



# Role of surface modification of CdS nanoparticles on the performance of hybrid photovoltaic devices based on p-phenylenevinylene derivate



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## HIGHLIGHTS

- A novel strategy to synthesize CdS nanocrystal modified with thiophenol (PHSH).
- CdS-PHSH NCs are used as an acceptor in a MEH-PPV.
- PI and PLRT measurement provided evidence for charge transfer at the interface.
- Thiophenol passivated CdS in conjunction with MEH-PPV is a promising composite for hybrid solar cell.

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## ABSTRACT

The role of organic capping ligand of semiconductor nanoparticles in dictating the interfacial charge transfer processes in hybrid semiconductor nanoparticles/polymer-based photovoltaic devices is investigated. Morphology, optical and structural study of the CdS nanoparticles and the hybrid material were accomplished using X-ray diffraction (XRD), absorption (UV–vis), atomic force microscopy (AFM), transmission electron microscopy (TEM), photoluminescence (PL) and time resolved photoluminescence spectroscopy (PLRT). A broad band absorption in UV–visible region and considerable fluorescence quenching of MEH-PPV in the composites are noted indicating a photo-induced charge transfer and dissociation of excitons. Time-resolved photoluminescence measurements indicating decreased lifetime further confirm this process. The solar cells open-circuit voltage and short-circuit current were improved using thiophenol modified CdS nanoparticles as electron acceptor in comparison to MEH-PPV only device demonstrating a promising approach to enhance charge transport in the hybrid nanoparticles–polymer composite photovoltaic cells (PV).

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## 1. Introduction

Hybrid nanoparticles–polymer composite have been progressively more studied due to the novel synergy effects on enhanced electronic and optical properties for many optoelectronic applications. By far, hybrid solar cells using conjugated polymers as electron donors and inorganic semiconductor nanoparticles as electron acceptors have attracted a lot of attention due to the combined merits of both materials: solution processability of conjugated polymers, high electron mobility and low-cost fabrication of inorganic semiconductor nanoparticles. Additionally,

nanoparticles in hybrid PV cells can absorb visible light, their band gap can be adjusted by variation of their size and surface passivation and it is possible to get one-dimensional morphology resulting in better pathways for electron transport. Up to now, several kinds of hybrid polymer solar cells have been reported using CdSe [1,2], CdS [3], TiO<sub>2</sub> [4] and ZnO nanoparticles [5] as electron acceptors. Because of the short exciton diffusion length (less than 10 nm) in semiconducting polymers, only excitons generated within 10–20 nm distance from the donor/acceptor interface can diffuse to the interface and dissociate into free carriers [6].

The exciton dissociation efficiency strongly depends on the morphology of the blend films, which is related to the degree of dispersion of the nanoparticles in polymer matrix [7,8]. That is one of the limiting factors for the efficiency of these devices [9]. Many

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studies have been done to achieve hydrophobic surfaces of inorganic semiconductor nanoparticles via surface modification with conductive ligands to reduce the polymer/inorganic nanoparticles phase separation in hybrid polymer solar cells [10,11]. Much effort has been put to understand and control the surface properties and interfacial interactions between the organic molecules and inorganic semiconductor, which can severely change the electronic properties of both components, critically affecting the performance of the final devices [10,11].

However, very few studies have been reported on the use of CdS as an important II–VI semiconductor in nanoparticles conjugated polymer composite for photovoltaic devices. Due to the relatively large band gap (2.42 eV) that absorbs light ranging from 300 to 512 nm, the high electron mobility and electron affinity of CdS, and the fact that large ratio of surface to volume of nanoparticles creates sufficient p–n interface areas for the exciton to be separated and to give rise to charge carriers, we expect that there is much more improvements of the photovoltaic device efficiency when hybrid CdS/conjugated is used.

It has been demonstrated that the performance of an organic/inorganic hybrid solar cell can be improved through interface modification with organic ligands molecules [14]. Ideally, ligands should possess head groups that have high affinity to nanoparticles and end groups that provide solubility. At the same time, these ligands are used to control the size of the nanoparticles and to reduce the surface traps. They are also necessary to stabilize and disperse nanoparticles in the polymer matrix, to improve the compatibility between the components of the hybrid system and to enhance electrons transfer and transport from polymer to NCs or from NCs to NC [12–15]. The most used ligands are pyridine, thiophenol which are added during the preparation of the blend films [16–18].

Several hybrid bulk heterojunction polymer solar cells have been reported including nanoparticles, after the modification of the surface by the ligands. Chen et al. [16] reported thiophenol as a surface ligand for enhancing photoluminescence quenching and PV properties in hybrid polymer/CdSe cells. Recently, Ligand effects in TiO<sub>2</sub> hybrid devices were examined [11]. Interestingly, power conversion efficiency (PCE) was improved when thiophenol was added as a ligand, likely due to low solubility of pristine TiO<sub>2</sub> nanorods in toluene. Nevertheless, there is less report on the interface modification in organic–CdS ordered hybrid composite today. Jiang et al. reported an efficiency of 0.25% with composite film CdS/P3HT by the addition of aromatic acid interface modifier [14].

In this paper, we report the synthesis and the characterization of CdS–thiophenol (CdS–PHSH) prepared by chemical route. This simple inexpensive method, exempt from extremely dangerous organometallic reagents, has led to new class of hybrid blends of conjugated polymers (MEH–PPV)/CdS–PHSH nanoparticles. Our aim is to give deeper insight into the structural and physical properties of the new material and the further understanding of the dominant processes in term of charge transfer and exciton dissociation. Improving the power conversion efficiently of hybrids PV cell and the performance of the device is our goal.

## 2. Experimental details

### 2.1. Chemicals

The chemicals used in this study were from Sigma, Aldrich, Merck and Fluka: Cadmium acetate dihydrate (C<sub>4</sub>H<sub>6</sub>CdO<sub>4</sub>·2H<sub>2</sub>O, ≥ 98%, Sigma–Aldrich), Thiourea (NH<sub>2</sub>CSNH<sub>2</sub>, ≥ 99%, Sigma–Aldrich), Thiophenol (C<sub>6</sub>H<sub>5</sub>SH, ≥ 99%, Aldrich) and Tetrabutylammonium perchlorate (TBAP, Merck). Conjugated polymer poly [2-methoxy-5-(2-ethylhexyloxy)-p-phenylenevinylene] (MEH–PPV) Fig. 1(a) and PEDOT:PSS

[poly (3,4-ethylenedioxythiophene)/poly-(styrene sulfonate)] were purchased from Sigma–Aldrich. All used solvents were of analytical grade and purchased from Aldrich. High-purity water was used for preparation of all aqueous solutions.

### 2.2. Sample preparation

#### 2.2.1. Preparation of CdS–PHSH nanoparticles

CdS nanoparticles were synthesized via wet chemical route using thiourea (NH<sub>2</sub>CSNH<sub>2</sub>) and cadmium acetate dihydrate (Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O) as starting material, and thiophenol ligands (PHSH). The synthesis procedure is described in reference [19,20]. In a typical experiment, firstly 5.7 mmol of cadmium acetate dihydrate and 13.8 mmol of capping agents were dissolved in 200 mL of deionized water to obtain a solution for which the pH was adjusted from 10 to 11 by drop wise addition of 1 M solution of KOH. Then, the solution was placed in a three-necked flask fitted with a septum and valves and was deaerated with N<sub>2</sub> bubbling for 30 min. A second aqueous solution of thiourea (2.88 mmol in 50 mL) was also prepared and added drop wisely to the initial solution under vigorous stirring. The precursors were converted to CdS nanoparticles by refluxing the reaction mixture at 100 °C for 2 h under N<sub>2</sub>. This conversion is accompanied by a change of the solution color to yellow. To isolate the CdS nanoparticles, the final solutions were concentrated down to 25 mL using evaporator. For the extraction, the particle was stirred in methanol solution for 1 h then filtered and dried in desiccators under vacuum. The thiols concentrations used in our preparation give a thiol/Cd ratio nearly equal to 2. This result may be due to the stoichiometric requirement which leads to a good coverage and a total saturation of the dangling bonds at the nanoparticles surface, leading to the inhibition of the non radiative transition [20].

#### 2.2.2. Cyclic voltammetry of CdS–PHSH nanoparticles

Cyclic voltammetry (CV) measurement has been performed of CdS thin film to understand the electro-chemical interaction between MEH–PPV and CdS–PHSH after mixing. The HOMO and LUMO values of CdS–PHSH nanoparticles were obtained via CV. The later measurements are recorded by an Applied Research potentiostat model 83965. An ITO-coated glass substrate has been used as the working electrode, a Pt wire as the counter electrode and Ag/AgCl as the reference electrode. Tetrabutylammonium perchlorate (TBAP) dissolved in acetonitrile (0.1 M) was used as supporting electrolyte. The electrochemical cell was externally calibrated by a ferrocene standard. Then, 0.01 M purified CdS–PHSH nanoparticles were dispersed in chlorobenzene to get a uniform solution and then coated on the surface of the working electrode, which had already been cleaned, polished and dried. Cyclic voltammograms were recorded at a scan rate of 20 mV/s.

#### 2.2.3. Fabrication of device

Composite material has been prepared by blending MEH–PPV with low concentration of chemically synthesized CdS nanoparticles modified by thiophenol, which exhibits good charge transport. The hybrid nanocomposite solution was prepared by dissolving 15 mg of MEH–PPV in chlorobenzene and 6 mg of CdS–PHSH (Fig. 1(b)). Nanoparticles were added to the solution making a 30% weight ratio to MEH–PPV. The poor compatibility between MEH–PPV and CdS is well resolved via CdS surface modification by thiophenol since both of them have benzyl groups [16,18]. The solution was stirred for 24 h before device fabrication. Photovoltaic devices were fabricated using a sandwich structure of ITO/PEDOT:PSS/MEH–PPV/CdS–PHSH/Al. ITO glass substrate was washed by deionized water, acetone and isopropyl alcohol. After that the substrate was patterned by etching with HCL and Zn dust to prevent the shortening in the device while making the contact for

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