

SYNTHESIS AND CHARACTERIZATION OF WATER-SOLUBLE CdSe NANOPARTICLES CAPPED BY AOT*

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Abstract Water-soluble CdSe nanoparticles were synthesized using AOT (sodium bis(2-ethylehexyl)-sulfosuccinate) as stabilizer, cadmium acetate and Na_2SeSO_3 as precursors in aqueous phase. The influence of some key factors, such as reaction time, temperature, concentration and molar ratio of precursors on the optical properties of CdSe nanoparticles was systematically investigated through UV-Vis and PL spectra. Powder X-ray diffraction (XRD) was used to characterize the crystalline structure of synthesized CdSe nanoparticles. As-prepared CdSe nanoparticles exhibit an apparent quantum confinement effect and typical hexagonal wurtzite structures. Finally, the optimal experimental conditions were obtained.

Keywords: AOT; CdSe; Nanoparticles; Aqueous phase.

INTRODUCTION

Owing to optical, photochemical, electrochemical and nonlinear optical properties, research on II-VI semiconductor nanoparticles has attracted much attention^[1–3]. Whereas, the most attractive potential applications of II-VI semiconductor nanoparticles are in biological fields such as fluorescent probes, which will play an important role in quantitatively marking molecules and cells. For example, Alivisatos^[4] and Nie^[5] successfully marked the fibroblasts of mouse by virtue of II-VI nanoparticles after treatment and introduced new methods of non-isotopic detection.

Among various kinds of II-VI semiconductor materials, CdSe nanoparticles are the most widely studied because of their tunable emission in the visible range. Up to now, organometallic approach^[6] has been widely used for the preparation of CdSe nanoparticles, but with disadvantages of complicated preparation process, strict and harsh conditions. Thus, it is necessary to prepare CdSe nanoparticles in water through simple, fast and convenient methods^[7–12] owing to the advantages of non-toxicity, stability and good biological compatibility. Wang *et al.*^[13] synthesized water-soluble CdSe nanoparticles by use of sodium hexametaphosphate (HMP), octyl mercaptan (OMT) and mercaptoacetic acid (TGA) or other thio-containing compounds as surfactants respectively. Yu^[14–17] prepared a series of high luminescent water-soluble semiconductor nanoparticles by virtue of mercaptoacetic acid, cysteamine, L-cysteine, sodium citrate, and so on as stabilizers. Yang^[18] synthesized monodisperse CdSe nanoparticles by using PVP as modifier in water.

AOT (sodium bis(2-ethylehexyl)-sulfosuccinate) is a commonly used surfactant in the synthesis of metal or semiconductor nanoparticles. Alivisatos^[19] synthesized CdS nanoparticles by using AOT as surfactant through reverse microemulsion method. Owing to the amphiphilic feature of AOT molecules, they can form ‘nano-

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reactor' in reverse microemulsion solution and then achieve the purpose of controlling the size of CdS nanoparticles. Prasad^[20] reported a method for preparing silver nanoparticles by using AOT as surfactant in aqueous phase. Silver nanoparticles could be transfer from water to organic phase after adding phase transfer agents. Moreover, it was indicated that silver nanoparticles can exist stably both in water and organic phase. The different modified mechanisms of AOT to the surface of nanoparticles in water and organic phase were intimately analyzed by FTIR spectra, which proved that AOT had a dual modified effect on the surface of silver nanoparticles.

In the present work, we used cadmium acetate and Na_2SeSO_3 as precursors, AOT as stabilizer and surfactants to synthesize CdSe nanoparticles in aqueous phase by changing reaction temperature, precursor concentration and precursor molar ratios.

EXPERIMENTAL

Chemicals and Apparatus

Chemicals

Cadmium acetate ($\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), selenium powder, AOT (sodium bis(2-ethylehexyl)-sulfosuccinate), anhydrous sodium sulfite (Na_2SO_3) and isopropanol were of analytical grade and were used without further purification. Redistilled water was used as received. The AOT used was import-packing products.

Apparatus

Absorption and fluorescent spectra were measured by a Lambda 25 UV-Visible spectrophotometer and an LS-55 fluorescence spectrophotometer which were both made from Perkin-Elmer Company.

Experimental Procedures

Preparation of Na_2SeSO_3

79 mg (1 mmol) selenium powder, 252 mg (2 mmol) Na_2SO_3 and 100 mL redistilled water were added into a two-neck flask. Under stirring and bubbling N_2 , the reaction with reflux condensation continued at 100 °C until the gray black selenium powder dissolved in water completely.

Preparation of CdSe nanoparticles

89 mg (0.2 mmol) AOT, 27 mg (0.1 mmol) cadmium acetate and 95 mL redistilled water were added into a two-neck flask. After heating to 70 °C under stirring and bubbling N_2 , 5 mL newly prepared Na_2SeSO_3 solution was added slowly into the flask. CdSe nanoparticles could be prepared at different temperature or time. Furthermore, effects of the concentration and ratio of precursors on the synthesis of CdSe nanoparticles were also investigated.

Preparation of powder CdSe nanoparticles

50 mL isopropanol was added into 300 mL as-prepared solution of CdSe nanoparticles. Powder CdSe nanoparticle samples were obtained through centrifugation and drying in vacuum oven at 40 °C.

RESULTS AND DISCUSSION

When the size of nanoparticles is less than the exciton Bohr radius, the absorption spectrum will shift to higher energy direction (blue shift) and presents discrete absorption band and spectral configuration, which is called the quantum size effect of nanoparticles. Owing to such an effect, absorption or fluorescence peaks show obvious blue shift with decreasing the size of nanoparticles.

Effect of Temperature

In order to investigate the effects of temperature on the synthesis of CdSe nanoparticles, the CdSe nanoparticles are synthesized under vigorous stirring and N_2 bubbling at different temperatures for 30 min with constant ratio 2:1:0.5 of AOT, cadmium acetate and Na_2SeSO_3 and concentration of cadmium acetate 1 mmol/L. Figure 1 shows the absorption and fluorescent spectra of CdSe nanoparticles at 55, 65, 70, 80 and 90 °C, respectively. For example, the absorption peaks of CdSe nanoparticles at above different temperatures show at 509, 528, 548,

574, 625 nm, respectively; moreover, the absorption band edges lie at 539, 569, 589, 650, 680 nm, respectively. Accordingly, the peaks of fluorescent spectra of CdSe nanoparticles are at 542, 550, 578, 587 and 583 nm, respectively. Based on the above data, we can see that the absorption and fluorescent peaks show an apparent red shift with the increase of reaction temperature, which indicated that the sizes of CdSe nanoparticles were strongly dependent on temperature. It was found that a symmetrical fluorescent peak with the full-width at half-maximum (FWHM) only 50 nm could be observed when the reaction temperature is at 70 °C, indicating a relatively narrow size distribution of CdSe nanoparticles.

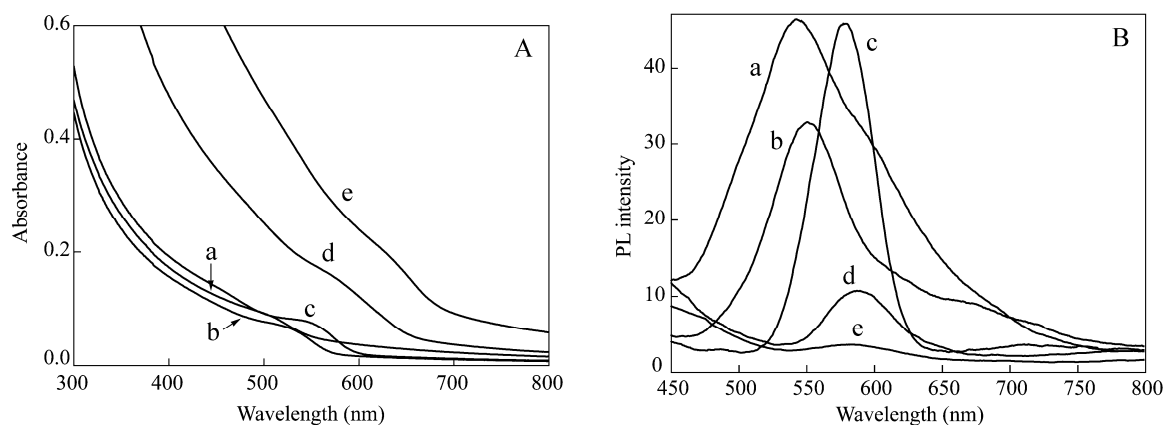


Fig. 1 UV-Vis absorption (A) and PL (B) spectra of CdSe nanoparticles prepared at different temperatures for 30 min with constant ratio 2:1:0.5 of AOT, cadmium acetate and Na_2SeSO_3 and concentration of cadmium acetate 1 mmol/L (a 55 °C, b 65 °C, c 70 °C, d 80 °C and e 90 °C)

Effect of the Precursor Concentration

With the constant ratio (2:1:0.5) of AOT, cadmium acetate and Na_2SeSO_3 , CdSe nanoparticles were synthesized under vigorous stirring and N_2 bubbling at different concentrations of cadmium acetate at 70 °C for 30 min. Figure 2 shows the absorption and fluorescent spectra of CdSe nanoparticles prepared at different precursor concentrations. The absorption peaks are at 526, 535 and 549 nm, and the emission peaks locate at 561, 569 and 597 nm corresponding to the precursor concentration of 1, 1.5 and 2 mmol/L, respectively. Obviously, the size of CdSe nanoparticles increases with precursor concentration, indicating that the precursor concentration can tune the size of CdSe nanoparticles readily.

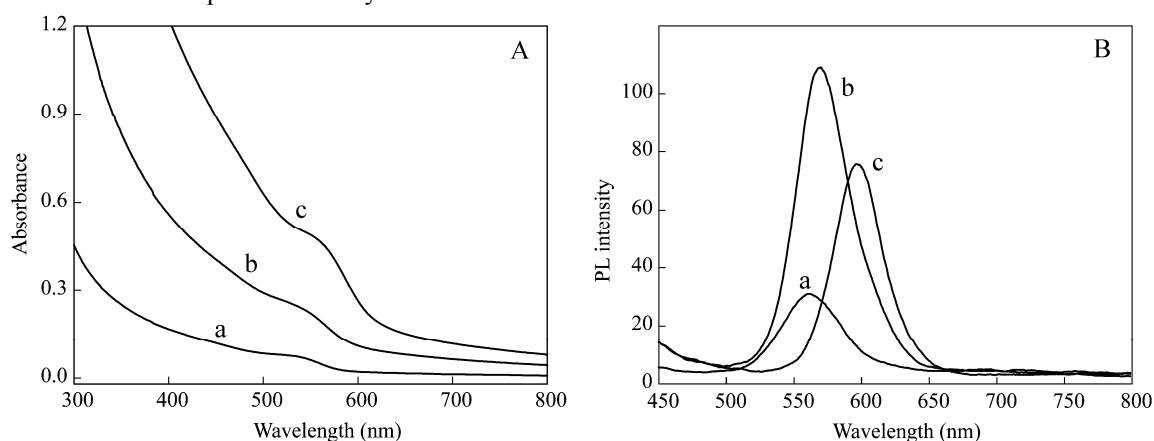


Fig. 2 UV-Vis absorption (A) and PL (B) spectra of CdSe nanoparticles prepared at different precursor concentrations with the constant ratio (2:1:0.5) of AOT, cadmium acetate and Na_2SeSO_3 (a 1 mmol/L, b 1.5 mmol/L and c 2 mmol/L)

Effect of Reaction Time

Keeping the ratio of AOT, cadmium acetate and Na_2SeSO_3 (2:1:0.5) and the concentration of precursor (1 mmol/L), CdSe nanoparticles were synthesized under vigorous stirring and N_2 bubbling at 70 °C for different reaction time. Effects of reaction time on the synthesis of CdSe nanoparticles were studied, and the corresponding absorption and fluorescent spectra are shown in Fig. 3. The absorption and fluorescent peaks shift toward long wavelength greatly with prolonging reaction time. It could be observed that the fluorescent peak shifts from 576 to 614 nm and PL intensity increases with reaction time prolonging within 30 min; while PL intensity decreases gradually after the reaction continued for another 30 min, which indicates that the size and fluorescent properties of CdSe nanoparticles are dependent on reaction time.

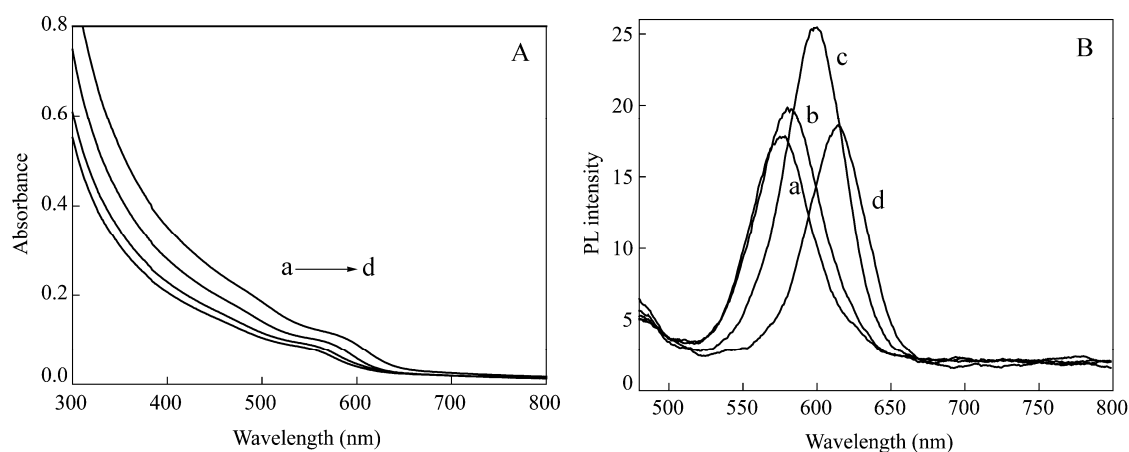


Fig. 3 UV-Vis absorption (A) and PL (B) spectra of CdSe nanoparticles prepared at different reaction time with constant ratio of AOT, cadmium acetate and Na_2SeSO_3 (2:1:0.5) and the concentration of precursor (1 mmol/L) (a 10 min, b 15 min, c 30 min and d 45 min)

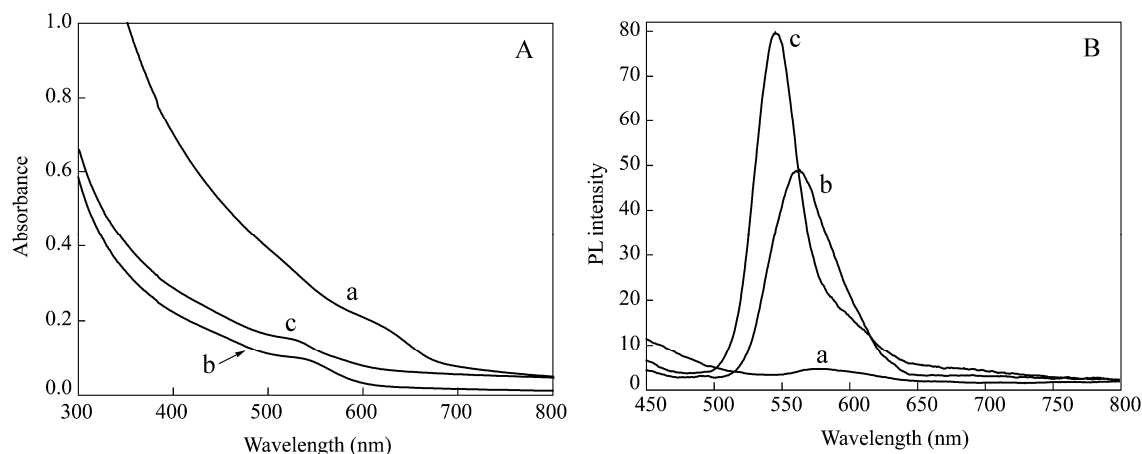


Fig. 4 UV-Vis absorption (A) and PL (B) spectra of CdSe nanoparticles prepared at different AOT: Cd^{2+} ratios with constant cadmium acetate and Na_2SeSO_3 ratio of 1:0.5 and precursor concentration of 1 mmol/L (a 1.5:1, b 2:1 and c 2.5:1)

Effects of AOT

AOT played an important role in modifying the nanoparticles surface, preventing the aggregation of nanoparticles efficiently and forming CdSe nanoparticles with narrow size distribution. Fixing molar ratio of cadmium acetate and Na_2SeSO_3 of 1:0.5 and precursor concentration of 1 mmol/L, CdSe nanoparticles were synthesized at 70 °C for 45 min with different amounts of AOT. Figure 4 shows absorption and fluorescent spectra of CdSe

nanoparticles with different molar ratios of AOT to Cd^{2+} (namely 1.5:1, 2:1 and 2.5:1). It could be observed that PL intensity of CdSe nanoparticles noticeably increases with the amount of AOT at a proper range because of surfactant surface modification of nanoparticles and making surface traps of nanoparticles decrease. Furthermore, it could also be seen that the absorption and fluorescent peaks of CdSe nanoparticles shift greatly toward high energy (blue shift) with the addition of more AOT, which explains that increasing amount of AOT properly is beneficial to synthesize CdSe quantum dots with small size.

Crystalline Structure Analysis

Wide-angle XRD powder pattern of CdSe nanoparticles is shown in Fig. 5. The diffraction peaks locate at 25.0° and 40.0° , 47.0° , which are in accordance with (002) and (103) planes of hexagonal wurtzite CdSe, respectively. Definitely, as-prepared CdSe quantum dots have the similar crystal structure to the bulk CdSe materials.

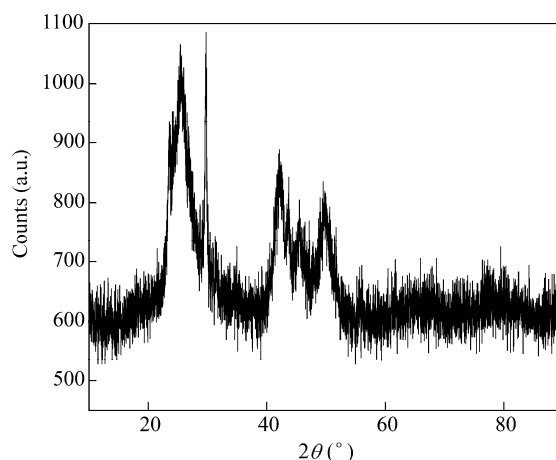


Fig. 5 XRD pattern of as-prepared CdSe nanoparticles

CONCLUSIONS

Stable CdSe nanoparticles capped by AOT were synthesized in aqueous phase by using cadmium acetate and Na_2SeSO_3 as precursors. The influence of some key factors, such as reaction time, temperature, concentration and molar ratio of precursors on the optical properties of CdSe nanoparticles were systematically investigated by UV-Visible absorption and PL spectra. The optimal experimental conditions are available, *i.e.* molar ratio of $n(\text{AOT}):n(\text{Cd}^{2+}):n(\text{SeSO}_3^{2-})$ is 2:1:0.5 at 70°C , for 30 min under N_2 atmosphere. Possibly, this method can be extended to prepare other water-soluble semiconductor nanocrystals, such as CdS and metal nanoparticles.

REFERENCES

- 1 Oded, O., Ran, T.V. and Ilina, B., J. Mater. Chem., 2009, 19: 7650
- 2 Jose, A.Y., Wang, A. and Peng, X.G., J. Am. Chem. Soc., 2001, 123 (36): 8844
- 3 Chander, R., Michael, K.F.L. and Manoj, V.W., Langmuir, 2006, 22 (11): 5018
- 4 Brucher, M., Moronne, M. and Gip, P., Science, 1998, 281(5385): 2013
- 5 Chan, W.C. and Nie, S.M., Science, 1998, 281(5385): 2181
- 6 Murray, C.B., Norris, D.J. and Bawendi, M.G., J. Am. Chem. Soc., 1993, 115 (19): 8706
- 7 Duck, J.S., Park, O.O. and Jung, H.J., Korean J. Chem. Eng., 2002, 19(3): 529
- 8 Wang, Y., Tang, Z.Y. and Miguel, A.C., J. Phys. Chem. B, 2004, 108: 15461
- 9 Shi, Z.X., Wang, Y.F. and Liu, J.J., Chinese J. Inorg. Chem., 2008, 24(7): 1186
- 10 Chen, X.F., Hutchison, J.L. and Dobson, P.J., J. Mater Sci, 2009, 44: 285

- 11 Himani, S., Shailesh, N.S. and Umesh, K., *J. Mater. Sci: Mater. Med.*, 2009, 20: 123
- 12 Zou, G.Z., *J. Chin. Chem. Lett.*, 2009, 20: 356
- 13 Xu, W.B., Wang, Y.X. and Liang, S., *Chinese J. Inorg. Chem.*, 2007, 23(7): 1220
- 14 Deng, D.W. and Yu, J.S., *Chinese J. Inorg. Chem.*, 2008, 24(5): 701
- 15 Wang, X.T., Yu, J.S. and Xie, Y., *Chinese J. Inorg. Chem.*, 2007, 23(7): 1185
- 16 Xie, Y., Xu, J.J. and Yu, J.S., *Chinese J. Inorg. Chem.*, 2004, 20(6): 663
- 17 Deng, D.W., Yu, Y.S. and Pan, Y., *J. Colloid Interface Sci.*, 2006, 299: 225
- 18 Yang, Y.J. and Bao, J.X., *J. Cryst. Growth*, 2005, 284(3–4): 453
- 19 Colvin, V.L., Goldstein, A.N. and Alivisatos, A.P., *J. Am. Chem. Soc.*, 1992, 114 (13): 5221
- 20 Prasad, B.V., Arumugam, S.K. and Tanushree, B., *Langmuir*, 2005, 21(3): 822