

QUANTUM DOTS SOLAR CELLS BASED ON CdS-TiO₂ PHOTOANODE

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Abstract: Various CdS quantum dots (QDs) have been synthesized on the TiO₂ nano porous by chemical bath deposition method with times different immersing. The size and morphology of CdS QDs can be observed from scan electron microscope and transmission electron microscopy images. Based on UV-Vis absorption measurement and photocurrent density-voltage characterization, the results display that compared with the device with the uniform size particles, the device with various size CdS QDs shows the better performance with higher short-circuit current density, open-circuit voltage, and power conversion efficiency.

Keywords: CdS QDs, solar cells.

I. INTRODUCTION

Quantum dots sensitized solar cells (QDSSCs) have attracted much attention because semiconductor nano crystals can bring many advantages to solar cells, such as low production costs, optical band gap can be easily adjusted by varying their sizes, due to quantum confinement effects, and the possibility for multiple exciton generation [1-13]. For these reasons, the semiconductor nano crystals are expected to boost the power conversion efficiency of solar cells. However, the performance of QDSSCs is still much worse than that of dye sensitized solar cells (DSSCs) up to now, which may be result from the poor light absorption [14-16]. As we know, the smaller size quantum dots (QDs) result in a larger band gap due to quantum confinement effect and the band gap determines the absorption wavelength of QDs [17-19]. Therefore, the light absorption of QDs can be adjusted by the size of the QDs [20-22]. So the absorption of a device sensitized by different size QDs together may be enlarged, resulting in the performance enhancement of the QDSSCs. Song and co-workers have successfully grown dual-sized CdS QDs on ZnO NWs through chemical bath deposition (CBD) method and sequential annealing process, and their results display that the strategy of co sensitization by dual-sized CdS QDs is effective to improve the performance of solar cell [23]. Furthermore, quantum dot-dye bilayer sensitization may be a good method to enlarge the light absorption, which is seldom reported.

In this work, we synthesized CdS-TiO₂ photo anodes by chemical bath deposition for to prepare solar cells. We have immersed TiO₂ films in CdS solution with different times that we can obtain the best peak of UV-Vis. Finally, based on the best peak of UV-Vis, we have prepared solar cells and obtained performance photovoltaic.

II. EXPERIMENT

Materials.

Cd(CH₃COO)₂·2H₂O (99%), KCl, Na₂S, Zn(NO₃)₂, S powder, Na₂SO₃, TiCl₄, TiO₂ paste obtained from Dyesol, Australia.

To prepare TiO₂ films

The TiO₂ thin films were fabricated by silk-screen printing with commercial TiO₂ paste. Their sizes ranged from 10 to 20 nm. Two layers of film with thickness of 8 μm (measured by microscope). Then, the TiO₂ film was heated at 400°C for 5 min, 500°C for 30 min. Afterward, the film was dipped in 40-mmol TiCl₄

solution for 30 min at 70°C and heated at 500°C for 30 min. The specific surface area of the meso porous TiO₂ were investigated by using the N₂ adsorption and desorption isotherms before and after the calcination. The surface area is 120.6 m²g⁻¹ (measured by BET devices). This result indicates that the synthesized material has wider meso porous structure.

To prepare TiO₂/CdS

The highly ordered TiO₂ were sequentially sensitized with CdS QDs by CBD method. The TiO₂ film was immersed CdS solution for different times from 1 hour to 5 hours and then rinsed with ethanol. Finally, CdS-TiO₂ films were annealing at 300°C in vacuum.

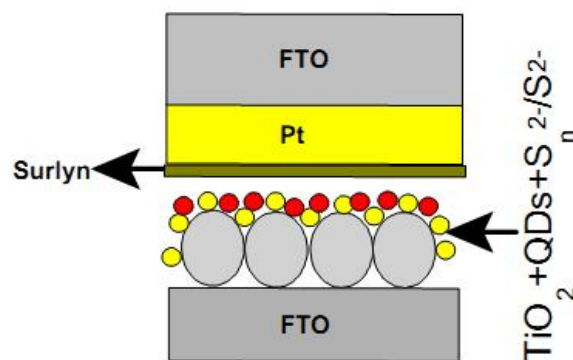


Figure 1. The diagram shows the instruction of the QDSSCs

Fabrication of QDSSCs

The polysulfide electrolyte used in this work was prepared freshly by dissolving 0.5 M Na₂S, 0.2 M S, and 0.2 M KCl in Milli-Q ultrapure water/methanol (7:3 by volume). The CdS/CdSe/ZnS co-sensitized TiO₂ photoanode and Pt counter electrode were assembled into a sandwich cell by heating with a Surlyn. The electrolyte was filled from a hole made on the counter electrode, which was later sealed by thermal adhesive film and a cover glass. The active area of QDSSC was 0.38 cm².

Characterizations and measurements

The morphology of the prepared samples was observed using field-emission scanning electron microscopy (FE-SEM, S4800). The crystal structure was analyzed with an X-ray

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diffractometer (Philips, Analytical X'pert, CuK α radiation). The absorption properties of the nanotube array samples were investigated using a diffuse reflectance UV-vis spectrometer (JASCO V-670). Photocurrent – Voltage measurements were performed on a Keithley 2400 sourcemeter using a simulated AM 1.5 sunlight with an output power of 100 mW/cm² produced by a solar simulator (Solarena, Sweden).

III. RESULTS AND DISCUSSION

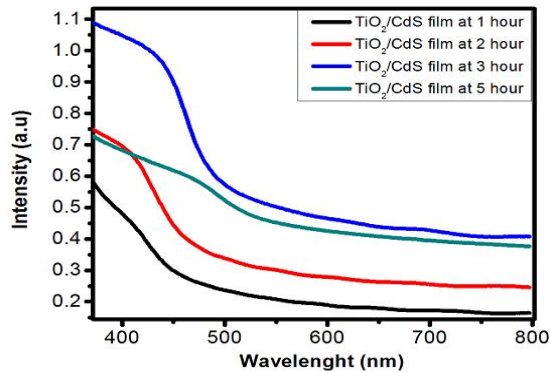


Figure 2. The absorption spectra of CdS-TiO₂.

Fig 2 shows the absorption spectra of CdS-TiO₂ at times from 1 hour to 5 hours that all peaks have wave in visible region from 400nm to 500nm. The changed peak of UV-Vis depending on the thickness is not large. However, the peak of U-Vis still moved a little forward the long wave when times changed from 1 to 3 hours. As the times is at 5 hours, the peak of UV-Vis unchanged. Finally, from above these sign, we think that CdS QDs have loaded on the TiO₂ films.

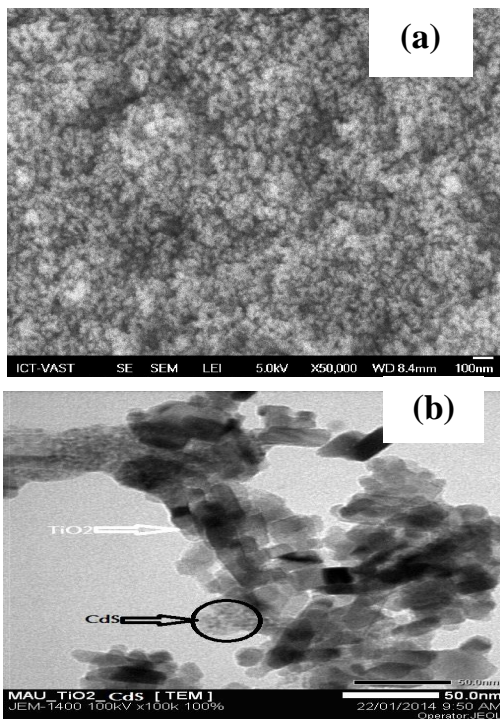


Figure 3. (a) FE-SEM image and (b)TEM image of TiO₂/CdS photo anode.

The FE-SEM and TEM are devices which can be used to research the size and morphology of CdS-TiO₂ photo anodes after CdS QDs loaded on TiO₂ films.

So, we can observe the size and morphology and thickness of photo anodes. Figure 3 shows FE-SEM image of TiO₂/CdS which was immersed at 3 hours and annealed at 300°C in vacuum. From FE-SEM, we shows that the photo anode is high porous with the mean size about 20 nm. Due to between TiO₂ nanoparticles have a lot of space, so the CdS QDs is easy loaded on the TiO₂ nanoparticles. The important things that photo anodes can be applied in solar cells. First, CdS QDs must load on the TiO₂ surface but not conglomerate on films. Second, the CdS QDs content not conglomerate bulk. For determination size of CdS QDs, we can use TEM image at Fig 3b. The size of CdS QDs can be determined about 3 nm.

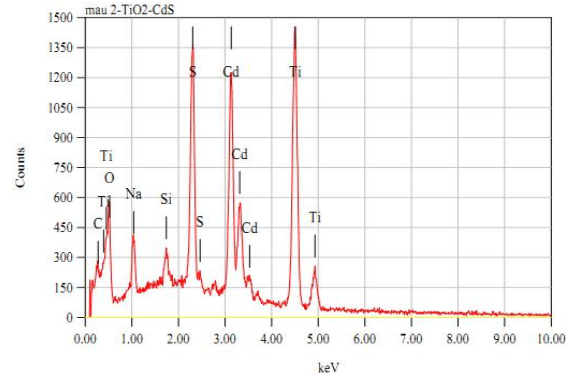
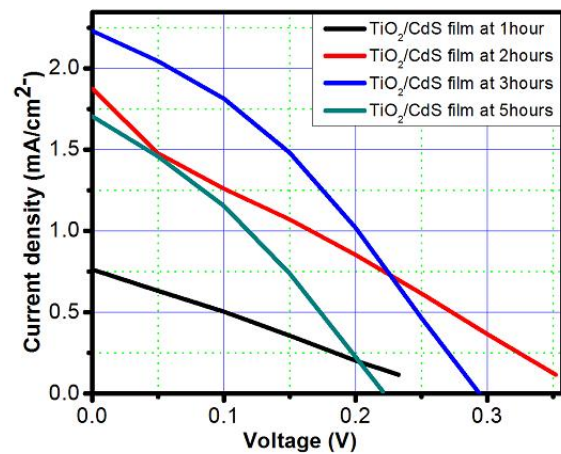


Figure 4. (a) EDS of TiO₂/CdS photo anode at 3 hours.

Table 1. Elements obtained in TiO₂/CdS photo anode at 3 hours.

Element	(keV)	Mass%	Atom%
C K	0.277	1.37	6.08
O K	0.525	2.25	7.49
Na K	1.041	1.88	4.37
Si K	1.739	1.11	2.11
S K (Ref.)	2.307	13.02	21.68
Ti K	4.508	31.41	35.02
Zn K	8.630	3.18	2.69
Cd L	3.133	48.96	23.26
Total		100.00	100.00

Figure 4 shows EDS of TiO₂/CdS photo anode in which we can observe Ti and O peaks of TiO₂, Cd and S of CdS QDs. The Si peak origin from FTO and C from solvent. So, from EDS, we think that CdS QDs have loaded on TiO₂ films.



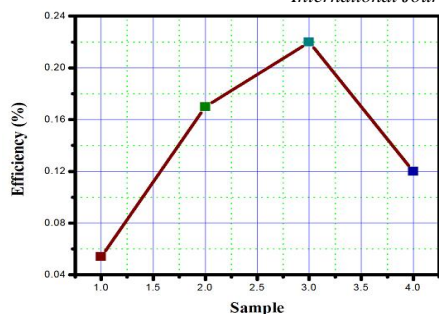
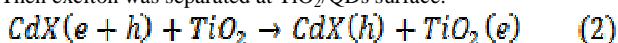


Figure 5. J-V curves of different QDSSCs.

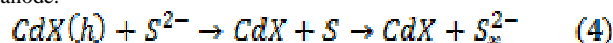
All QDs were corroded and reduced the absorption when they linked with I/I^{3-} electrolyte. As mentioned above, we have used Sulfide electrolyte to replace I/I^{3-} electrolyte because CdS QDs were corroded in I/I^{3-} electrolyte. For QDSSCs, electronics can be separated in QDs when they were illuminated.



Then exciton was separated at TiO_2/QDs surface.



Red and Ox is the redox and oxidation process at cathode and anode.



The transferred electrons in CdS- TiO_2 depend on the size of QDs and injection process in TiO_2 . The highest efficiency of the QDSSCs obtained 0.22 % when TiO_2/CdS photo anode was immersed at 3 hours. As the photo anode was immersed at 5 hours that the efficiency decreased.

Table 2. The dynamic resistance of QDSSCs were determined by one J-V.

Samples	R_s (Ω)	R_{SH} (Ω)	Efficiency η (%)
TiO ₂ /CdS immersed 1 hour	218	647.2	0.054
TiO ₂ /CdS immersed 2 hours	132.6	1758	0.17
TiO ₂ /CdS immersed 3 hours	53.8	2177	0.22
TiO ₂ /CdS immersed 5 hours	107	1690	0.12

The fill factor (FF) depend on open circuit voltage (V_{OC}), the series resistance (R_s) and recombination in QDSSCs. From Table 2, we can observe that V_{OC} depend on thickness. The V_{OC} values of TiO_2/CdS change from 0.24 V to 0.33 V when FF increase from 0.24 to 0.34. The FF is low because of large recombination in QDSSCs. Moreover, the FF was effected by the series resistance and shunt resistance in solar cells. From Table 2, R_s values change from 53.8 to 218 Ω which is large. So, the electronics is trammed when they move in solar cells to pass contacts. The same, R_{SH} value become low and cause the low efficiency.

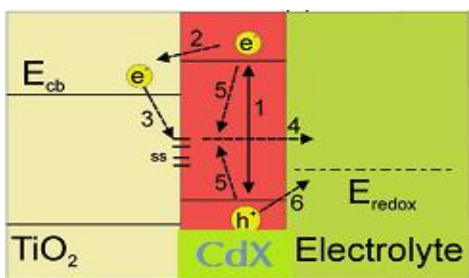


Figure 6. Diagram shows the main processes in QDSSCs: (1) created exciton, (2) injected electrons in TiO_2 , (3) trapped electrons at states surface, (4) transferred electrons from states surface to

electrolyte, (5) recombination in semiconductor and (6) injected holes in electrolyte.

First, there were a lot of created excitons and recombination in CdS QDs when the photo anode was illuminated, (1). Electrons in CB_{TiO_2} injected directly in semiconductor. Moreover, electrons were trapped by states surface (2) and then we also injected in electrolyte (3) or recombined with the holes in QDs (4). The (1), (2), (6) processes is useful when QDSSCs is active. However, the other processes cause the decreased efficiency of solar cells.

4. CONCLUSIONS

We have succeed the QDSSCs based on the different CdS- TiO_2 photo anodes that the absorption of photo anode at 3 hours is the best correspond to the highest efficiency. However, the performance photovoltaic is about 0.22 % because there are a lot of recombination in solar cells and the low fill factor. In addition, CdS QDs have a lot of defects, so the injection electrons from CdS QDs to TiO_2 reduced.

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