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Fabrication of CdSeS Alloyed Quantum Dots and Study on Fluorescence Lifetime

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Recently, various types of quantum dots (QDs) have been synthesized and widely used in optoelectronic devices and biomedical researches. Alloyed QDs, which are well-known for their superior optical properties such as fluorescence stability and high photoluminescence intensity, have been synthesized with combination of various starting materials. The band gap energy of semiconductor can be controlled through change of the ingredient and the inner structure. In this work, we have synthesized CdSeS alloyed QDs by using one pot reaction with coordinating solvent. Cadmium oxide (CdO), selenium powder (Se), and sulfur powder (S) were used as precursor for the preparation of alloyed QDs. The typical size of the QDs was about 3.3 nm. With the S content decreased, the fluorescence spectra were red-shifted, and fluorescence lifetime was decreased.

Keywords alloyed QDs; composition; lifetime

1. Introduction

Recently various types of QDs have been prepared and used in optoelectronics and biotechnology [1–3]. QDs are nano-sized semiconductors with unique optical properties such as size-adjustable PL intensity, narrow emission spectrum, and high photostability against photobleaching. Several applications have been developed including light emitting diodes [4], lasers [5], solar cells [6,7], biomedical tags [8], and temperature sensors [9]. Over the last two decades various QDs have been synthesized. Among them, CdSe, CdSe/ZnS, and CdTe with different sizes and emission wavelengths have been extensively studied. But the size dependence of optical properties of QDs hinders the expanding of QD applications especially in the field of nanotechnology and biotechnology. It is also difficult to control the size of QDs as the reaction time is usually very fast. Recently various alloyed QDs have been synthesized. Alloyed QDs have merits to engineer their band gap energy by changing the ingredient and the inner structure. Fluorescence life time is very important especially for the application of QD LED, fluorescence resonance energy transfer (FRET) sensor, and bio labeling. Recently several types of QDs were synthesized and used in our lab for the application of FRET sensor, temperature sensor, and DNA sensor [10–13]. For the application of alloyed QDs to those sensors, systematic investigations of their optical properties are necessary. In this study, we have synthesized alloyed CdSeS QDs with different ratio of Se

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Table 1. The actual ratio of alloyed CdSeS QDs from SEM/EDX analysis.

Samples	Reagents		Se:S Actual Atomic%	Composition Ratio
	Se(g)	S(g)		
a	0.001	0.020	1.37 :65.71	1:47.96
b	0.003	0.012	3.53 :80.21	1:22.72
c	0.005	0.011	9.05 :72.39	1:8.00
d	0.016	0.007	12.54:71.98	1:5.74
e	0.022	0.005	43.56:20.87	1:0.48

to S. The fluorescence spectra and life time of alloyed QDs depending on the composition was studied.

2. Experimental

2.1. Material and Reagents

Oleic acid (OA, 90%), trioctylphosphine (TOP, 90%), tri-n-octylamine (TOA, 98%), cadmium oxide (CdO, 99.99+%), sulfer powder (S, 99.98%) and selenium powder (Se, 99.5+%) were purchased from Aldrich. Ethanol (EtOH) was purchased from Duksan Pure Chemicals. All reagents were used without any further purification.

2.2. Instruments

Photoluminescence spectra were obtained using a QuantaMaster PTI spectrofluorometer (Photon Technology International, Birmingham, NJ, USA). The excitation wavelength was

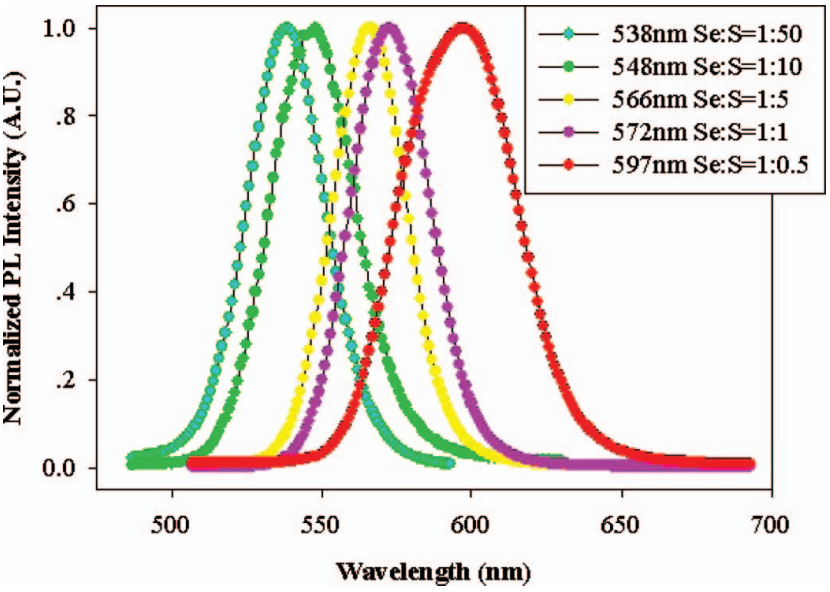

Figure 1. PL spectra of alloyed CdSeS QDs.

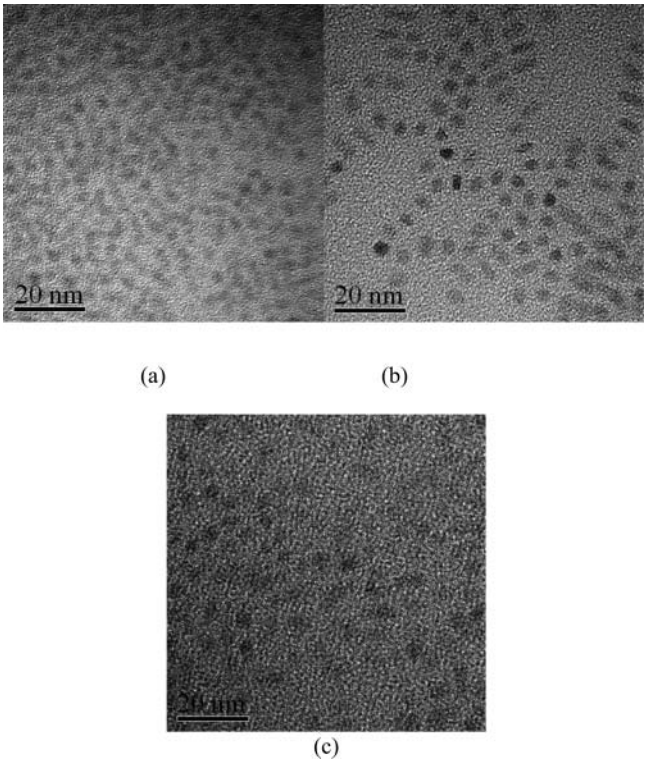

Figure 2. TEM image of alloyed CdSeS QDs. (a) Sample a, Se:S = 1:50; (b) Sample c, Se:S = 1:5; (c) Sample e, Se:S = 1:0.5.

467 nm and emission spectra were collected. The alloyed CdSeS QDs are dissolved in chloroform with 1 ppb. TEM image was obtained using FEI TECNAI G2 transmission electron microscope. SEM/EDX data were obtained using HITACH S-4700 scanning electron microscope. The fluorescence lifetime data were obtained from the EasyLife II (PTI). The alloyed CdSeS QDs are dissolved in chloroform with 1 ppm.

2.3. Synthesis of CdSeS Nanocrystals

The alloyed CdSeS QDs were synthesized by the method reported previously with slight modification [14]. 0.05 g of CdO, 0.56 ml of OA and 15 ml TOA were mixed in a 100 ml three-necked flask and heated to 300°C with vigorous stirring under N_2 gas. A colorless solution was obtained after 30 min. While the temperature was maintained at 280°C, 1 ml of stock solution of Se and S in TOP was rapidly injected into the solution. The molar ratio of Se to S was varied (1:0.5, 1:1, 1:5, 1:10, 1:50) for the preparation of the stock solution. Table 1 shows the amount of Se and S used in the reactant. After 1 min of reaction, cold ethanol was added to quench the reaction, and CdSeS QDs were precipitated. The particles were purified by centrifugation (10,000 rpm, 20 min) and the QDs were re-dispersed in chloroform. The purification step was repeated three times.

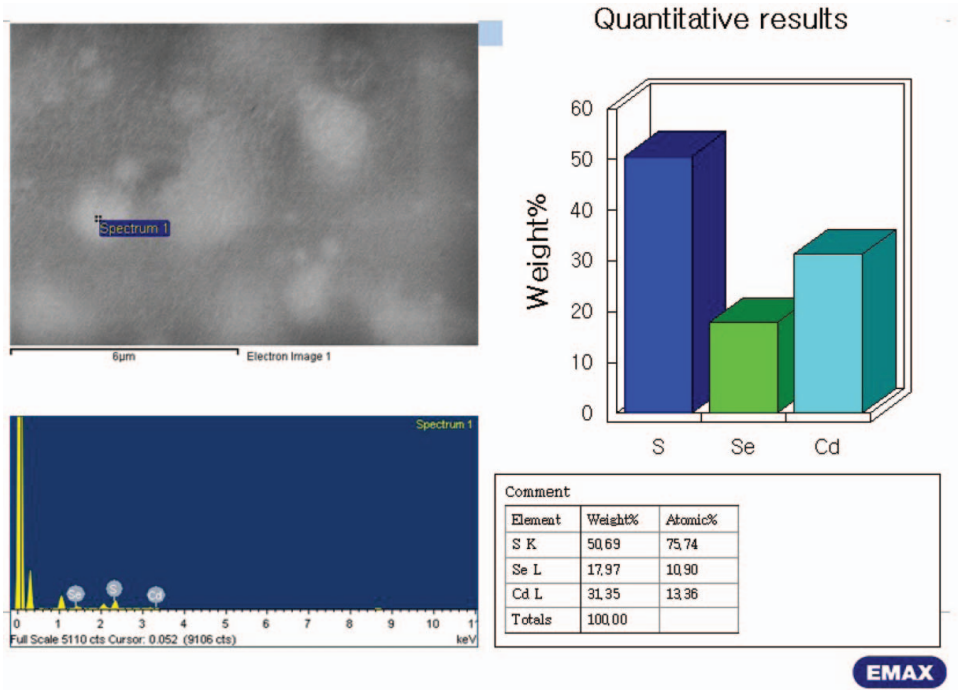

Figure 3. SEM/EDX data of the alloyed QDs, sample c.

3. Results and Discussion

Five different colors of QDs were synthesized with different molar ratio of Se to S in the reactant. The PL spectra of QDs in chloroform (1 ppb) were measured using QuantaMaster PTI spectrofluorometer. Figure 1 shows normalized PL emission spectra of the samples

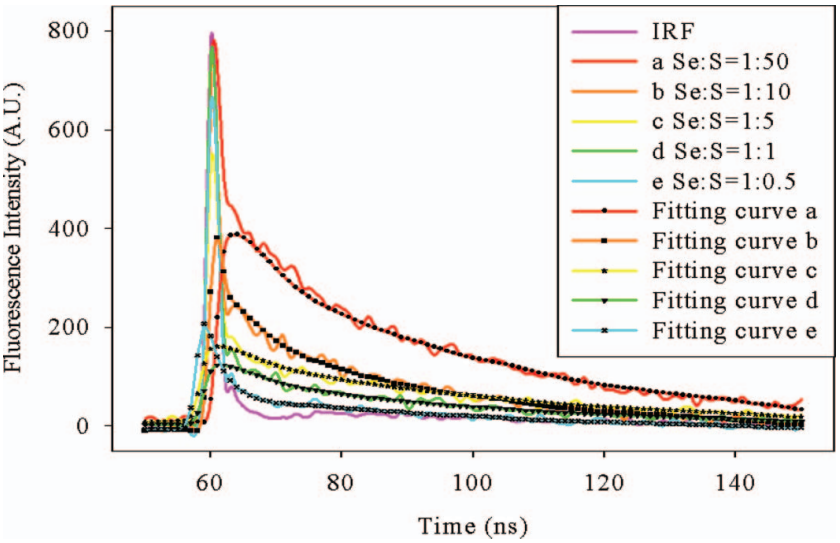

Figure 4. Lifetime spectra of alloyed CdSeS QDs.

Table 2. (a) Lifetime data of QDs; (b) Statistical parameters of Lifetime.

(a)

Samples	τ_1 (ns)	τ_2 (ns)	F_1	F_2	t(ns)
a	0.07289	18.3	0.00011	0.9999	18.3
b	0.06224	15.37	0.01021	0.9898	15.3
c	0.06083	14.23	0.0188	0.9812	14.2
d	1.0825	12.6	0.1328	0.8672	12.4
e	1.0243	11.96	0.2052	0.7948	11.7

(b)

Samples	Chi-square	Durbin Watson	Z
a	1.025	1.8182	−0.1852
b	1.055	1.7547	−0.0008
c	0.981	1.9876	−0.0443
d	1.074	1.848	−0.00726
e	0.924	1.771	0.06189

where emission maximum peak was at 538, 548, 566, 572 and 597 nm, respectively. As the ratio of Se to S was increased, the PL emission spectra of QDs were red-shifted. The figure also shows that the peak width is increased gradually (FWHM is 28 for sample a and 41 nm for sample e) with the increase of the ratio, which means that more uniform QDs can be obtained with higher content of S. The QDs were well dispersed in chloroform, and the dispersion was maintained for quite a long time with constant fluorescence intensity. Figure 2 shows TEM images of sample a, c, and e. The figure shows that QDs with more uniform size distribution in round shape can be obtained with higher content of S, which is coincide with Figure 1. The average size of the QDs was 3.4 nm. The figure also shows that even with the similar size, QDs show different PL spectra with different composition. SEM/EDX data were used to obtain the actual ratio of Se to S in the synthesized alloyed QDs. Figure 3 shows the SEM/EDX image and molar ration of Cd, Se, and S in sample c (Se to S, 1:5). The actual molar ratio of Se to S for the samples was listed in Table 1. The table shows that though the actual molar ratio of Se to S is not same with that in reactant, the relative amount of S is gradually decreased as with reactant. Fluorescence lifetime of QDs was measured with EasyLife II as shown in figure 4. Biexponential decay was used to simulate PL decay of QDs which can be described with the following equation.

$$D(t) = F_1 \exp(-t/\tau_1) + F_2 \exp(-t/\tau_2), \tag{1}$$

$$< t > = \left(F_1^* \tau_1^2 + F_2^* \tau_2^2\right) / \left(F_1^* \tau_1 + F_2^* \tau_2\right), \tag{2}$$

where D(t) is the delta function generated decay, F_1, F_2 are the decay parameters, τ_1 is the shorter lifetime, τ_2 is the longer lifetime, and <t> is the average lifetime. The curve fitting was performed using software of Easylife II. As we set the fit parameters for double exponential, the lifetime data were analyzed with two parts, shorter-lifetime and longer lifetime. The shorter lifetime, τ_1 is characterized as band to band recombination and the

longer lifetime $\tau 2$ is characterized as surface-related recombination [15]. Using these two equations and curve fitting software of EasyLife II which is based on Marquardt algorithm, the lifetime t for QDs was obtained. Table 2 shows the life time obtained from curve fitting together with statistical parameters. The best fit is determined when chi-square is minimized. If the standard deviations are estimated correctly, a perfect fit to the data will produce a chi-square close to 1.0. The parameter of Durbin Watson and Z indicates the satisfaction of the fitting curve. The fitting is likely satisfactory if the Watson's value is higher than 1.75 and Z's value is higher than -1.96. The table shows that curve fitting for PL decay is satisfactory for all samples. The table also shows that with decrease of S content, shorter life time was observed for CdSeS alloyed QDs.

4. Conclusion

CdSeS alloyed QDs were prepared with different molar ratio of Se to S in reactant. With decrease of S content, larger size distribution of QDs were obtained, and PL spectra were red shifted. By using curve fitting, PL decay of QDs was analyzed to give life time. With decrease of S content, shorter life time was observed.

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