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Abstract. The present work demonstrates the synthesis of a hybrid accepter material containing amino-functionalized graphene oxide (GO) and an inorganic semiconducting material, cadmium selenide (CdSe). First, amino-functionalized graphene was synthesized and then nanocrystals (NCs) of CdSe were in situ grown in the functionalized-(GO) matrix named f-GCdSe. Structural studies such as x-ray diffraction, and a scanning electron microscopic were employed to investigate the growth of CdSe NCs in the graphene matrix. To understand the charge generation and transfer process at the donor/acceptor interface, the absorption, photoluminescence (PL), and transient absorption spectroscopic (TAS) studies have been carried out in poly(3-hexylthiophene) (P3HT)/f-GCdSe thin films. PL quenching in P3HT/f-GCdSe thin film suggests that charge transfer takes place at the donor/acceptor interface. TAS shows higher optical density and long lived free carriers for P3HT/f-GCdSe thin film. These results suggest that f-GCdSe is an excellent electron–acceptor material for organic photovoltaic devices. © 2015 Society of Photo-Optical Instrumentation Engineers (SPIE) [DOI: 10.1117/1.JNP.9.093048]

Keywords: graphene; cadmium selenide; nanostructure; acceptor; transient absorption spectroscopy; charge transfer.

Paper 15045 received Jun. 10, 2015; accepted for publication Sep. 11, 2015; published online Oct. 13, 2015.

1 Introduction

The past decade has witnessed a lot of advancement in the area of organic photovoltaic (OPV) technology by scientists and engineers. Recently, double digit power conversion efficiency has already been achieved by many groups.1–3 The main attractive aspect of OPV devices over traditional Si solar cells is their cost-effectiveness as they can be easily manufactured by roll-to-roll processes. In addition, OPV has a better performance in low light, can be transparent and colorful, and has greater flexibility and lower weight. However, the disadvantage of OPV is their low efficiency in comparison to traditional silicon solar cells. To make polymer-based solar cells an economically viable alternative, the efficiency of these devices needs to be increased. The limited efficiency of the OPV is due to the poor carrier mobility,4 short exciton diffusion length,5 charge trapping,6 and the mismatch of the absorption spectrum of the active layer and the solar emission.7 To address these fundamental limitations of polymer solar cells, inorganic NCs are blended with organic materials which integrate the benefits of both classes of materials. Various NCs including CdS,8 cadmium selenide (CdSe),9,10 CdTe,11 PbS,12 ZnO,13 and TiO2 14 have been widely studied for hybrid solar cell fabrication. However, the efficiency of organic/inorganic hybrid solar cells reported so far is still less than 5%, which is still far from the requirement for the next-generation solar cell for commercial applications. A major
challenge in developing high-performance organic/inorganic hybrid solar cells is the effective separation of photogenerated electron–hole pairs and the transfer of the electrons to the electrode.

Various strategies have been employed to enhance the separation of photogenerated electron–hole pairs in hybrid devices. One way to improve charge separation is to develop an organic/inorganic nanocomposite. It has been observed that C₆₀ played an effective role in the capture and transfer of photogenerated electrons in a CdSe-C₆₀ composite employed in quantum dot (QD) sensitized solar cells.¹⁵ Similar results have also been reported with CdS–CNT nanostructure as the light-harvesting assembly.¹⁶ Compared with C₆₀ and CNT, graphene, a monolayer of sp²-hybridized carbon atoms arranged in an archetypal two-dimensional (2-D) lattice, is more efficient for the application in OPV due to its supreme structural and electrical properties.¹⁷ The high surface area, superior room temperature electron mobility of the order of $2.5 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,¹⁸ and tunable bandgap make it an excellent electron acceptor in OPV devices.¹⁹ The high carrier mobility of graphene can facilitate electron transport to the photoanode, thereby decreasing the probability for carrier recombination and extending its lifetime.²⁰,²¹ The high surface area provides large donor/acceptor interface for charge separation. Moreover, it is well known that high loading of nanocrystals (NCs) is necessary for better charge transport in organic/inorganic hybrid solar cells. Consequently, excessive volume fraction increases the risk of aggregation. In functionalized-graphene (f-G), the functional groups can act as anchor sites for inorganic NCs and prevent their aggregation.²² Furthermore, modification of the graphene surface with QDs causes fluorescence quenching due to the electrons flowing from the conduction band of the QD to the graphene sheets.²³ Therefore, the hybrid nanostructures based on graphene can be considered as the potential acceptor material for organic solar cells.

Hence, it is of great interest and importance to bind CdSe NCs onto graphene because the combination and interaction between NCs and graphene will lead to multifunctional or even completely new properties in such a nanocomposite.²⁴,²⁵ Herein, we report the in situ synthesis of CdSe NCs in a functionalized graphene matrix, wherein the strategy of in situ growing CdTe NCs onto a P3HT matrix has been adopted.¹¹ The f-GCdSe nanocomposite shows a very fast and dramatically enhanced photoresponse, which makes it an excellent electron–acceptor material for OPV devices.

2 Synthesis of Functionalized-Graphene/Cadmium Selenide Nanocomposites

Prior to in-situ synthesis of CdSe NCs in functionalized graphene, an aqueous suspension of graphene oxide (GO) was synthesized from natural graphite powder using modified Hummer’s method.²⁶ In a typical process, 3.5 g graphite was charged into a 500 ml beaker and heated for 10 s in a microwave oven to expand the graphite powder. The powder was mixed with 500 ml concentrated H₂SO₄ at 0°C with continuous stirring. Then 21 g of KMnO₄ was slowly added and maintained below 20°C. The temperature was then increased to 35°C, and then 70°C for 2 h with continuous stirring. The flask was then chilled again in the ice bath, and distilled water (ice) was slowly added, maintaining the temperature below 70°C. The mixture was stirred for 1 h and subsequently diluted with 5 L of deionized water. A 50 ml of H₂O₂ (30 wt. %) was added, and vigorous bubbles appeared as the color of the suspension changed from dark brown to yellow. The suspension was centrifuged and washed several times with 10% HCl solution until the pH of the GO dispersion reached 6. The as-synthesized GO dispersion was a paste with a concentration of 1.0 wt. % GO. The calculated amount of GO was then treated with SOCl₂ in dimethylformamide followed by octadecylamine (ODA) at 150°C for 24 h to yield functionalized graphene. The in situ synthesized CdSe NCs in graphene were named as f-GCdSe and are schematically illustrated in Fig. 1. In a typical synthesis of f-GCdSe, 100 mg of functionalized graphene has been allowed to react with 0.1 mmol of cadmium acetate dihydrate at 150°C in the medium of ODA and the reaction temperature was increased to 300°C for 2 h. The selenium precursor was prepared by treating 0.2 mmol of selenium powder (Acros Organics) in trioctylphosphine (Sigma Aldrich), at 300°C for 30 min under nitrogen flow. The Se precursor was then injected into the functionalized graphene-Cd solution and the mixture was allowed to react for
30 min at 300°C under nitrogen flow. The growth of CdSe NCs is completed when the color of the solution turns to dark orange. After the completion of the reaction, the unreacted cadmium acetate and precursor of Se were removed by treating the nanocomposites with hexane. The reaction mixture was separated by centrifugation and dried in vacuum at 40°C. Similarly, another composition of functionalized graphene containing a different molar ratio of Cd-acetate was synthesized and was designated as f-GCdSe2 of 0.2 mmol.

3 Results and Discussion

3.1 Structural Study

The XRD patterns of nanocomposite powder were recorded using Rigaku Ultima x-ray diffractometer (40 KV, 30 mA, \( \lambda = 1.54059 \) A, Cu-K\(_{\alpha 1} \)) and are shown in Fig. 2. The XRD pattern of the f-G sample shows a broad peak at 20 deg. The broad diffraction peak of f-G can be attributed to two factors: first, the small sheet size (1 \( \mu \)m and below) and, second, a relatively short domain order or turbostratic arrangement of f-GO stacked sheets, each of which broadens the XRD peak.\(^{27}\) In comparison, XRD data of f-GCdSe show an additional peak at 20°-25.2 deg, 42.4 deg, and 49.5 deg which is ascribed to the presence of CdSe NCs in the f-G matrix.

![Fig. 1 Schematic illustration of the in situ growth of the cadmium selenide (CdSe) nanocrystals (NCs) in the f-graphene oxide/P3HT matrix.](image1)

![Fig. 2 X-ray diffraction (XRD) spectra of: (a) f-graphene oxide (f-GO), (b) f-GCdSe1, and (c) f-GCdSe2 nanocomposites.](image2)
These peaks at $2\theta \sim 25.2$ deg, 42.4 deg, and 49.5 deg correspond to the (111), (220), and (311) planes, respectively, of the zinc blend phase of CdSe. The XRD peaks are broadened due to the small size of CdSe NCs. In the XRD spectra of f-GCdSe, the low intensity of the CdSe peaks at $2\theta \sim 42.4$ deg and 49.5 deg may be attributed to the low concentration of CdSe in f-GO. These results are in good agreement with scanning electron microscopy (SEM) micrographs shown in Fig. 3(a). On the other hand, the peak at $2\theta \sim 19$ deg in f-GCdSe2 almost disappears due to the higher concentration of CdSe in f-GCdSe2, which is also evident in Fig. 3(b). The nanoscale morphology is a crucial parameter to understand the effectiveness of the interface for exciton splitting into free charge carriers and the formation of a percolation network for efficient transport of charge carriers to the electrodes. The surface morphologies of the f-GCdSe1 and f-GCdSe2 nanocomposite films have been examined by SEM and are presented in Fig. 3. These SEM micrographs were observed by a field emission SEM (Jeol FESEM-7600F). It is quite clear that CdSe NCs are evenly distributed within the hybrid system with a low CdSe NCs content [Fig. 3(a)], while NCs are massively phase separated or aggregated from the f-GO matrix at the higher NCs content [Fig. 3(b)]. An even more drastic contrast between organic and inorganic phases can be observed in f-GCdSe2.

### 3.2 Raman Analysis

Raman spectroscopy was performed on a Thermoscientific Raman microscope (DXR) under 532-nm excitation at low power levels to avoid laser heating. The Raman spectra of f-GO and f-GCdSe nanocomposites are shown in Fig. 4. f-GO, fGdSe1, and fGdSe2 exhibit characteristic D-bands at 1342, 1346, and 1343 cm$^{-1}$ and G-bands at 1583, 1578, and 1576 cm$^{-1}$, respectively. The D-band may be assigned to local defects and disorders, whereas the G-band originates from symmetric stretching of the sp$^2$ C-C bond. It can be clearly noticed that the G-band of the fGdSe nanocomposite shows a red shift in comparison to the f-GO. This shift indicates the interaction between graphene and CdSe nanoparticles, which is a prerequisite for charge transfer between CdSe and graphene. The shape and position of the 2D-band dramatically change on incorporating CdSe into f-GO, as shown in Fig. 4. The 2D-band in fGdSe can be resolved into two or more components, whereas the monolayer f-GO has a single component. According to this graph, it can also be seen that the symmetric and sharp 2D-band at 2677 cm$^{-1}$ is the best indicator for less than five layers of graphene. The center of the 2D-band of fGdSe nanocomposites shows a blue shift and can be resolved into two or more components, which further confirms the incorporation of CdSe nanocrystals in a graphene matrix.

### 3.3 Spectroscopic Properties

The sample for spectroscopy measurement was prepared by spin-coating of polymer solution onto a glass substrate at 2000 rpm for 60 s and was then annealed at 393 K for 30 min. Absorption spectra were taken on a Shimadzu UV-1601 spectrophotometer. The normalized
UV-Vis absorption spectra of the nanocomposites’ thin films with different concentrations of f-GCdSe in P3HT are shown in Fig. 5. The maximum absorption of pristine P3HT films was observed at 522 nm, which corresponds to the $\pi-\pi^*$ transition of the conjugated chain in the P3HT.\(^{32}\) It can be seen that the P3HT/f-GCdSe thin films have almost the same absorption range and peaks as that of P3HT film in the wavelength range from 350 to 650 nm, with the exception of a broad band that occurs in the blue region as compared to pristine P3HT. This is caused by the absorption of CdSe NCs in this region as evidenced from absorption spectra of f-GCdSe shown in the inset of Fig. 5. The absorption spectrum of the P3HT/f-GCdSe shows no significant change as compared to pristine P3HT, which implies that in the P3HT/f-GCdSe thin films, no significant ground-state interactions take place between the two materials, and hence no charge transfer occurs in the ground state.

For bulk heterojunction photovoltaic cells, photo-induced charge transfer from the donor polymer to the acceptor is usually needed for the photocurrent generation. Photoluminescence (PL) in conjugated P3HT is well known to arise from radiative recombination of polaron-exciton pairs into Franck–Condon (FC) states,\(^{33}\) and PL quenching of an appropriate donor polymer by
a suitable acceptor gives an indication of an effective photo-induced charge transfer from the
donor to the acceptor.34 In Fig. 6, the PL spectra of pristine P3HT film have been compared with
that of different nanocomposites’ films containing 20%, 40%, 60%, and 80% of f-GCdSe in
P3HT. These spectra were taken on an A Shimadzu RF-5301PC with an excitation wavelength
of 525 nm. It can be observed from Fig. 6 that the P3HT thin film shows strong PL between 600
and 800 nm. The PL intensity of the nanocomposite films is significantly reduced at 40% con-
centration of f-GCdSe in polymer. With the increase of f-GCdSe concentration in polymer, the
PL intensity decreases further. The reduced PL intensity of the composites relative to the pristine
P3HT indicates that the charge transfer, and thus the exciton dissociation at the interface of
f-GCdSe and P3HT.11 These results show that the excited fluorophore in the P3HT backbone
is quenched by the electronic interactions at the P3HT and f-GCdSe interfaces. By referencing
previous work with PCBM34 and carbon nanotubes,35 this efficient quenching of the PL emission
shows that f-GCdSe is expected to be an effective electron–acceptor material for OPV
applications.

Figure 7(a) shows the transient absorption spectra (TAS) of P3HT, P3HT/f-G, and P3HT/
f-GCdSe thin films. A GL-301 PTI dye laser module was used in conjunction with the PTI GL-
3300 nitrogen laser to provide a variable wavelength source of excitation (400 to 750 nm). It is
clear from the figure that P3HT/f-GCdSe films have a very high optical density (ΔOD) as com-
pared to pristine P3HT as well as P3HT/f-G. In the P3HT film, only the polarons generated by
interchain charge separation contribute to the mid-IR signal.36 In the composite, both the prod-
ucts of interchain charge separation (polarons in polymer) and interfacial electron transfer (pos-
itive polarons in polymer and injected electrons in CdSe) can contribute to the observed IR
signal. The enhanced optical density of the composite film indicates photo-induced charge sep-
aration resulting in an increase of the yield for free carrier generation, and a higher sum of the
mobilities of free carriers because of the contribution of the electron mobility in the f-GCdSe.
Charge separation will also result in longer photocarrier lifetimes due to the electron and the hole
residing in two different phases in the composite material. P3HT decay is short lived and appears
cruelly in the first order with a half life of approximately 1.2 μs, while the composite signal
decay continues over 5 orders of magnitude in time up to 10 ms. Furthermore, the average emis-
sion lifetimes of P3HT, P3HT/f-GO, and P3HT/f-GCdSe are 0.5, 0.75, and 0.69 μs, respectively.
The increase in the lifetime for P3HT/f-GO compared with P3HT indicates that there is photo-
generated electron transport from P3HT to f-GO. On the other hand, the lifetime for P3HT/
f-GCdSe decreases from 0.75 to 0.69 μs, which may be attributed to electron transfer from
P3HT to CdSe and then to graphene as shown in Fig. 7(b).

Fig. 6 Photoluminescence (PL) spectra of P3HT, P3HT/f-G-CdSe nanocomposite thin films after
excitation by radiation of 525-nm wavelengths.
4 Conclusions

In conclusion, the successful in situ incorporation of CdSe NCs in a reduced graphene matrix has been demonstrated. Structural and morphological studies reveal that CdSe NCs are uniformly distributed in the carbon matrix. PL quenching in P3HT/f-GCdSe suggests that charge transfer takes place between P3HT and f-GCdSe NCs. Charge transfer between donor and acceptor is further confirmed by time resolved absorption spectroscopy, which shows higher optical density and long lived free charge carriers. These results suggest that f-GCdSe is an excellent electron–acceptor material for OPV devices.

References


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