

Chapter 2

Green Synthesized CdSe Quantum Dots Capped by 3-Mercaptopropionic Acid Sensitized Solar Cells

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Abstract In this paper, the green synthesized CdSe quantum dots (QDs) capped by 3-mercaptopropionic acid (MPA) sensitized solar cells are fabricated. Glycerol is chosen as the solvent to prepare the CdSe QDs, which makes the whole reaction is environmental-friendly. After MPA ligand exchanging, the as-synthesized CdSe QDs maintain the original absorbance at ca. 500 nm, coherence to the maximum absorbance of the solar spectrum. The strong photoluminescence quenching of the MPA capped QDs increases the nonradiative decay processes and is beneficial to the electron transfer. Then the MPA ligand exchanged QDs were assembled onto mesoscopic TiO₂ film to integrate into QD sensitized solar cells. The power conversion efficiency of the QD-sensitized solar cells reaches 0.12 % under sun illumination (AM 1.5, 100 mW cm⁻²) and relatively mechanism is discussed.

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2.1 Introduction

Dye-sensitized solar cells (DSSC) are considered to be a low-cost alternative to conventional solid-state solar cells. DSSC are based on photosensitization of mesoporous TiO_2 films by adsorbed sensitizers, such as Ruthenium complexes and organic dyes with the power conversion efficiency up to 11 % [1]. Besides, semiconductor nanocrystals-quantum dots (QDs) such as CdS, CdSe, PbS, PbSe and InP [2–10], which absorb light in the visible region, can also serve as sensitizer of DSSCs. The specific advantages of QDs over organic materials in light harvest come from the quantum confinement effect due to its size-dependent bandgap. Moreover, by using QDs, it is possible to utilize hot electrons to generate multiple electron-hole pairs per photon through the impact ionization effect [11]. QD-sensitizer also has a higher extinction coefficient than conventional dyes, which can reduce the dark current and increase the overall efficiency of a solar cell. Since QDs' proper energy level is suitable for electrons effectively transfer to the conduction band of TiO_2 or ZnO upon visible light irradiation, the maximum efficiency theoretically predicted for quantum dots-sensitized solar cells (QD-SSC) (44 %) is higher than that for DSSC using organic sensitizers (33.5 %) and for traditional Si solar cells (35 %).

Among various semiconductor QDs, CdSe QDs are suitable to integrate to solar cells because of its absorption in the visible region. Over the past two decades, various approaches have been explored to synthesize CdSe QDs. Although Zhang et al. [12] synthesized high quality scalable CdSe QDs, the trioctylphosphine (TOP) used as the solvent is highly toxic. More recently, focus of investigations turns to the water-phase synthesis of CdSe QDs [13, 14] in order to realize green synthesis of this QDs.

It is known that QD-SSC's performance largely benefit from the solubility and surface modification of the QD sensitizers which significantly influence charge transfer behavior [15]. In most cases, the surfactants used for preventing aggregation during the growth of the QDs contain long alkyl chains, like oleic acid (OA) [16]. In order to improve the charge transfer between nanocrystals and polymer, as well as electron transfer between QDs, extensive investigations on the surface modification of nanocrystals have been reported based on short insulating ligands, which leads to a relatively improved efficiency of solar cells. For example, pyridine treatment of the QDs is the most commonly used and effective procedure for improving device efficiency [17]. Olson et al. reported on a CdSe/P3HT blended device using butylamine as a shorter capping ligand for CdSe nanocrystals (NCs) [18]. Considering that 3-mercaptopropionic acid (MPA) is a kind of short-chain ligand and according to the well-known hard and soft acids and bases theory [19], the hard-hard or soft-soft molecules or ions can form a strong binding. The Cd^{2+} and Se^{2-} ions are classified as soft ions and have stronger interaction with soft “–SH (from MPA)” but not hard “–COOH (from OA)” So the MPA can form rather strong bonding with CdSe.

In this paper, we choose water phase glycerol as solvent to prepare the CdSe QDs. The reaction is environmental-friendly and energy saving, with which we have realized the in situ observation and control of the whole procedure. Then the long chain ligands olic acid (OA) of CdSe QDs was exchanged by the short chain ligands MPA. The MPA-capped CdSe QDs with absorbance of ca. 500 nm, which is coherence to the maximum absorbance of sun spectrum, were assembled onto mesoscopic TiO₂ film, choosing platinum as the counter electrode and fabricated into QD sensitized solar cells. With the increase of MPA, the energy conversion efficiency (ECE) increases from 0.08 to 0.12 % under the sun illumination (AM 1.5, 100 mW cm⁻²).

2.2 Experimental

The preparation of CdSe quantum dots: The Se precursor for the present work was prepared by mixing the selenium powder (0.005 mol) (A. R, Shanghai Meixing Chemical Co., Ltd.), sodium sulfite (0.01 mol) (A.R, Sinopharm Chemical Reagent Co., Ltd.), sodium hydroxide (0.01 mol) (A.R, Shanghai Aijian ready-made Reagent Co. Ltd.) and deionized water (50 ml) with N₂ protection and magnetic stirring. The mixture was heated to boiling while the solution turned from red brown to the black precipitated. Then sodium hydroxide (0.01 mol) was added, and after returning for 4 h, the reactants were cooled down to the room temperature followed by nitrogen protection for 30 min.

The Cd precursor was prepared by mixing water, ethanol and oleic acid (A.R, Jiangsu Yonghua Fine Chemicals Co., Ltd.) together in volume ratio of 10:30:8. Cadmium acetate 0.001 mol (A.R, Sinopharm Chemical Reagent Co. Ltd.) and sodium hydroxide (0.7 g) were added as precipitation agents to the mixed solvent (48 ml). The mixture was under the N₂ protection until it became clear and transparent. The reaction temperature was 120 °C.

The CdSe QDs were synthesized by adding 10 ml Se precursor solution to the 48 ml Cd precursor solution, under N₂ protection and magnetic stirring. The reactions were carried out at 120 °C for 5, 10, 15, 20, 25 and 30 min, respectively. The samples were centrifuged with ethanol, and dispersed in hexane.

The ligand exchange of olic acid (OA) acid-capped CdSe QDs to 3-mercaptopropionic acid (MPA)-capped CdSe QDs: Mix 3-Mercaptopropionic acid (MPA) (with molar ratio of 5,10, 20 and 30 comparing to CdSe QDs), 0.3 mL H₂O and 1 mL methanol, adjusting the pH value of the solution around 12 with 40 wt% of NaOH solution. Then, add 5 ml CdSe solution (in hexane, at 120 °C in 30 min). After stirring the above mixed solution for 2 h, 7 mL H₂O was added. The whole solution are kept standstill for 5 min, which is layered with the bottom layer of yellow mixed CdSe QDs and MPA and the up layer of transparent hexane. The bottom layer is used in the solar cell fabrication. And the four samples (molar ratio MPA/QDs = 5, 10, 20 and 30) are named I, II, III and IV, respectively.

The preparation of CdSe QDs sensitized solar cells-The preparation of anode: The fluorine-doped SnO_2 (FTO) glass ($7 \Omega/\square$) was first cleaned in a detergent solution using an ultrasonic bath for 10 min and then washed with water and ethanol with the same method. A layer of TiO_2 past (P25) was coated on the FTO glass plates by screen-printing. Then, the FTO glass was kept in a clean box for 3 min and then dried for 6–8 min at 125°C . This procedure is repeated for 6 times and the final thickness of TiO_2 film is $12 \mu\text{m}$ and area is 25 mm^2 . The electrodes coated with the TiO_2 pastes were gradually heated under an airflow at 125°C for 20 min, 325°C for 5 min, 375°C for 5 min, 450°C for 15 min and finally at 500°C for 15 min. The FTO glass with the TiO_2 film is treated at 70°C in 30 min with 40 mM TiCl_4 solution, then washed with water and ethanol and sintered at 500°C for 30 min ($2^\circ\text{C}/\text{min}$), and then kept at room temperature for 20–24 h. After that, the TiO_2 anode was immersed in the MPA-capped CdSe QDs for 24 h.

The preparation of the counter electrode: To prepare the counter electrode, a hole ($d = 1 \text{ mm}$) was drilled in the FTO glass by sandblasting. The perforated FTO glass was washed with H_2O as well as with 0.1 M HCl solution in ethanol by ultrasonic bath for 10 min. After wiping off residual organic matter by heating in air for 15 min at 400°C , the Pt past was deposited on the FTO glass by screen-printing technique, and sintered at 400°C for 30 min.

The encapsulation of the CdSe QDs sensitized solar cells: Seal the anode and Pt-counter-electrode, and the polysulfide electrolyte (consisting of 2 M Na_2S and 3 M S) was infused into the solar cells.

The high resolution transmission electron microscopy (HRTEM) (JEM–201, American FEI Company) was used to characterize the morphology of the CdSe QDs. The optical absorption spectra (a Lambda 950 UV-Visible Spectrophotometer, Perkin Elmer, Waltham, MA) and the photoluminescent (PL) spectra (model Fluorolog-3-P, France JobinYvoncompany, model Cary 500, American Varian company) were used to test the optical properties of CdSe QDs. Current density-voltage measurements under AM 1.5 G $100 \text{ mW}/\text{cm}^2$ illumination are used to characterize the efficiency of the CdSe QDs sensitized solar cells.

2.3 Results and Discussion

Characterization of CdSe QDs: Figure 2.1(a–d) presents HRTEM, absorption spectra and luminescence spectra of the synthesized CdSe QDs. From Fig. 2.1a, b it is seen that oval shaped CdSe QDs show an excellent monodispersity with the size distribution mainly close to 3–4 nm as shown in the inset of Fig. 2.1a, while the existence of lattice fringe indicates that the products have excellent crystallinity. With the prolonged reaction time from 5 to 30 min, the color of real samples changed from yellow, orange to red (the inset of Fig. 2.1b). From the absorption spectra of the CdSe QDs it is seen that absorption peaks appear at 475–500 nm, coherence to the maximum remittance region of the solar spectrum. An obvious

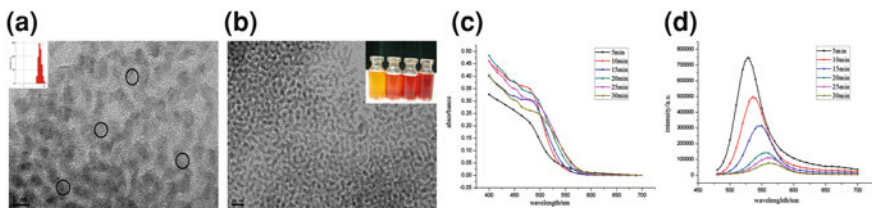


Fig. 2.1 **a** HRTEM of CdSe QDs (scale bar 5 nm) and its size distribution, **b** HRTEM of CdSe QDs (scale bar 20 nm) and the real sample of CdSe QDs, **c** absorption spectra of the QDs at 120 °C in different reaction time, and **d** emission spectra of the QDs at 120 °C in different reaction time excited at 460 nm

blue shift of the absorption peak comparing with that of the bulk CdSe (717 nm) proves occurrence of the band-gap broadening phenomenon as a consequence of the quantum size effect. Furthermore, with the increased reaction temperature, the size of products grew larger; the quantum size effect thus reduces, leading to the red shift of the absorption peak due to narrowing of the band-gap. This tunable band-gap of CdSe QDs is suitable to be applied in solar cells as sensitizers. Figure 2.1d shows the normalized emission spectra of CdSe QDs. Under the excitation of blue light (460 nm), a broad emission band is observed peaking in the green to yellow region and showing obvious red shift with the increasing reaction time also due to the quantum size effect.

Characterization of MPA capped-CdSe QDs: Because MPA contains short alky chains, while olic acid has long alky chains, after MPA capping, samples I, II, III and IV show the monodispersity (Fig. 2.2a–d) inferior to that of olic acid capped CdSe QDs (Fig. 2.1a, b). With the increased MPA/QDs molar ratio (5, 10, 20 and 30), the aggregation of the CdSe QDs becomes more severe. MPA can be a large driving force in nanocrystal aggregation which improves the charge transport [20–22]. It is expected to increase relatively power conversion efficiency of solar cells [23, 24].

Figure 2.3 illustrates the absorption spectra of MPA capped samples I, II, III and IV where samples I and II shows the similar spectra to that of CdSe QDs capped by olic acid (Fig. 2.1c), i.e., ligand exchanging doesn't affect the QDs absorption. However, with the further increased quantity of MPA (samples III and IV), absorption peaks become undetectable; proving the aggregation among MAP capped QDs again, coinciding with the result of HRTEM (Fig. 2.2).

In contrast, strong photoluminescence quenching was observed in the case of MPA replaced QDs, as shown in Fig. 2.4, comparing to the MPA-free CdSe QDs' (Fig. 2.1d). With the increased molar ratio MPA/QDs = 5, 10, 20 and 30, emission intensity decreased obviously. This phenomenon could be attributed to the removal of excess oleic acid ligands accumulated around the QDs, resulting in the increase of nonradiative decay processes [25–27], which is beneficial to the electron transferring from the conduction band of CdSe to TiO₂'s [28–31].

Current and voltage measurements: The current density (J) and voltage (V) were measured under AM 1.5 G 100 mW/cm² illumination on samples I, II, III

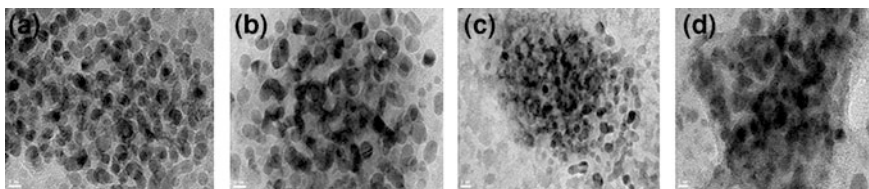


Fig. 2.2 HRTEM photos of samples I, II, III and IV (a, b, c and d)

Fig. 2.3 Absorption spectra of samples I, II, III and IV

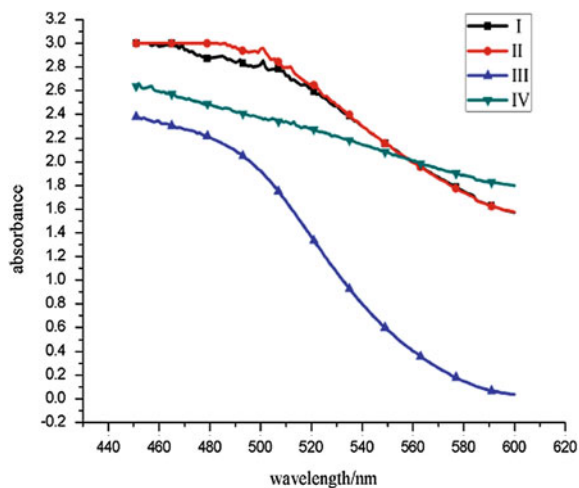
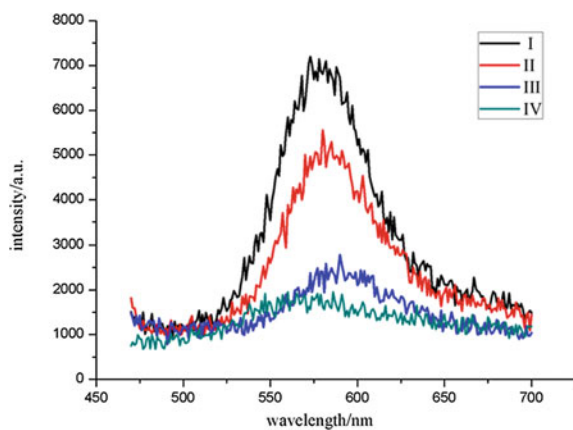


Fig. 2.4 Emission spectra of samples I, II, III and IV excited at 460 nm



and IV being assembled onto the mesoscopic TiO_2 film. As shown in Fig. 2.5 and Table 2.1, the optimal results have been obtained from the sample IV, that is, an open-circuit voltage (V_{oc}) of 300.11 mV, a short-circuit current density (J_{sc}) of 1.12 mA/cm^2 , a fill factor (FF) of 0.36, and a PCE of 0.12 %.

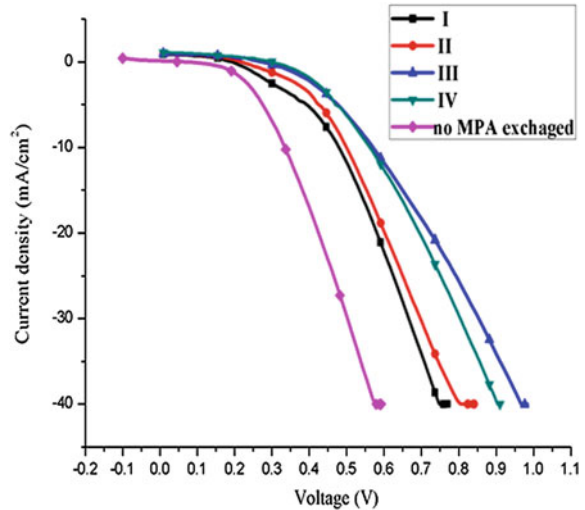


Fig. 2.5 the sealed solar cells’ I–V curves of sample I, II, III and IV and no MPA exchanged CdSe QDs

Table 2.1 parameters obtained from the I–V curves of QD-SSCs with different mol ratio of MPA/CdSe QDs

Sample number	Different mol ratio of MPA/CdSe QDs	η (%)	FF	V_{oc} (mV)	J_{sc} (mA cm ⁻²)
No MPA exchanged CdSe QDs	0:1	0.00	0.26	69.81	0.12
I	5:1	0.08	0.45	191.11	0.90
II	10:1	0.10	0.46	215.12	0.99
III	20:1	0.11	0.41	275.82	1.00
IV	30:1	0.12	0.36	300.11	1.12

From Fig. 2.5 and Table 2.1 it is also seen that the PCE of devices is sensitive to the molar ratio of MPA/CdSe QDs. With the increase of the MPA loading, the increase of PCE can be observed while the MPA free CdSe QDs has no such an effect. This is because when oleic acid ligands accumulated around the CdSe QDs, their monodispersity is excellent, and this is not beneficial for the electron transfer between QDs and leads to the increase of radiative of the electrons as proved by the strong emissions, resulting in no power conversion efficiency of solar cells. However, when olic acid is replaced by MPA, especially, with the increase of MPA (samples II, III and IV), the aggregation among QDs occurs. Therefore, electron transfer and the nonradiative decay processes are enhanced, i.e. after the solar illumination, the electrons preferentially transfer to the conduction band of TiO₂ from the conduction band of CdSe QDs. The efficiency of the solar cells increases thus to 0.08, 0.10, 0.11 and 0.12 %, respectively.

2.4 Conclusion

In this paper, the CdSe quantum dots (QDs) are green synthesized by the glycerol solvent. The long chain ligands olic acid of CdSe QDs was replaced by the short chain ligands of MPA. The as-synthesized CdSe QDs with the absorbance at ca. 500 nm, coherence to the maximum absorbance of sun spectrum, were assembled onto mesoscopic TiO₂ film, choosing platinum as the counter electrode to prepare the CdSe QDs sensitized solar cells. With the increase of the quality of MPA, the power conversion efficiency of the QD-sensitized solar cell reaches 0.12 % under the sun illumination (AM 1.5, 100 mW cm⁻²).

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