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QUANTUM DOTS SOLAR CELLS BASED ON CdSe-TiO₂ PHOTOANODE

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Abstract:- CdSe quantum dots (QDs) have been synthesized by using Colloid method and they were applied in Quantum dots Solar cells (QDSSCs) based on CdSe-TiO₂ photo anode which were prepared by using chemical bath deposition (CBD) method with different immersing times. The size and morphology of CdSe QDs can be observed from scan electron microscope (SEM) and transmission electron microscopy (TEM). 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 CdSe QDs obtained efficiency of 0.575%.

Keywords: CdSe 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 CdSe 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 dualsized CdSe 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 CdSe-TiO₂ photo anodes by chemical bath deposition for to prepare solar cells. We have immersed TiO₂ films in CdSe 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, Se powder, S powder, Na₂SO₃, TiCl₄, TiO₂ paste obtained from Dyesol, Australia.

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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 layes of film with thickness of 8 μ m (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/CdSe

The highly ordered TiO_2 were sequentially sensitized with CdSe QDs by CBD method. The TiO₂ film was immersed CdSe solution for different times from 1 hour to 5 hours and then rinsed with ethanol. Finally, CdSe-TiO2 films were anealing at 300°C in vacuum.

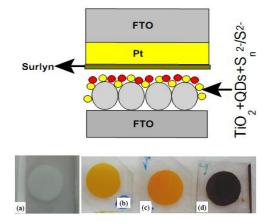


Figure 1. The diagram shows the instruction of the QDSSCs and images of different CdSe-TiO₂ photo anodes.

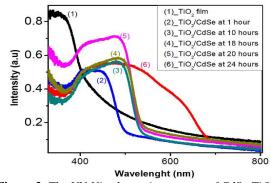
Fabrication of QDSSCs

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 by an X-ray diffractometer (Philips, Panalytical X'pert, CuKα 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 by 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



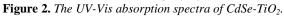


Fig 2 shows the absorption spectra of CdSe-TiO₂ at times from 1 hour to 24 hours that all peaks have wave in visible region from 420 nm to 620 nm. The changed peak of UV-Vis defending on the thickness is not large. However, the peak of UV-Vis still moved a strong forward the long wave when times changed from 1 to 24 hours. As the times is at 20 hours, the peak of UV-Vis is the highest. Finally, from above these sign, we think that CdSe QDs have loaded on the TiO₂ films.

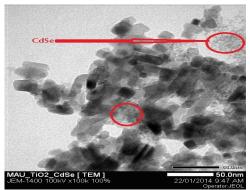


Figure 3. TEM image of TiO₂/CdSe photo anode.

The FE-SEM and TEM are devices which can be used to research the size and morphology of CdSe-TiO₂ photo anodes after CdSe 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/CdSe 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 CdSe QDs is easy loaded on the TiO₂ nanoparticles. The important things that photo anodes can be applied in solar cells. First, CdSe QDs must load on the TiO₂ surface but not conglomerate on films. Second, the CdSe QDs content not conglomerate bulk.

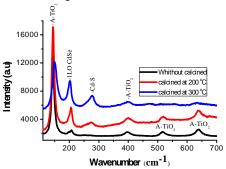


Figure 4. Raman spectrum of TiO₂/CdSe photo anode corresponding with different temperatures calcination.

From raman (Fig 4), we can see that peaks appeared at 144 cm⁻¹, 397 cm⁻¹, 517 cm⁻¹, 638,5 cm⁻¹ to corresponding to anatase phase of TiO₂ **Error! Reference source not found.** When the temperature increased, the peaks shifted toward short wavenumber. Beside, 1LO and 2 LO peaks of CdSe QDs appear at 206,5cm⁻¹, 405 cm⁻¹ due to CdSe QDs formed on TiO₂. For 300°C, 1LO peak shifted toward 202cm⁻¹ since crystal size increased. On the other hand, at 200°, 300°C the raman appear at 275 cm⁻¹ mode corresponding to oscillation of the link Cd-S because of thiol group **Error! Reference source not found.**. This result is entirely consistent with the predictions from X-ray diffraction diagram.

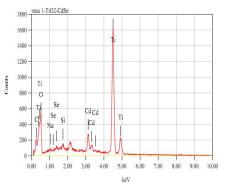


Figure 4. (a) EDS spectra of TiO₂/CdSe photo anode at 20 hours.

 Table 1. Elements obtained in TiO2/CdSe photo anode at 20 hours

Element	(keV)	Mass%	Atom%		
C K	0.277	2.55	9.45		
ОК	0.525	4.68	13.41		
Na K	1.041	0.3	0.58		
Si K	1.739	0.86	1.37		

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Se L	1.379	1.43	0.81
Ti K	4.508	72.01	67.05
(Ref.)			
Cd L	3.133	17.96	7.13
Total		100.00	100.00

Figure 4 shows EDS of $TiO_2/CdSe$ photo anode in which we can observe Ti and O peaks of TiO_2 , Cd and S of CdSe QDs. The Si peak origin from FTO and C from solvent. So, from EDS, we think that CdSe QDs have loaded on TiO_2 films.

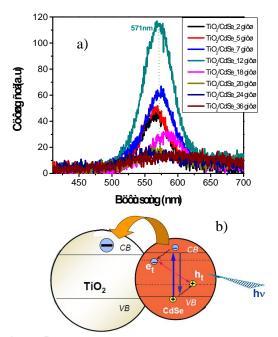


Figure 5. a) PL of samples depend on deposition times and b) instruction energy of photo anodes.

Intensity of PL for all samples reduced as deposition times increased due to:

When CdSe QDs absorb photons, electrons were created in

conductor follow as:

 $CdSe + hv \rightarrow CdSe(h^+ + e^-)$ (1)

e - h couple can combinated and radiated:

 $CdSe (h^+ + e^-) \rightarrow CdSe + hv' (2)$

Next, electrons were injected in conductor ban of TiO_2 . So, intensity of PL reduced:

 $CdSe (h^+ + e^-) + TiO_2 \rightarrow CdSe(h^+) + TiO_2(e^-) (3)$

Table	2.	The	dynamic	resistance	of	QDSSCs	were
determi	ined	by on	e J-V.				

Solar Cells	J_{SC}	$V_{oc}(V)$	Fill	efficiency
	(mA/cm^2)		factor FF	η(%)
TiO ₂ /CdSe at 1 hour	0.256	0.31	0.25	0.02
TiO ₂ /CdSe at 10 hours	0.59	0.32	0.24	0.046
TiO ₂ /CdSe at 18 hours	2.08	0.33	0.27	0.184
TiO ₂ /CdSe at 20 hours	5.47	0.33	0.31	0.575

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	TiO ₂ /CdSe at 24	2.13	0.29	0.24	0.15	
	hours					

The fill factor (FF) defend on open circuit voltage (V_{OC}), the series resistance (R_S) and recombination in QDSSCs. From Table 2, we can observe that V_{OC} defend on thickness. The V_{OC} values of TiO₂/CdSe change from 0.29 V to 0.33 V when FF increase from 0.24 to 0.31. The FF is low because of large recombination in QDSSCs.

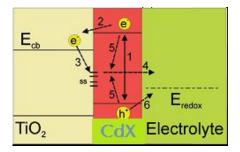


Figure 6. Diagram shows the main processes in QDSSCs: (1) created exciton, (2) injected electrons in TiO_2 , (3) trapped electrons at states surface, (4) transferred electrons from states surface to electrolyte, (5) recombination in semi conduction and (6) injected holes in electrolyte.

First, there were a lot of created excitons and recombination in CdSe QDs when the photo anode was illuminated, (1). Electrons in CB_{TiO2} injected directly in semi conduction. 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.

IV. CONCLUSIONS

We have succeed the QDSSCs based on the different CdSe-TiO₂ photo anodes that the absorption of photo anode at 24 hours is the best correspond to the highest efficiency. However, the performance photovoltaic is about 0.575 % because there are a lot of recombination in solar cells and the low fill factor. In addition, CdSe QDs have a lot of defects, so the injection electrons from CdSe QDs to TiO₂ reduced.

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