

Synthesis of CdSe quantum dots (QDs) via a hot-bubbling route and sensitized solar cells assembly

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CdSe quantum dots (QDs) were synthesized via a hot-bubbling route. The synthetic parameters including temperature, growth time, and feeding ratio Cd/Se were studied to show great influence on the optical properties. More than 5.0g CdSe QDs were obtained in a lab-scale synthesis at 210°C. The prepared CdSe QDs had been transferred into aqueous solution via ligand exchange. To expand the spectral response in photovoltaic devices, CdSe QDs were deposited on mesoporous TiO₂-SiO₂ electrode, and the solar cells (SCs) were prepared. It was found that the sensitization solar cells, for the TiO₂-SiO₂/CdSe(hot-bubbling) device, showed a power conversion efficiency of 1.94% under the illumination of one sun (AM1.5, 100mW/cm²), which was about as the same as the TiO₂-SiO₂/CdSe(hot-injection) device ($\eta=1.74\%$). This research provides an alternative in the manufacturing the CdSe QDs that could find applications in photoelectrical devices.

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1. Introduction

Since the sandwich architecture for the dye-sensitized solar cells (DSSCs) was developed by Grätzel in 1991 [1], it has drawn much attention [2-4]. Up to now, the highest efficiency of DSSCs reached over 20% [5]. Quantum dots (QDs) can also serve as solar cells sensitization [6-9] because they can transfer electrons to large band gap semiconductors. Quantum dots sensitized solar cells (QDSSCs) have been attracting much attention because of the specific advantages of QDs. First, size quantization effect allows one to tune the visible response and vary the band energies to modulate the vectorial charge transfer across different-sized particles [10]. In addition, QDs can generate multiple excitons carriers with a single photon through impact ionization [11]. Up to now, more methods such as hot-injection [12], sol-gel route [13], electrostatic deposition [14], gas evaporation [15], micelles [16], solvent growth [17] and so on [18-20] have been developed for the synthesis of II-VI QDs. However, all the above reported methods are not advantage in terms of their tiny scale, the high cost of precursors (tetradecyl phosphonic acid (TDPA), dodecylamine (DDA)) and the inconvenience for one-pot operation (liquid-liquid reaction). The scalable synthesis of CdSe QDs with continuous operations has barely been reported.

In this research, we report large-scale synthesis of high-quality CdSe QDs. More than 5.0 g CdSe QDs were obtained in a lab-scale synthesis. A hot-bubbling strategy was proposed in which H₂Se was continuously bubbled

into a hot solution of cadmium oleate with a flow of inert gas. This route has such characteristics as superior heat transfer compared to the liquid-liquid reactions, faster mass transfer due to the presence of gas reactants, ease of rate control of the reaction, and a wide range of temperature choice which affords the possibility of annealing the quantum dots. This gas-hot liquid reaction provides a burst of homogeneous nucleation, a continuous operation, a good control over the final size and an opportunity for scaling up. Therefore, this hot-bubbling synthetic approach is featured by both the advantages of hot-injection and the gas-aqueous solution reactions, and this process is more applicable to the fixed or packed fluidized bed reactor if we take the cost effect and safety into consideration. In addition, we also utilized the synthesized CdSe QDs as sensitizers for solar cells, and deposited CdSe QDs on mesoscopic TiO₂-SiO₂ electrode. A wider range of optical response and a higher photon-to-current conversion efficiency were obtained on the sensitized solar cells.

2. Experiment

2.1. Synthesis of CdSe QDs

For a typical synthesis, 280 mg CdO, 1.4 ml oleic acid (OA), and 100 mg trioctylphosphine oxide (TOPO) were mixed with 8 mL ODE, and was loaded into a 50 mL four-necked flask. The reaction flask was then transferred

to a Schlenk line and placed under vacuum, heated gradually to 100°C to remove residues of volatile solvents. The system was then switched to N₂ flow, and the temperature was increased to 250°C. After a period of time (~20 min) the solution became colorless and transparent, *i.e.*, the cadmium oleate was produced. The H₂Se gas was prepared from NaBH₄, Se and H₂O, and was bubbled into cadmium oleate solution with a steady N₂ flow (5 L·min⁻¹) as carrier gas.

Toluene, methanol and isopropanol were added into the final reaction solution, and the mixture was centrifuged at 15000 r.p.m. for 20 minutes. Then the upper liquid was poured out, the precipitate was CdSe quantum dots. The procedure was repeated three times. Finally, the precipitate was stored in toluene for use.

2.2. Preparation of TiO₂-SiO₂ photoanode

The TiO₂-SiO₂ paste was made as follows [21]. TiO₂ (10g) mixed with SiO₂ (0.5g), acetic acid (3ml), water (12ml) and ethanol (50ml) was grinded for 15 min. After the grinded paste was mixed with ethanol (300ml), terpineol (40g) and ethyl cellulose (6g), the mixture was homogenized by stirring and ultrasonic treatment. A layer of film was fabricated on the F-doped tin oxide (FTO, 20V/A) surface by screen-printing method. Then, the TiO₂-nano-SiO₂ film was obtained after annealed at 500°C for 30 min. CdSe QDs were added into TiO₂-nano-SiO₂ films using the spin-coating method. Thus, the TiO₂-nano-SiO₂ photoanode could be gotten.

2.3. Fabrication and measurement of QDSSCs

The CdSe-modified TiO₂-nano-SiO₂ electrode was incorporated as the active photo-anode. The Pt coated FTO conductive glass was used as the counter electrode. The two electrodes were sandwiched by thermal adhesive film (Surlyn1702, Dupont). The electrolyte solution consisted of Na₂S (0.5M), S (0.8M), and KCl (0.2M) [22]. The electrolyte was filled through a hole made on the counter electrode [23]. Photocurrent-voltage (J-V) measurement was performed with the solar simulator (94063A, Newport), equipped with the 1000W xenon lamp (6272NS, Newport) and the Keithley digital source meter (2400, USA). The QTest Station 1000 ADI system (Crowntech Inc.) illuminated with a 300W Xe were used during the measurements of incident photon to current conversion efficiency (IPCE).

3. Results and discussion

3.1. Influence of temperature

To study the influence of temperature, the syntheses temperature were enhanced from 150°C to 270°C with a

same molar ratio of Cd:Se=2:1. The growth time was also fixed. Correspondingly there is a red-shift in the position when the temperature is enhanced from as shown in Fig. 1. The fwhm (full width of half maximum) in the PL peaks (band gap) is the smallest at 210°C. This indicates the size of the particles grows larger and the size distribution becomes better at 210°C.

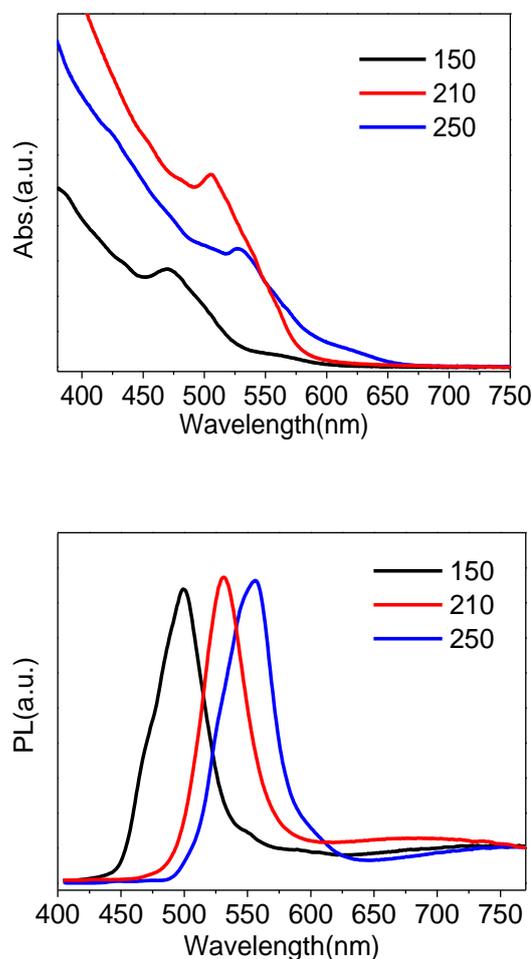


Fig. 1. Absorption and PL spectra of the CdSe QDs synthesized at different temperatures with a fixed feed molar ratios of Cd:Se=2:1 (color online)

3.2. Influence of growth time

To get knowledge of the evolution for the CdSe QDs, we conducted the time-resolved experiments at 150°C when we fixed the ratio of Cd:Se at 3:1. With the reaction time prolonging, the color of solution turns from yellow to dark yellow. The evolution of the absorption and emission spectra was displayed in Fig. 2. It was found that both the absorption onsets and PL band emission shift to the longer wavelength region as expected. The broad peak at 680 nm does not shift much which can be a characteristic of similar surface trapping sites of the synthesized QDs.

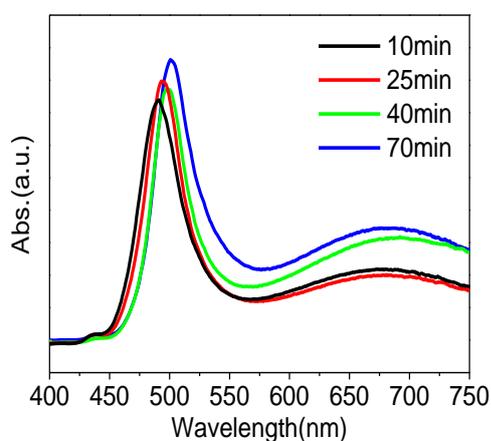
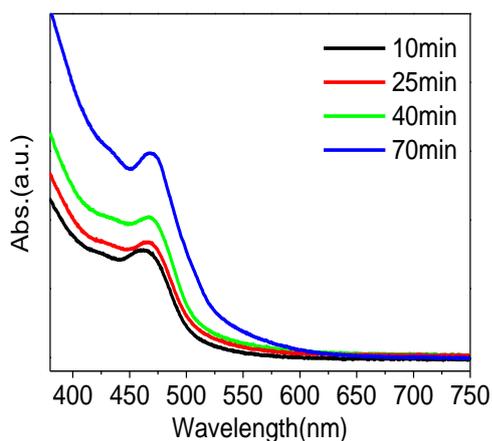


Fig. 2. The absorption and PL spectra of the evolution for the CdSe QDs synthesized at 150°C with a ratio of Cd:Se=3:1 (color online)

3.3. Influence of Cd/Se feed ratio

In this experiment the molar ratio of Cd/Se precursors was varied from 2:1 to 4:1 when the synthesis was carried out at a temperature of 210°C, and the growth time was fixed at 50 min. In Fig. 3, it is worth to note that the first excitonic absorption peak exhibits a red-shift from 488 nm to 508 nm with the decreasing Cd/Se ratio from 2:1 to 4:1. The red-shift was also found in the corresponding PL profiles from 518 nm to 528 nm. This demonstrates that the size of the CdSe QDs was bigger and bigger.

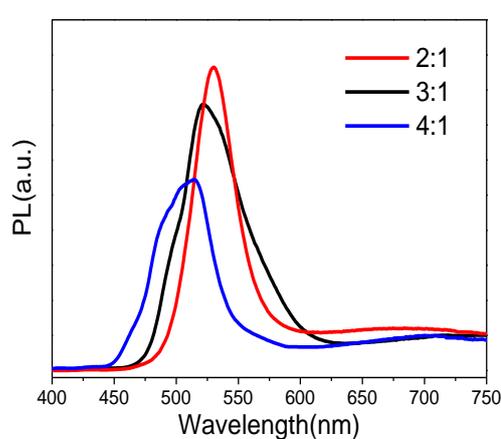
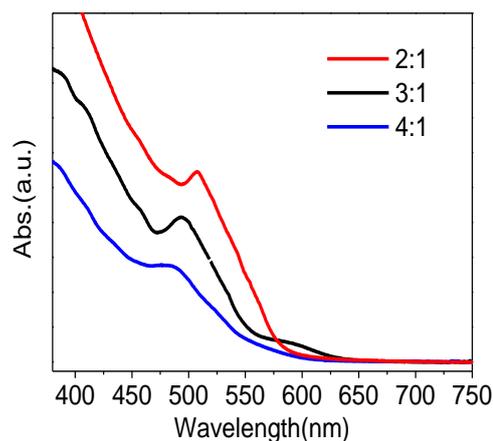


Fig. 3. Absorption and PL emission spectra of CdSe QDs under different Cd/Se ratios (color online)

3.4. CdSe QDs sensitized solar cells

To study the photovoltaic performance, we fabricated the standard QDSSCs using the TiO₂-nano-SiO₂ hybrid films as photoelectrode. Fig. 4 presents the J–V characteristics of the fabricated solar cells, and the parameters from J–V curves were described in Table 1.

Table 1. Parameters obtained from the J–V profiles of various QDSSCs

Electrode	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	η(%)
TiO ₂ -SiO ₂ / MPA-CdSe(hot-bubbling)	0.58	10.5	0.33	1.94
TiO ₂ -SiO ₂ / MPA-CdSe(hot-injection)	0.58	10.1	0.31	1.74

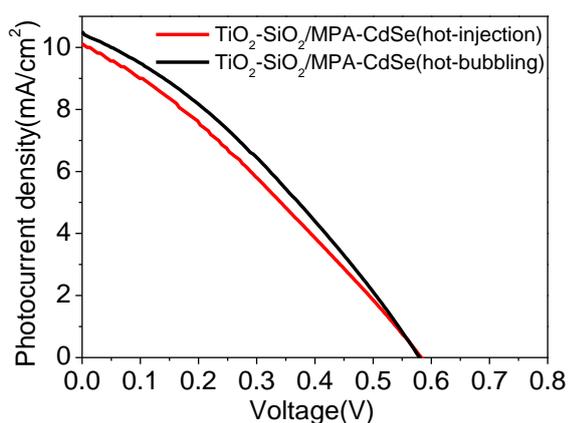


Fig. 4. J-V characteristics of QDSSCs for various photoelectrodes

The most notable variation is the short circuit current (J_{sc}) density and the power conversion efficiency (η). For the $\text{TiO}_2\text{-SiO}_2\text{/MPA-CdSe(hot-bubbling)}$ device, the power conversion efficiency is 1.94%, which is about as the same as the $\text{TiO}_2\text{-SiO}_2\text{/MPA-CdSe(hot-injection)}$ device. The increment of J_{sc} from 10.5mA/cm^2 is achieved. The result indicates that MPA-CdSe (hot-bubbling) QDs-sensitized solar cells can lead to a significant efficiency. The reason is that the size distribution of CdSe (hot-bubbling) QDs is uneven. And the micro/meso-pores in the hybrid film were utilized better. There is the improvement in the light harvesting capacity of the photoelectrode, and the efficiency was notable. The IPCE profiles are given in Fig. 5, and the profile resembles the absorption spectra of CdSe QDs reasonably well. All solar cells show photocurrent responses below 600 nm. A maximum IPCE value of 50% is observed for the $\text{TiO}_2\text{-SiO}_2\text{/MPA-CdSe(hot-bubbling)}$ device. IPCE values of the $\text{TiO}_2\text{-SiO}_2\text{/MPA-CdSe(hot-injection)}$ device shows lower efficiencies with a maximum IPCE of 40%. These lower IPCE values indicate that a larger fraction of carriers are lost to charge recombination within the particle or at the CdSe(hot-injection)/ $\text{TiO}_2\text{-SiO}_2$ interface. The results show that the MPA-CdSe (hot-bubbling) QDs increases the IPCE value.

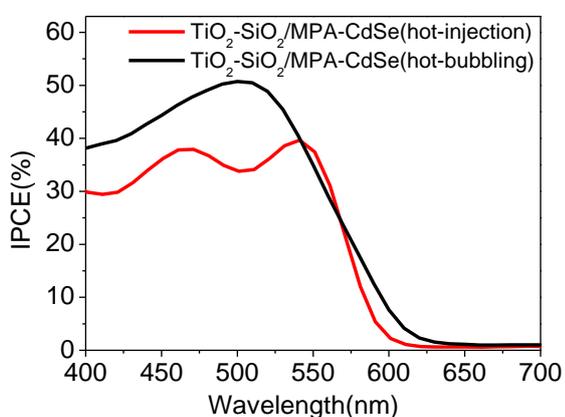


Fig. 5. IPCE characteristics of QDSSCs for various photoelectrodes

4. Conclusions

In summary, we developed a hot-bubbling strategy for continuous operation and large-scale preparation of mono-dispersed CdSe QDs. The optical properties of the QDs can be tuned by control of synthetic parameters such as reaction temperature, growth time, feeding ratio of Cd/Se. By control of the growth time, reaction temperature and feeding ratio of Cd/Se, the wavelengths of the Uv-vis and PL can be tuned. The sensitization of mesoporous $\text{TiO}_2\text{-SiO}_2$ electrode was successfully prepared and the CdSe quantum dots were used to sensitize the solar cells. The power conversion efficiency of the sensitized solar cells reaches 1.94% under the illumination of one sun (AM1.5, 100mW/cm^2). This research provides an alternative in the manufacturing the CdSe QDs that could find applications in photoelectrical devices.

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