SYNTHESIS OF NOVEL FUNCTIONALIZED-GRAPHENE/QUANTUM DOTS HYBRID SYSTEM FOR SOLAR CELLS APPLICATION

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ABSTRACT

The present work demonstrates the synthesis of a novel hybrid accepter material containing amino-functionalized graphene oxide 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-graphene oxide matrix named f-GCdSe. Structural studies like X-ray diffraction (XRD), Scanning Electron Microscopic (SEM) were employed to investigate the growth of CdSe NCs in 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 at the donor/acceptor interface. TAS shows higher optical density and longer lived free carriers for P3HT/f-GCdSe thin film. These results suggest that f-GCdSe is an excellent electron acceptor material for OPV devices.

Keywords: Acceptor, functionalized graphene, CdSe nanocomposites, spectroscopy,

1   INTRODUCTION

Since the past decade a lot of advancement has been accomplished by scientists and engineers in the area of organic photovoltaic (OPV) technology. Recently, double digit power conversion efficiency (PCE) 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 have better performance in low light, can be transparent and colorful, and have greater flexibility and lower weight. The downside of OPV is that their efficiency is still much lower than traditional Silicon solar cells. To make polymer based solar cells an economically interesting alternative, the efficiency of these devices must be increased. The limited efficiency of the OPV is due to the poor carrier mobility [4], the short exciton diffusion length [5], the 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 have been blended with organic materials which integrate the benefits of both classes of materials. Various NCs including CdS [8], CdSe [9,10], CdTe [11], PbS [12], ZnO [13] and TiO_2 [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 some distance from the requirement for the next generation of solar cells. 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.

Graphene, a monolayer of sp^2-hybridized carbon atoms arranged in archetypal two-dimensional lattice, has attracted tremendous attention of OPV scientist and engineers in recent years. The high specific surface area for a large interface, superior electrical mobility up to 10000 $cm^2V^{-1}s^{-1}$, and tunable band gap would make it an excellent electron acceptor in OPV devices [15]. 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 [16, 17]. Herein we report the novel *in-situ* synthesis of CdSe NCs in functionalized graphene matrix, wherein the strategy of *in-situ* growing CdTe NPs onto P3HT matrix has been adopted [11]. The f-GCdSe nanocomposite shows very fast and dramatically enhanced photoresponse, which makes it an excellent electron acceptor material for OPV devices.

2   SYNTHESIS OF FUNCTIONALIZED-GRAPHENE/CdSe NANOCOMPOISTES

Prior to *in-situ* synthesis of CdSe nanocrystals in functionalized graphene, aqueous suspension of graphene oxide (GO) has been synthesized from natural graphite powder using modified Hummers method [18]. 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. The resulting graphite was put in 500ml concentrated H_2SO_4 at 0 ℃ with continuous stirring. Then, 21 g of $KMnO_4$ was slowly added and maintained the temperature at 20 °C. The temperature was then elevated to 35 °C, and then 70℃ for 2 h with continuous stirring. The flask was then chilled again in the ice bath, and distilled water (ice) was slowly added, maintaining temperature below 70 °C. The mixture was stirred for 1 h and subsequently diluted with 5 L of deionized water. 50 ml of
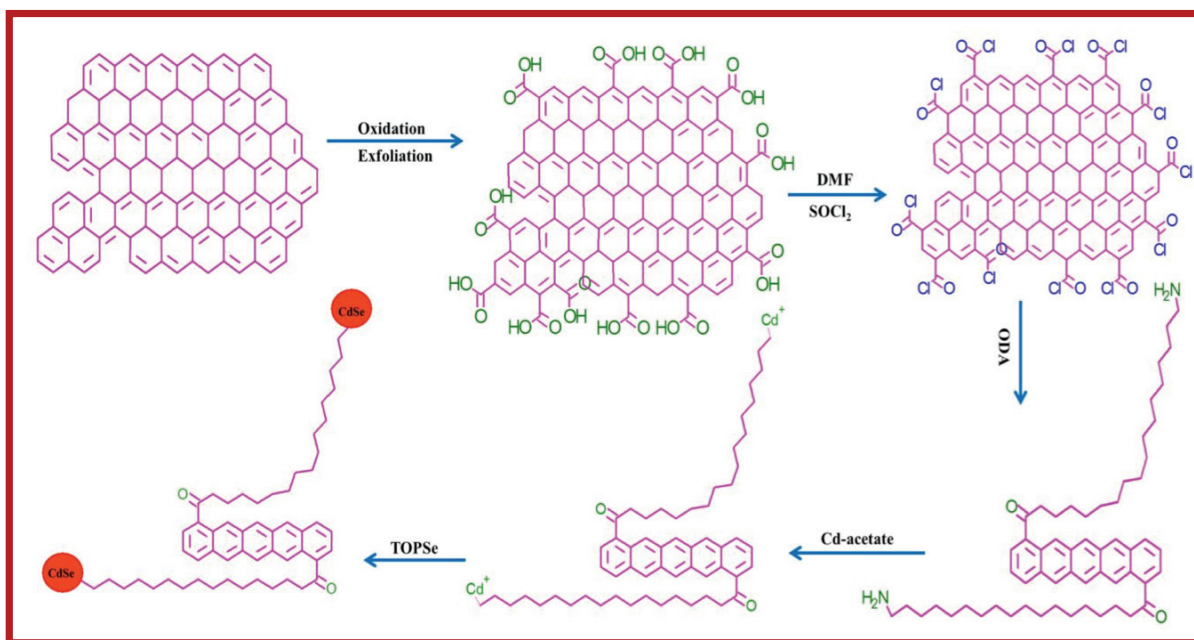
Scheme I: *Schematic illustration of the in-situ growth of the CdSe NCs in the f-graphene oxide P3HT matrix.*

H_2O_2 (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 treated with $SOCl_2$ in DMF followed by octadecylamine ODA at 150°C for 24 hrs to give functionalized graphene. *The in-situ* synthesized CdSe NCs in graphene was named as f-GCdSe and schematically illustrated in scheme I. In a typical synthesis of f-GCdSe, 100 mg of functionalized graphene was allowed to react with 0.1mmol of cadmium acetate dihydrade at 150 °C in the medium of ODA and the reaction temperature was increased to 300 ^{0}C for 2 hrs. The selenium precursor has been prepared by treating 0.2 mmol of selenium powder (Acros Organics) in trioctylphosphine (TOP) (Sigma Aldrich, USA), at 300°C for 30min under nitrogen flow. The Se precursor was then injected in to the functionalized graphene-Cd solution and the mixture was allowed to react for 30 mins at 300°C under nitrogen flow. Growth of CdSe NCs was gets completed when color of the solution turned to dark orange. After the completion of the reaction, the unreacted cadmium acetate and precursor of Selenium were removed by treating nanocomposites with hexane. The reaction mixture was separated by centrifugation and dried in vacuum at 40 °C. Similarly, other compositions of functionalized graphene containing different mole ratios of Cd-acetate were synthesized and are designated as f-GCdSe2 for 0.2 mmol.

3 RESULTS AND DISCUSSION

3.1. Structural Study

The XRD of the f-GO and f-GCdSe nanocomposite are shown in Figure 1. The XRD of nanocomposites powder were recorded using Rigaku Ultima X-ray diffractometer (40 KV, 30 mA, λ=1.54059 A, Cu-K$_{\alpha 1}$). The XRD pattern of the f-GO samples shows a broad peak at 20°. The broad diffraction peak of f-GO can be attributed to two factors: first, the small sheet size (1 μm and below) and, second, a relatively short domain order or turbostratic arrangement of f-GO stacked sheets, each of which broadens the XRD peak [19]. In comparison, XRD data of f-GCdSe shows additional peaks at $2\theta \sim 25.2^{°}$, $42.4^{°}$and $49.5^{°}$ which are attributed to the presence of CdSe NCs in f-GO matrix. These peaks at $2\theta \sim 25.2^{°}$, $42.4^{°}$ and $49.5^{°}$ corresponds to the (111), (220) and (311) planes, respectively, of Zinc blend phase of CdSe [20]. The XRD peaks are broadened due to the small size of CdSe NCs. In the XRD spectra of f-GCdSe1, intensity of CdSe peaks at $2\theta \sim 42.4^{°}$ and $49.5^{°}$ are very low attributed to low concentration of CdSe in f-GO. This can also observed from SEM images shown in Figure 2(a). On the other hand peak at $2\theta \sim 19°$ is almost disappear in f-GCdSe2 due to higher concentration of CdSe in f-GCdSe2 which is also evident in Figure 2(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 morphology of the f-GCdSe1 and f-GCdSe2 nanocomposite films have been examined by scanning electron microscopy (SEM) are presented in Figure 2. The SEM micrographs were observed by a field emission scanning electron microscopy (Jeol FESEM-7600F) . It is quite clear that CdSe NCs are evenly distributed within the hybrid system at low CdSe NCs content (Figure 2a) while NCs are massively phase-separated or aggregated from the f-GO matrix at higher NCs content (Figure 2b). An even more drastic contrast between organic and inorganic phases can be observed in f-GCdSe2.
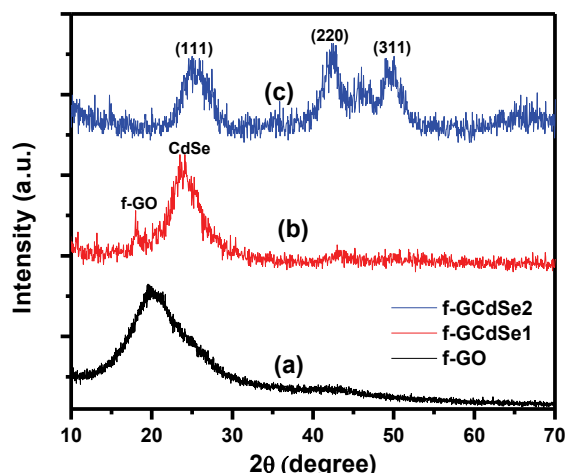
Figure 1 *XRD spectra of (a) f-graphene oxide (f-GO), (b) f-GCdSe1 and (c) f-GCdSe2 nanocomposites*

Figure 2. *SEM micrograph of* **(a)** *f-GCdSe1 and* **(b)** *f-GCdSe2*

3.2. Spectroscopic Properties

The sample for spectroscopy measurement were prepared by spin-coating of polymer solution onto glass substrate at 2000 rpm for 60 sec. and annealed at 393K for 30 min. Absorption spectra were taken on Shimadzu UV-1601 spectrophotometer. The normalized UV-Vis absorption spectra of the nanocomposites thin films with different concentrations of f-GCdSe2 in P3HT are shown in Figure 3.
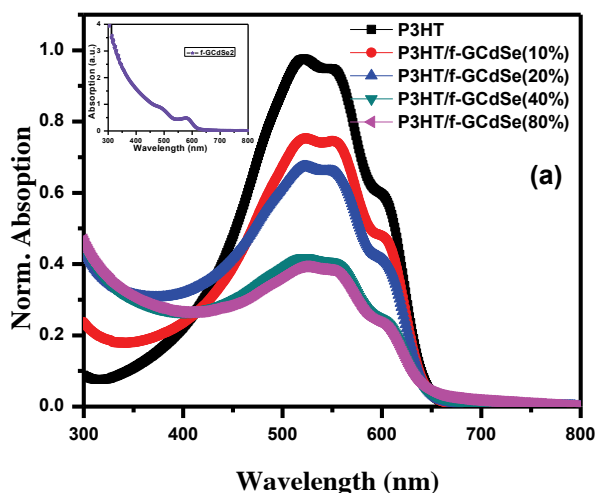

Figure 3. *Normalized absorption spectra of P3HT and P3HT/f-GCdSe nanocomposites films with different concentration of f-GCdSe in P3HT. Inset shows absorption of f-GCdSe solution dissolved in tetrahydrofuran. Percentage of f-GCdSe in P3HT are mentioned in bracket*

The maximum absorption of pristine P3HT films has been observed at 522 nm which corresponds to the π-π* transition of the conjugated chain in the P3HT [21]. It can be seen that the P3HT/f-GCdSe thin films has almost the same absorption range and peaks as that of P3HT film in the wavelength range from 350 to 650 nm, except that the absorption spectrum has been broader in blue region as compared to pristine *P3HT*. This
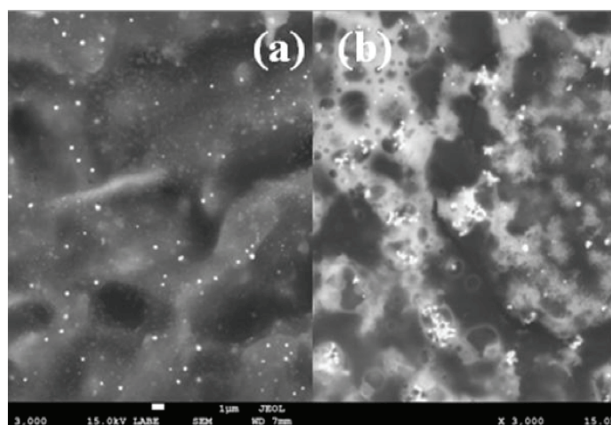
should be caused by the absorption of *CdSe* NCs in this region as evidenced from absorption spectra of *f-GCdSe* shown in the inset of Figure 3. The absorption spectrum of the *P3HT/f-GCdSe* shows no significant change as compared to pristine *P3HT*, this implies that in the *P3HT/f-GCdSe* thin films, no significant ground-state interactions take place between the two materials, and hence, no charge transfer occurs in the ground state.

For bulk hetrojunction (BHJ) photovoltaic cells, photoinduced 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, [22] and PL quenching of an appropriate donor polymer by a suitable acceptor gives an indication of an effective photoinduced charge transfer from the donor to the acceptor [23]. In Figure 4 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. Photoluminescence spectra were taken on a Shimadeza RF-5301PC photoluminescence, with excitation wavelength 525 nm. It can be observed from the Figure 4 that the P3HT thin film shows strong photoluminescence between 600 and 800 nm. PL intensity of the nanocomposite films significantly reduces at 40% concentration of f-GCdSe in polymer. With increase of f-GCdSe concentration in polymer, the PL intensity decreases further. Reduced PL intensity of the composites relative to the pristine P3HT, indicates that charge transfer, thereby exciton dissociation at interface of f-GCdSe and P3HT [11]. These results show that the excited fluorophore in the P3HT backbone was quenched by the electronic interactions at the P3HT and f-GCdSe interfaces. By referencing previous work with PCBM [23] and carbon nanotubes, [24] this efficient quenching of the PL emission shows that f-GCdSe is expected to be an effective electron-acceptor material for organic photovoltaic applications.

Figure 5 shows the transient absorption spectra of P3HT, P3HT/f-GO 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 (400-750nm).
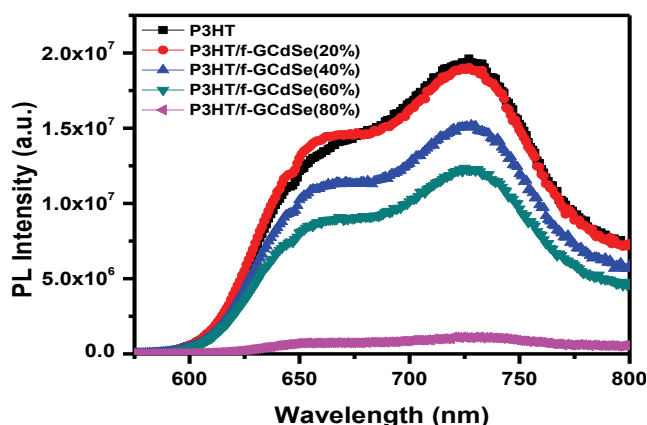
Figure 4. *Photoluminescence spectra of P3HT, P3HT/f-GCdSe nanocomposites thin films after excitation by radiation of 525 nm wavelength*

It is clear from the Figure that P3HT/f-GCdSe films have very high optical density (ΔOD) as compared to pristine P3HT as well as P3HT/f-GO. The enhanced optical density ΔOD of the composite film indicates photoinduced charge separation occurs resulting in (a) an increase of the yield for free carrier generation, and (b) a higher sum of the mobilities of free carriers because of the contribution of the electron mobility in the f-GCdSe.
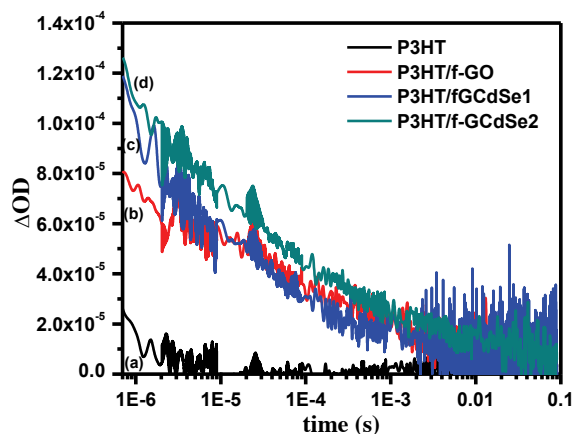

Figure 5: *Transient Absorption spectroscopy of (a) P3HT, (b) P3HT/f-GO, (c) P3HT/f-GCdSe1 and (d) P3HT/f-GCdSe2 thin films.*

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 crudely first order with a half life of approximately 0.5µs while composite signal decay continues over 5 orders of magnitude in time, up to 10 milliseconds .

4 CONCLUSIONS

In conclusion, the successful *in-situ* incorporation of CdSe nanocrystals in f-graphene oxide matrix has been demonstrated.

Structural and morphological studies reveal that CdSe NCs are uniformly distributed in carbon matrix. PL quenching in P3HT/f-GCdSe suggest that charge transfer between P3HT and f-GCdSe nanocrystals. Charge transfer between donor and acceptor is further confirmed by time resolved absorption spectroscopy which shows higher optical density and longer lived free charge carries. These results suggest that f-GCdSe is an excellent electron acceptor material for OPV devices.

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