Expanding the photoresponse range of TiO_2 nano by CdS/CdSe/ZnS quantum dots co-modification

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ABSTRACT.

In this work, the CdS and CdSe QDs modification expands the photoresponse range of TiO_2 nanoparticles from ultraviolet region to visible range. It is demonstrated that sequentially assembled CdS and CdSe QDs significantly improved the light harvesting ability and photocurrent efficiency, and a high incident photon to current conversion efficiency of 1.52 % was obtained. Further coating the TiO_2/CdS/CdSe electrodes with a barrier layer of ZnS QDs increases the efficiency to 264 %.

***Keyword**: passivation, solar cells, quantum dots.*

INTRODUCTION

Recently, the scientists in the world have interested in the quantum dots solar cells (QDSSCs) based on the TiO_2 subtrate. The QDSSCs based on the QDs have more advantages than the Dye sensitized solar cells (DSSCs) based on the molecules for some reasons: (1) the molecules only absorb the light in visible, (2) and are unstable in the air enviromental. Beside the disadvantages of the moleccules, the QDs has some advantages such as quantum confinement effect, the higher coefficients than the dyes, the generation of multiple electron – hole pairs by a single incident photon [1-2]. Moreover, the tunable adsorption band of the QDs can be perform by the changed their size for the light harvesters in QDSSCs [3].

For those reasons, the QDSSCs were promised to become the candidate for the high efficiency. Firstly, Vogel and colleagues prepared the QDSSCs based on CdS QDs and obtained the low efficiency [4]. In 2008, many scientists only studied the single QDs as CdS, CdSe, PbS… for the application in the QDSSCs. Therefore, the results obtained the low efficiency. For the next years, the series articles focus on the improving efficiency of the QDSSCs with the subject such as: to improve the adsorption of the photoanodes [5], [6]; to use the different methods such as chemical bath deposition (CBD), successive ionic layer adsorption and reaction (SILAR)... [7]; to apply the core – shell QDs to reduce the surface states in the QDs [8]. However, the efficiency of the QDSSCs was still lower than the efficiency of the DSSCs at the present due to the high surface states at the TiO_2/QDs contact and the large diffusion resistance in the TiO_2 film.

In this work, the CdS and CdSe QDs modification expands the photoresponse range of TiO_2 nanoparticles from ultraviolet region to visible range. It is demonstrated that sequentially assembled CdS and CdSe QDs significantly improved the light harvesting ability and photocurrent efficiency, and a high incident photon to current conversion efficiency of 1.52 % was obtained. Further coating the TiO_2/CdS/CdSe electrodes with a barrier layer of ZnS QDs increases the efficiency to 264 %.

EXPERIMENT

The films were coated with TiO_2 layers by silk-screen printing, and were then annealed at 500°C for 30 minutes. Their sizes ranged from 10 nm to 30 nm. The thickness of the TiO_2 films was approximately 4 µm, as measured by a stylus. Then,

the films were dipped in 40 mmol $TiCl_4$ solution for 30 minutes at 70°C and sintered at 500°C for 30 minutes.

TiO_2/CdS/CdSe/ZnS films were synthesized using the SILAR and colloidal synthesis methods. First, the TiO_2 film was dipped in 0.5 M Cd^{2+}-ethanol solution for 1 minute and rinsed with ethanol. Then, the film was dipped for 1 minute in 0.5 M S^{2-}-methanol solution and rinsed with methanol after being dried in air (a SILAR cycle). The number of CdS QDs increased by repeating the assembly cycles with three cycles. Second, the TiO_2/CdS assembly was immersed in CdSe solution (size ~3 nm) for 20 hours before being dried at room temperature. For the ZnS passivation layers, TiO_2/CdS/CdSe photoanodes were dipped into 0.1 M Zn^{2+} and 0.1 M S^{2-}-solutions for 1 minute and rinsed with pure water between the two dips (a total of two cycles). Finally, the films were annealed in a vacuum environment at 300°C to prevent oxidation. The TiO_2/CdS/CdSe/ZnS thickness was measured using a stylus. The average thickness of CdS (3 cycles), CdSe (20 hours), and ZnS (2 cycles) were 351.9 nm, 80 nm and 257.8 nm respectively.

Fabrication of QDSSCs

The structure of the QDSSCs was designed using a Surlyn between the photoanodes and counter electrodes at 170°C. The electrolyte was filled from a hole made on the counter electrode. The active area of the QDSSCs was 0.38 cm^2. The polysulfide electrolyte consisted of 0.5 M Na_2S, 0.2 M S and 0.2 M KCl in Milli-Q ultrapure water/methanol (7:3 by volume).

Characterization

The morphologies of the samples were investigated using transmission electron microscopy (TEM). The crystal structure was analyzed using an X-ray diffractometer (Philips, PANalytical X'Pert, CuKα radiation). The absorption properties of the samples were investigated using a diffuse reflectance UV–vis spectrometer (JASCO V-670). Photocurrent – voltage measurements were performed on a Keithley 2400 source meter using a simulated AM 1.5 sunlight with an output power of 100 mW/cm^2 produced by a solar simulator (Solarena, Sweden).

RESULTS AND DISCUSSIONS

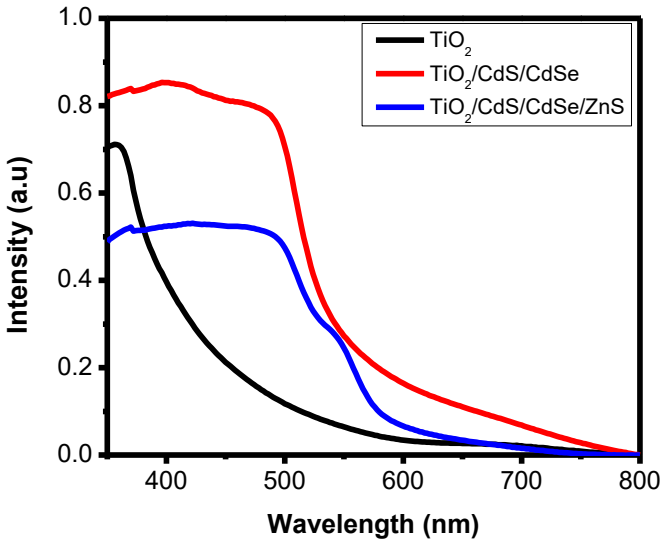

Figure 1. The UV-Vis of the TiO_2/CdSe photoanodes.

The optical properties of the three electrodes are studied by their UV–vis absorption spectra. The absorption edge, obtained from the intersection of the sharply decreasing region of a spectrum with its baseline, of the as prepared TiO_2 films extended to around 380 nm (Figure 1), corresponding to a band gap of 3.2 eV of anatase TiO_2. The absorption edges locate at 500 nm for the TiO_2/CdS, and 550 nm for the TiO_2/CdS/CdSe/ZnS electrodes. These band gaps are wider than the values reported for bulk CdS and CdSe (2.25 and 1.7 eV, respectively), which could be attributed to the quantum confinement effect of the QDs. The absorbance of the co-sensitized TiO_2/CdS/CdSe film is higher than that of either the the TiO_2/CdSe film, which result is reproducible under carefully Figure 1. The enhanced absorption is likely indicating that the TiO_2/CdS/CdSe have complementary and enhancement effects due to the wider absorption of CdSe and the good charge transport mobility of CdS. After coating a layer of ZnS shell, the absorption is sharply increased and a red shift of the absorption edge is observed, which is similar to the previous observation on the CdSe/ZnS core-shell structure.

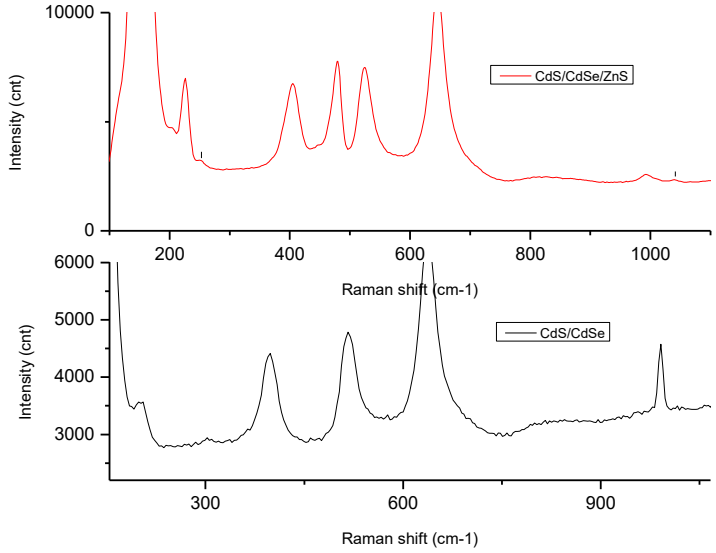

Figure 2. The Raman of the TiO_2/CdSe photoanodes.

The Raman of the photoanodes have been investigated by us to determine the structural materials. From the Raman (Figure 1), we noted that the TiO_2 structure is Anatase correspond to the E_g mode at 134 cm^{-1}. In addition, we also noted the

three 201, 395 và 515 cm^{-1} modes correspond to the CdS, CdSe cubic. The results show that CdS, CdSe QDs deposited on the TiO_2 subtrate.

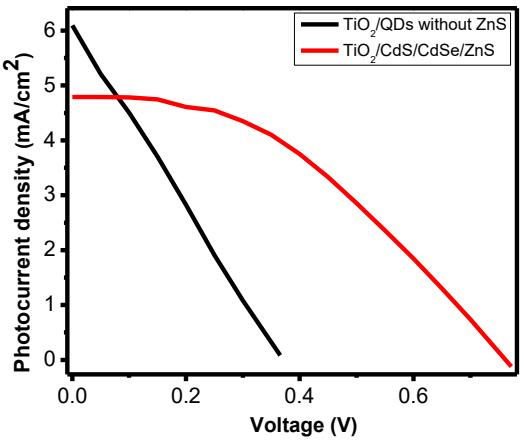

Figure 3. The I-V curves of the QDSSCs.

Table 1. The parameters of the QDSSCs obtained to the I-V curves

No	QDSSCs	R_S (Ω)	R_{ct2} (Ω)	R_{ct1} (Ω)	Efficiency η(%)
1	TiO_2/CdSe	6.04	0.35	0.255	0.575
2	TiO_2/CdS/CdSe/ZnS	4.79	0.76	0.41	1.52

For determined the effect of the ZnS passivation on the performance efficiency, we investigated to the I-V curves of the QDSSCs based on the different photoanodes. The Figure 3(b) shows the I-V curves of the QDSSCs with the different photoanodes. The QDSSCs based on the TiO_2/CdS/CdSe/ZnS photoanode were determined to open circuit (V_{OC}) of 0.76 V, short current (J_{SC}) of 4.79 mA/cm^2, fill factor of 0.41 and efficiency (**η**) of 1.52 %. The result agree well with the UV-Viss. The obtained performance efficiency were low when the QDSSCs based on the photoanodes without ZnS passivation layers. To explain for the reason, we noted that the QDs with ZnS passivation reduced the recombination processes at the QDs surfaces.

CONCLUSIONS

The QDSSCs based on the TiO_2/CdS/CdSe/ZnS photoanodes have successfully prepared. It is demonstrated that sequentially assembled CdS and CdSe QDs significantly improved the light harvesting ability and photocurrent efficiency, and a high incident photon to current conversion efficiency of 1.52 % was obtained.

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REFERENCES

1. Nozik, A, J (2005), Exciton Multiplication and Relaxation Dynamics in Quantum Dots: Applications to Ultrahigh-Efficiency Solar Photon Conversion. *Inorg. Chem. 44*, 6893-6899.
2. Wu. Jiang, Wang. Zhiming M. (2014), Quantum Dot Solar Cells. *Springer-Verlag New York*, Volume 15.
3. Guyot-Sionnest, P (2008), Colloidal Quantum Dots. *C. R. Physique*. *9*, 77-787.
4. Vogel R, Pohl K, Weller H. (1990), Sensitization of highly porous polycrystalline TiO_2 electrodes by quantum sized CdS, *Chem Phys Lett*,174,241-6.
5. Lee Y. L, Lo Y. S. (2009), Highly efficient quantum-dot-sensitized solar cell based on co-sensitization of CdS/CdSe, *Advanced Functional Materials*, 19, 604–609.
6. Zhang Q, Zhang Y, Huang S, Huang X, Luo Y, Meng Q, Li D. (2010), Application of carbon counterelectrode on CdS quantum dot-sensitized solar cells (QDSSCs), *Electrochemistry Communications*,12, 327–30.
7. Chen J, Zhao DW, Song JL, Sun XW, Deng WQ, Liu XW, Lei W. (2009), Directly assembled CdSe quantum dots on TiO_2 in aqueous solution by adjusting pH value for quantum dot sensitized solar cells, *Electrochemistry Communications*, 11, 2265–7.
8. Yu X-Y, Lei B-X, Kuang D-B, Su C-Y. (2012), High performance and reduced charge recombination of CdSe/CdS quantum dot-sensitized solar cells, *J Mater Chem*, 22, 12058–63.