



## Preparation and Characterization of Quantum Dots Sensitized Solar Cells Based on $\text{TiO}_2/\text{CdS}:\text{Mn}^{2+}/\text{CdSe}$ Photoanode

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**Abstract:** In this study, we have prepared and investigated the optical properties of the  $\text{TiO}_2/\text{CdS}:\text{Mn}^{2+}/\text{CdSe}$  photoanode as the function of  $\text{Mn}^{2+}$  doping concentration and thickness. The results show that the peaks of the UV-Vis spectra shifted toward longer wavelength while  $\text{Mn}^{2+}$  doping concentrations or thickness of the films were changed. The main cause of the red-shifting in UV-Vis spectra may come from the increasing of photoanode light-harvesting capacity. In addition, the results also demonstrated by the boosting performance of quantum dots sensitized solar cells from 2.07% for  $\text{TiO}_2/\text{CdS}/\text{CdSe}$  photoanode to 2.5% for  $\text{TiO}_2/\text{CdS}:\text{Mn}^{2+}/\text{CdSe}$  photoanode.

**Keywords:** Solar cells, nano CdS, nano CdSe.

### 1. Introduction

Quantum dots sensitized solar cells (QDSSCs) can be regarded as a derivative of dye sensitized solar cells (DSSCs) by replacing dye molecules with quantum dots (QDs). QDs have been chosen as a main photosensitizer in solar cells since they have several optical and electrical advantages, including: tunable band gap depending on the QD size due to the quantum confinement effect, higher absorption coefficient than most organic dyes, and multiple exciton generation (MEG) effect [1-3]. Moreover, QDs can generate multiple electron-hole pairs from a single incident photon absorption (MEG), which allowed the power conversion efficiency (PCE) of QDSSCs overcome the Shockley – Queisser limit of traditional Si solar cells. Therefore, QDSSC is expected to create a great potential for breakthrough

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efficiency [4]. First considerable research in this field belonged to Vogel and coworkers on nanocrystal CdS QDSSCs, despite of very low PCE. Until 2008, most of researched QDSSCs still used only single QD so the light absorbing domain is limited and the efficiency cannot be improved. Thereafter, several researches had been focused on enhancing the QDSSCs PCE, such as: extending the photoanode absorption [2-6]; using several photoanode preparation methods: chemical bath deposition (CBD), successive ionic layer absorption and reaction (SILAR), etc... [7]; applying the core-shell structure to improve the recombination process of QDs surface traps and the electron injection into TiO<sub>2</sub> [8]; using the linkers of TiO<sub>2</sub> and QDs [9-10]. However, high PCE of QDSSCs has been not archived until now. Recently, Tubtimtae et.al. reported the PCE of QDSSCs reached 3.1% [11]. Therefore, multiple problems need to be researched on applying QDs to solar cell, including: (1) synthesis QDs having compatible electrical and optical properties; (2) the optimum binding of QDs and TiO<sub>2</sub>; (3) optimal surface trap-states treatment methods to increasing the QDs stability in electrolyte [12-13]; (4) preparing QDSSCs with tandem structure to extend the light absorption domain (from ultraviolet to near-infrared region) for enhancing the QDSSCs PCE [4-6, 14-15]. Some researchers had been conducted recently on doping transitional metal ions into pure QDs, such as PbS nanocrystal doping Hg<sup>2+</sup> [8] and CdSe:Cu<sup>2+</sup> [11]. The appearance of a dopant energy level in the band gap of pure QDs increases the photon absorption capacity and then enhances the current density of QDSSCs [10-11]. Therefore, doping transitional metal ions into pure QDs is an effective method for improving the PCE of QDSSCs.

In this research, we doped ions Mn<sup>2+</sup> into pure CdS nanocrystals of TiO<sub>2</sub>/CdS:Mn<sup>2+</sup>/CdSe photoanode and the optical properties of the photoanode have been investigated by the function of ion doping concentration and layer thickness. Finally, we fabricated the QDSSCs based on the optimal photoanode.

## 2. Materials and methods

### 2.1. Photoanode preparation

Preparation of mesoporous TiO<sub>2</sub> films: FTO glass substrates (Dyesol, TEC15, 1.4x2.1cm) were prepared by following steps: ultrasonic cleaning in soap solution for 30mins followed with deep washing in pure water and ethanol; dipping in 40mM TiCl<sub>4</sub> solution at 70°C in 30mins then washing with deionized water and drying before using. Mesoporous TiO<sub>2</sub> films were prepared onto cleaned FTO substrates via doctor-blading method followed with sintered at 500°C for 30mins.

Preparation of TiO<sub>2</sub>/CdS:Mn<sup>2+</sup> photoanodes: Prepared TiO<sub>2</sub> films were immersed into the mixture of Cd<sup>2+</sup> and Mn<sup>2+</sup> ionized solution for 5mins at room temperature, then rinsed with ethanol to remove excess precursors and dried before the next dipping. The films were next dipped into S<sup>2-</sup> solution for 5mins at room temperature followed with rising by methanol and drying. These steps are called one SILAR cycle. This process was repeated from 1 to 5 times.

Preparation of TiO<sub>2</sub>/CdS:Mn<sup>2+</sup>/CdSe photoanodes: The TiO<sub>2</sub>/CdS:Mn<sup>2+</sup>/CdSe photoanodes were prepared similarly as described above. Briefly, the TiO<sub>2</sub>/CdS:Mn<sup>2+</sup> layers were immersed into Cd<sup>2+</sup> ionized solution for 5mins at room temperature, then rinsed with ethanol to remove excess precursors and dried. The films were next dipped into Se<sup>2-</sup> solution for 5mins at room temperature followed by rinsing by methanol and drying. This cycle was repeated 3 times.

Preparation of QDSSCs: The polysulfide electrolyte was prepared by dissolving 0.5 Na<sub>2</sub>S.9H<sub>2</sub>O, 0.2M S and 0.2M KCl in the mixture of deionized water and methanol solution (ratio 7:3 in volume). For the Pt cathode preparation, commercial Pt paste were doctor-bladed onto cleaned FTO glass

substrates then sintered at 500 °C for 30mins. Completed QDSSCs consisted of photoanode and counter electrode adhesive by surlyn layer heated at 170 °C.

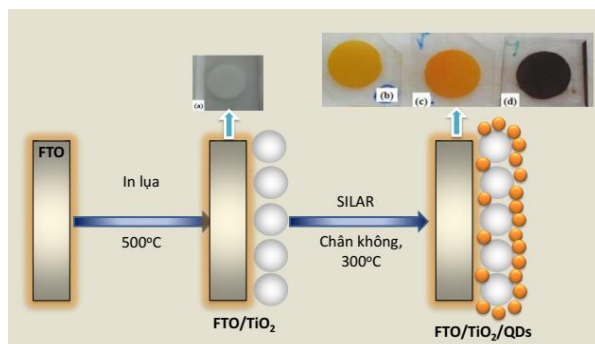


Figure 1. Schematic of the photoanode  $\text{TiO}_2/\text{CdS}:\text{Mn}^{2+}/\text{CdSe}$  preparation.

## 2.2. Measurement

Field-effect scanning electron microscope (FESEM) of Ho Chi Minh City Institute of Physics was used to investigate the surface morphology and composition of the photoanode. The UV-Vis spectra was characterized by the JASCO V-670 device of Applied Physical Chemistry lab of University of Science, Vietnam National University – Ho Chi Minh City. X-ray diffraction (XRD) spectra and photocurrent-voltage (I-V) curves were analyzed by devices of two aforementioned offices.

## 3. Results and discussion

$\text{TiO}_2$  plays the role of intermediate layer for QDs assembling. The thicker the layer was the more QDs assembled. However, the thickness of  $\text{TiO}_2$  layer had been optimal since the decreasing of PCE and the increasing of internal resistance of QDSSCs when the thickness of  $\text{TiO}_2$  layer increased. The transmittance of photoanode with a different  $\text{TiO}_2$  layer had been investigated. In Fig. 2a, the photoanode included single  $\text{TiO}_2$  layer was inequality and limited, which leads to the transmittance of  $\text{TiO}_2$  layer was equivalent with FTO substrate. When the amount of  $\text{TiO}_2$  layer was more than 3, the optical properties of photoanode was declined since the decreasing of transmittance and the quality of the electrode. Therefore, two layers of  $\text{TiO}_2$  were prepared on FTO for QDs assembling.

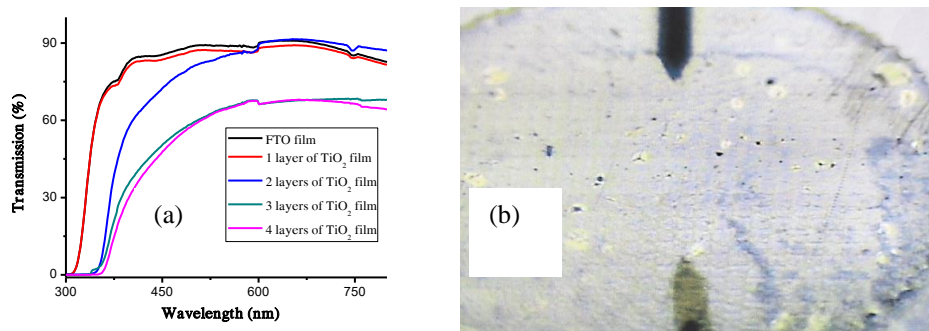


Figure 2. (a) The transmittance of electrode with different number of  $\text{TiO}_2$  doctor-bladed layer and (b) the thickness of  $\text{TiO}_2$  layer measured by stylus.

Stylus had been carried out for measuring the thickness of  $\text{TiO}_2$  layer and the results were approximately 11-12 $\mu\text{m}$  (Fig. 2b)

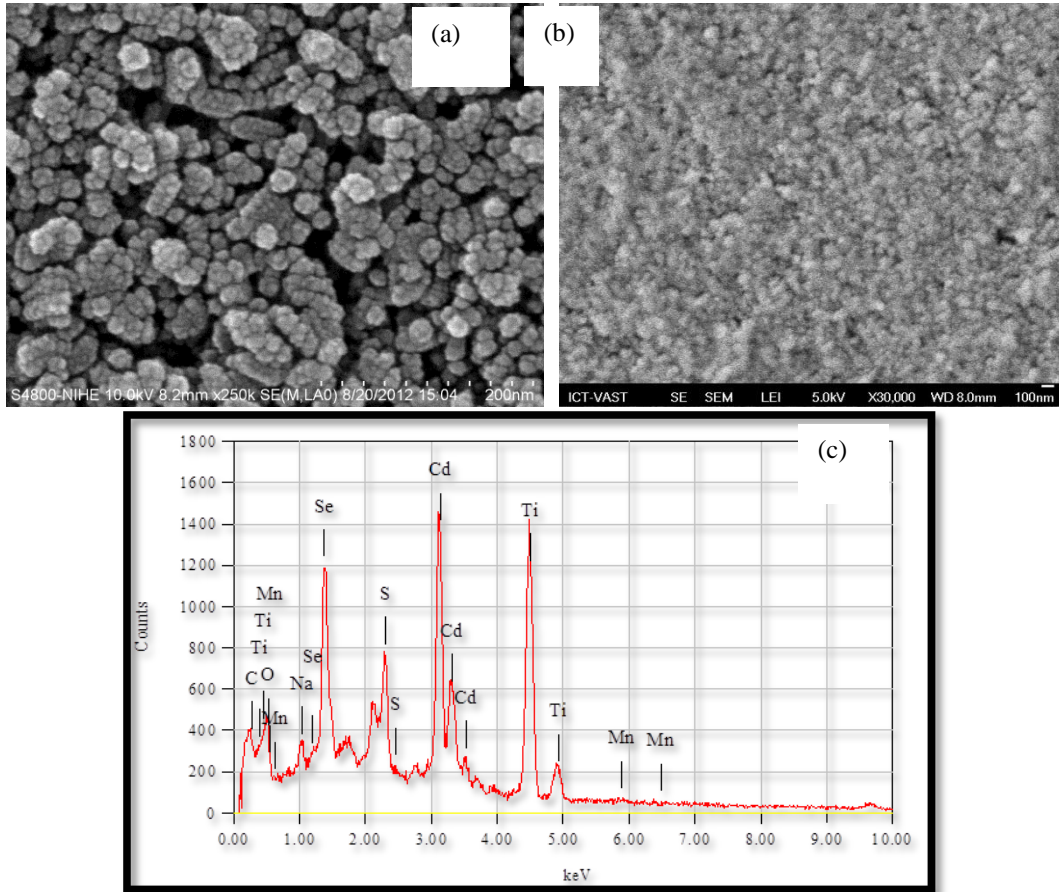


Figure 3. FE-SEM image of (a)  $\text{TiO}_2$  and  $\text{TiO}_2/\text{CdS}:\text{Mn}^{2+}/\text{CdSe}$  film, (c) EDX of  $\text{TiO}_2/\text{CdS}:\text{Mn}^{2+}/\text{CdSe}$  film.

The surface morphology of the photoanode had been investigated. The FESEM image of  $\text{TiO}_2/\text{CdS}:\text{Mn}^{2+}/\text{CdSe}$  photoanode at 100nm resolution was demonstrated (Fig. 3b). The layer had high porosity, the average dimension of nanoparticles was a few dozen of nanometers. Because of huge size  $\text{TiO}_2$  nanoparticles (Fig. 3a), the layer had high porosity and there were more spaces between particles, which lead to the higher assembled ability of  $\text{CdS}:\text{Mn}^{2+}$  and  $\text{CdSe}$  QDs onto the surface of  $\text{TiO}_2$  nanoparticles. There are two main problems which had been investigated for applying the photoanode for QDSSCs, including: (1) QDs had been assembled on the surfaces of  $\text{TiO}_2$  nanoparticles instead of sticking on the layer; (2) the concentration of assembled QDs onto  $\text{TiO}_2$  layer could not form bulk morphology.

The energy peaks related to Ti and O element in  $\text{TiO}_2$  were clearly founded in the energy dispersive X-ray (EDX) spectra of  $\text{TiO}_2/\text{CdS}:\text{Mn}^{2+}/\text{CdSe}$  photoanode. Cd, Se, and S – energy peaks were also illustrated in the spectra, corresponded to the composition of  $\text{CdS}$  and  $\text{CdSe}$  nanocrystal. Si and C – energy peaks had been originated from FTO and excessive organic solution remaining in the layer (since the electrodes were sintered in vacuum), respectively. Mn – energy peaks came from the

anion precursor solution. The EDX spectra confirmed that QDs had been assembled and crystallized on the TiO<sub>2</sub> layer (Fig. 3c and Table 1).

Table 1. EDX quantitative analysis of TiO<sub>2</sub>/CdS:Mn<sup>2+</sup>/CdSe photoanode

Elements (k)	Energy (KeV)	Ratio of mass (%)	Error (%)	Ratio of Atom (%)
C	0.277	1.54	0.06	8.21
O	0.525	0.97	0.14	3.90
Na	1.041	0.68	0.26	1.91
Si	1.739	0.43	0.59	0.98
S	2.307	4.92	0.05	9.84
Ti	4.508	23.25	0.02	31.12
Mn	5.894	0.52	1.87	0.60
Se	1.379	20.08	0.04	16.30
Cd	3.133	47.06	0.02	27.16
Total		100.00		100.00

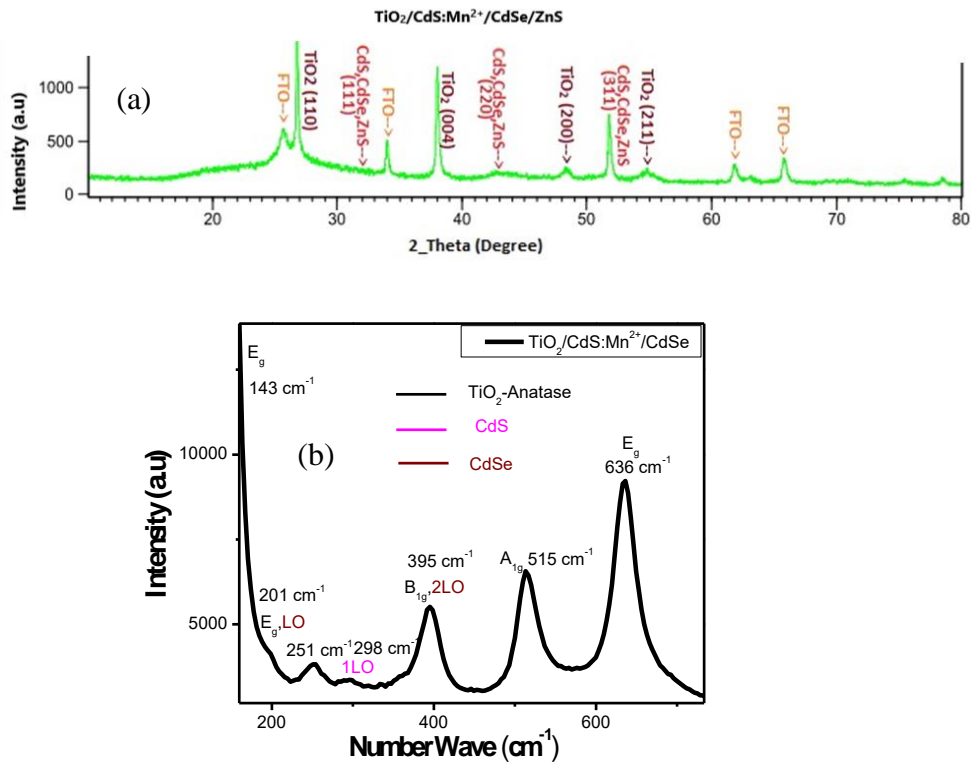


Figure 4. (a) X-ray diffraction (XRD) and (b) Raman scattering spectra of TiO<sub>2</sub>/CdS:Mn<sup>2+</sup>/CdSe photoanode

As can be seen in Fig 4a, it is immediately obvious that the XRD of TiO<sub>2</sub>/CdS:Mn<sup>2+</sup>/CdSe/ZnS appears the peaks at 32°, 43.1° and 52° positions corresponding to the (111), (220) and (311) planes, which indicates an upstanding CdS, CdSe and ZnS zinc Blende. It is a completely suitable result for JCPDS No. 05-5666, JCPDS No. 88-2346, JCPDS No. 41-1019, respectively. Moreover, the left peaks of XRD pattern can be assigned the TiO<sub>2</sub> anatase (JCPDS No. 21-1272). This implies that CdS:Mn<sup>2+</sup>, CdSe and ZnS nanoparticles have absorbed on TiO<sub>2</sub> films. These results were also affirmative through

Raman scattering spectra of same components photoanode (Fig. 4b). The oscillated mode at  $143\text{cm}^{-1}$ ,  $251\text{cm}^{-1}$ ,  $515\text{cm}^{-1}$ , and  $636\text{cm}^{-1}$  featured for the anatase-phase of  $\text{TiO}_2$  nanoparticle and the others at  $201\text{cm}^{-1}$ ,  $298\text{cm}^{-1}$  and  $395\text{cm}^{-1}$  corresponded to cube  $\text{CdS:Mn}^{2+}$  and  $\text{CdSe}$  nanocrystal.

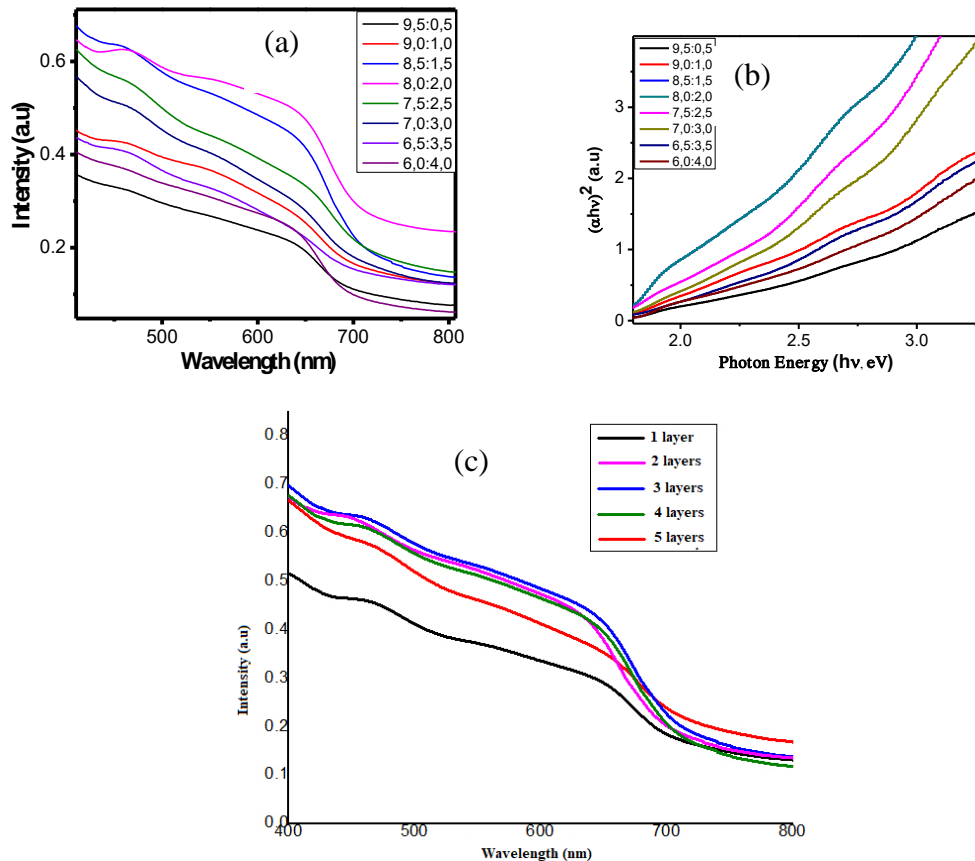


Figure 5. (a) UV-Vis spectra and (b) inferred  $(\alpha hv)^2$  versus  $(hv)$  curves of  $\text{TiO}_2/\text{CdS:Mn}^{2+}/\text{CdSe}$  photoanode at different Cd:Mn ratio; (c) UV-Vis spectra of photoanode at different thickness.

The UV-Vis spectra of prepared  $\text{TiO}_2/\text{CdS:Mn}^{2+}/\text{CdSe}$  photoanode with 3 SILAR cycles of  $\text{CdS:Mn}^{2+}$  and  $\text{CdSe}$  nanocrystal had been investigated in the wavelength region from 300 to 850nm (Fig. 5a). Because of a large band gap energy (3.2eV in bulk),  $\text{TiO}_2$  nanoparticles absorbed weakly in the visible domain. The absorption edge of  $\text{TiO}_2/\text{CdS}$  photoanode was at approximately 460nm corresponded to the significant absorption region of  $\text{CdS}$  nanocrystal, which were mentioned in other publications [16, 17]. When ion  $\text{Mn}^{2+}$  were doped into  $\text{CdS}$  nanocrystal and the  $\text{CdSe}$  QDs were assembled, the photoanode absorbance increased significantly and the absorption edge shifted to a approximately 620nm region at the ratio of Cd:Mn = 8:2. The intensity and position of absorption peaks were slightly different at others ratio Cd:Mn.

The relationship between the absorbance ( $\alpha$ ) and the incident photon energy ( $hv$ ) in UV-Vis spectra in the strong absorption region of semiconductors can be derived by Tauc equation [18]

$$\alpha hv = \alpha_0 (hv - E_g)^n \quad (1)$$

With  $\alpha_0$  is an independent constant with incident photon energy and  $E_g$  is the semiconductor band gap energy. The constant  $n$  in the equation (1) was the power factor of the optical transitions in the semiconductor, depend on these transitions and structure of semiconductor (amorphous or crystal). This constant can be 1/2, 2, 3/2, or 3 depending on the nature of semiconductor [18]. By plotting all the curves illustrated the relationship between the absorbance ( $\alpha$ ) and the incident photon energy ( $h\nu$ ) of  $\text{TiO}_2/\text{CdS}$  and  $\text{TiO}_2/\text{CdS}/\text{CdSe}$  photoanode with all possible value of  $n$ , the most accordant and fully symmetric curve was at  $n = 1/2$ . As can be seen in Fig. 5b, there was a linear region in the relationship between  $(\alpha h\nu)^2$  and incident photon energy ( $h\nu$ ). The effective band gap can be estimated by extrapolating the linear portion. The band gap energy of  $\text{TiO}_2/\text{CdS}:\text{Mn}^{2+}/\text{CdSe}$  nanocrystal with ion  $\text{Mn}^{2+}$  doping concentration varied from 5% to 40% were 1.93eV, 1.91eV, 1.90eV, 1.89eV, 1.88eV, 1.91eV, 1.92eV and 1.90eV, respectively. These values are larger than 1.7eV of CdSe band gap energy in bulk [18], indicated that synthesized particles were in nanoscale.

Besides Cd:Mn ratio, the number of SILAR cycle of the  $\text{CdS}:\text{Mn}^{2+}$  nanocrystal synthesis was also an important factor determined the crystal properties. The higher the SILAR cycle was the greater the nanocrystal was and the smaller the bandgap energy of semiconductor was. Since the photoanode need to be in tandem structure, the amount of SILAR cycle had been optimal. The optical properties of  $\text{CdS}:\text{Mn}^{2+}$  nanocrystal at different SILAR cycle from 1 to 5 had been investigated by UV-Vis spectra of  $\text{TiO}_2/\text{CdS}:\text{Mn}^{2+}/\text{CdSe}$  photoanode.

The UV-Vis spectra of  $\text{TiO}_2/\text{CdS}:\text{Mn}^{2+}/\text{CdSe}$  photoanode was illustrated in Fig. 5c. When the SILAR cycle increased from 1 to 3 cycles, the absorption edges were red-shifted, obviously from 610 to 620nm region and the absorbance increased rapidly. The energy band gap of the semiconductor decreased when the dimension of particles increased was the possible reason for the changing in UV-Vis spectra. At 4 and 5 SILAR cycles, the red-shift of absorption edge was changed insignificantly compared to 3 SILAR cycles since the crystal dimension reached a saturation state and the gap space between  $\text{TiO}_2$  nanoparticles were fully filled by  $\text{CdS}:\text{Mn}^{2+}$  nanocrystal [19-21].

Table 2. Photovoltaic parameters obtained from I-V curves of QDSSCs with different Cd:Mn ratio

Cd:Mn	Absorption peak (nm)	Band gap (eV)	FF	$J_{sc}(\text{mA}/\text{cm}^2)$	$V_{oc}(\text{V})$	$\eta(\%)$
9,5:0,5	644	1,93	0,291	7,780	0,417	0,947
9,0:1,0	648	1,91	0,348	7,738	0,411	1,110
8,5:1,5	651	1,90	0,347	12,008	0,460	1,990
8,0:2,0	657	1,89	0,34	12,5	0,49	2,5
7,5:2,5	658	1,88	0,341	11,520	0,476	1,876
7,0:3,0	650	1,91	0,374	9,566	0,458	1,619
6,5:3,5	646	1,92	0,325	9,230	0,442	1,332
6,0:4,0	651	1,90	0,346	8,617	0,430	1,285

Table 3. Photovoltaic parameters obtained from I-V curves of QDSSCs with different thickness layers

Photoanodes	FF	$J_{sc}(\text{mA}/\text{cm}^2)$	$V_{oc}(\text{V})$	$\eta(\%)$
$\text{TiO}_2/\text{CdS}:\text{Mn}^{2+}(1)/\text{CdSe}(3)$	0,529	5,425	0,430	1,398
$\text{TiO}_2/\text{CdS}:\text{Mn}^{2+}(2)/\text{CdSe}(3)$	0,420	9,070	0,466	1,747
$\text{TiO}_2/\text{CdS}:\text{Mn}^{2+}(3)/\text{CdSe}(3)$	0,34	12,5	0,49	2,5
$\text{TiO}_2/\text{CdS}:\text{Mn}^{2+}(4)/\text{CdSe}(3)$	0,451	8,690	0,489	1,910
$\text{TiO}_2/\text{CdS}:\text{Mn}^{2+}(5)/\text{CdSe}(3)$	0,434	7,990	0,4644	1,612



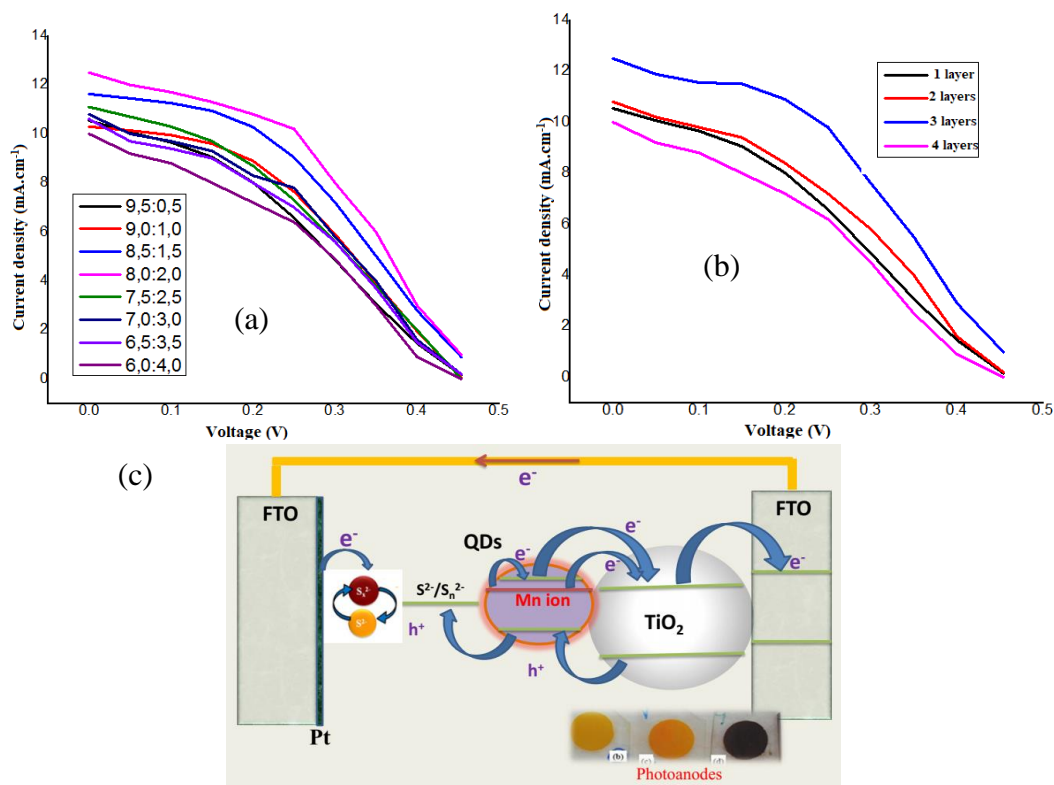


Figure 6. I-V curves of QDSSCs in the function of (a) Cd:Mn ratio and (b) thickness layer; (c) structure diagram of QDSSCs.

The PCE of QDSSCs using pure CdS nanocrystal was 1.52%. When ion  $\text{Mn}^{2+}$  were doped, photovoltaic parameters of QDSSCs enhanced significantly. At 20% ion  $\text{Mn}^{2+}$  doping concentration, the short-circuit current density, open-voltage and fill factor were  $J_{\text{SC}} = 12.5 \text{ mA/cm}^2$ ,  $V_{\text{OC}} = 0.49 \text{ V}$ , and  $\text{FF} = 0.34$ , respectively, and the PCE of QDSSCs reached 2.5%. The enhancing of photovoltaic parameters and PCE of doped QDSSCs can be came from these possible reasons: (1) the doped photoanode had higher absorbance and could generate more excited electrons; (2) the absorption edge of  $\text{CdS}:\text{Mn}^{2+}$  photoanode shifted towards longer wavelength (red-shift) so more photons in the visible region can be absorbed; (3) ion  $\text{Mn}^{2+}$  generated an intermediate energy level in the band gap of CdS nanocrystal so incident photons which had energy smaller than semiconductor band gap can be absorbed then generated more excited electrons, as was demonstrated by the enhancing of the short-circuit current density of doped QDSSCs compared to undoped cells. Thus, doping ion  $\text{Mn}^{2+}$  into CdS nanocrystal plays an important role in improving the PCE of QDSSCs.

The photovoltaic parameters and PCE of QDSSCs were enhanced significantly when the ion  $\text{Mn}^{2+}$  doping concentration increased from 0.1 to 0.2. Specifically, QDSSCs included photoanode with 20% ion  $\text{Mn}^{2+}$  doping concentration reached the PCE of 2.5% (increased 164% to undoped QDSSCs) with the short-circuit current density, open-voltage and fill factor were  $J_{\text{SC}} = 12.5 \text{ mA/cm}^2$ ,  $V_{\text{OC}} = 0.49 \text{ V}$ , and  $\text{FF} = 0.34$ , respectively. More excited electrons were generated since the absorbance of photoanode increased (at 20% ion  $\text{Mn}^{2+}$  doping concentration, the photoanode had highest absorption as illustrated in Fig. 5a) accompanied by a tandem structure in the energy level of photoanode which facilitated carrier diffusion, lead to the increasing of the short-circuit current density and PCE of QDSSCs.



However, the photovoltaic parameters and PCE of QDSSCs decreased when the doping concentration overcame 0.2. The PCE reached 2.5% and 1.227% at 20% and 50%  $\text{Mn}^{2+}$  ion doping concentration, respectively. This reduction can be explained by the decreasing of photoanode absorbance at 50% compared to 20% doped photoanode, which lead to the decline of excited electron generation. From this result, it can be inferred that the PCE of QDSSCs would be decreased if ion  $\text{Mn}^{2+}$  doping concentration continued increasing since the CdS nanocrystal lattice reached the saturation state [22].

#### 4. Conclusions

We successfully fabricated QDSSCs with  $\text{TiO}_2/\text{CdS}:\text{Mn}^{2+}/\text{CdSe}$  photoanode with different ion  $\text{Mn}^{2+}$  doping concentration and  $\text{CdS}:\text{Mn}^{2+}$  thickness layer. By optimizing preparation parameters, the PCE of QDSSCs reached a value as large as 2.5% at 20% doping concentration and the number of  $\text{CdS}:\text{Mn}^{2+}$  SILAR cycle was 3.

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