

HARVESTING LIGHT ENERGY WITH CdSe/ CdSe (SILAR) /ZnS (SILAR) NANOCRYSTALS MOLECULARLY LINKED TO MESOSCOPIC TiO₂ FILMS FOR QUANTUM DOT SOLAR CELLS

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Abstract: On paper, we have prepared TiO₂/MPA/CdSe/ZnS by Successive ionic layer adsorption and reaction (SILAR). The results show that a significant improvement of the light to electric power conversion efficiency of quantum dot sensitized solar cells with a polysulfide electrolyte which can be achieved as using bi functional surface modifiers (SH-R-COOH, Mercaptopropionic acid (MPA)). The injected charge carriers in a CdSe-modified TiO₂/MPA film can be collected at a conducting electrode to generate a photocurrent. The TiO₂/MPA/CdSe/ZnS composite, employed as a photo anode in a photo electrochemical cell, exhibits a photon to charge carrier generation efficiency η , the short circuit current J_{SC} , open circuit voltage V_{OC} , and fill factor FF correspond to 0.909 %, 6.67 mA/cm², 0.43 V, 0.31.

Keywords: Defect states, Solar cell, SILAR.

I. INTRODUCTION

There are many methods which have been employed to synthesize semiconductor quantum dots (QDs) in recent years. These methods include the reverse micelle [4], epitaxial, colloidal, hydrothermal [2,3]. to depend on the aims of the different applications. The quantum dots have shown potential applications in thin film light emitting devices (LED), nonlinear optical devices, fluorescent labels for biological applications, solar cells, displays, sensors or biosensors, lasers. A large of number of high quality quantum dots as such CdS, CdSe, CdTe were successfully synthesized.

In this paper, CdSe QDs and TiO₂/CdSe films have been prepared via a colloidal route using Mercaptoethanol (Thioglycol) as a capping agent. We have successfully fabricated the CdSe QDs and TiO₂/CdSe thin films by dipping technology. We researched optical characteristic of CdSe QDs and TiO₂/CdSe films for the application in the solar cell. Dye sensitized solar cell bases wide band gap semiconductors have the potential advantages of lower cost production and versatility in comparison to the conventional solid state cells. We have prepared CdSe/ZnS thin films by using chemical bath deposition (CBD). Results expand the photo response range of TiO₂ meso porous from ultraviolet region to visible range to study the effects of co modification by CdS, CdSe and ZnS QDs on the photovoltaic response of TiO₂ meso porous-based QDSSC.

Highly ordered TiO₂ meso porous were fabricated by electrochemical anodization. The TiO₂ meso porous were treated by CBD of CdSe and ZnS QDs and were used as photo anodes in QDSSC. We demonstrated that the co-modified TiO₂ mesoporous possess superior photovoltaic response compared to the single QD sensitized devices, and the final TiO₂/MPA/CdSe/ZnS photo anode leads to high efficiency QDSSCs.

II. EXPERIMENT

Materials. Cd(CH₃COO)₂·2H₂O (99%), Dimethyl formamide (DMF) C₃H₇NO (99%), Mercaptoethanol (Thioglycol) HOCH₂CH₂SH (99%), Sodium selenite pentahydrate Na₂SeO₃·5H₂O (98%), acetone, obtained from Merck, Mercaptopropionic 99%, Merck. TiO₂ paste obtained from Merck.

Preparation of TiO₂ films: TiO₂ thin films were fabricated by printed silk with TiO₂ paste commercial with size from 10nm to 20nm. Film were printed one layer with thickness of 2 μ m (measured by Alpha step unit device). Then, It was heated by the process: TiO₂ film was heated at 325°C for 5min, at 375°C for 5min, at 400°C for 15min, at 500°C for 15min and dipped in solution TiCl₄ 40mmol for 30min at 70°C, and final were heated at 500°C for 30min.

Preparation of TiO₂/MPA/CdSe films: Mixture TiO₂ was dipped in a solution of (MPA 5ml +50 ml acetone) at 100°C during 4hours. After it was washed three times with acetone, and was brought outside to dry naturally. Continue dipping in the solution CdSe with different time periods to change the thickness of the film. Then, it takes three times to wash in solvent acetone. Finally, it was heated in a vacuum environment with different temperatures to avoid oxidation.

Preparation of TiO₂/MPA/CdSe/ZnS films: The highly ordered TiO₂/MPA/CdSe were sequentially sensitized with CdSe and ZnS QDs by using CBD. First, the CBD process of CdSe QDs, Se aqueous solution was prepared by mixing Se powder and Na₂SO₃ in 50ml pure water, after adding NaOH 1M at 70°C for 7h. In the CBD process of CdSe QDs, the TiO₂/MPA/CdSe samples were first dipped into 0.5M Cd(CH₃COO)₂ ethanol solution for 5min at room temperature, rinsed with ethanol, and then dipped into a Se aqueous solution for 5min at 50°C and rinsed again with pure

Publication History

Manuscript Received : 14 December 2014
Manuscript Accepted : 24 December 2014
Revision Received : 28 December 2014
Manuscript Published : 31 December 2014

water. The two-step dipping procedure is termed as one CBD cycle. Repeating the CBD cycle would increase the amount of CdSe QDs (a total of four cycles). The CBD method was also used to deposit the ZnS passivation layer. The TiO₂/MPA/CdSe/CdSe (SILAR) samples were coated with ZnS by twice dipping alternately into 0.1M Zn(NO₃)₂ and 0.1M Na₂S solutions for 5min/dip, rinsing with pure water between dips (a total of two cycles). Finally, it was heated in a vacuum environment with different temperatures to avoid oxidation.

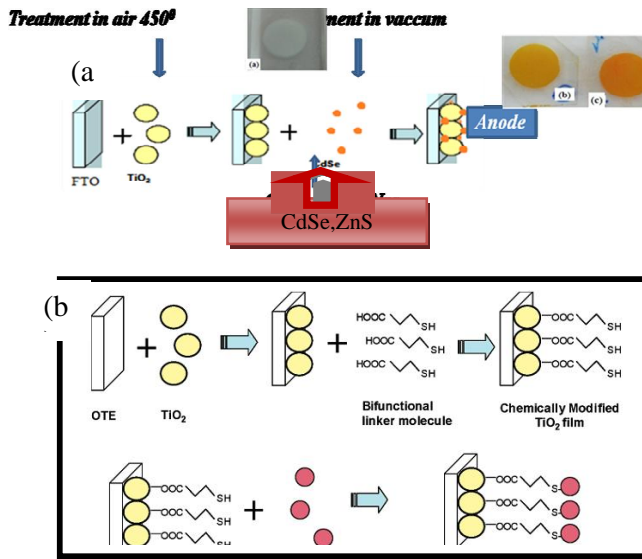


Figure 1. The diagram shows the process to prepare (a) the TiO₂/CdSe/ZnS and (b) TiO₂/MPA/CdSe/ZnS photo anode.

3. RESULTS AND DISCUSSION

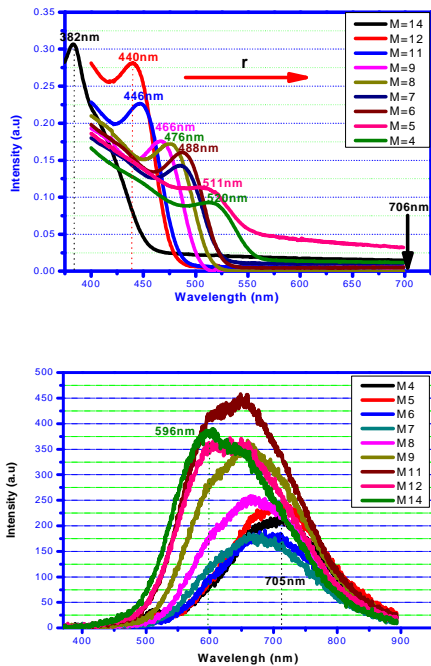


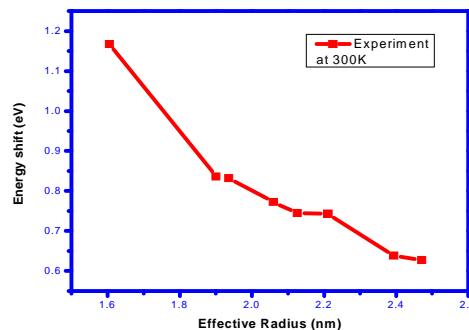
Figure 2. Shows the absorption (left) and Photoluminescence spectra (right) of CdSe QDs corresponding M=4, 5,6,7,8,9,11,12,14.

Figure 2 (left) shows the absorption spectra of CdSe QDs with the different values M (M = Cd²⁺/thioglycol), all samples are shown effects quantum that is very strong, the peak of the absorption spectrum changed from 382nm to 520nm corresponding size particle changed from 1.6nm to 2.5nm (shows in Table 1) smaller than the radius of Borh (a_B = 5nm of CdSe bulk material) is calculated by the approximate equation [16]. Related to the shift in color from light yellow to dark red. Therefore, the results obtained with CdSe QDs are applied model strong confinement quantum (R < a_B) [15]. The organic molecules -thiol- group limited interaction between the QDs CdSe and therefore reducing link between the QDs together, QDs stabilized because the electric charge moved from the QDs to ligand field [Sachleben 1998]. During this process we have chosen thioglycol, it enveloped the QDs CdSe when the newly formed. When M values increasing, the thioglycol less envelopment than so the particle size increases correspond with the shift peak absorption of light toward the red (the color change to red). Peak of absorption spectra of the samples was attributed to the shift that is due to shift between the two basic exciton 1S_{3/2}-1S_e [16].

Table 1. Describes the change of the particle size on the concentrate of M.

Sample	λ (nm)	E _g ^{eff} (ev)	R (nm)
M=4	520	2.384	2.471
M=5	511	2.426	2.393
M=6	488	2.540	2.211
M=7	488	2.540	2.211
M=8	476	2.605	2.126
M=9	466	2.660	2.060
M=11	446	2.780	1.936
M=12	440	2.818	1.901
M=14	428	3.246	1.605

Figure 3 shows the difference in energy between the two absorption spectrum and the PL spectrum of the same. An energy shift change from 0.6eV to 1.2eV corresponds to the change of the effective radius from 1.6nm to 2.5nm. Due to existence of the surface states in CdSe quantum dots. The state is the main surface defect inside the QDs, resulting in recombination with electrons. When electrons receive excitation energy from the valence to conductor band and then returned immediately recombination with state surface inside the energy gap of CdSe QDs.



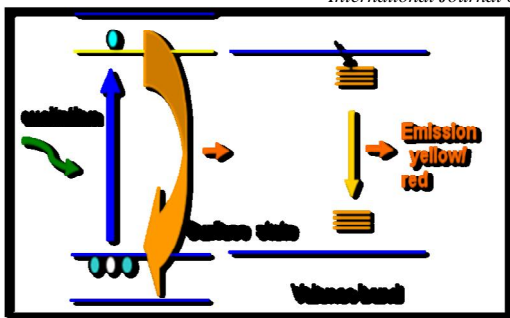


Fig. 3. Shows the energy shift of CdSe at 300K to depend on effective radius (left) and diagram shows the surface states in CdSe QDs.

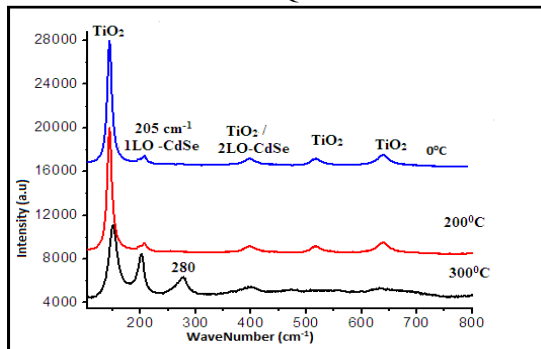


Figure 4. Raman spectrum of TiO₂/CdSe thin films at different temperature.

In the Raman spectrum, there are three peaks at 201cm⁻¹, 402cm⁻¹ and 601cm⁻¹. These are the peaks corresponding to the phonon of longitudinal optical vibration in CdSe, the first lies at 201cm⁻¹ (longitudinal optical - LO), the second at 402cm⁻¹ is the second harmonic of the first peak (2LO), the third at 601cm⁻¹ is the third harmonic of the first peak (3LO). Origin of branch LO and the interactions between photons with surfaces of CdSe QDs depend on the size of electron-hole pair interaction. Each peak is asymmetrical tends to stretch toward the low frequency, which is attributed to the surface vibration. Blue-shifted were also seen in the two peaks LO and 2LO at 201cm⁻¹ and 402cm⁻¹ of CdSe powder in comparing with the peaks 210cm⁻¹ and 418cm⁻¹ [2] of CdSe bulk. The red-shifted proved that CdSe QDs, with high ratio area/volume, were created in the sample. Raman spectra of TiO₂/CdSe thin films at different temperatures, show both anatase of TiO₂ and a zinc blend of CdSe structure.

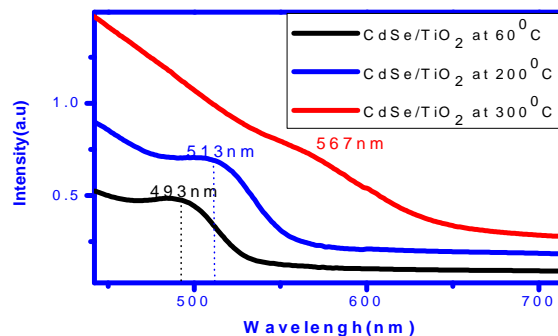
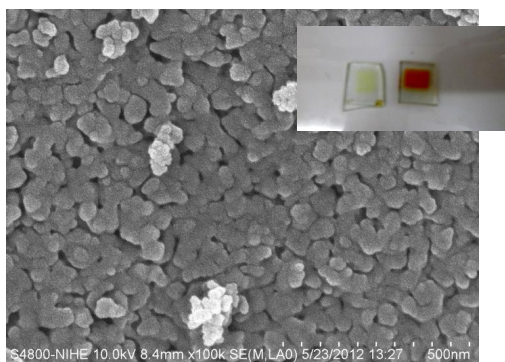


Fig. 5. Image FE-SEM and the absorption spectrum of TiO₂/CdSe photo anode.

Image FE-SEM of CdSe/TiO₂ anode films with pH ~10, deposition was carried out for 24h at room temperature. Growth of CdSe, white TiO₂ film electrode became red in color after annealing 300°C was homogeneous and strongly adherent to the substrate. Fig.5 shows the surface morphologies of porous TiO₂/CdSe the film is smooth and uniform with equally distributed nanometer sized grains. In the absorption spectrum of self-grown CdSe porous TiO₂ film, there is a considerable red-shift with respect to the porous TiO₂, confirming the invasion of CdSe self-grown nanoparticles. As annealing temperature increases to 300°C, CdSe nano crystals increase in size. But size distribution also increases.

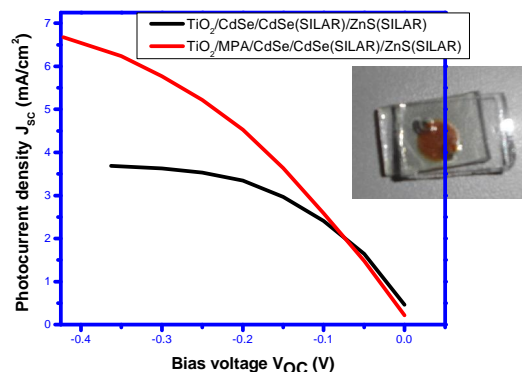


Figure 6. J–V curves of the samples solar cell with TiO₂/CdSe/CdSe (SILAR) /ZnS (SILAR) and TiO₂/MPA/CdSe/CdSe (SILAR) /ZnS (SILAR) anode.

Table 3. Photovoltaic parameters of solar cell with TiO₂/CdSe/CdSe (SILAR)/ZnS (SILAR) and TiO₂/MPA/CdSe/CdSe (SILAR) /ZnS (SILAR) anode.

Sample	TiO ₂ /CdSe/CdSe (SILAR)/ZnS(SILAR)	TiO ₂ /MPA/CdSe/CdSe (SILAR)/ZnS(SILAR)
J _{sc} (mA/cm ²)	3.689	6.676
V _{oc} (V)	0.388	0.43
Fill factor	0.422	0.314
Efficiency	0.603	0.91
η(%)		

A relative energy level of different components is shown in Fig. 7 (a). According to the data reported in the

literatures [11,12], the band gap of TiO_2 (3.2eV) limits its absorption range below the wavelength of about 400nm. CdSe has a higher conduction band (CB) edge than TiO_2 , which is favorable for electron injection. However, with a band gap of 1.7eV, the absorption of bulk CdSe is also limited below approximately 760nm. The conduction band of CdSe is slightly lower than that of TiO_2 , so the electrons would flow from CdSe to TiO_2 [13]. In addition, we have coated two layers ZnS QDs, which could be attributed to several reasons. First, as the absorption edge of ZnS is at about 345nm, a higher absorption can be obtained due to the complement of the absorption spectrum of the ZnS with that of the CdSe and CdS QDs. Second, ZnS acts as a passivation layer to protect the CdS and CdSe QDs from photocorrosion. Thus, the photoexcited electrons can efficiently transfer into the conduction band of TiO_2 . Third, the outer ZnS layer can also be considered to be a potential barrier between the interface of QDs materials and the electrolyte. ZnS has a very wide band gap of 3.6eV, it is much wider than that on the CdS and CdSe QDs. As a result, the leakage of electrons from the CdSe and ZnS QDs into the electrolyte can be inhibited. As a result, an ideal model for the cosensitized TiO_2 electrode is shown in Fig. 7 (b). After the CdSe and ZnS QDs are sequentially deposited onto a TiO_2 film, A cascade type energy band structure is constructed for the cosensitized photoanode. The best electron transport path is from the conduction band of ZnS and finally reaching the conduction band of TiO_2 . Meanwhile, this stepwise structure is also favorable for the hole transport. As a result, an efficiency is obtained on the $\text{TiO}_2/\text{CdS}/\text{CdSe}/\text{ZnS}$ (SILAR) /ZnS (SILAR) electrode of 0.603101%. To improve the significantly photoresponse, we have capped TiO_2 and quantum dots by MPA. As a result, a higher efficiency is obtained on the $\text{TiO}_2/\text{MPA}/\text{CdSe}/\text{CdS}$ (SILAR) /ZnS (SILAR) electrode of 0.909 %. This would decrease significant loss of electrons occurs due to scattering as well as charge recombination at TiO_2/CdSe interfaces and internal TiO_2 grain boundaries.

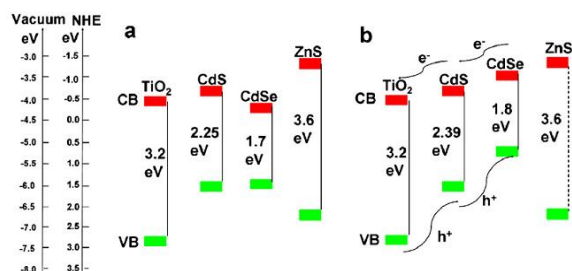


Figure 7. (a) Relative energy levels of TiO_2 , CdS, CdSe and ZnS in bulk phase, (b) the proposed energy band structure of the $\text{TiO}_2/\text{CdS}/\text{CdSe}/\text{ZnS}$ nanostructure interface. All the energy levels are referenced to NHE scale. CB and VB are conduction band and valence band [11,12].

III. CONCLUSIONS

We have successfully fabricated solar cells based on the photo anodes which is sequentially modified by CdSe and ZnS QDs. The co-sensitized electrode exhibited significantly improved photo response compared to the single type QDs sensitized electrodes, including both expanded spectral response range and enhanced efficiency performance. Such improvement is mainly attributed to the overlap of the absorption spectra of the different materials and the

formation of an ideal stepwise band structure which is advantageous to the transport of excited electrons and holes across the composite electrode. The resulted $\text{TiO}_2/\text{MPA}/\text{CdSe}/\text{CdS}$ (SILAR) /ZnS (SILAR) photo anode exhibits a maximum efficiency value of 0.909 % compared with $\text{TiO}_2/\text{CdSe}/\text{CdS}$ (SILAR) /ZnS (SILAR) anode is 0.603 %.

ACKNOWLEDGMENTS

This work was supported by Dong Thap University.

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