

Optical Properties of Ternary Alloyed $Zn_xCd_{1-x}Se$ Semiconductor Nanocrystals

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ABSTRACT

In this study, ternary alloyed $Zn_xCd_{1-x}Se$ ($x=0, 0.2, 0.5, 0.8$ and 1) semiconductor nanocrystals with high quality are synthesized by a high temperature decomposition route. The effect of Zn content (x) of $Zn_xCd_{1-x}Se$ semiconductor nanocrystals on their physical properties is investigated by controlling the Zn/Cd ratios. The optical properties and morphologies of the prepared nanocrystals are measured by FL, UV-Vis and TEM techniques. The actual composition of the prepared nanocrystals based on the ICP results is $Zn_{0.03}Cd_{0.97}Se$, $Zn_{0.12}Cd_{0.88}Se$, and $Zn_{0.38}Cd_{0.62}Se$ when Zn content is 0.2, 0.5, and 0.8, respectively. The fluorescence properties of the obtained alloyed $Zn_xCd_{1-x}Se$ nanocrystals possess pure green light color and narrow particle size distribution (FWHM=28-30 nm). It is found that the emission wavelength of nanocrystals shifts from 510 to 545 nm with increasing Zn content from 0 to 0.8, although based on the TEM measurements, the particle sizes of $Zn_xCd_{1-x}Se$ nanocrystal for different Zn content (0-0.8) are almost about 3.2 nm. Therefore, the wavelength shift and nonlinear optical property of the $Zn_xCd_{1-x}Se$ nanocrystals is not caused by the particle size but the compositional effect..

Keywords: semiconductor nanocrystal; compositional effect; $Zn_xCd_{1-x}Se$ nanocrystals ; fwhm ; FL.

1 INTRODUCTION

Semiconductor nanocrystals also known as quantum dots (QDs), have been investigated widely in the last decade due to their unique chemical and physical properties. The continued interests in semiconductor nanoparticles can be attributed to the size-dependent optical and electronic properties displayed by these quantum-confined materials. The small size of these compounds results in the three-dimensional confinement of the bulk charge carriers and the corresponding transformation of the bulk energy bands into discrete molecular energy states. This bulk-to-molecular transition is continuous, so that the band gap of the nanocrystalline material can be tuned to a desired energy by controlling the particle size [1-2]. Besides, for the nanocrystals with sizes of several nanometers, the huge surface energy is noted because most of the atoms are located on the surface. Therefore, surface modification is used in order to increase the quantum efficiency of

photoluminescence. Therefore, a proper handling of the surface is essential to obtain highly luminescent QDs. The adjustable and sharp emission characteristics of these materials make them interesting candidates for light emitting diodes [3-6], laser [7,8], biological labels [9-11], and solar cells [12,13].

The luminescence efficiency of nanocrystals can be improved by the following four ways: (1) Remove the lattice defect by heat treatment under high temperature in order to decrease the probability of trapped electron [14]. (2) Passivate the particle surface by bonding with an organic molecular and to improve the surface stability of nanocrystal by reducing the lone pairs [15]. (3) Modify the surface by inorganic molecules (called core-shell structure) for the sake of increasing the electron-hole recombination efficiency [16,17]. (4) Form an alloyed nanocrystals so as to eliminate the lattice mismatch and stress on the core-shell structures [9,12].

On the other hand, the current focus on the synthesis of semiconductor nanocrystals is to develop efficient routes for the synthesis of high quality and monodispersed nanocrystalline materials. The ternary alloyed systems such as $Zn_xCd_{1-x}Se$ [9,18,19], $CdSe_xTe_{1-x}$ [10], $Zn_xCd_{1-x}S$ [12], CdS_xTe_{1-x} [20] and CdS_xSe_{1-x} [21] are obtained by a two-step route, i. e. the alloyed nanocrystal is formed by a core-shell structure through an annealing process. Moreover, ternary $Zn_xCd_{1-x}S$ and $Zn_xCd_{1-x}Se$ can also be synthesized using a low temperature molecular precursor approach [22]. Because of the interesting optical properties of ternary alloyed nanocrystals which can be controlled without changing the particle size, more and more research have been focused to develop a fast procedure to produce a high quality QDs in the range of visible light. In this study, an effective one-pot synthetic strategy has been developed to make a series of high-quality ternary alloyed $Zn_xCd_{1-x}Se$ nanocrystals by controlling the Zn content, and the amount of Zn effect on the optical property during the preparation has been also elucidated.

2 EXPERIMENTAL PROCEDURE

2.1 Chemicals

Cadmium oxide (CdO, 99.998 %) was purchased from Alfa Aesar. Zinc oxide (ZnO, 99.99 %), stearic acid (SA, 99

%), selenium powder (Se, 99.999 %), trioctylphosphine (TOP, 90 %), Hexyldecylamine (HDA, 90 %), and Trioctylphosphine oxide (TOPO, 90 %) were obtained from Aldrich. Hexane (99.7 %) and methanol (99 %) were provided by Mallinckrodt Chemicals. All chemicals were used as received without further purification.

2.2 Preparation of $Zn_xCd_{1-x}Se$ nanocrystals

Total amount of 0.3 mmol of CdO and ZnO were mixed with SA used as complex agent in a three-necked flask and then heated to 230 °C under argon until a clear solution was formed to prepare the cadmium/zinc-SA precursors. The solution was then allowed to cool down to room temperature, and a white solid precipitate was obtained. After cadmium/zinc-SA precursor was formed, the mixture surfactants, TOPO and HDA, were added into three-necked flask and stirred together under Ar at room temperature, and then the sample was reheated up to 320 °C to form a transparency solution. Se-TOP precursor, prepared by 1.5 mmol of Se dissolved in mixed TOP and hexane, was swiftly injected into the three-neck flask. The reaction time was about 1~2 s, and the mixed solution was swiftly cooled down to stop reaction. Samples were precipitated with hot anhydrous methanol for purification process. The precipitate was dissolved in hexane to remove unreacted reagents for further measurement.

2.3 Characterization

The optical properties of samples were measured by Fluorescence Spectrophotometer (FL, Hitachi F-7000) and UV-Vis spectrometer (UV-Vis, Jasco V-670 spectrometer), respectively. Quantum efficiencies (QY) of samples were determined by using fluorescent dye (Rhodamine 6G in methanol) as reference sample. Transmission electron microscope (HRTEM, JEOL JEM-2010) was used to analyze the morphologies of samples. The compositions of alloyed nanocrystals were conducted by Inductively-coupled plasma atomic emission spectrometry (ICP-AES).

3 RESULTS AND DISCUSSION

Fig. 1 shows the UV-Vis and FL spectra of ternary alloyed $Zn_xCd_{1-x}Se$ nanocrystals. The emission wavelength of CdSe with Cd/Se =1/5 is 512 nm and the QY is 58 %. Compared to the Peng's result, it is noted that a high QY of CdSe with green light can be prepared within a very short period of time in this study [23]. Besides, the FL and UV-vis absorption spectrum is extremely sharp with a FWHM about 25 nm and the stokes shift about 10 nm. The result also shows that to form a SA-Cd complex is quite important for boosting the QY of CdSe nanocrystals. Primary amines have shown the most promising results for achieving high FL efficiency for a variety of semiconductor nanocrystals

[24-26] and the function of SA is proven to be helpful for the formation of large-sized CdSe [27]. Moreover, when Zn content is 0.2, the band edge absorption and emission are 510 and 523 nm, respectively. Stokes shift is 13 nm and the FWHM is 28 nm. When Zn content increases to 0.5, the band edge absorption and emission increases to 525 and 534 nm, respectively. When increasing the Zn content up to 0.8, the band edge absorption and emission are 536 and 545 nm, respectively. This result indicates that those samples have a narrow size distribution and a pure green color emission. The QYs of ternary alloyed $Zn_xCd_{1-x}Se$ with $x=0.2, 0.5,$ and 0.8 are 89, 81, and 45 %, respectively. In addition, only one emission peak with narrow FWHM can be observed for all samples, implying that either pure CdSe or ternary alloyed $Zn_xCd_{1-x}Se$ nanocrystals are formed. In order to confirm the stoichiometric ratio of Cd and Zn, the ICP is used to measure the exact composition of those samples. From the ICP results, the actual composition of ternary alloyed $Zn_xCd_{1-x}Se$ ($x=0.2, 0.5, 0.8$) is $Zn_{0.03}Cd_{0.97}Se,$ $Zn_{0.12}Cd_{0.88}Se,$ and $Zn_{0.38}Cd_{0.62}Se,$ respectively, meaning that ternary alloyed $Zn_xCd_{1-x}Se$ nanocrystals can be prepared successfully under high Zn concentration by one step alloying route. For low Zn concentration, the doping effect is obvious. Moreover, the QY of ternary alloyed nanocrystal is higher than that of CdSe although the QY is decreased slightly with increasing the Zn content from 0.2 to 0.5. However, the QY decreases dramatically for higher Zn content of 0.8. Besides, this result implies that even the concentration of Cd is reduced, $Zn_xCd_{1-x}Se$ nanocrystal with high QY also can be prepared. Peng et al. have mentioned that for the CdSe with an initial Cd/Se of 1:10, its PL QY is high to 80 %, which is consistent with our results.

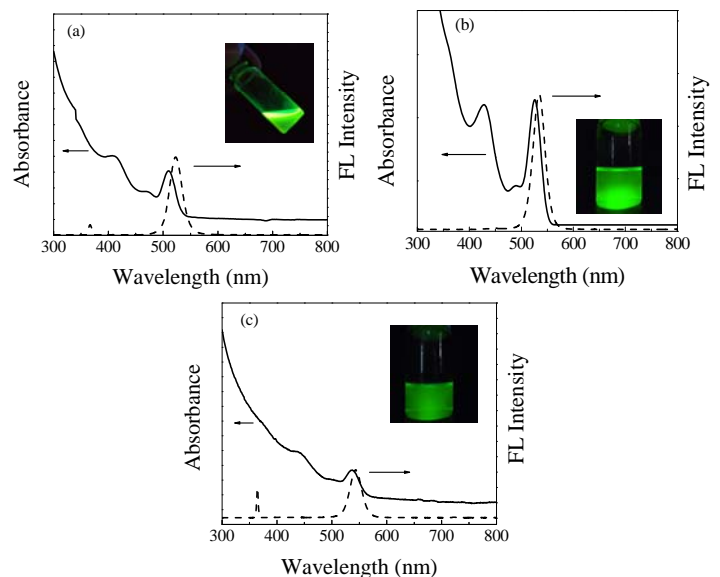


Fig. 1 Fluorescence and UV-Vis spectra of $Zn_xCd_{1-x}Se$ nanocrystals. (a) $x=0.2$, (b) $x=0.5$, (c) $x=0.8$.

The fluorescence spectra of ternary alloyed $Zn_xCd_{1-x}Se$ nanocrystals is shown in Fig. 2. The emission wavelength of $Zn_xCd_{1-x}Se$ nanocrystals shifts from 510 to 545 nm obviously when increasing the amount of Zn from 0 to 0.8. When Zn content is 1 (ZnSe), it can not observe any emission wavelength, meaning that ZnSe can not be prepared under this condition. We find that the emission wavelength of ternary alloyed $Zn_xCd_{1-x}Se$ ($x=0.2$ to 0.8) nanocrystals is located between CdSe and ZnSe. The band gap of CdSe and ZnSe is 1.74 and 2.8 eV, respectively. This phenomenon implies that the ternary alloyed $Zn_xCd_{1-x}Se$ shows a nonlinear optical property, which may be caused by the compositional or particle size effect. However, from the TEM graphs of ternary alloyed $Zn_xCd_{1-x}Se$ nanocrystals shown in Fig. 3, the particle size of ternary alloyed $Zn_xCd_{1-x}Se$ nanocrystals is 3.1, 3.1, 3.2, and 3.3 nm for Zn=0, 0.2, 0.5, and 0.8, respectively, suggesting that the nonlinear optical property of ternary alloyed $Zn_xCd_{1-x}Se$ nanocrystals are caused by the compositional effect. Bailey et al. have mentioned that the relation of the anion-cation bonding to their equilibrium positions leads to local structural disordering and a particularly large band gap reduction in CdSeTe-type semiconductor alloys [10]. Therefore, a nonlinear optical can be observed. In our study, we believe that a similar mechanism is operative in ZnCdSe-type semiconductor alloys when the Zn content is not high enough. The results of emission wavelengths, particle sizes, QYs, and actual compositions of ternary alloyed $Zn_xCd_{1-x}Se$ nanocrystals are listed in Table 1. A large red-shift of $Zn_xCd_{1-x}Se$ nanocrystal is observed with increasing the Zn more fractions from 0 to 0.38 (emission wavelength is between 510 to 545 nm) and the particle size is also almost the same. Zhong et al. have mentioned that a large blue-shift of $Zn_xCd_{1-x}Se$ nanocrystal is observed with increasing the Zn more fractions from 0 to 0.67 (emission wavelength is between 615 to 500 nm) and the particle size also increases from 5.2 to 7.5 nm. The optical properties of $Zn_xCd_{1-x}Se$ nanocrystals show linear optical property and

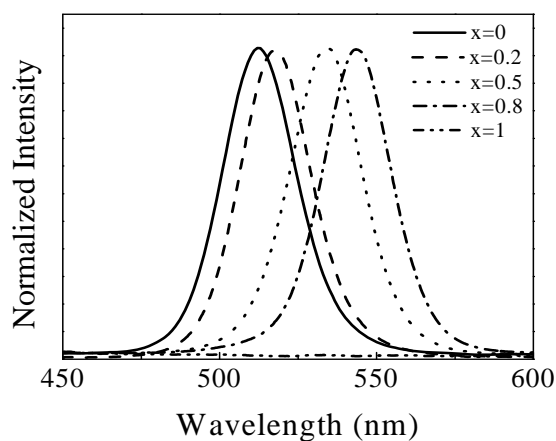


Fig. 2 The FL spectra of $Zn_xCd_{1-x}Se$ nanocrystal.

high QY due to larger particle size, high crystallinity, hardened lattice structure, decreased inter-diffusion and spatial composition fluctuation [9]. The emission peak of composition-tunable $Zn_xCd_{1-x}Se$ nanocrystals moves to short wavelength when increases the Zn content. Bailey pointed out that the optical properties of $CdTe_{1-x}Se_x$ nanocrystals are nonlinear and the emission peak for $CdTe_{1-x}Se_x$ nanocrystals are out of the range of CdSe and CdTe [10]. According to a theoretical model developed by Bernard and Wei, the nonlinear effect of alloyed nanocrystal is due to the following factors: (1) different atomic size of different ions, (2) different electronegativity values, and (3) different lattice constants [28,29]. In our study, the emission peaks of ternary alloyed $Zn_xCd_{1-x}Se$ nanocrystals are between those of ZnSe and CdSe. However, when the actual Zn mole fraction increases from 0 to 0.38, a significant red-shift of ~35 nm is observed. This nonlinearity results from the different reactivity and atomic radii of the Zn and Cd. From ICP results it can be seen very clearly that the Zn content in actual composition of alloyed nanocrystals is much lower than that of the theoretical composition. Therefore, the emission properties of ternary alloyed nanocrystals may be dominated by CdSe under lower Zn content. When the Zn content is higher than a certain value, the emission wavelength of ternary alloyed $Zn_xCd_{1-x}Se$ nanocrystals may either shift to short wavelength or appear two wavelengths. In this situation, the optical properties of ternary alloyed nanocrystals may be dominated by ZnSe and the QY also decreases. In our study, the actual Zn content in alloy is not high enough, and the nonlinear optical properties can be observed.

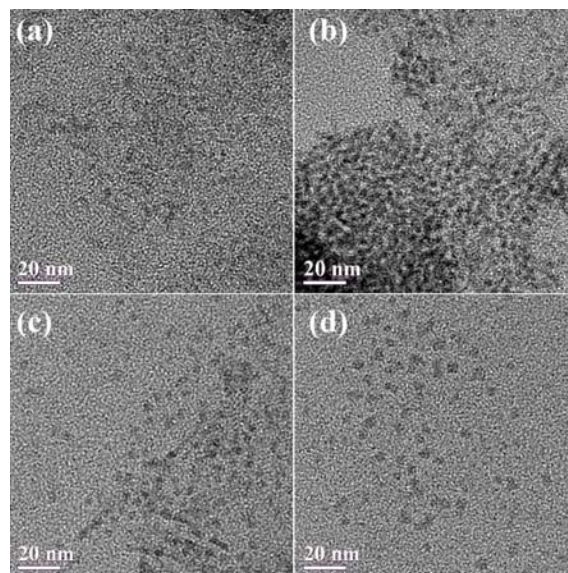


Fig. 3 TEM images of $Zn_xCd_{1-x}Se$ nanocrystals. (a) $x=0$, (b) $x=0.2$, (c) $x=0.5$, (d) $x=0.8$.

4 CONCLUSIONS

Table 1 Physical properties of ternary alloyed $Zn_xCd_{1-x}Se$ nanocrystals

Theoretical Composition	Emission Wavelength (nm)	Particle Size (nm)	QY (%)	Actual Composition
CdSe	510	3.1	58	-
$Zn_{0.2}Cd_{0.8}Se$	523	3.1	89	$Zn_{0.03}Cd_{0.97}Se$
$Zn_{0.5}Cd_{0.5}Se$	534	3.2	81	$Zn_{0.12}Cd_{0.88}Se$
$Zn_{0.8}Cd_{0.2}Se$	545	3.3	45	$Zn_{0.38}Cd_{0.62}Se$
ZnSe	-	-	-	-

In this study, ternary alloyed $Zn_xCd_{1-x}Se$ nanocrystals with high QY are synthesized by a high temperature decomposition route. The results display that not only Stokes shift but also the FWHM of ternary alloyed $Zn_xCd_{1-x}Se$ nanocrystals is very small, implying that a narrow size distribution and saturated color of ternary alloyed $Zn_xCd_{1-x}Se$ nanocrystals could be obtained. The Zn content of ternary alloyed $Zn_xCd_{1-x}Se$ nanocrystals affects their optical properties significantly. When increasing the amount of Zn, the emission peak is red-shifted from 510 to 545 nm and the QY decreases from 89 to 45 % slightly. From the TEM analysis, those samples have almost the same particle size, indirectly suggesting that the nonlinear optical property of alloyed $Zn_xCd_{1-x}Se$ is caused by the Zn effect instead of the size effect. One-pot preparation method in this study is not only to reduce the concentration of Cd but can maintain the QY of nanocrystals. This method would be also a new class of colloidal chemistry.

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