

Effects of bifunctional linker on the performance of P3HT/CdSe quantum dot-linker-ZnO nanocolumn photovoltaic device

Tsung-Wei Zeng, I-Shuo Liu, Fang-Chi Hsu, Kuo-Tung Huang, Hsueh-Chung Liao, and Wei-Fang Su*

Department of Materials Science and Engineering, National Taiwan University, Taipei 106, Taiwan
*suwf@ntu.edu.tw

Abstract: We study the effects of bifunctional linker on the photovoltaic properties of P3HT/CdSe quantum dot-linker-ZnO nanocolumn heterostructure. The CdSe quantum dots are bound on the surface of ZnO nanocolumns through either aliphatic linker of 3-aminopropyl trimethoxysilane(APS) or aromatic linker of p-aminophenyl trimethoxysilane(APhS) using simple solution process. As compared to CdSe bound by aliphatic linker(APS), while CdSe is bound by aromatic linker(APhS), more than one fold increase of short circuit current density (J_{SC}) of the device obtained under irradiance, which is attributed to a more efficient charge transfer dynamics at interface. In addition, the ZnO-APhS-CdSe/P3HT devices possess about 4.8 folds in power conversion efficiency as compared to ZnO/P3HT device as the results of reduction in shunt loss and interfacial recombination.

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1. Introduction

The polymer solar cell power conversion efficiencies of over 5% has been achieved by using a mixture comprising conjugated polymer as the donor and PCBM as the acceptor [1,2]. Polymer based solar cells have received much attention for fabrication of large area and low cost solar cells through solution processes [3]. Based on conjugating polymers, there are many alternative materials and structures of photovoltaic cells providing advantageous features. Conjugated polymers have been widely combined with n-type inorganic semiconductors [4–6]. ZnO has received attention due to it offers high electron mobility and good air stability [7]. ZnO can be grown as nanostructured films and allows facile control over the desired morphology [8,9]. For a firstly prepared P3HT/ZnO nanorod arrays solar cell, an efficiency of 0.53% has been obtained demonstrates ZnO nanorod arrays may serve as a promising electron acceptor due to the direct charge transport route within polymer-inorganic heterojunction devices [10].

Properly modifying the P3HT/ZnO nanorod array heterojunction can improve the photovoltaic conversion efficiency [11,12]. Anchoring the dye molecule to the ZnO nanorods in the P3HT/ZnO photovoltaic cell as an interfacial layer between the donor and acceptor [13,14], leads to rapid charge separation and retarded recombination at the interface. Alternatively, coating the ZnO nanorods with a thin shell of inorganic TiO₂ significantly increases the open circuit voltage and fill factor of P3HT/ZnO photovoltaic cell which is attributed to an efficient exciton dissociation and a retarded recombination [15,16].

In this study, a thin and conformal shell of CdSe quantum dot is anchored by bifunctional linkers on the ZnO nanocolumns. In prior studies, the techniques of coating CdSe on TiO₂

nanoporous film has been demonstrated in solar cell applications. The efficient CdSe quantum dot sensitized TiO₂ mesoporous solar cells have been reported by improved layer adsorption processes [17]. Additionally, the use of absorbed molecular in the CdSe quantum dot sensitized TiO₂ mesoporous solar cells is under sought to improve the solar cell efficiencies [18]. In our study, coating a CdSe quantum dot thin shell on semiconductor oxide electron accepting materials is introduced into the P3HT/ZnO nanocolumn heterostructure. This CdSe layer can serve as buffer layer to mediate charge transfer and to suppress the surface recombination and thus increase open circuit voltage in the ZnO nanocolumn/P3HT heterostructure. This approach provides opportunities for further control of the quantum dot properties, such as size and shape, which facilitating tailoring of CdSe buffer layer properties [19].

The charge transfer in the ZnO nanocolumn-bifunctional linker-CdSe quantum dots heterojunction is believed dependent on the type of linker because the type of linker molecule between the quantum dots and the ZnO affects the electronic structure at the interface [20]. In this study, we have assembled ZnO nanocolumn-bifunctional linker-CdSe quantum dots/P3HT photovoltaic devices to evaluate the influence of the introduced linker-CdSe at ZnO nanocolumns/P3HT interfaces on overall device performance.

2. Experimental

CdSe nanocrystals were prepared using the method described in the literature [21]. Briefly, CdO (0.041g, 99.99%, Aldrich), trioctylphosphine oxide (TOPO, 6.1g, 90%, Aldrich), and hexadecylamine (HDA, 3.05g, 90%, Tokyo Kasei) were loaded into a 50ml flask. The mixture was then heated to about 320°C under Ar flow with stirring. Once the color of the solution changed from brick red to transparent, the temperature of the solution was cooled to 240°C and a solution of Se powder (0.025g, 99%, Aldrich) dissolved in tri-n-butylphosphine (TBP, 1ml 95%, Acros) was quickly injected into the flask. After the injection, the CdSe quantum dots were allowed to age at 240°C for 1 min before cooling to room temperature under Ar atmosphere. CdSe quantum dots were isolated by adding 1.5ml of methanol (99.99%, Acros) to the cooled reaction vessel followed by centrifugation. Repeated methanol washings followed by centrifugation removed excess TOPO and obtained TOPO passivated CdSe quantum dot powder.

The ZnO nanocolumns were grown on ITO substrate using chemical bath deposition. The preparation of ZnO nanocolumns for the device follows the procedures reported in the literature with modifications [22]. The nucleation layer solution was obtained by adding 0.5M zinc acetate and 0.5M ethanolamine into 2-methoxyethanol and was stirred at 60°C for two hours until transparent. The solution was then cast onto pre-cleaned ITO substrate through sonication in ethanol. Following spin coating, the substrate was thermal annealed at 300°C for half an hour. After this step, the nucleation thin film was immersed into a mixture of 0.05M zinc nitrate and 0.05M hexamethylenetetramine in deionized water and was hydrothermally grown at 90°C for an hour. The as grown ZnO nanocolumn substrate was then rinsed by ethanol and deionized water for several times, followed by thermal treatment at 300 °C for 30 minutes.

The 3-aminopropyl trimethoxysilane (APS, Acros) modified(anchored) ZnO nanocolumn was prepared following the method described in the literature [23]. Firstly, a ZnO nanocolumn film on substrate (0.5 × 0.5cm²) was immersed in 6g of anhydrous dimethyl sulfoxide (DMSO, Acros) and 0.54g of 3-aminopropyl trimethoxysilane was added into this system at room temperature. This system is heated to 130°C for 2hr, and then the mixture was cooled to room temperature. The obtained ZnO nanocolumn film was washed three times with ethanol. To bound the CdSe nanoparticles on APS anchored ZnO for the preparation of CdSe-APS-ZnO heterostructure film on substrate, the TOPO capped CdSe nanoparticles (0.03g) were dispersed in 3ml of toluene and the APS modified ZnO film on substrate was immersed into the mixture and then stirred for 24hr. The produced CdSe-APS-ZnO film on substrate was washed three times with toluene to remove excess CdSe nanoparticles.

To prepare p-aminophenyl trimethoxysilane (APhS, Gelest) modified ZnO nanocolumns, the preparation method is similar to that of APS modified ZnO nanocolumns. A ZnO nanocolumn film on substrate ($0.5 \times 0.5\text{cm}^2$) was immersed in 6.0g of anhydrous DMSO (Acros) and then 0.64g of p-aminophenyl trimethoxysilane was added into the system at room temperature. The reaction is heated to 130°C for 2hr, and then the system was cooled to room temperature. The APhS modified ZnO nanocolumn film on substrate was washed three times with ethanol. To prepare CdSe-APhS-ZnO film on substrate, the TOPO capped CdSe nanoparticles (0.03g) were dispersed in 3ml of toluene and the APhS modified ZnO film on substrate was immersed into the mixture and then stirred for 24hr. The prepared CdSe-APhS-ZnO film on substrate was washed three times with toluene to remove excess CdSe nanoparticles.

For the photovoltaic device fabrication, the solution of P3HT in chloroform (30mg/ml) was cast onto the ZnO nanocolumn substrate at 750rpm, resulting $\sim 700\text{nm}$ thick films. Silver electrode was then thermal deposited on top of P3HT layer to accomplish the device. The device was then subsequently tested in the air under AM 1.5G ($100\text{mW}/\text{cm}^2$) simulated sunlight irradiation (Newport Corp.). The light intensity was calibrated with a standard silicon solar cell. The steady-state photoluminescence (PL) spectroscopy was gathered by exciting the samples with a continuous wave He-Cd laser (325nm). The study of the electrochemical impedance spectroscopy of the devices is performed with frequency ranging from 0.1m to 2 MHz under the application of dc voltage = 0.1 V and small ac voltage = 10mV (ZAHNER elektrik).

3. Results and discussion

Figure 1 depicts the surface modification procedures of ZnO nanocolumns. The fabrication of the CdSe quantum dot-linker-ZnO nanocolumn heterostructure follows the concept in the literature [23]. According to Fig. 1, the TOPO capped CdSe quantum dots is bound on the rod-shaped ZnO film. The first reaction of the ZnO nanocolumns with 3-aminopropyl trimethoxysilane (or p-aminophenyl trimethoxysilane) produces APS-bound ZnO columns (or APhS-bound ZnO columns), which in a subsequent reaction with TOPO-stabilized CdSe quantum dots in toluene. The symbols CdSe, ZnO, ZnO-APS-CdSe, and ZnO-APhS-CdSe used here represent TOPO capped CdSe quantum dots, ZnO nanocolumn film, APS as a linker between ZnO nanocolumns and CdSe quantum dots, and APhS as a linker between ZnO nanocolumns and CdSe quantum dots, respectively.

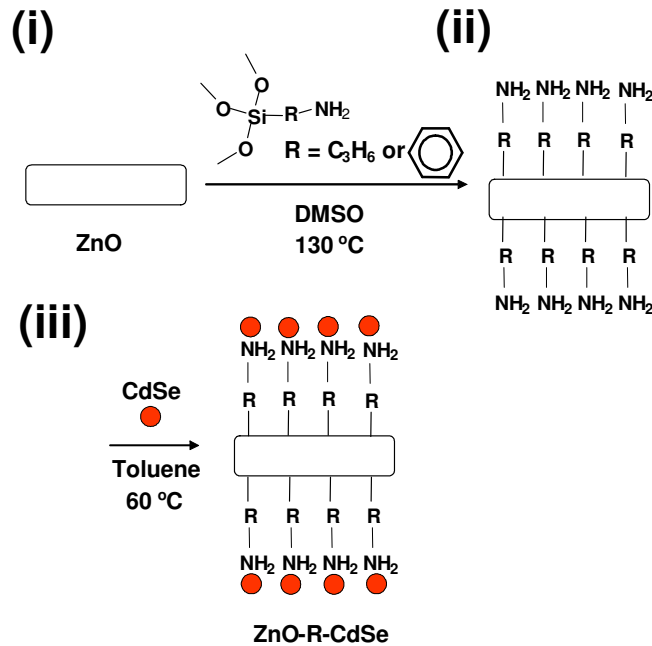


Fig. 1. Schematic illustration of the binding of CdSe quantum dots to ZnO nanocolumns by linker.

In the following, the ZnO nanocolumn-linker-CdSe quantum dot/P3HT photovoltaic devices have been made to study the influence of ZnO-CdSe interfacial properties on overall photo to electric conversion. Energy levels of CdSe, ZnO and P3HT are as shown in Fig. 2. The size quantization effect is expected to shift both the conduction band to a high potential value and the valence band to a low potential value as compared to bulk material. The increasing in the conducting band potential of CdSe quantum dot will increase the conducting band difference between ZnO nanocolumn and CdSe quantum dot leading to efficient electron transferring from CdSe quantum dots to ZnO nanocolumns. The P3HT has been chosen as the hole conductor and also an light absorber in producing CdSe quantum dots sensitized ZnO nanocolumns device owing to the suitable energy levels and outstanding hole mobility. The devices of ZnO-APS-CdSe/P3HT, ZnO-APhS-CdSe/P3HT and a control device of ZnO/P3HT were made.

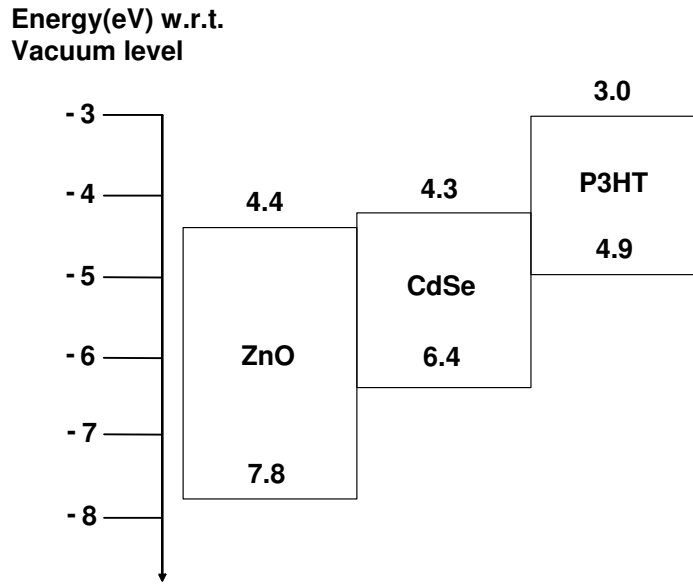


Fig. 2. Energy level diagram for a CdSe quantum dots coated ZnO nanocolumns with P3HT.

Figure 3(a) shows the effect of interfacial treatment on the current-voltage characteristics of ZnO nanocolumns/P3HT devices in dark. The inclusion of the linker-CdSe layer dramatically suppresses the dark current; a result which has been partially attributed to the presence of linker-CdSe can block possible shorting paths along the junctions, such as by minimizing the direct contact between P3HT and ITO through defect in the imperfect ZnO dense layer [13]. The surface modification at ZnO/P3HT interface may thereby reduce the shunt losses for photovoltaic devices under illumination.

Figure 3(b) displays the IV characteristics of the devices under simulated sun light irradiance. The type of linker between the CdSe and ZnO plays an important role in determining electron transfer rate and leads to distinct short circuit density and fill factor. As the CdSe layer is attached by APS, the short circuit current density (J_{SC}) in the device is about 40% of that attached by APhS which is resulted by the hindrance for electron forward induced by insulating aliphatic linker. Charge transfer across the $-(CH_2)_3-$ linkage is found less effective than across the aromatic ring in prior study [24].

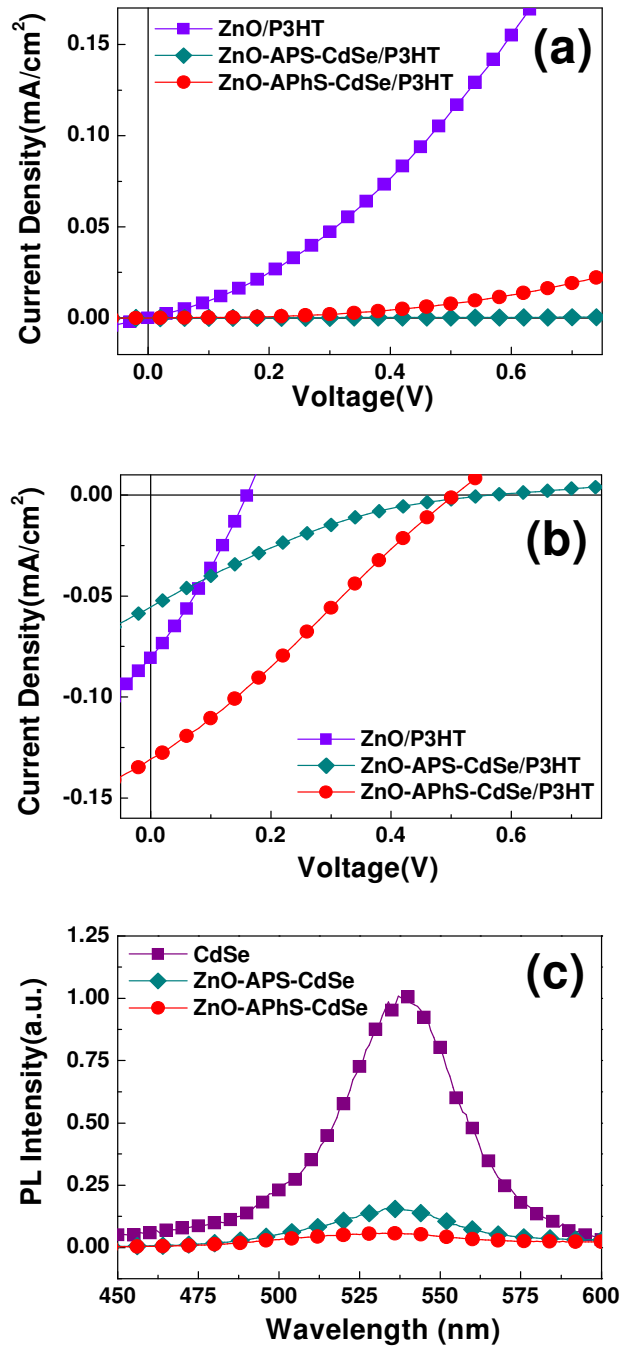


Fig. 3. Current density versus voltage of ITO/ZnO nanocolumn/P3HT/Ag without and with a CdSe quantum dot layer attached by APS or APhS at the ZnO nanocolumn/P3HT interface (a) in dark and (b) under illumination. (c) Photoluminescence spectra of CdSe-linker-ZnO as compared to CdSe thin film.

In the CdSe quantum dot sensitized TiO₂ mesoporous solar cell, the use of absorbed molecule affects the position of the conduction band of acceptor induced by molecular dipole

[18]. Similarly, in CdSe-linker-ZnO heterostructure, the linker may create additional energy offset between the conduction band of CdSe with respect to ZnO conduction band leading to different charge injection rate. The created energy diagram offset is induced by the absorbed molecular dipole. For further studies, varying the molecular structure and dipole moment of the linker can increase the offset, leads to increased driving force and photocurrent. Therefore, not only fine tuning the bandgap of quantum dot in such type cells is possible, using a variety of bifunctional linkers offers the possibility for fine tuning the energy diagram offset between the CdSe quantum dot and ZnO nanocolumn and making it easier to maximize this type photovoltaic cell power conversion efficiency.

The device with introduced the CdSe nanocrystals layer anchored by APhS exhibits 1.6 fold J_{SC} and 3.3 fold V_{OC} , as compared to the control cell in the ZnO/P3HT configuration which is attributed to the contribution from the retarded surface recombination, shunt losses and altered charge separation dynamics. The open circuit voltage is increased more than two times due to the CdSe layer blocking the possible shorting pathways along the junctions and lowering the interfacial charge recombination rate by separating the electron in the ZnO and hole in the P3HT physically. The charge separation is occurred at ZnO/CdSe and CdSe/P3HT interfaces instead of ZnO/P3HT. Our photoluminance (PL) measurements on the sample of CdSe-APhS-ZnO and CdSe-APS-ZnO show an effective PL quenching as compared to CdSe thin film as shown in Fig. 3(c). The amount of CdSe quantum dot in this thin film is equal to that in the samples of CdSe-linker-ZnO. This result indicates the exciton dissociation and charge transfer take place at CdSe-linker-ZnO. Thus the light absorption of the CdSe thin shell coated on ZnO can contribute to the photocurrent in the devices with CdSe layer.

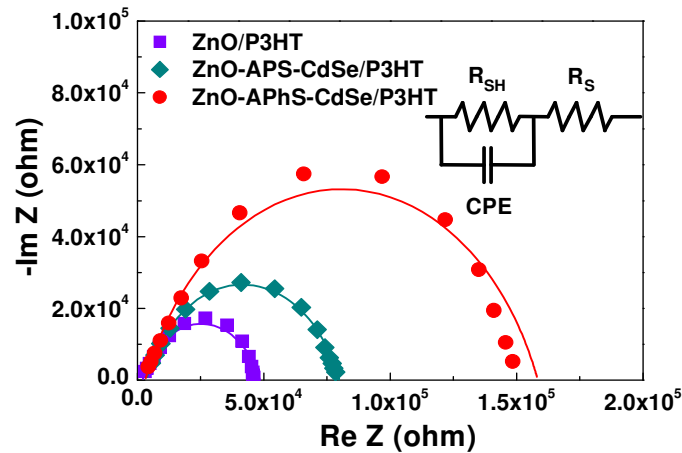


Fig. 4. The electrochemical impedance spectroscopy for the devices of ITO/ZnO nanocolumn/P3HT/Ag without and with a CdSe quantum dot layer attached with different linkers under illumination (the equivalent circuit is shown in the inset).

Through modification at ZnO nanocolumns, the shunt losses for ZnO/P3HT photovoltaic devices can be reduced as shown in the electrochemical impedance spectroscopy of the devices under illumination (Fig. 4). We fit the experimental data using the simplest equivalent circuit model [25]. With the capacitance component replaced by a constant phase element (CPE), which describes the porous and none ideal electrode surface. The shunt resistances (R_{SH}) extracted from the intercepts at the low frequency of the Nyquist plot are 4.6×10^4 , 7.6×10^5 , and 1.6×10^6 ohm for the reference device, APS-CdSe, and APhS-CdSe modified devices, respectively. In the modified devices, the increased shunt resistance is due to the reduction of electron-hole recombination at the interfaces. The device with APhS linker

possess lower interface recombination rate than the one with APS and the control device without CdSe layer.

4. Conclusions

The IV evaluation of ZnO nanocolumn based photovoltaic devices under irradiance demonstrates the key role played by the surface modifications of ZnO through attaching a CdSe layer. The CdSe layer can serve as a buffer layer [26,27] between the electron donor and acceptor phases. The types of linker that influence the charge transfer rate at the interface of ZnO and CdSe lead to distinct photo to electric conversion efficiency. Through attaching a thin layer of CdSe quantum dot by an aromatic linker, the device efficiency is about 4.8 folds of a ZnO nanocolumn/P3HT device.

Acknowledgments

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