

ENHANCING THE EFFICIENCY OF FTO/ZnO NANORODS/P3HT/Ag HYBRID SOLAR CELLS BY SENSITIZING CdS QUANTUM DOTS

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ABSTRACT

An improvement in the performance of the inverted organic solar cells based on zinc oxide/ poly(3-hexylthiophene)(ZnO/P3HT) is modified by deposited cadmium sulfide quantum dots (CdS QDs) were prepared via successive ionic-layer adsorption and reaction (SILAR) on ZnO nanorods (ZNRs). The size of CdS QDs on the ZNRs surface were controlled when the QDs were prepared from varied concentration of precursor solutions (0.01, 0.05 and 0.10) M using 5 SILAR cycles of deposition for 5 min in each solution. The results of photocurrent-voltage (I-V) measurement showed that CdS modification first can improve all photovoltaic parameters and increase the power conversion efficiency of the hybrid solar cells and then decreased as concentration of precursor solutions increased. A maximum power conversion efficiency (PCE) of 0.52% was obtained for the CdS QDs at the concentration 0.05 M, which was increased almost three times compared with the solar cell without using CdS QDs. Open circuit voltage (V_{oc}) and short circuit current (J_{sc}) improved with increasing concentration of precursor solutions up on 0.05 M, which can reduce charge carrier recombination in the interface between ZNRs and P3HT after deposit CdS QDs.

Keywords: Hybrid solar cells; ZnO nanorods; CdS quantum dots; P3HT; SILAR;

INTRODUCTION

A hybrid polymer solar cell is a promising photovoltaic technology due to its advantageous offering environmental stability, low-cost manufacturing and versatile applicability [1-3]. Inverted organic solar cells (IOSC) utilize the high electron mobility to overcome charge-transport limitations associated with organic devices. Zinc oxide

(ZnO) has been considered as a good semiconductor material for the IOSC due to its high electron mobility and the high chemical and thermal stability [4, 5]. ZnO nanorods (ZNRs) have some advantages for optoelectronic devices compared with ZnO bulk including the large surface area to significantly increase the junction area and the improved carrier confinement in one dimension. Various polymer/ZnO hybrid solar cells have been reported [1, 6], but the power conversion efficiencies (PCE) of these devices are still low and need to be improved [4, 7]. Moreover comparing to traditional dye sensitizers, semiconductor quantum dots (QDs) have been regarded as possible alternative sensitizers. Recently, many studies have reported that it is possible to utilize hot electrons to generate hole-electron pairs per photon due to depositing semiconductor QDs [3]. The deposition of QDs has been regarded to be of great promise in enhancing PCE of the IOSC. Various II-VI compound semiconductors used for QDs such as PbS, CdSe and CdS, where the CdS is the most common used as absorbers [5]. Among the advantages of QD as a light absorber is tunable energy gaps, the ability of multiple exciton generation, low fabrication cost, and high absorption coefficient [8, 9]. Chemical bath deposition (CBD) [10, 11] and successive ionic layer adsorption and reaction (SILAR) [12, 13] are the most common wet chemical approach used to deposit QDs. Among the two methods, SILAR technique consider an easy and effective method to deposit QDs [12, 14]. It has the advantage of depositing QDs with controlled size and volume by varying the parameters such as precursor concentration (cationic and anionic solution), number of deposition cycles, and duration time of deposition. Different parameters used appear to give different cell performances [15–17].

In this paper, we fabricated inverted organic solar cells (IOSC), ZNRs with a diameter of ~46 nm and a length of ~377 nm served as acceptor and poly (3-hexylthiophene) (P3HT) was spun-coating as a doner. CdS QDs were synthesized on the surface of ZNRs by the SILAR technique. We also focus on the relationships between the precursor concentration for CdS QDs and the solar cell performance.

EXPERIMENTAL

Materials

All chemicals and Materials used in our experiments (fluorine-doped tin oxide (FTO~7 Ω /sq), zinc acetate dehydrate ($Z(\text{CH}_3\text{COO})_2 \cdot (\text{H}_2\text{O})_2$), hexamethylenetetramine (HMT), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), diethanolamine (DEA), cadmium acetate dehydrate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) and poly (3-hexylthiophene) (P3HT)) were purchased from Sigma-Aldrich.

Preparation of ZnO Nanorods

Firstly the FTO glass substrate (~7 Ω /sq) cleaned with acetone and 2-propanol each for 18 min consecutively in tightly closed containers in ultrasonic. Next, it was placed in deionized water in ultrasonic for 15 min. The hot air was used for drying process. The sol-gel method was used in the seeding process, (DEA) was added to ethanol with stirring for 2 min by using a magnetic stirrer at room temperature of 26 °C. Then, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ was added to the mixture of DEA and ethanol with stirring on 400

rpm for 30 min at 60 °C . The solution was kept one day for stability. The solution was deposited on a previously cleaned FTO by the spin coating process at 3000 rpm for 30 Sec, this process was repeated three times and the samples were annealed at 300 C for 1 h in air. FTO substrate coated with the ZnO seed layer was placed vertically in an aqueous solution of 0.04 M ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and (HMT) at 90 °C for 45 min in a laboratory oven. Finally, the samples were removed from the aqueous solution, rinsed with deionized water and dried.

Preparation of CdS QDs.

The CdS QDs were deposited on ZNRs surface using the SILAR approach. For depositions CdS QDs appropriate cationic and anionic precursor solutions were prepared. ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) and Na_2S aqueous solution were used to prepare Precursor solutions. For the preparation of CdS QD, the ZNRs coated FTO glass was first dipped in ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) aqueous solution of different concentration for 5 min. This was followed by deionized water rinsing and drying before dipping into the same concentration of ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) aqueous solution for the same defined period. The process was completed with deionized water for rinsing and drying. The two steps dipping and rinsing processes are considered as one SILAR cycle. Finally, the sample was rinsed with ethanol and deionized water for 1 min and dried at (120 °C) and kept in ambient conditions for use. The amount of CdS can be increased according to the requirement of the experiment by repeating the number of cycles.

Device Fabrication.

Polymer (poly(3-hexylthiophene)(P3HT)) solution with concentrations of 35 mg/ml was prepared by dissolving in chlorobenzene followed by stirring in the dark for overnight at 40 °C, the solution must totally dissolve. P3HT was spin-coated onto the ZNRs with various concentrations of CdS QDs. A layer of P3HT was deposited on CdS/ZnO arrays by spin coating at (600 rpm for 45 s), followed by subsequent drying at (1000 rpm for 1 min) in a glove box. Finally, the Ag electrodes with a thickness of 100 nm were deposited without further heat treatment by using magnetron sputtering with an effective working area of 0.07 cm² through mask for each device.

Characterization.

Morphological properties of the ZNRs with various concentrations of CdS QD were characterized by field emission scanning electron microscope (FESEM, JEOL JSM-7600F). The optical absorption spectra of the samples were obtained in a range from 350 to 800 nm using UV–vis spectrometer (UV-1650PC Shimadzu). Photocurrent-voltage (I-V) characteristics of the devices were measured by using Keithley 237 source measurement unit under dark condition and under illumination at 100 mW cm⁻² from a solar simulator with AM 1.5G filter .

RESULTS AND DISCUSSION

In this study, CdS QDs have been sensitized via SILAR method on the surface of ZNRs. Three different precursor concentrations (0.01, 0.05, 0.10) M was used for both

anion and cation precursors to deposit CdS QDs. Figure 1(a-d) shows FESEM top view imaging for ZNRs without CdS QDs and CdS QDs deposition on ZNRs surface. ZNRs size appears to be a little larger compared to that in the pristine ZNRs Figure 1 (a). The morphology of nanorod remains constant and the ZNRs become rough covered with a number of small nanoparticles compared with the very smooth surface without CdS QDs, implying the formation of CdS onto the ZNRs surface. It can be observed that the diameters of the CdS QDs are changed with the increasing precursor concentration and some small dots can clearly be found on the surface of the ZNRs.

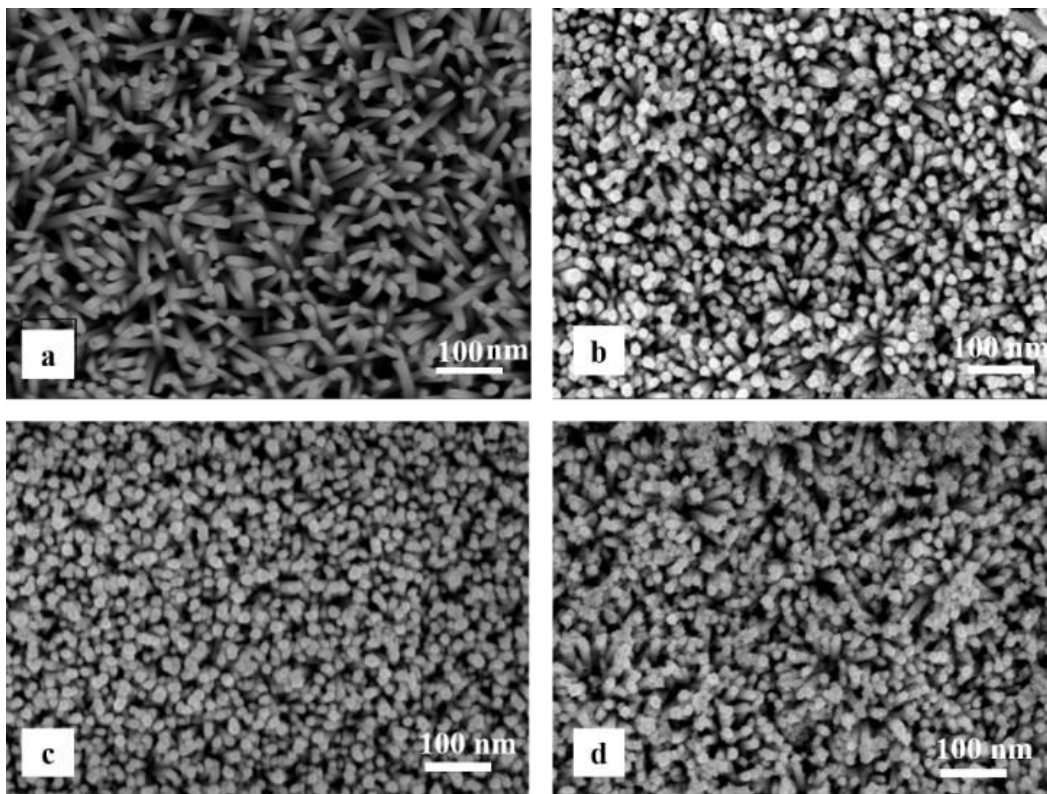


Figure 1: FESEM top-view images of the ZNRs /CdS QDs with different concentration (a) 0 M (b) 0.01 M (c) 0.05 M and (d) 0.10 M

Figure 2 shows the optical properties of ZNRs and ZNRs after coated with CdS QDs were measured by UV–Vis spectrophotometer in the wavelength range of 350-800 nm to evaluate the amount of the CdS incorporated with different precursor concentration on the FTO/ ZNRs. As shown in the Figure 2, FTO/ ZNRs can only absorb the wavelength shorter than 370 nm for the high energy light because of its large energy gap (3.6 eV). After the deposition of CdS QDs on ZNRs by SILAR, the absorbance of the wavelength in the region of 370– 520 nm increases with precursor concentration as expected.

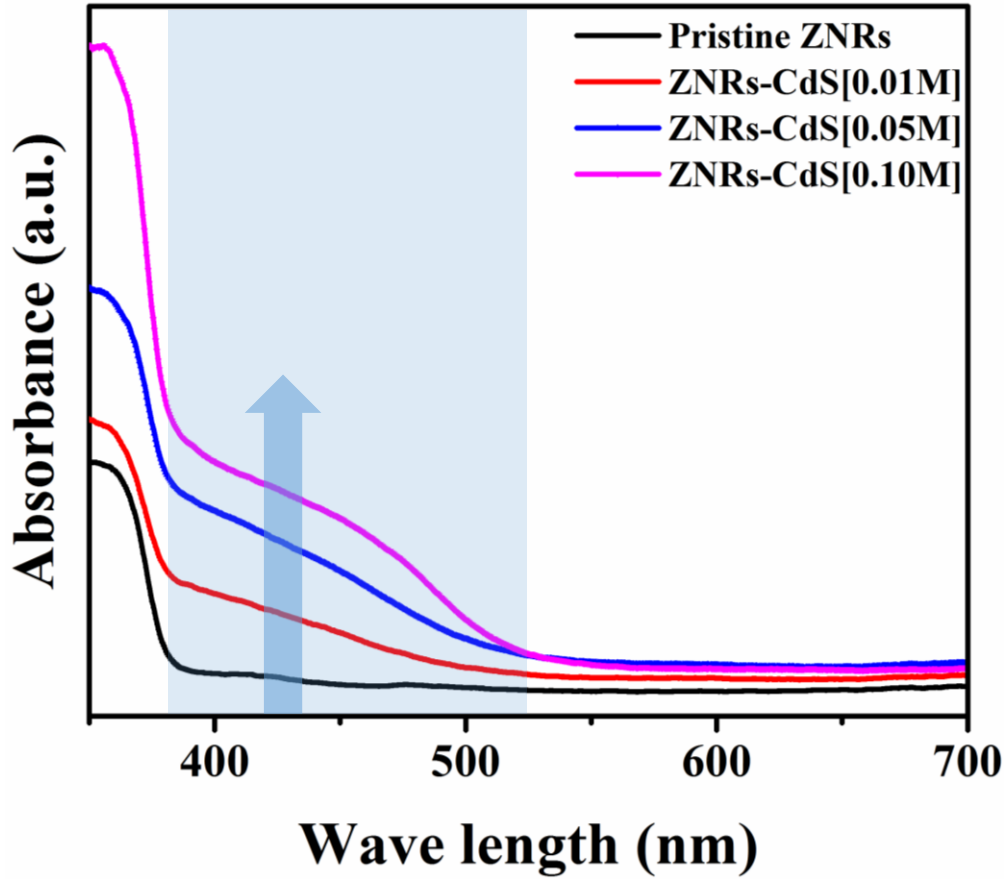


Figure 2: UV-Vis spectra for ZNRs /CdS QDs prepared using various precursor concentrations

The band gap energy of the QDs was estimated from Tauc plot, in which $(\alpha h\nu)^2$ against incident photon energy ($h\nu$) was plotted. Here α is the absorption coefficient, h is the Planck's constant, and ν is the frequency of the incident photon. Tauc plot for CdS QD/ZNRs with different CdS concentration is shown in Figure (3). According to Tauc equation [18, 19], it is suggested that the light absorption range of semiconductor is relative to its band gap (E_g) and the light absorption range will enlarge as E_g decreases. The band gap of CdS (about 2.4 eV) is narrower than that of ZnO (3.2 eV), and as a result, the ZnO/CdS electrodes absorb a wider light range after the deposition of CdS on ZNRs.

According to quantum size effect [20], the increase in grain size results in the decrease in band gap. Consequently, the electrons require lower energy to excite from the valence band to the conduction band, which results in the red-shift in UV-vis absorption spectra. This is similar to the results as other reported [21, 22]. The band gap energy of the CdS QDs is obtained by extrapolating the straight line portion of the horizontal axis. The higher sized QD particle can be obtained with a higher precursor concentration due to decrease the band gap energy as the increase of precursor concentration.

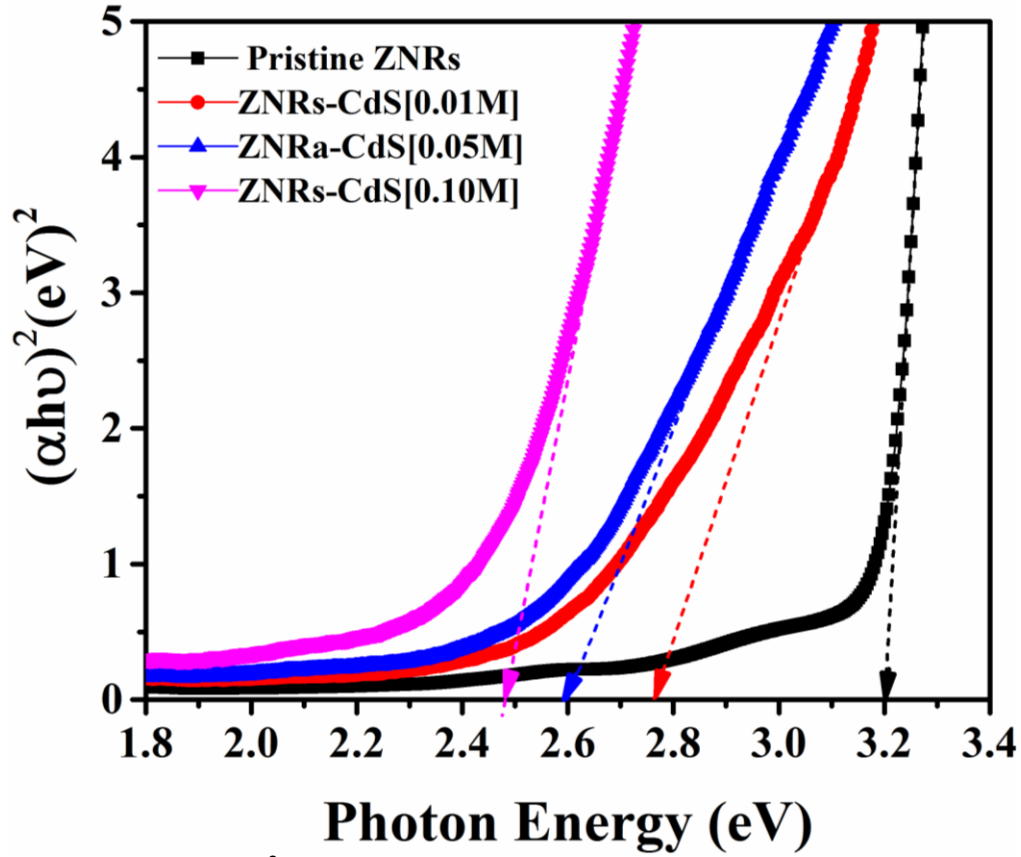


Figure 3: Plot of $(\alpha h\nu)^2$ versus photon energy for ZNRs /CdS QDs with varying precursor concentrations

The size of the QDs can be estimated using the following Eq. [23-26]:

$$\Delta E = E_1 - E_g = \left(\frac{h^2}{8r^2} \right) \left(\frac{1}{m_e} + \frac{1}{m_h} \right) \quad (1)$$

where ΔE is the band gap energy shift, E_1 is the band gap of the QD, E_g is the band gap of the bulk materials, r is the radius of the QD, h is the Plank's constant, and m_e and m_h are the effective masses of electron and hole, respectively. For CdS material, $m_e = 0.18m_o$, $m_h = 0.53(m_o = 9.11 \times 10^{-31} \text{ kg})$, and $E_g = 2.4 \text{ eV}$ [27, 28]. Generally, in crystals, as the grain size increases, the band gap energy is reduced. Table 1 summarizes the band gap energy and diameters of QDs together with the corresponding cell performance parameters.

Table 1: The energy gap, estimated QDs Diameter and IOSC performance parameters for CdS QDs prepared using different precursor concentrations

Precursor Concentration [M]	QD band gap [eV]	Estimated QD diameter [nm]	J_{sc} [mA/cm ²]	V_{oc} [V]	FF [%]	PCE [%]
0	3.2	-	0.75	0.44	0.47	0.16
0.01	2.77	5.48	1.74	0.46	0.48	0.38
0.05	2.61	7.26	2.3	0.48	0.47	0.52
0.10	2.48	11.73	2.1	0.48	0.45	0.45

Figure (4) shows the I-V curves for inverted organic solar cells (IOSC) fabricated with different precursor concentration of CdS QDs. The solar cell parameters obtained from these curves are listed in Table 1. In addition, the energy band gaps and the estimated diameters of the QDs are listed in this Table. It is interesting to note that the device with a higher precursor concentration of CdS QD does not show the highest cell efficiency. The highest efficiency (0.52%) is obtained at the 0.05 M precursor concentration of CdS QDs. Moreover, the diameter of the QDs is 7.26 nm at the same concentration (0.05 M) which is estimated from Eq (1). When the precursor concentration is high, a large number of QD are formed on the ZNRs. Therefore, more QDs particles are produced [28] and it is suspected that the efficiency is limited due to the aggregating of QDs on the top part of the ZNRs [28, 29]. As a result, QDs deposition will continue to form on the top surface only and the easy electron transfer from QD to the ZNRs surface will be obstructed, leading to the low current generation and hence low efficiency. Fill factor of the devices does not change much with various concentrations as it depends on the resistance of the cell.

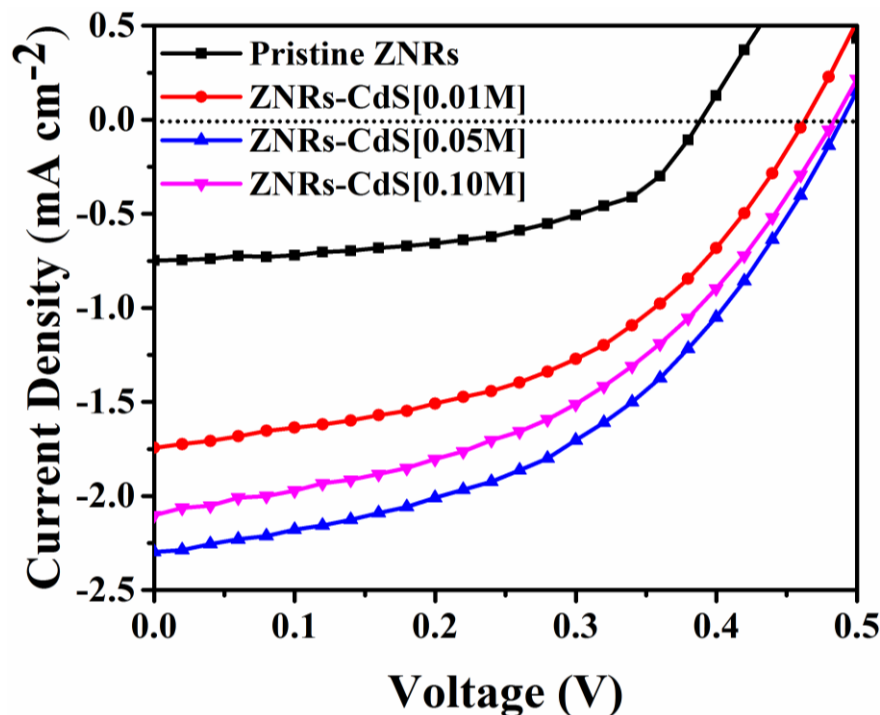


Figure 4: J–V curves of the devices for ZNRs /CdS QDs with different concentrations under illumination

Based on the results listed in Table 1, the most efficient inverted organic solar cells can be fabricated with 0.05M precursor concentration for CdS QDs using 5 cycles with a 5min duration for deposition in each solution.

CONCLUSIONS

In Summary, Inverted organic solar cells (IOSC) based on P3HT and ZNRs have been fabricated. ZNRs were modified with CdS QDs deposited by SILAR technique. The performance of the IOSC was dependent on the different precursor concentration of CdS QDs. The power conversion efficiency (PCE) of the devices was improved from 0.16 to 0.55% after the CdS QDs modification at the optimized fabrication condition. The performance of the devices first increased and then decreased as the precursor concentration increased. When the number of dipping cycles was 5 cycles, the ZNRAs /CdS QDs showed maximum J_{sc} and V_{oc} value than those without CdS deposition. The corresponding estimated QD diameter size for CdS QD is 7.44 nm. To obtain the best performance in IOSC, CdS QDs must be deposited from a precursor concentration of 0.05 M using 5 SILAR cycles with 5min duration of deposition in each solution.

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