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# The enhanced current density of the quantum dots solar cells based on $CdSe:Mn^{2+}$ crystalline

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## ABSTRACT

In this work, the pure CdSe and Mn-doped CdSe quantum dots were synthesized by Successive ionic layer absorption and reaction method for the high performance of quantum dots sensitized solar cells. Relevant molar concentrations of $Mn(CH_3COO)_2.2H_2O$ were changed at 0.1 mM, 0.2 mM, 0.3 mM, 0.4 mM, and 0.5 mM as mixing with $Cd(CH_3COO)_2.2H_2O$ anion source corresponding to x represent for the $Mn^{2+}$-doped molar concentration. As a result, the quantum dots Solar cells were successfully prepared with the enhanced short current density from 7.63 $mA/cm^2$ to 18.99 $mA/cm^2$ for $Mn^{2+}$ ions doped on CdSe nanoparticle corresponding to the enhanced efficiency of quantum dots solar cells from 1.64% for pure CdSe nanocrystal to 3.77% for $Mn^{2+}$ ions doped on pure CdSe nanoparticle. Actually, $Mn^{2+}$ dopant rises in the conduction band of pure CdSe nanocrystal, reduces recombination, enhances the efficiency of high harvesting, improve the charge transfer and collection. In addition, $Mn^{2+}$ dopant can rise in the conduction band levels of pure CdSe nanocrystal, which leads to reduce the charge recombination, enhances the light-harvesting efficiency and improve the charge diffusion and collection. Correspondingly, the photoluminescence decay and Electrochemical Impedance Spectra were carried to determine the lifetime of excited electrons and dynamic resistances in QDSSCs.

## 1. Introduction

Dye sensitized solar cells (DSSCs) have received widely academic and commercial interest due to low cost and high conversion efficiency. However, dye molecular as a sensitizer has a narrow absorption and limits to absorb in the visible region. Besides, this material poses some drawbacks as the Shockley-Queisser limit [1–3]. Recently, semiconductor quantum dots (QDs) have been drawing great attention as a material-sensitizer for application in the quantum dots sensitized solar cells (QDSSCs) due to their optical properties of these materials tunability, owing to the high molar extinction coefficient, hot electron injection and multiple exciton generation effect (MEG) [1–3]. Moreover, in view of multiple exciton generation effect the theoretical photovoltaic conversion efficiency can reach up to 44%, which is much higher than 31% for single $E_g$ because of the Shockley-Queisser limit [4]. As for QDs' advantages concerned, to improve the efficiency conversion of photovoltaic and UV–Vis spectra in the visible region, $TiO_2$/CdS/CdSe/ZnS photoanode has been synthesized by successive ionic layer adsorption and reaction (SILAR) and colloidal synthesis methods [5,6]. The photoanodes can absorb plenty of photons in each region. Furthermore, the ZnS coating forms a potential barrier between the nanocrystal and the electrolyte and blocking the electrons in the conduction band (CB) transfer from the nanocrystal to the electrolyte and reduce the defect states in the nanocrystal [7]. Now dopant materials in the QDs are widely used to modify the intrinsic properties of host semiconductor nanocrystals, such as electrical conductivity properties [8,9]. Doping of the QDs with transition metal ions ($Mn^{2+}$, $Cu^{2+}$,..) have become more interesting because the dopant materials can be tuned the optical [10–12]. Doping of 3d transition metal such as Mn in II−VI semiconductor quantum dots (QDs) have been widely investigated for very high Mn emission quantum yield (QY) [13] and long emission lifetime for energy storage [14–16]. Therefore, metal ions doped on pure CdSe nanocrystal can be a useful way for high efficiency QDSSCs [17].

In order to boost the performance, $Mn^{2+}$ ions doped on CdSe nanoparticles with the different compositions of ions (x = 0 to 0.4) and

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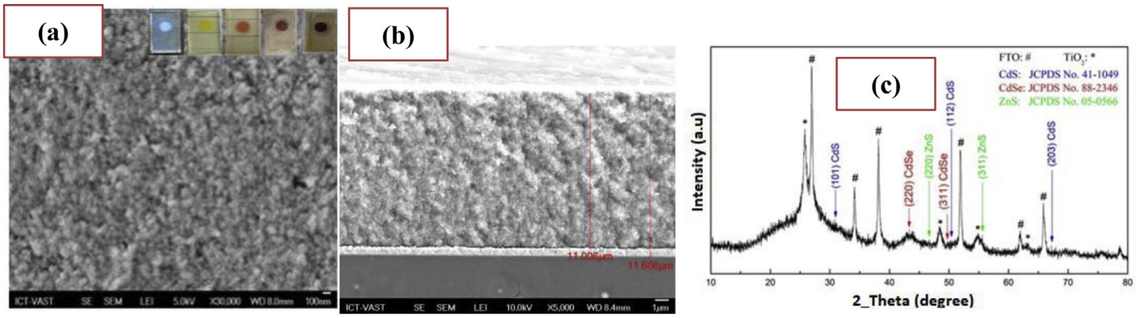

**Fig. 1.** (A) FESEM image of $TiO_2/CdS/CdSe(3)Mn^{2+}(0.2)/ZnS$ at 100 nm and (b) Cross - section of anode at 1 mμ, (c) XRD of $TiO_2/CdS/CdSe(3)Mn^{2+}(0.3)/ZnS$.

the thickness of films (y = 1 to 3 layers) by SILAR was illustrated. Moreover, the significant effects of $Mn^{2+}$ ions on optical, physical, chemical and photovoltaic features of QDSSCs can be studied by the UV–Vis spectra and Tauc equation to determine $E_g$, CB, and VB positions of $Mn^{2+}$ ions doped on pure CdSe nanoparticles. In the same way, the lifetime of excited electrons and the dynamic resistances in QDSSCs, which can be determined by photoluminescence (PL) decay and Electrochemical Impedance Spectra (EIS), respectively, are used to explain the obtained results.

## 2. Experiment

In this experiment, fluorine-doped tin oxide (FTO) glass substrate with sheet resistance 7 $\Omega sq^{-2}$ was used for the photoanode and the counter electrode. First, the FTO substrate was ultrasonically cleaned using ethanol for 30 min, followed by deionized (DI) water for 15 min. The nanoporous $TiO_2$ film was made on the well-cleaned substrate by doctor blading method followed by sintering at 500 °C for 30 min. The CdS, CdSe and Cu-doped CdSe QDs were deposited onto $TiO_2$ nanoparticle film in turn through successive ionic layer adsorption and reaction (SILAR) process. For CdS QDs, $TiO_2$ film wase dipped into a $Cd(CH_3COO)_2.2H_2O$ ethanol solution (0.1 M) for 5 min, rinsed with ethanol and dried, successively dipped into a $Na_2S.9H_2O$ methanol solution (0.1 M) for another 5 min, rinsed with methanol and dried. The two-step dipping procedure was termed as one SILAR cycle. The process was repeated 3 times and the obtained $TiO_2$ film decorated with CdS QDs were named as $TiO_2$/CdS film [18–21].

For the CdSe and Mn-doped CdSe QDs, the Se powder was mixed with $Na_2SO_3$ (0.6 M) and 100 ml pure water at 70 °C for about 7 h. To accommodate the doping of Mn metal ion, relevant molar concentrations of 0.1 mM, 0.2 mM, 0.3 mM, 0.4 mM, and 0.5 mM of $Mn(CH_3COO)_2.2H_2O$ were mixed with $Cd(CH_3COO)_2.2H_2O$ anion source. The SILAR process of CdSe and Mn-doped CdSe QDs were similar to that of CdS except that 15 min and 50 °C were required for dipping the $TiO_2$/CdS film in the Se aqueous solution. Different electrodes were named as $Cd_{1-x}Mn_xSe$ with x represent for the $Mn^{2+}$-doped molar concentration. Finally, the electrode was coated with ZnS passivation layer by dipping alternately into 0.1 M $Zn(NO_3)_2.6H_2O$ and 0.1 M $Na_2S.9H_2O$ DI water solution for 5 min each. This process was repeated 2 times to get the optimal thickness [18–21].

Polysulfide solution was made by dissolving 0.5 M $Na_2S.9H_2O$, 0.2 M S and 0.2 M KCl in DI water/methanol (7:3 by volume). The $Cu_2S$ counter electrode was synthesized through chemical bath deposition according to the previous publication [22]. Briefly, 0.24 g $CuSO_4$ was dissolved in 60 ml DI in a glass bottle. $N_2$ was bubbled through the water for 10 min to remove the dissolved oxygen from the system. Then 0.37 g $Na_2S_2O_3.5H_2O$ was mixed in the solution, and the color turned to light green. Afterwards, a clean FTO glass was immersed in the solution, with its conductive surface facing down and had an angle against the wall. The system was then settled in the water bath of 90 °C and kept for 1 h. The $Cu_2S$ crystal would directly grow onto the conductive surface of FTO glass. Finally, the as-prepared $Cu_2S$coated FTO glass sample was rinsed with deionized water and dried in air. The post-heat treatment was carried out in $N_2$ atmosphere at 200 °C for 30 min.

### 2.1. Characterization

The morphologies of the samples were investigated using scanning electron microscopy (SEM). 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 simulated AM 1.5 sunlight with an output power of 100 $mW cm^{-2}$ produced by a solar simulator (Solarena, Sweden). The electrochemical impedance spectroscopy (EIS) was carried out with the use of an impedance analyzer (ZAHNER CIMPS). The photoluminescence (PL) spectra were measured by excitation wavelength of 430 nm at room temperature using Shimadzu luminescence spectrometer RF-5301PC.

## 3. Results and discussion

Fig. 1a shows a typical FE-SEM image of $TiO_2/CdS/CdSe(3)Mn^{2+}(0.2)/ZnS$ with the mood surface morphology. Here, a ZnS passivation is coated the CdS, CdSe nanocrystal by SILAR to reduce the recombination of exciton electrons with holes and electrolyte. In fact, the ZnS is absorbed into $TiO_2/CdS/CdSe:Mn^{2+}$ which do not change color of anode. Besides, average cluster size of anode can be determined ~50 nm by the FESEM image (Fig. 1a) and thickness of the film determined approximately 11.606 μm by a cross – section (Fig. 1b). Firstly, Looking at Fig. 1c, it is immediately obvious that the XRD of $TiO_2/CdS/CdSe(3):Mn^{2+}(0.2)/ZnS$ appears the peaks at 47.4° and 55.7° positions corresponding to the (200) and (111) planes which indicates an upstanding ZnS zinc Blende. It is a completely suitable result for JCPDS No. 05–5666. Secondly, it also shows the peaks at 43.3° and 50.0° positions corresponding to the (220) and (311) planes of CdSe zinc Blende (JCPDS No. 88–2346) and the peaks at 30.7°, 50,6° and 67.2° corresponding to (101), (112), (203) planes of CdS zinc Blende (JCPDS No. 41–1019), respectively. Finally, the left peaks of XRD characterize $TiO_2$ anatase (JCPDS No. 21–1272). This implies that CdS, $CdSe(3)Mn^{2+}(0.2)$ and ZnS nanoparticles have absorbed on $TiO_2$ films.

For QDSSCs, a band alignment of nanoparticles in anode is quite necessary for us to explain the diffraction and movement of excited electrons in the conduction band levels of semiconductor. Bulk CdSe has a band gap energy of 1.76eV [23], which limits its ability to absorb in the visible region and the CB of CdSe become lower than that of $TiO_2$. Thus, the excited electrons are against when they move to $TiO_2$. On the contrary, the CB of bulk CdS is higher than that of $TiO_2$ which is driving force the excited electrons to $TiO_2$ easier [18]. The band alignment of bulks $TiO_2$, CdS, ZnS is shown in Fig. 4. CdS/CdSe co-sensitized can significantly improve the performance of QDSSCs [23,24]. In addition, Lee and co-workers said that the Fermi energy of CdSe nanoparticles shifted above while that of CdS nanoparticles shifted down as CdS/CdSe co-sensitized [23] to make $TiO_2 < CdS < CdSe$ structure. Therefore,