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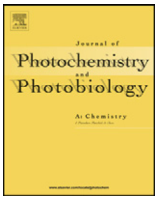

Polymer-quantum dot-carbon nanotube composites formation under visible light irradiation

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ABSTRACT

A facile method for preparation of polymer-CdSe quantum dot (QD)-carbon nanotube (CNT) composite under visible light irradiation is described. This photochemical method for such composite formation is based on a photoinduced hole transfer from the CdSe core to the ligand resulting in the formation of polymeric quantum dots on the surface of the CNT. Transmission electron microscopy (TEM), scanning electron microscopy (SEM), and energy dispersive X-ray (EDX) methods were used to confirm the formation of thiophene based polymer-QD-CNT composites. The composites maintain the quantum confinement characteristics of the CdSe nanoparticle, retaining its broad absorption in the spectrum of the sun. The composites thus produced can, therefore, be potentially used as the absorbing material in photovoltaic cells.

1. Introduction

With ever increasing demand for clean renewable energy resources, the search for cost-effective solar cells continues to grow in this decade. Silicon solar cells are expensive to make, install and maintain; and polycrystalline semiconductor thin films, though less expensive, are inefficient [1–3]. Polymer-based solar cells have the potential to deliver higher efficiency at lower cost and are prepared from flexible plastics easily [4–8]. But low-cost and stable materials that can capture and efficiently transport photogenerated electrons/holes to external electrodes are still being sought [9–16].

The advantages of using semi-conducting quantum dots (QDs) as solar energy conversion materials are due to their tunable bandgap and high absorption coefficients [9,17], multiple excitons (electron/hole pairs) generation with single photon absorption [18,19], easy formation of different forms in sheets or in three-dimensional arrays, and low cost. QDs can be produced in bulk materials via chemical manufacturing techniques. The crucial step to achieve high power conversion efficiency lies in the rapid trapping and transferring of the electron or hole, formed in QD by absorption of photon, to the external electrodes before it undergoes recombination. Therefore, efforts have been focused on designing efficient electron or hole transfer from QDs [20,21]. Conductive polymers such as polypyrrole, polyaniline, poly(para-phenylene vinylene), and polythiophene which has π electron in the backbone are good charge carrier. QD-conductive polymer inorganic–organic hybrid composites having dual properties, those of the QD and the conductive polymers, are expected to be promising materials for photovoltaic cells [1,22–26]. Carbon nanotube (CNT) with its high electronic conductivity, elasticity, and optical transparency is also considered to be efficient trapper and transporter of the exciton from QDs [1,9,27,28]. Therefore, polymer-QD-CNT composites would provide the benefits of CNTs while retaining the advantages of QD-conductive polymer composites. Formation of CNT composites has, however, been challenging; and two distinct approaches have been employed in this purpose. One method attaches presynthesized nanoparticles to the CNT; the other grows nanoparticles directly on the CNT [29,30]. At the same time, preparing either conductive polymer-QD or CNT-QD composites is complicated chemical procedure [27]; and there are few reports of fabrication of conductive polymer-QD-CNT composites. Recently, we reported functionalization of CNTs using 5-mercapto-2,2′-bithiophene (BTSH) functionalized metal nanoparticles [31]. A crosslinked-like polymerized nanostructure around the CNT is formed under UV light irradiation of the ligand. In addition, we reported a facile method for the formation of QD-polymer composites using the photo-induced hole transfer from the QD to the ligand [32]. Inspired by these findings, we sought to employ the

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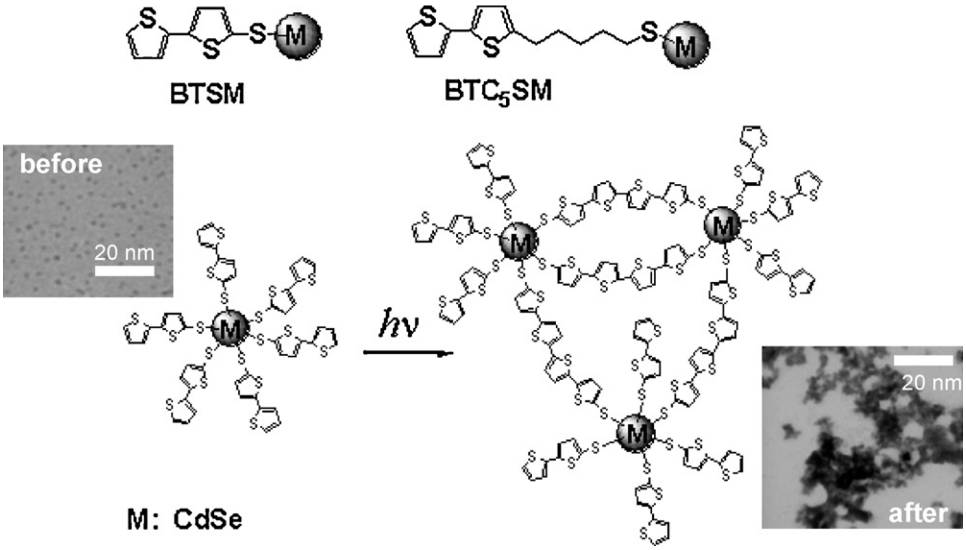

Fig. 1. The structures of BTSCdSe and BTC_5SCdSe; and schematic drawing showing polymerization of BTSM upon visible light irradiation of CdSe QD core. Insets show TEM images of BTSCdSe QD before and after visible light (≥450 nm) irradiation.

photo-induced hole transfer method, used for the preparation of polymer-QD composites, in developing a facile method to produce a thiophene based polymer-QD-CNT composites.

We report herein polymer-QD-CNT composites formation by visible light irradiation. BTSH modified CdSe QDs (BTSCdSe) was prepared and was dispersed with CNTs. When subject to visible light (≥450 nm) irradiation of the QD core, photo-induced hole transfer from the CdSe QD to the BTS ligand results in formation of polymeric QD on the CNT surface. The hole transfer forms bithiophene radical cation that initiates the formation of crosslinked-like thiophene polymers from the surface of QD; and the resulting polymeric QD wraps around the surface of CNT to form polymer-QD-CNT composites. For control, CdSe QD modified with BTC_5SH where the biothiophene unit is separated by five methylene groups from the CdSe core was prepared and was dispersed with CNT. Due to the separation of the QD core from the bithiophene unit by the five $-CH_2-$ groups the hole transfer from QD to the ligand is prevented. Therefore, upon visible light irradiation of the QD core no polymerization or formation of composites was observed. The formation of polymer-QD-CNT composites in case of BTSCdSe-CNT was confirmed by transmission electron microscopy (TEM), and scanning electron microscopy (SEM). Energy dispersive X-ray (EDX) analysis of the CNT surface provided further evidence for the formation of the composites.

2. Materials and methods

2.1. Materials

5-Mercapto-2,2′-bithiophene (BTSH) was synthesized according to literature procedures [33,34] and 5-(5-mercaptopentyl)-2,2′-bithiophene (BTC_5SH) was synthesized in our lab [31,35]. Trioctylphosphine oxide (TOPO) modified CdSe QD (~3.5 nm) were synthesized following the directions in previous reports [36,37]. BTSH and BTC_5SH functionalized CdSe QDs (BTSCdSe and BTC_5SCdSe) were prepared by ligand exchange reactions. TOPO modified CdSe QD were mixed with BTSH or BTC_5SH in toluene and stirred for one day under argon. The solution was then triturated with methanol and the surface modified QDs are isolated by centrifugation. The precipitates were washed with methanol several times to remove all the displaced TOPO and unreacted ligands. The final residues were dissolved in toluene. Exchange reactions and subsequent procedures were carried out in the dark. Single wall CNT (SWCNT) (Pure HiPco, <15% Ash content) or multiwall CNT (MWCNT) (O.D.: 10–30 nm, I.D.: 5–10 nm, length: 0.5–50 μm) (<1%, w/w) were added into the BTSCdSe or BTC_5SCdSe solution and sonicated for at least 15 min to ensure good dispersion of the CNTs and QDs. The solution was then irradiated using a Xe lamp (ORIEL Corp. Model, 68805) equipped with a light filter (≥450 nm) for 30 min. After centrifugation, the precipitates were washed with methanol and toluene several times. The final precipitate was dispersed in toluene by sonication for product characterization. All solvents were ACS-grade products.

2.2. Electron microscopy

TEM images were taken on a ZEISS EM10 transmission electron microscope operating at 30–80 kV. The sample was dropcast from toluene solutions onto formvar-carbon coated 300-mesh copper grids and air-dried before viewing under the TEM. Samples for SEM, recorded on a FEI Inspect F (SN-D8580) electron microscope at 5 kV, were prepared by placing a few drops of the sample solution onto a copper film placed on an aluminum stub. The samples were allowed to dry before viewing under the electron microscope. EDX were carried out using the same equipment with an EDX detector.

2.3. Ultraviolet–visible absorption and fluorescence spectroscopy

Ultraviolet–Visible (UV) absorption spectra were measured using MultiSpec-1501 (Shimadzu). The emission spectra and emission lifetimes were measured using a SPEX Fluorolog-3 (Jobin Yvon Inc.; source – 450 W Xe Arc Lamp) equipped with Time Correlated Single Photon Counting (TCSPC); source – 465 nm NanoLED, detector-TBX-04 photomultiplier tube.

3. Results and discussion

Recently, using ultrafast (fs) laser flash photolysis [31,35], we observed efficient charge transfer between a bithiophene ligand and QD core. We observed concomitant photoinduced polymerization of BTSH modified QD (BTSCdSe) from excitation of the CdSe nanocore with visible light [31,35]. This represents an easy method for fabrication of polymer nanomaterial composites given that no