Synthesis and optical properties of water-soluble CdTe_{1-x}Se_x quantum dots with ultra-long fluorescence lifetime

Zhizhong Han^{a*}, Lili Ren^b, Li Chen^a, Min Luo^a, Haibo Pan^{b, c*}, Chunyan Li^a, Jinghua Chen^a,

^a School of Pharmacy, Fujian Medical University, Fuzhou, Fujian 350122, China

^b College of Chemistry, Fuzhou University, Fuzhou, Fujian 350116, China

^c Fujian Key Lab of Medical Instrument and Pharmaceutical Technology, Fuzhou University,

Fuzhou, Fujian 350116, China

*Corresponding authors

Telephone: 86-591- 22866127; Fax: 86-591-22866127

E-mail: zzhan@fjmu.edu.cn (Z. Han); hbpan@fzu.edu.cn (H. Pan)

Abstract

Water-soluble ternary-alloyed $\text{CdTe}_{1-x}\text{Se}_x$ quantum dots (QDs) have been synthesized via a simple one-pot approach in aqueous phase. The as-prepared $\text{CdTe}_{1-x}\text{Se}_x$ QDs show good crystallinity, excellent monodispersity, and a narrow size distribution with average size of 3.0 nm. Lattice parameters and band gaps of the ternary-alloyed $\text{CdTe}_{1-x}\text{Se}_x$ ($0 \leq x < 1$) QDs are regulated respectively in linear and quadratic relationships with the Se content (x). By tuning composition, the photoluminescence (PL) emission wavelength of $\text{CdTe}_{1-x}\text{Se}_x$ can cover from 528.9 to 689.3 nm, and gradually moved to longer wavelengths with a decrease content of Se (x). The lifetime of $\text{CdTe}_{1-x}\text{Se}_x$ QDs is decreased gradually with the Se content (x) augment, attributing to the decreasing lattice spacing resulting from substitution of the larger Te atoms with the smaller Se atoms, bringing about a incremental plasmonic coupling effect at smaller inter-lattice fluorophore distance. However, the as-prepared $\text{CdTe}_{1-x}\text{Se}_x$ QDs ($0 \leq x < 1$) have significantly longer fluorescence lifetimes of >80 ns with the maximum lifetime up to 174.64 ns. The longer life is good for the application of photoelectric conversion, fluorescent biomedical imaging and detecting.

Keywords

$\text{CdTe}_{1-x}\text{Se}_x$; Quantum dots; Composition control; Photoluminescence; Fluorescence lifetime; Water-soluble

1. Introduction

Alloy quantum dots (QDs) could provide an additional degree of freedom in selecting desirable properties for nanoscale engineering because their physical and optical properties depend on both size and composition [1]. Compared with traditional organic dyes, QDs have many excellent optical properties, e.g., narrow and symmetric emission spectra, higher reliability and stability against irradiation, and broad absorption range. Therefore, QDs are attractive materials for various applications, such as biological detection and labeling, light-emitting diodes, solar cells, photocatalysts, etc. [2-5].

In general, the band gap of binary QDs can only be tuned by controlling the particle size due to the quantum size effect. However, since super-tiny particles are unstable and large particles greater than the exciton Bohr radius are not favorable for the emission efficiency, tuning the band gap by simply adjusting the particle size would limit in broadening the emission range and achieving monochromatic fluorescence. In contrast, composition control is a more feasible route to fabricate semiconductor with tunable band gaps, and specific band gap can be conveniently achieved through variation of the composition in multi-component QDs even under a specific size. For these reasons, a great variety of multi-component QDs have been extensively investigated [6-9]. Among these multi-component QDs, CdTeSe can efficiently emit light in NIR wavelength window and be potentially applied in biomedical imaging and detecting field [10]. Although these alloyed QDs were successfully synthesized, they were mostly prepared by organometallic method which restricted their direct applications in hydrophilic systems. However, to date, few works have been focused on investigated the composition-tunable properties of water-soluble ternary CdTe_{1-x}Se_x QDs.

The fluorescence lifetime is important, because it determines the time available for the fluorophore to interact with or diffuse in its environment, and hence the information available from its emission. In general, the fluorescence lifetime for single QDs is 10 - 40 ns [11]. The fluorescence time of CdTeSe/ZnS QDs is only 31 ns [12]. CdSeTe QDs synthesized in oil phase have a fluorescence lifetime of 30 - 40 ns [13]. Cichy and his co-workers prepared ternary AgInS₂ quantum dots with a longer fluorescence lifetime of 100 ns [14], which is also shorter than that for the as-prepared QDs in this work. The small fluorescence lifetime will limit the application of QDs, specially for biomedical analysis and imaging. Here, monodisperse compositionally controlled CdTe_{1-x}Se_x QDs with longer fluorescence lifetime were prepared through a single injection of two seemingly noninteracting anion precursors into a reaction vessel. The obtained CdTe_{1-x}Se_x QDs were capped with 3-mercaptopropionic acid (3-MPA). The mercapto group of 3-MPA is conjugated with the Cd²⁺ ion on the surface of CdTe_{1-x}Se_x QDs, while the carboxylate group is ionized in the water to make CdTe_{1-x}Se_x QDs water-soluble. Additionally, detailed structural and optical characterization of the as-prepared ternary alloys QDs were carried out and used to investigate the regulation mechanism.

2. Experimental section

2.1 Materials

Tellurium powder (Te, 99.999%) was purchased from Alfa Aesar. Selenium powder (Se, 99.95%) was obtained from Shanghai Meixing Chemical Company. 3-Mercaptopropionic acid (MPA, >99%) was obtained from Sigma-Aldrich. Cadmium acetate (Cd(CH₃COO)₂, 99%) and NaBH₄ (96%) were obtained from Sinopharm Chemical Reagent Company. All other chemicals

were of analytical grade.

2.2 Synthesis of CdTe_{1-x}Se_x QDs with homogeneous composition

The synthesis of CdTe_{1-x}Se_x alloy nanocrystals was based on the synthesis of CdTe previously [15]. All reactions were conducted under argon atmosphere. Typically, 53.3 mg of Cd (CH₃COO)₂ and 100 mL of 3-MPA solution (0.5 mM, pH 10~11) were deaerated with nitrogen bubbled in a 250 mL three-neck round-bottom flask for 60 min. Then, the solution was heated to 100 °C. A selenium stock solution (0.3 M, NaHSe) was prepared by dissolving 0.0487g of Se and 0.1256g of NaBH₄ in 2.0 mL of deionized water and stirring in ambient temperatures and anaerobic environment to achieve complete dissolution. Similarly, a tellurium stock solution (0.3 M, NaHTe) was prepared by adding 0.778 g of Te and 0.1256 g of NaBH₄ to 2.0 mL of deionized water and hitting to 40-60 °C for dozens of minutes until all tellurium had dissolved. To prepare nanocrystals of CdTe_{1-x}Se_x, a solution composed of 83.3x μL of Te stock solution and 83.3 (1 - x) μL of Se stock solution was swiftly injected into the flask. The temperature was then cooled to 30 °C, and the nanocrystals were allowed to grow until the desired size had been achieved. A series of alloyed CdTe_{1-x}Se_x (x = 1, 0.75, 0.67, 0.51, 0.33, and 0) QDs was prepared by changing ratio of Se and Te in the solution. Once synthesized, the nanocrystals were isolated by precipitation with a mixture of acetone and ethanol, then centrifuged, and the resulting nanocrystal pellets were resuspended in deionized water.

2.3. Characterization

High-resolution transmission electron microscopy (HRTEM) images were taken on a Tecnai G2 F20 S-TWIN (FEI, USA). TEM samples were prepared by placing a drop of nanocrystals diluted in ethanol to an optical density < 0.1 onto an ultrathin carbon-on-Formvar TEM grid (Ted

Pella, Inc.), wicking away any excess solvent. X-ray diffraction (XRD) scans were obtained using a Scintag X1 automated powder X-ray diffractometer with a Peltier-cooled solid-state detector, and a zero-background, Si (510) sample support. UV-vis absorption and diffuse reflectance spectra were measured on a Perkin-Elmer Lambda 900 spectrophotometer. The optical band gap was calculated by the wavelength at the band edge of specific peak. Photoluminescence (PL) spectra were taken on a Cary Eclipse (Varian, USA) at room temperature. Fluorescence emission decay measurements were performed on an FLS 920 Steady state lifetime fluorescence spectrometer (Edinburgh Instruments, Edinburg, UK). The quantum yield (QY_x) of the as-prepared QDs was calculated by the following equation:

$$QY_x = QY_r \frac{I_x}{I_r} \frac{A_r}{A_x} \frac{n_x^2}{n_r^2} \quad (1)$$

Where quinine sulfate in 0.1 M H_2SO_4 was chosen as a standard sample with $QY_r = 54\%$ and $n_r = 1.33$ [16]. The as-prepared QDs were dispersed in deionized water with $n_x = 1.33$.

3. Results and discussion

3.1. Homogeneity and structure of $CdTe_{1-x}Se_x$ QDs

Fig. 1a shows the XRD patterns of the QD samples. It presents clearly that all peaks of $CdTe_{1-x}Se_x$ ($x = 0$) correspond well to the cubic CdTe (JCPDS #65-1047 and JCPDS #65-1046). The peaks located at 24.53° , 40.59° and 48.01° are assigned to (111), (220) and (311) plane of CdTe (F-43m), respectively, and the peak located at 30.75° is assigned to (200) plane of CdTe (Fm-3m). Similarly, the peaks located at 25.48° , 42.21° and 49.96° in curve of $CdTe_{1-x}Se_x$ ($x = 1$) correspond well to the cubic CdSe (F-43m, JCPDS #65-2891). However, a linear change to higher angle is observed for the three main peaks of $CdTe_{1-x}Se_x$ ($x = 0.33$ to $x = 1$), and the main peaks

are located between CdTe and CdSe standard values. Similar to the sintered $\text{CdTe}_{1-x}\text{Se}_x$ films prepared by layer-by-layer approach [17], the present samples ($x = 0.33$ to $x = 0.75$) are inferred to be cubic $\text{CdTe}_{1-x}\text{Se}_x$ QDs, and three peaks for $\text{CdTe}_{1-x}\text{Se}_x$ QDs are assigned to (111), (220) and (311) plane, respectively. As shown in Fig. 1b, the lattice parameter (a) of the $\text{CdTe}_{1-x}\text{Se}_x$ QDs represents a linear relationship with the Se content (x), and this trend is consistent with the Vegard's law [18], resulting from substitution of the smaller Se atom radius (1.16 Å) with the larger Te atom radius (1.432 Å). Specifically, as Se ions were replacing gradually by Te ions, it is believed that relaxation of the anion-cation bonds to their equilibrium positions leads to local structural ordering and a linear lattice parameters increase by degrees in $\text{CdTe}_{1-x}\text{Se}_x$ QDs. XRD patterns of $\text{CdTe}_{1-x}\text{Se}_x$ QDs suggest the formation of homogeneous alloy rather than a physical mixture of CdTe and CdSe, and the wide and weak diffraction peaks observed from each of the samples are due to the nanoscale size of the $\text{CdTe}_{1-x}\text{Se}_x$ QDs. Average crystalline size of the $\text{CdTe}_{1-x}\text{Se}_x$ QDs was estimated at ~ 3 nm by Debye–Scherer equation after modified instrument's factors (Table 1), which exhibits the grain size do not decrease obviously with increasing Se content.

Fig. 1. (a) XRD patterns and (b) lattice parameter of $\text{CdTe}_{1-x}\text{Se}_x$ QDs ($0 \leq x \leq 1$).

Table. 1 The crystalline size of CdTe_{1-x}Se_x QDs.

Samples	CdSe	CdTe _{0.25} Se _{0.75}	CdTe _{0.33} Se _{0.67}	CdTe _{0.49} Se _{0.51}	CdTe _{0.67} Se _{0.33}	CdTe
crystalline size (nm)	2.9	3.0	3.1	3.0	3.0	3.1

From HRTEM images (Fig. 2), it shows that the different as-prepared QDs have highly crystalline and axiolitic structure. The average diameters of the CdTe_{1-x}Se_x QDs ($x = 0.33, 0.49, 0.75$) are all around 3 nm, in consistent with the results of crystalline size calculation, indicating that the obtained CdTe_{1-x}Se_x QDs have good monodispersity with relatively narrow size distribution. The results of XRD and HRTEM suggest that the effect of Se content on size of QDs is weak, which is due to the larger lattice energy of CdSe (749 kcal/mol) compared to CdTe (680 kcal/mol) and the small size of the as-prepared ternary QDs [17]. By examining several isolated particles under high magnification, the average lattice fringe of CdTe_{0.49}Se_{0.51} QDs is estimated to be 3.55 Å (Fig. 2d), correspond to the (111) plane of CdTe_{0.49}Se_{0.51} QDs. To date, it is first found such high quality crystalline of hydrophilic CdTe_{0.49}Se_{0.51} QDs synthesized in aqueous phase.

Fig. 2. HRTEM images for the as-prepared (a) CdTe_{0.33}Se_{0.75}, (b) CdTe_{0.75}Se_{0.25} and (c) CdTe_{0.49}Se_{0.51} QDs, (d) amplifying images of the circled area in Fig. 2 (c).

3.2. Optical properties and bowing constant of CdSe_xTe_{1-x} QDs

To investigate band gap engineering of CdTe_{1-x}Se_x QDs, we collected UV-vis diffuse reflection absorption spectra of the as-prepared CdTe_{1-x}Se_x QDs (Fig. 3). From Fig. 3a, it can be seen that all spectra of CdTe_{1-x}Se_x QDs ($0 < x < 1$) show higher light absorption factor compared with that for binary CdTe QDs and CdSe QDs, and they also exhibit a steep absorption edge and can be tuned to cover almost the UV and visible spectrum. The absorption edges of CdTe_{1-x}Se_x QDs display a systematic shift to longer wavelength from 578 nm (2.01 eV), 659 nm (1.84 eV), 664 nm (1.80 eV), 693 nm (1.72 eV) and 718 nm (1.70 eV) to 722 nm (1.69 eV) with decreasing Se content (x) in the ternary CdTe_{1-x}Se_x QDs ($0 \leq x \leq 1$), respectively, demonstrating that band gap is able to be tuned stem from stoichiometrial variation in the ternary alloy semiconductors. While the lattice parameter of ternary alloys changes linearly with composition, band gaps (E_g) often vary nonlinearly [19]. To a approximation, the variation is quadratic as shown in Eq. 2 [20].

$$E_g(\text{CdTe}_{1-x}\text{Se}_x) = xE_g(\text{CdSe}) + (1 - x) E_g(\text{CdTe}) - bx(1 - x). \quad (2)$$

where b is a bowing parameter, describing the extent of nonlinearity. In our case, the variation of the band gaps of the CdTe_{1-x}Se_x with Se content (x) is shown in Fig. 3b and can be fitted with a quadratic function of $E_g(\text{CdTe}_{1-x}\text{Se}_x) = 0.50x^2 + 0.15x + 1.69$ ($0 \leq x \leq 1$) with a bowing parameter of 0.50 eV, which is not surprising if we consider the main factors that contribute to nonlinear behavior in alloys. According to a theoretical model developed by Zunger and co-workers [20], the observed band gap bowing is due to the disparity ion size between Se and Te ions, different electronegativity between Se and Te ions, and diverse lattice constant for binary CdSe and CdTe QDs (Fig.1b). As Scheme 1 shown, when Se ions are replaced gradually by Te ions, the conduction band (CB) is lowered and the value band (VB) is raised for the ternary QDs, leading to

the nonlinear reducing of band gap. These results demonstrate that, by modulating composition of the ternary alloys, we can readily obtain various band gaps (and other properties) while it would be difficult to achieve by binary QDs. Band gap of binary QDs can only be tuned by changing the size of QDs because of the quantum confinement effect, but it is hard to perfectly control the size, which will affect the stability and electrochemical performance of the binary QDs.

Fig. 3. (a) UV-vis diffuse reflection absorption spectra and (b) the band gaps of the as-prepared CdTe_{1-x}Se_x QDs.

Scheme 1. Structure and energy band diagrams of CdSe, CdTe and ternary CdTe_{1-x}Se_x QDs.

Fluorescence analysis and researching, as an important characterization method in many areas such as biological detection and photoelectrochemical direction etc., is in favor of further research on photogenerated charge transfer characteristics of nanomaterials. In this work, we also

investigated the effects of reactant composition on PL emission peaks and fluorescence lifetime of CdTe_{1-x}Se_x QDs. As shown in Fig. 4a, CdTe_{1-x}Se_x QDs have different PL emission peaks by tuning composition, exhibiting a emission range from 528.9 to 649.3 nm (Table 2). PL emission peaks of CdTe_{1-x}Se_x QDs are located between the CdSe QDs and CdTe QDs peaks and gradually moved to longer wavelengths with a decrease content of Se (*x*). The fluorescence energy depends on the energy gap, so the regulation of PL emission peaks is according to that of band gap for different CdTe_{1-x}Se_x samples. In addition, the emission FWHM of ternary QDs fluctuates from 47 to 58 nm. The FWHM of PL spectra is related to the size distribution of the prepared QDs [21]. The smaller FWHM indicates that the size distribution of the ternary QDs is narrow, which is demonstrated with HRTEM results (Fig. 2). Fig. 4b shows typical fluorescence images of ternary-alloyed QDs with varied compositions illuminated by 380 nm, a series colours of alloyed QDs are from light blue, green to red. These data indicate that the ternary-alloyed QDs exhibit unique composition- dependent optical properties.

The effects of reactant composition on emission decay of CdTe_{1-x}Se_x QDs were also investigated and are illustrated in Fig. 4c, recorded with 373 nm diode laser excitation. The samples are stable enough to record luminescence measurements under low intensity excitations. As observed in the previous studies, both heterogeneity of samples and varying degrees of surface defects introduce multi-exponential decay behavior to the charge recombination process [22,23]. In this work, the luminescence decay was multi-exponential, and the traces were fitted with three exponential kinetics. For comparison purpose, we also determined the average emission lifetimes based on Eq. 3 [24] and the results are summarized in Table 2.

$$\langle \tau \rangle = \sum (a_i \tau_i^2) / \sum (a_i \tau_i) \quad (3)$$

The results indicate that the fluorescence lifetimes of alloyed QDs are associated with reactant composition, the fluorescence decay of CdTe is much slower than that of CdSe, leading to shortened fluorescence lifetimes from 174.65 ns for CdTe to 42.16 ns for CdSe, and 120.53, 105.82, 94.59, 87.85 ns for ternary CdTe_{1-x}Se_x QDs with $x = 0.33, 0.51, 0.67, 0.75$, respectively. The shortened lifetime mechanism can be explained as follows: the decreasing lattice spacing, resulting from substitution of the larger Te atoms with the smaller Se atoms and bringing about a incremental plasmonic coupling effect at smaller inter-lattice fluorophore distance. Further, the decay rate is accelerated, and the lifetime of ternary-alloy CdTe_{1-x}Se_x QDs is decreased gradually with the Se content (x) augment. However, compared with fluorescence lifetime of CdSeTe QDs (30 - 40 ns) synthesized previous in oil phase [13], CdTe_{1-x}Se_x ($0 \leq x < 1$) QDs in this work have significantly longer fluorescence lifetimes of > 80 ns. The longer lifetime may be owing to excellent water-solubility. They are well suited for time-resolution fluorescent analysis, imaging, and photo-electric conversion. The longer lifetime of CdTe_{1-x}Se_x ($0 \leq x < 1$) QDs is good for the separation of electron-hole pairs and can improve the photoelectric conversion efficiency. Moreover, the relatively QYs of CdTe_{1-x}Se_x ($0 \leq x < 1$) QDs are between 18.07% and 38.59% (Table 2).

Fig. 4. (a) PL emission peaks, (b) fluorescence images and (c) fluorescence lifetime of $\text{CdTe}_{1-x}\text{Se}_x$ QDs with Se content (x) changed.

Table. 2 PL characteristic parameters of $\text{CdTe}_{1-x}\text{Se}_x$ QDs.

Samples	PL Emission wavelength (nm)	Lifetime value (ns)	Quantum yield
CdSe	528.9	42.16	18.07%
$\text{CdTe}_{0.25}\text{Se}_{0.75}$	555.7	87.85	28.52%
$\text{CdTe}_{0.33}\text{Se}_{0.67}$	586.1	94.59	29.07%
$\text{CdTe}_{0.49}\text{Se}_{0.51}$	618.5	105.82	31.18%
$\text{CdTe}_{0.67}\text{Se}_{0.33}$	647.5	120.53	34.56%
CdTe	689.3	174.64	38.59%

4. Conclusions

We report the synthesis of water-soluble homogeneously cubic $\text{CdTe}_{1-x}\text{Se}_x$ QDs using 3-MPA as a stabilizer for the first time. The band gap of these $\text{CdTe}_{1-x}\text{Se}_x$ QDs can be tuned by composition control, enabling the selection of more than one desired property (e.g., fluorescence) for specific applications. The dependence of the band gap on composition is found to be nonlinear, with a bowing constant of 0.50 due to the disparity ion size and electronegativity between Se and Te ions and diverse lattice constants for binary CdSe and CdTe QDs. PL emission peaks of $\text{CdTe}_{1-x}\text{Se}_x$ QDs are located between CdSe and CdTe QDs peaks with a emission range from 528.9 to 649.3 nm and gradually moved to longer wavelengths with a decrease content of Se (x).

Especially, the as-prepared ternary QDs show extraordinary fluorescence lifetimes (>80 ns), which will be used for time-resolution fluorescent analysis, imaging, and photoelectric conversion.

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