if it assists with the 2-D assembly of these nanoparticles on G or rGO better. We considered two promising candidates, as shown in Figure 4.24. Capping reagent S1 is a carboxylic acid which can ionize into a negatively charged species, while capping reagent S2 is a positively charged capping reagent. If the Cu$_2$S nanoparticles are capped by these capping reagents, the carboxylic acid groups or trimethylaminium groups are exposed at the outer surface because sulfur atom has much stronger interactions with copper atom. Due to the charged nature of these capping reagents which makes the as-prepared Cu$_2$S nanoparticles also charged. Therefore, there exists electrostatic repulsion between the Cu$_2$S nanoparticles. Thus we hope by employing these unique capping reagents, superlattice of the Cu$_2$S nanoparticles on G or rGO sheets can be realized.

S1 is commercially available, but for S2 we had to synthesize it. The synthetic route of S2 is shown in Figure 4.25. The synthesis of S2 starts from 11-bromo-1-undecene followed by the introduction of the positively charged moiety. The second step is a
radical reaction which introduces the sulfur group into the molecule. AIBN acts as the initiator and the formed radical react with thioacetic acid to form thioacetyl radical which later undergoes a radical addition reaction with 11-bromo-1-undecene. The last step is the de-protection of the acetyl group under the presence of excess HCl and reflux.

With these two charged capping reagents in hands, we proceeded to investigate their effect on the Cu$_2$S nanoparticles. Figure 4.26 shows the SEM images of the Cu$_2$S nanoparticles deposited on the rGO sheets with S1 as capping reagent. The rGO sheets are 100% fully covered with the Cu$_2$S nanoparticles. This is because there exist very strong interactions between Cu$_2$S nanoplates and the rGO sheets, for example, hydrogen bonds between the carboxylic group of S1 and the oxygen atoms in the rGO sheets. The Cu$_2$S nanoplates are hexagonal in shape. In addition, we can spot some superstructures on the rGO sheets.
Figure 4.26. Typical SEM images of the Cu$_2$S nanoparticles on rGO sheets with S1 as capping reagent.

Figure 4.27 shows the TEM images of the as-synthesized Cu$_2$S nanoplates with S2 as capping reagent on the rGO sheets. We could see some very interesting superstructures of the Cu$_2$S nanoplates on the rGO sheets. These nanoplates stand upright on the rGO sheets and self-assemble into superstructures in a face-to-face fashion. The interspace between two adjacent nanoplates is very interesting. However, we could also observe some nanoplates which stand on the rGO in a random way. Two limitations of this superstructure are that it cannot form long-range periodicity and the size distribution of the nanoplates is not uniform.

Figure 4.27. TEM images of the as-synthesized Cu$_2$S nanoparticles on rGO with S2 as capping reagent.

To our disappointment, we did not successfully deposit the Cu$_2$S nanoplates onto the G sheets with these two capping reagents. Presumably, it is because the nanoplates are
capping by the positively charged surfactant with a bulkier tail comparing to DDT. This bulky tail structure possesses detrimental effect on the deposition of the nanoplates onto the graphene sheets.

4.5 Summary

In summary, we have demonstrated a novel and efficient method to deposit Cu$_2$S nanoparticles onto G and rGO sheets which involves a two-phase hydrothermal reaction. The principle of the design is that the formation of the nanoparticles occurs at the interface between the organic phase and the water phase while the graphene sheets also exist at the interface. Therefore, there is a high chance that the Cu$_2$S can be successfully deposited onto the graphene sheets in despite of the weak interactions between the Cu$_2$S nanoparticles and the graphene sheets. To investigate if 2-D assembly of the nanoparticles on G could take place, we tried to self-assemble the Cu$_2$S nanoparticles onto the G sheets using four capping reagents with different characteristics. In most cases, we successfully deposited the Cu$_2$S nanoparticles onto the G or rGO sheets but only attained limited success with the self-assembly of 2-D superstructure on G.

4.6 References


Chapter 5

Conclusion

In this project, we demonstrated that graphene, as a two dimensional macromolecule, can be non-covalently functionalized by organic small molecules as well as inorganic nanoparticles to form graphene hybrids. The functionalization will tailor the electronic and electrochemical properties of graphene. Moreover, interesting properties could arise from this hybridization too.

In Chapter 2, we synthesized two pyrene ferrocene molecules and non-covalently functionalized graphene with them in which the pyrene ferrocene molecules acted as electrochemical and fluorescent probes for investigating the interactions between graphene and the organic molecules. The strong interactions between graphene and pyrene ferrocene molecules leads to an interesting change of the fluorescent and electrochemical properties of the molecules which can be easily characterized by fluorescence spectroscopy and cyclic voltammetry. Specifically, the addition of graphene to the solution of PyFc1 yields a remarkable enhancement of fluorescence emission by a factor of 47; while in the case of PyFc2, the fluorescence emission is diminished by a factor of 2.5. Moreover, the electrochemical properties of both molecules are strongly affected by graphene as well. The differences in electrochemical and fluorescent properties were correlated to the different binding modes of the molecules on graphene. In PyFc1, the pyrene moiety and the ferrocene moiety are not co-planar; therefore, the pyrene moiety can stack onto graphene while leaving the ferrocene moiety point away from graphene substrate. However, PyFc2 is a planar molecule. Both the pyrene moiety and the ferrocene moiety can stack onto graphene perfectly. Due to the $\pi-\pi$ interactions between graphene and the molecules, there is electron communication between them. The electron or energy transfer
between graphene and the molecules also gives rise to interesting non-linear optical limiting properties.

In Chapter 3, we synthesized the thiophene-acrylonitrile-carbazole oligomer (TACO) which exhibits aggregation-dependent dual emissions property due to the large band gap between its two excited states. Specifically, the anomalous S2 emission is dominating in dilute solution. In the aggregated state, however, the relative peak intensities of S2 compared to S1 are now reduced greatly. This trend is more pronounced for emission from the solid film. It was found that GO can induce the aggregation of TACO onto the GO sheets in THF/water mixture solvent which results in the emergence of a new fluorescent peak. Moreover, the GO and TACO blend exhibits remarkable nonlinear optical limiting performances in the femtosecond time scale. The femtosecond scattering centers and femtosecond charge transfer are thought to play the crucial roles in this nonlinear optical limiting observation.

In Chapter 4, we devised a novel and efficient method to deposit Cu$_2$S nanoparticles onto G and rGO sheets which involves a two-phase hydrothermal reaction. The principle of the design is that the formation of the nanoparticles occurs at the interface between the organic phase and the water phase while the graphene sheets also exist at the interface. Therefore, there is a high chance that the Cu$_2$S can be successfully deposited onto the graphene sheets in despite of the weak interactions between the Cu$_2$S nanoparticles and the graphene sheets. To investigate if 2-D assembly of the nanoparticles on G could take place, we tried to self-assemble the Cu$_2$S nanoparticles onto the G sheets using four capping reagents with different characteristics. In most cases, we successfully deposited the Cu$_2$S nanoparticles onto the G or rGO sheets but only attained limited success with the self-assembly of 2-D superstructure on G.

To sum up, we non-covalently functionalize G with organic molecules and inorganic nanoparticles. However, we failed to attain broad application with the as-synthesized graphene hybrids. Nevertheless, we comprehensively studied the electronic and
electrochemical properties of the hybrids; as a result, interesting observations arose. The significance of the work is that we set examples of how to deposit various types of materials onto G. Particularly, in the case of Cu$_2$S, we facilitate the deposition of Cu$_2$S nanoparticles onto G by employing a two-phase hydrothermal method. This two-phase method is of great potential, because Cu$_2$S can be easily replaced by other inorganic materials such as CuInS$_2$, Fe$_2$S, etc. By doing so, interesting properties like photovoltaic property may also arise. In the cases of conjugated organic molecules, due to the strong pi-pi interactions between G and organic molecules, it is relatively easy to tailor and characterize G’s properties. As there are literally unlimited numbers of conjugated organic molecules out there, it is highly likely that G’s properties can be tailored extensively by careful screening.

In prospect, my research has laid the foundation of future researches. Specifically, we can continue to screen conjugated organic molecules and investigate the properties of the G hybrids. Hopefully, we can obtain more interesting properties or more profound NLO properties. In addition, we can continue the functionalization of G with inorganic materials. Thus, interesting properties like photovoltaic and NLO properties could be achieved.

With so many remarkable properties, I believe that graphene hybrids will revolutionize the 21st century. But, prior to that, much more work still needs to be done.