

Fluorescence and Electroluminescence Quenching Evidence of Interfacial Charge Transfer in Poly (3-hexylthiophene): Graphene Oxide Bulk Heterojunction Photovoltaic Devices

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Current solar cell production is dominated by silicon (Si), which holds nearly 90% of the market. However, worldwide electricity production using Si solar cells is limited by the shortage of Si and by the high cost of their production. Low-cost, stable, and highly efficient solar cells are needed to provide a clean, renewable source of electricity worldwide. Several types of organic photovoltaics (OPVs) are under development to meet this challenge. The most common type, possessing a donor–acceptor heterojunction (HJ),^{1,2} achieves only limited efficiency because of the conflict between the need for a thick donor layer for maximum light absorption and the bottleneck of a short exciton diffusion distance.³ Low charge transfer mobility and poor stability of organic semiconductors under sunlight irradiation are additional factors limiting the overall performance of these devices. Most often, fullerene is used as the acceptor for conjugated polymer-based OPVs.⁴ Carbon nanotubes have been used as acceptors as well.⁵ Development of new electron acceptor materials for controlling the charge separation interface and decreasing the cost of OPVs is critical for further improving the efficiency and practical applications of OPV devices.

Graphene has been researched intensely over the past decade, with work focusing on its synthesis, electronic properties, and practical applications.^{6–9} Its charge carriers exhibit giant intrinsic mobilities, as high as $7 \times 10^4 \text{ cm}^2/\text{V}\cdot\text{s}$.¹⁰ It is also known to be a good electron acceptor. The bandgap of

ABSTRACT We present electrochemical studies of graphene oxide (GO) nanosheets and demonstrate the fluorescence and electrogenerated chemiluminescence quenching capability of GO nanosheets that are transferred into chloroform from aqueous solution utilizing a novel, surfactant-assisted method. Electrochemical studies indicate that GO can be reduced upon charge injection. Fluorescence quenching of the conjugate polymer poly (3-hexylthiophene) (P3HT) in both solution and solid films is demonstrated to show that GO can be used as an electron acceptor in a bulk heterojunction organic photovoltaic (OPV) device. OPV devices were then fabricated with an ITO/PEDOT:PSS/P3HT-GO/Al structure. Devices containing GO exhibited an increase in short-circuit current (I_{sc}) and conductivity but a decrease in open circuit potential (V_{oc}). These results display the potential for nonorganically functionalized GO to be used as an acceptor material in future OPV devices. The results also indicate that GO can increase the conductivity of the nanocomposite film so that charge recombination is an issue in such a device. The increased conductivity and fluorescence quenching are also supported by electrogenerated chemiluminescence (ECL) of P3HT/GO composite films.

KEYWORDS: graphene · graphene oxide · fluorescence quenching · organic photovoltaic · cyclic voltammetry · electrogenerated chemiluminescence

graphene can be manipulated by adsorbing different molecules on the surface and edges of graphene, as predicted by recent computational studies.^{11,12} Recently, chemical routes have been developed to obtain single sheets of graphene from graphene oxide (GO), which is the oxidized form of graphene with its surface and edges modified with hydroxyl, carboxyl, and epoxide groups.^{13,14} Such modification will affect the electronic structure of the graphene plane and could lead to an excellent electron acceptor for use in OPV devices. Organic solar cells utilizing reduced GO (r-GO) as a transparent anode have been explored recently,^{15–17} while little attention

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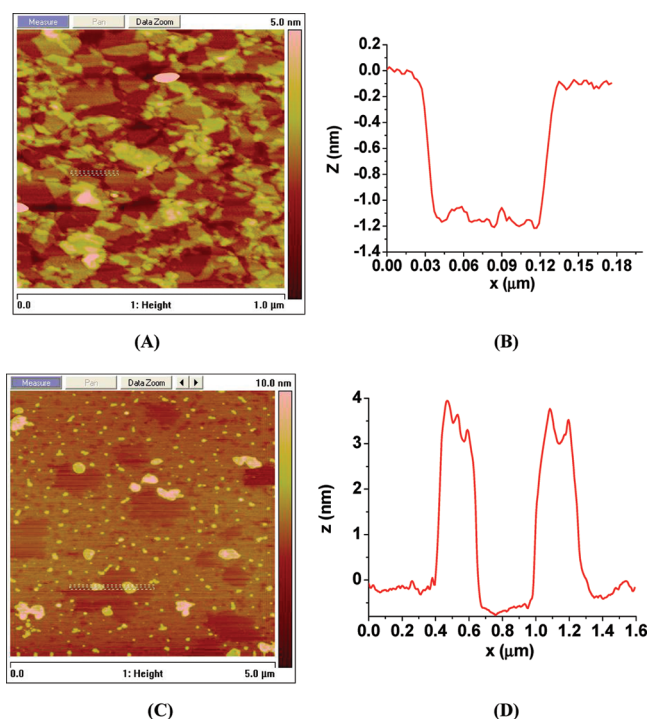


Figure 1. AFM images (A and C) and depth profiles (B and D) of GO nanosheets before (A and B) and after (C and D) being transferred to organic phase.

has been paid to utilizing GO nanosheets as an electron acceptor in OPVs.¹⁸ More recently, Chen and co-workers developed an OPV using GO as an electron acceptor.^{19,20} However, the electrochemical characteristics of GO and charge-transfer mechanism of these devices containing GO are not fully understood. Fluorescence quenching in conjugated polymers blended with r-GO has also been studied by Bardeen and co-workers.²¹ In this report, we present electrochemical studies of GO nanosheets that are transferred into chloroform from aqueous solution utilizing a novel, surfactant-assisted method and the application of GO nanosheets in a bulk-heterojunction (HJ) organic solar cell. Fluorescence and electrogenerated chemiluminescence (ECL) quenching in conjugated polymers blended with GO are studied in order to understand the photovoltaic performance of the poly (3-hexylthiophene) (P3HT)/GO photovoltaic system.

RESULTS AND DISCUSSION

Transfer of GO Sheets into Organic Solvent. To allow for easy construction of OPV devices by wet techniques, such as spin-coating, it is of course desirable to have the materials dissolved in a volatile, organic solvent. Previous work on OPV devices utilizing GO has made use of organically functionalized GO sheets, which are directly soluble in organic solvents.^{19,20,22} However, organic functionalization of GO could lead to undesirable effects on the electronic properties (such as highest occupied/lowest unoccupied molecular orbital levels) that make GO an effective electron acceptor.

An alternative method that has been reported involves the use of quaternary ammonium-based surfactants to transfer GO from an aqueous to organic solvent.²³ The drawbacks to this method are that it requires careful regulation of the pH of the aqueous solution and that the final concentration of GO in organic solvent is dependent on the initial concentration of the aqueous solution.

As an alternative, we employ a method that uses a surfactant, didodecyldimethylammonium bromide (DDAB), to isolate a solid GO product that can be readily dispersed in chloroform. Addition of DDAB, followed by mild sonication, causes the surfactant molecules to attach to the GO sheets *via* ionic interactions. Following centrifugation and drying, a solid product containing GO and DDAB can be isolated. It should be noted, however, that it is currently unknown to the authors as to the weight ratio of GO to DDAB in the final product.

AFM and Raman of Transferred GO Nanosheets. Figure 1 shows typical atomic force microscopy (AFM) images and depth profiles of the GO sheets before and after being transferred into chloroform. GO nanosheets from aqueous solution are found to be as thin as 1.2 nm and have an extended planar structure with sharp edges in comparison to the ones transferred into chloroform. This can be explained by the folding of GO nanosheets and aggregation during the process of phase transfer in the presence of DDAB. The Raman spectrum (Figure 2) of the transferred GO has two bands, G and D, respectively.^{24,25} The G band is attributed to the in-phase vibration of the graphite lattice at 1575 cm^{-1} . The D band refers to the

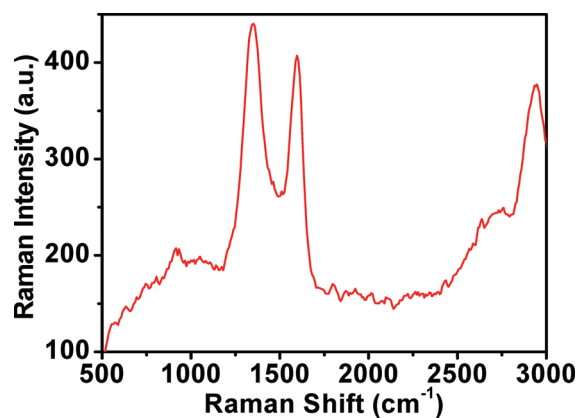


Figure 2. Typical Raman spectrum obtained from GO transferred into organic solvent.

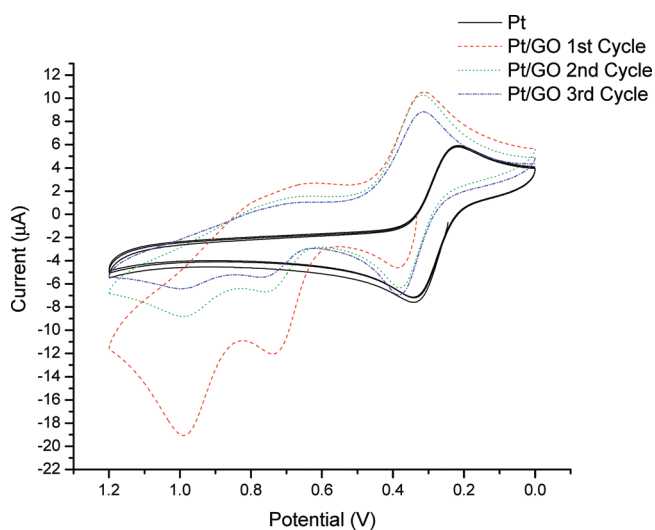


Figure 3. Consecutive anodization of a GO thin film on a Pt electrode in acetonitrile containing 0.1 M LiClO₄ as a supporting electrolyte. One mM ferrocene methanol is used as an internal standard. Counter and QRE electrodes were Pt and Ag wires, respectively.

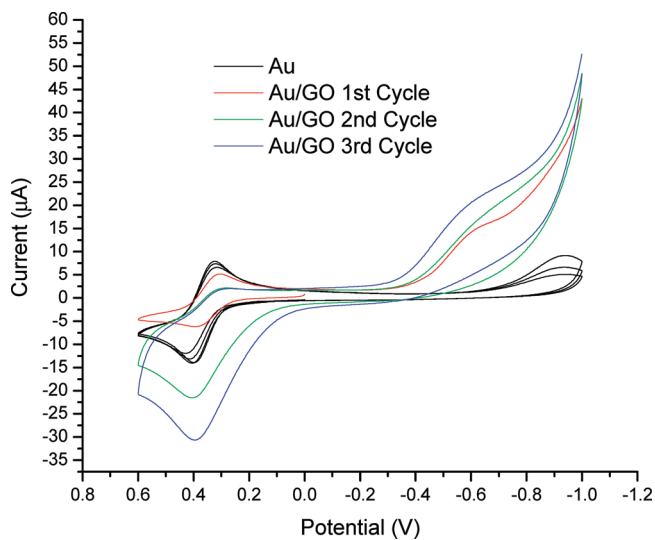


Figure 4. Consecutive reduction of a GO thin film on a Au electrode in acetonitrile containing 0.1 M LiClO₄ as a supporting electrolyte. One mM ferrocene methanol is used as an internal standard. Counter and QRE electrodes were Pt and Ag wires, respectively.

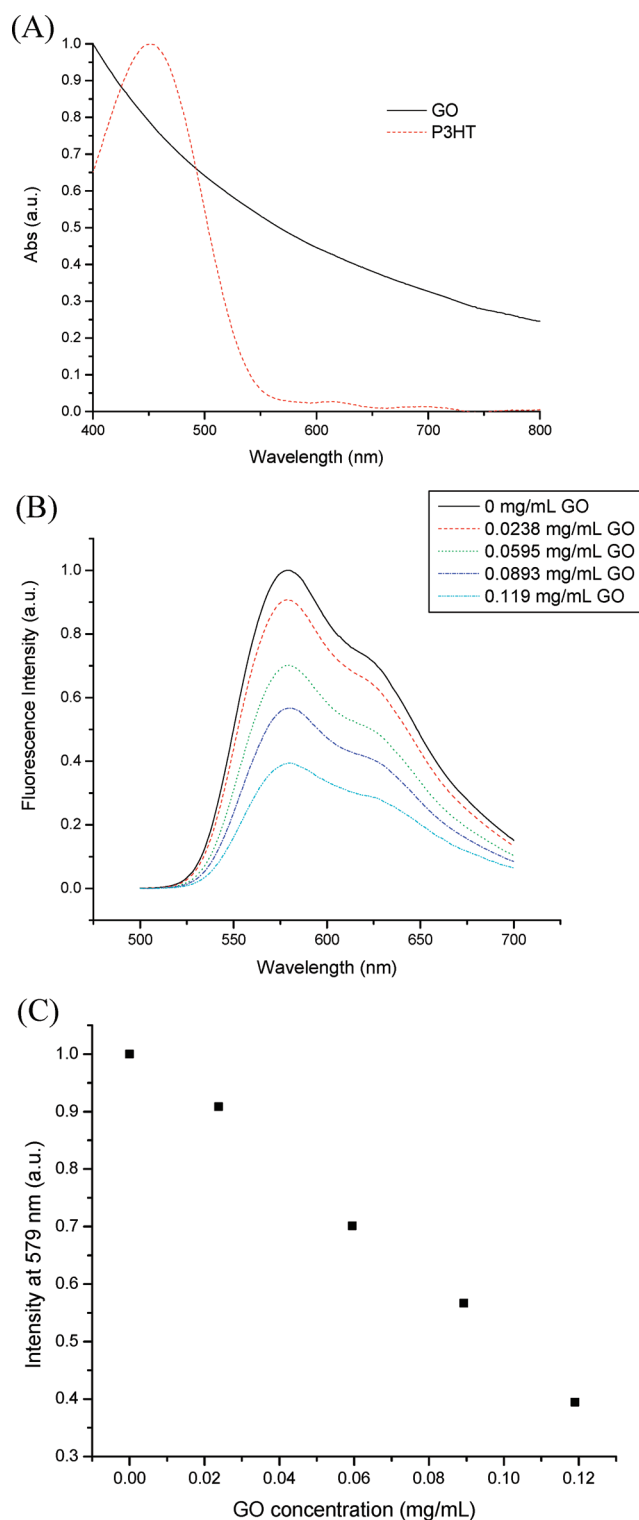


Figure 5. (A) Normalized absorbance spectra of P3HT and GO in CHCl₃. (B) Normalized PL of solutions of 0.0952 mg/mL P3HT in CHCl₃ with and without various concentrations of GO. Excitation wavelength: 450 nm. (C) Plot of fluorescence peak intensity versus GO concentration for the same samples as in Figure 1.

disorder band caused by the graphite edges at approximately 1355 cm^{-1} . The strong photoluminescence (PL) background is from the defects present on GO nano-sheets.^{26,27} The PL intensity from GO is found to be dramatically enhanced in chloroform due to the effect of solvent polarity.²⁸

Electrochemical Characterization of GO. The electrochemical properties of GO were investigated by cyclic voltammetry (CV). Films of GO, drop cast from CHCl₃ solution, were used in this study, using a Ag wire quasi-reference electrode (QRE) and ferrocene MeOH as an internal reference. As can be seen in Figure 3, the GO

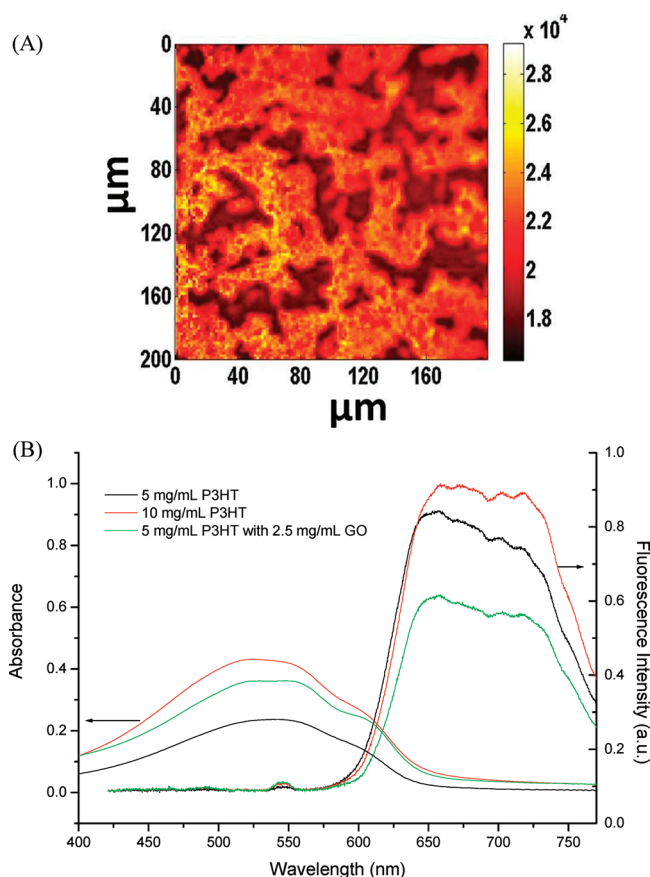


Figure 6. (A) Typical PL image of a spuncast P3HT/GO film. (B) Absorption and normalized PL spectra of thin films spuncast from solutions of 5 mg/mL P3HT, 10 mg/mL P3HT, and a mixture of 5 mg/mL P3HT and 2.5 mg/mL GO. Excitation wavelength: 532 nm.

films exhibited two oxidation peaks in their CVs, both appearing to be due to irreversible processes. Because of the observed stability of the ferrocene MeOH reference, these peaks could most likely be attributed to the oxidation of the surfactant used to stabilize the GO nanosheets. The anodic current decreases upon the complete oxidation of DDAB. The peaks attributed to ferrocene subsequently get more pronounced because of the decrease in the double-layer charging current caused by the surfactant. The CV's for the reduction of GO can be seen in Figure 4. Apparent here is an increase in the oxidative current of ferrocene after reduction of GO, along with an irreversible reduction peak of ferrocene. The irreversible behavior of ferrocene at electrochemically reduced GO film can be explained by the interrupted mass-transfer activities of ferrocene (Fc) in the porous GO electrode. Strong surface adsorption of ferrocene on the GO surface and desorption after oxidation may also cause such irreversible behavior. In addition, partial oxidation of r-GO in the positive potential range will cause the r-GO film to be less conductive, limiting Fc^+ reduction. The increase in oxidative current can be attributed to increased conductivity of the GO film after reduction, since the current also

increases for the GO reduction peak with each subsequent cycle.

Fluorescence Quenching of P3HT by GO. Fluorescence quenching experiments were performed on solutions and thin films containing P3HT and GO. Quenching of the PL of P3HT upon addition of GO provides evidence for charge transfer between P3HT molecules and GO sheets. Results from the liquid samples can be seen in Figure 5. It can be seen that upon addition of GO, the fluorescence of P3HT is reduced significantly. Also, a linear relationship is observed between the peak height and the GO concentration. This is consistent with the reduction in fluorescence intensity being due to quenching of the P3HT by GO and not to reabsorption or scattering effects.

Similar results can be seen for thin films of P3HT/GO in Figure 6. The fluorescence image of one of these films shown in Figure 6A displays localized fluorescence quenching in the vicinity of GO. Figure 6B shows the related absorption and PL spectra which illustrate these effects quantitatively. It should be noted that the films applied from a solution of 5 mg/mL P3HT and 2.5 mg GO had a higher absorption than those applied from a solution of only 5 mg/mL P3HT. This is due to the increase in the spin-coated film thickness due to the added mass of the GO. However, even with the increase in photon

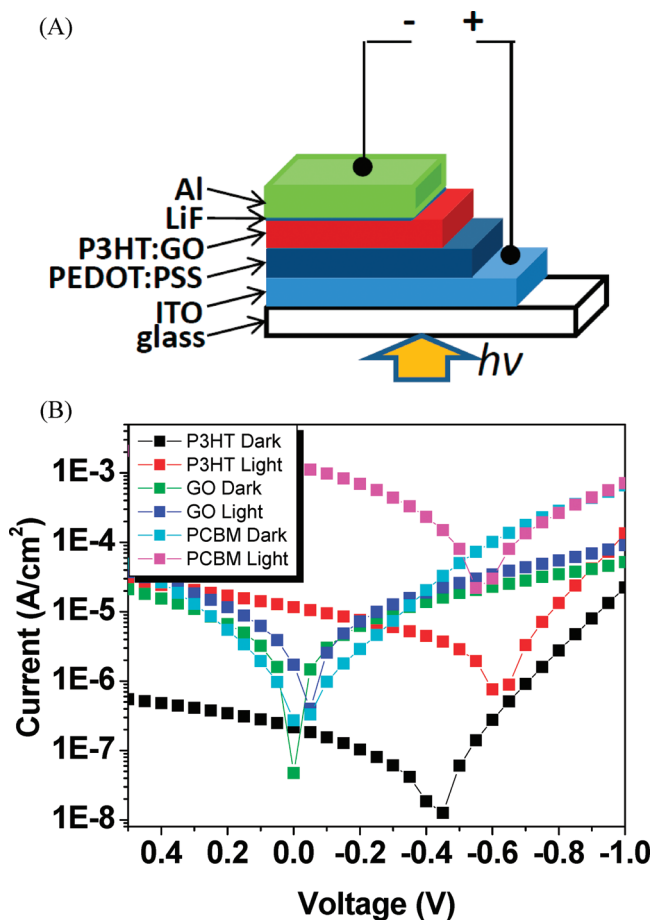


Figure 7. (A) Schematic of a typical OPV containing GO nanosheets. (B) Dark and light $I-V$ curves of an OPV device containing only P3HT, a device containing P3HT/GO, and a device containing P3HT/PCBM (spuncast from a solutions of 5 mg/mL P3HT, 5 mg/mL P3HT and 5 mg/mL GO, and 5 mg/mL P3HT and 5 mg/mL PCBM, respectively).

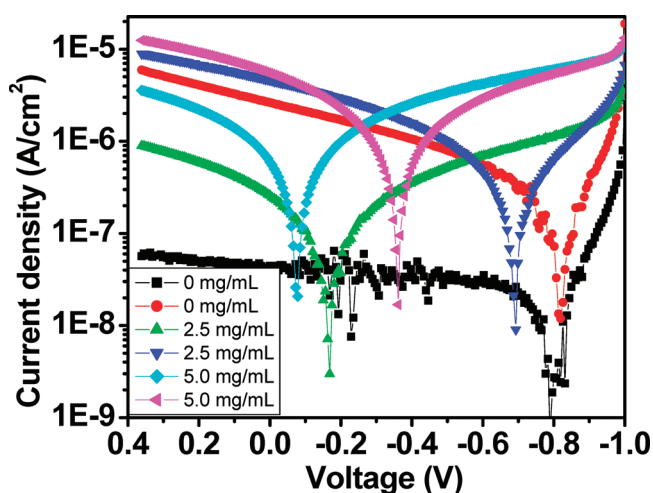


Figure 8. Photocurrent of OPV devices containing various amounts of GO (spuncast from a solution of 10 mg/mL P3HT and GO in the concentrations labeled).

absorption by P3HT, the P3HT/GO films exhibited a significant reduction in fluorescence intensity when compared to the films containing only P3HT. The fluorescence quenching can be explained by Förster resonance energy-transfer activities because GO absorbs light in a broad range from visible to NIR. Direct charge

transfer may be possible because some regions of the GO nanosheets are also electron-rich like graphene, as we will show in the following device characterization results.

Construction and Characterization of OPV Devices. The OPV devices (Figure 7A) used in this study were constructed

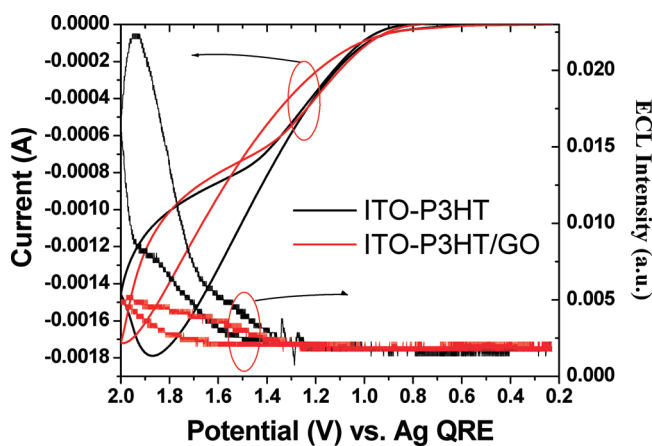


Figure 9. Current and ECL response of P3HT and P3HT-GO films in acetonitrile containing 0.1 M LiClO_4 and 0.1 M tripropylamine. Counter and QRE electrodes were Pt and Ag wires, respectively. Scan rate: 0.05 V/s; 300 V DC on PMT. Both samples were supported on ITO glass by spin coating.

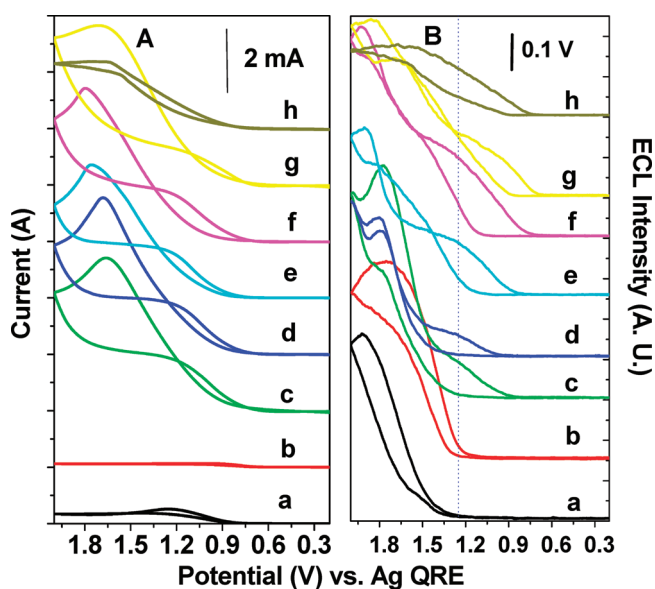


Figure 10. Current and ECL response of P3HT-GO films of varying concentrations in acetonitrile containing 0.1 M LiClO_4 and 0.1 M tripropylamine. (a) bare Pt electrode; (b) GO-coated Pt electrode; (c) P3HT-coated Pt electrode; (d) P3HT:GO (10:1) (w/w); (e) P3HT:GO (10:2); (f) P3HT:GO (10:3); (g) P3HT:GO (10:5); and (h) P3HT:GO (10:10). Counter and QRE electrodes were Pt and Ag wires, respectively. Scan rate: 0.1 V/s; 500 V DC on PMT. All samples were supported on ITO glass by spin coating.

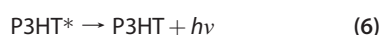
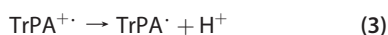
by common wet-techniques. A thin layer of PEDOT:PSS was first applied to thoroughly cleaned ITO glass. The active layer, which consists of the P3HT/GO mixture, was then applied by spincoating from a solution of both in CHCl_3 to create a bulk heterojunction between the donor and acceptor materials. LiF (~ 1 nm) and Al (~ 100 nm) layers were subsequently applied onto the active layer by thermal evaporation, completing the devices.

Devices were primarily characterized by measuring their current–voltage (I – V) curves under dark and illuminated conditions. Curves for a device consisting of only P3HT, P3HT and GO, and P3HT and PCBM can be seen in Figure 7B. The first notable difference between the three is the dark current. While there is a virtually negligible dark current in

the P3HT device, there is an appreciable dark current in those containing P3HT/GO and P3HT/PCBM. This suggests that the addition of GO and PCBM causes a significant increase in the conductivity of the film. The photocurrent density of P3HT/GO is found to be much less than P3HT/PCBM cell, and GO actually decreases both the short circuit current and open circuit voltage compared to PCBM. This indicates that GO is causing the excitons to recombine at a rapid rate even though it can quench the PL of P3HT. Some other effects, such as the interactions of excited states with the charged species (residual surfactant and counterions), may be the cause of the poor device performance. Figure 8 shows the dependence of the P3HT/GO cell characteristics on the amount of GO. Both dark current and photocurrent density increase with the amount of GO,

yet the device performance is not greatly improved by GO because of the poor charge collection and transport in the P3HT/GO device. The P3HT/GO device performance could be improved by removing the charged residues in the film and optimizing the GO particle size and doping level. The small dark current for the P3HT only device at 0 V in both Figures 7B and 8 is caused by stored charge at the electrode/polymer interface, which is initially introduced at the start of the voltage scan. This charge storage phenomenon can cause a distortion of the I - V curve, which can manifest in the form of an observed hysteresis effect.^{29–31}

In order to further confirm the enhancement of GO on conductivity and PL quenching, we also studied the ECL of the GO-P3HT nanocomposite film. ECL is a light-emitting process generated by electrochemical means and has been widely used in solid light-emitting devices, colorimetric biomolecular sensors, and clinical chemistry.^{32,33} ECL is important for quantitative and qualitative analysis as well as early stage diagnosis of diseases and device fabrication. The ECL of P3HT can be generated at a solid electrode through an oxidation–reduction mechanism in the presence of a co-reactant, here tripropylamine (TrPA), given by



where P3HT and TrPA are both oxidized to radical cations at a solid electrode (*e.g.*, Pt). Deprotonation of the TrPA radical cations forms TrPA radicals which annihilate with neutral P3HT molecules to form radical anions of P3HT. The reduced P3HT and oxidized P3HT will react with each other to form an excited state of P3HT, which undergoes radiative relaxation to produce

light. As shown in Figure 9, we observe enhanced current densities at the low potential range due to the presence of GO, while the ECL intensity is much lower than the one without GO. This result is consistent with our fluorescence quenching and photovoltaic characterization. Resonance energy transfer or charge transport are responsible for the fluorescence quenching. We also investigated the influence of the amount of GO doped in P3HT on the ECL, and the results are shown in Figure 10. Two controls (a and b) without P3HT show that ECL can be obtained even at a bare Pt electrode above 1.2 V with TrPA oxidation starting at 0.8 V. The sluggish kinetics do not decrease the intensity of the ECL observed with the GO electrode because of the higher surface area of the GO functionalized electrode. It cannot be concluded from the present literature what the light emitting species are for samples a and b in Figure 10B. They may actually be trace amounts of contaminants in the electrolyte solution or on the Pt electrode. In the presence of P3HT, we observed strong ECL even around 0.8 V. The decrease in the ECL turn on potential with increasing GO content is attributed to the improved local conductivity of P3HT film on the Pt surface in the presence of GO nanosheets. The decrease of ECL intensity at 1.8 V upon GO doping is due to the ECL quenching. This is because excited states of P3HT are readily quenched by GO through charge transfer or fluorescence resonance energy transfer. These results are consistent with our fluorescence quenching and photovoltaic device results.

CONCLUSIONS

We presented here systematic studies on the electrochemistry of GO phase-transferred from water into chloroform. Fluorescence energy transfer and ECL of P3HT:GO have been demonstrated. Photovoltaic device characterization also indicates that GO can facilitate charge recombination due to its relatively conductive characteristics. This suggests that an electron-blocking layer between ITO and P3HT and/or a hole-blocking layer is needed in order to increase the charge separation efficiency.

MATERIALS AND METHODS

Synthesis of Graphitic Oxide. GO was synthesized from graphite powder (Sigma Aldrich; 20 μm particle size). Preoxidation was performed by placing 20 g of graphite powder in an 80 °C solution containing P_2O_5 , $\text{K}_2\text{S}_2\text{O}_8$, and H_2SO_4 ; the resulting blue-gray solution was then allowed to cool to room temperature, and the solid was rinsed with enough DI water to bring the solid to a neutral pH.³⁴ After drying the preoxidized material for 24 h, it was further oxidized *via* the Hummer's method to produce GO.³⁵ The blue-gray powder was placed into a 0 °C H_2SO_4 bath. Slowly 15 g of KMnO_4 was added with

constant stirring. During addition of the KMnO_4 , the solution was not allowed to increase in temperature above 20 °C. The solution was left to stir at 35 °C for 2 h. Then 230 mL of DI H_2O was added, and the solution was stirred for another 30 min. The reaction was subsequently terminated with the addition of 700 mL of DI H_2O and 12.5 mL of 30% H_2O_2 solution. The resulting solution is a dark-yellow color. After rinsing with 2 L of a 10% HCl solution, the solid product was isolated by vacuum filtration and dissolved in DI H_2O at a concentration of 2%. This solution was then subjected to dialysis to remove undesired ions and to prevent aggregation of the final

graphene product. After dialysis, the solution is about 0.5%; this solution was diluted 20 times and subjected to ultrasonication for 30 min at 30% amplitude with a 400 V Branson digital sonifier. Larger particles were then separated by centrifugation at 3200 rpm for 1 h, discarding the precipitate.

Transfer of GO to Chloroform. Enough DDAB was added to a stock solution of GO in H₂O to yield a mass ratio of about 1:4 GO to DDAB, respectively. This solution was sonicated for 15 min to stimulate interaction between the GO sheets and the surfactant. The solution was then centrifuged at 10 000 rpm for 15 min. After pouring off the supernatant, the solid GO/surfactant product was dried in air in a 100 °C oven overnight. The solid was subsequently diluted to the desired concentration with CHCl₃ and sonicated overnight to disperse.

Preparation of Thin Films for Fluorescence Measurements. Solutions containing varying amounts of P₃HT and GO in CHCl₃ were spuncast onto clean cover glass slides (0.15 mm thick) at 2000 rpm for 20 s in air. A Nano-View 200-2/M nanopositioner (Mad City Laboratories, Madison, WI) was mounted to the top of an Olympus IX-71 inverted microscope for scanning the samples. The GO sample was excited using a 532 nm laser and imaged with a ×100 numerical aperture oil-immersion objective (NA = 1.3). The PL signal was then split, sending one part into a spectrometer with a liquid nitrogen cooled digital CCD spectroscopy system (Acton Spec-10:100B, Princeton Instruments, Trenton, NJ) through a monochromator (Acton SP-2558, Princeton Instruments, Trenton, NJ) for PL spectrum collection and the other to an avalanche photo diode (APD, SPEM-AQRH-15, PerkinElmer) for PL imaging. A PC 6602 card from National Instruments Inc. was used for data acquisition. Data collection and control of the photon counter and nanopositioner were done using Labview 8.5 (National Instruments, Inc.). To account for roughness and variation in the composition of the films, 100 spots on each sample were chosen at random, and the resulting spectra were averaged together. Absorbance spectra of solutions and films were obtained using a Varian Cary 50 UV–vis spectrophotometer. Fluorescence of liquid samples was taken using a Horiba Jobin Yvon FluoroMax-3 spectrofluorometer.

Fabrication of PV Devices. ITO glass slides were cleaned by sonicating for 10 min each in a detergent solution, acetone, and isopropanol. A layer of PEDOT:PSS was then applied by spin-casting (4000 rpm, 20 s) under a N₂ atmosphere. Samples were subsequently annealed at 200 °C for 1 h under N₂. The P₃HT/GO active layer was spuncast over the PEDOT:PSS layer (2000 rpm, 20 s), also under N₂. The LiF and Al layers were then applied by thermal evaporation. *I*–*V* curves and action spectra of the PV devices were obtained using a Keithley 2400 multimeter. A Newport 66902 Xenon Arc lamp through an Oriel AM 1.5 was used for illumination of the devices. Illumination intensity was 100 mW/cm².

ECL Measurements for P₃HT/GO Thin Film Electrode. A home-built electrochemical cell with its bottom opened to accommodate a transparent thin film electrode was used for the ECL measurements. Pt and Ag wire electrodes were used as counter and quasireference electrodes, respectively. A bipotentiostat CHI 760C (CH Instruments, Inc., Austin, TX) was used for ECL generation with its auxiliary signal channel input connected to a 1931-C high-performance low-power optical meter (Newport Corporation, Irvine, CA), through which the electroluminescence signal was detected by a photomultiplier tube (PMT) and amplified.

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