

Fabrication and Optical Properties of Water Soluble CdSeS Nanocrystals Using Glycerin as Stabilizing Agent

Fengrui Jiang, Guolong Tan*

State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan, China

Abstract

Herein we present an unusual phosphine-free method to fabricate water soluble CdSeS nanocrystals in cubic structure. In this method, glycerin was used as a stabilizing agent replacing tri-*n*-octylphosphine oxide (TOPO). Water solution of Na₂SeO₃ in polyethylene glycol was utilized as Se source. 3-Mercaptopropionic acid (MPA) provides S source. The phosphine-free Se and S sources were found to be highly reactive and suitable for the synthesis of CdSeS nanocrystals. XRD and HRTEM images confirm the formation of CdSeS nanocrystals in zinc blende structure. The absorption peaks on UV-vis spectra of as-prepared CdSeS nanocrystals are tunable from 330 nm to 440 nm, which blue shifts to shorter wavelength side in comparison with that of pure CdSe nanocrystals. The cubic CdSeS nanocrystals demonstrate narrow PL emissions spectra between 464 and 615 nm. Transmission electron microscopy images show the uniformity for the size distribution of the ternary QDs. Series water soluble CdSe_{1-x}S_x ($x = 0 \sim 1$) nanocrystals have also been synthesized using Na₂SeO₃ and Na₂S solution as the Se-S co-sources. Tunable band gap energies of CdSe_{1-x}S_x ($x = 0 \sim 1$) nanocrystals upon chemical composition x have been achieved, the gap ranges from 290 nm to 558 nm.

Citation: Jiang F, Tan G (2013) Fabrication and Optical Properties of Water Soluble CdSeS Nanocrystals Using Glycerin as Stabilizing Agent. PLoS ONE 8(10): e77253. doi:10.1371/journal.pone.0077253

Editor: Arum Han, Texas A&M University, United States of America

Received: May 27, 2013; **Accepted:** September 9, 2013; **Published:** October 21, 2013

Copyright: © 2013 Jiang, Tan. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

Funding: The financial support is from the Natural Science Foundation of Hubei Province (2010CDA078). The funders had no role in study design, data collection and analysis, decision to publish, or preparation of the manuscript.

Competing Interests: The authors have declared that no competing interests exist.

* E-mail: gltan@whut.edu.cn

Introduction

Over the past decades, scientists have discovered new species ranging between molecules and solids with unique size dependent physical and chemical properties [1–3]. One prominent example are colloidal semiconductor nanocrystals (NCs) [4], which have found their way into various applications such as LEDs, [5–8] solar cells [9,10] and fluorescent labeling [11,12]. To achieve the widespread use of QD-based devices and systems, it would be important to develop safe, economical, and environmentally friendly large-scale syntheses of high-quality QDs.

For the synthesis of colloidal II–VI QDs, earlier efforts focused more on binary systems, such as CdSe and CdS QDs, and recent efforts more on ternary systems, such as CdTeSe [13–15], CdSeS [16–18], ZnCdSe, and ZnCdS QD alloys [19–25]. For the ternary QDs, bandgap engineering can be achieved via control of their sizes, constituent stoichiometry, and internal structures (such as homogeneous vs. gradient). For homogeneous ternary QDs, their compositions play an essential role affecting both the confinement potential and the interfacial strain; thus, their band gap energy can be tuned, even at a constant size [26]. For example, alloyed CdSeS nanocrystals can be tuned readily to emit in the wavelength range of 480–540 nm, which is not easily achieved with binary CdSe or CdS QDs alone [4,27–30]. The ternary QDs reported by other research groups were from hot-injection approaches using of Tri-*n*-octylphosphine (TOP)/tri-*n*-octylphosphine oxide (TOPO) or other long chain organic compounds [26,31] as the capping agent at high temperature.

The high-temperature synthesis method usually involves the reaction of a cadmium compound with a phosphine complex of

selenium and sulfur [4,30–33]. The product often exhibits high PL QY and photostability. However, the organic compounds and phosphines (e.g., trioctylphosphine (TOP) and tributylphosphine (TBP)) are usually toxic and expensive. The Se and S precursor is still almost invariably a Se- or S-phosphine complex. The use of such capping agents requires very stringent experimental conditions, such as an inert atmosphere and high temperature [15]. Meanwhile, these phosphines or other organic compounds are not water soluble. Therefore, it is still a challenge to develop new synthesis routes leading to water soluble ternary semiconductor nanocrystals with uniform size by a phosphine-free method, which is affordable and could be easily scaled up. One of the most important aspects is the capping agent, which could stabilize nanocrystals in solutions. In contrast, by using polymeric stabilizers to synthesize nanocrystals is an easy, safe way and is much cheaper than that employing TOP/TOPO as the capping agent. In general, polymer stabilizer only requires ambient laboratory conditions [34,35].

In this work, glycerin has been used to replace TOPO as a new kind of capping agent and phosphine-free Na₂SeO₃ solution as Se source, 3-mercaptopropionic acid (MPA) and Na₂S as the S source to produce CdSeS nanocrystals, which is water soluble and could be stabilized in the solution for several months without having its color and optical properties changed.

Results and Discussion

1.1. Structure determination

CdSeS nanocrystals were thus produced through the reaction of Cd source with Se source from Na_2SeO_3 and S source from MPA. Figure 1 shows the X-ray diffraction pattern of CdSeS nanocrystals. It can be seen that the as-prepared CdSeS nanocrystals exhibit cubic structure. All the diffraction peaks locate within the angle positions between that of cubic CdSe (JCPDS 65–2891) and cubic CdS (JCPDS 65–2887). The diffraction peaks at 25.47° , 42.22° and 49.91° correspond to the lattice planes of (111), (220) and (311), suggesting that the nanoparticles are in zinc blende structure and are in good agreement with the reported data on $\text{CdSe}_{1-x}\text{S}_x$ nanoparticles [17,36–39]. The lattice parameter of the CdSeS nanocrystals has been determined to be $a = 1.9769\text{\AA}$ from the XRD pattern through Bragg equation. By using the formula of (a_1 (CdS) = 1.9266\AA , a_2 (CdSe) = 2.0144\AA ; a_x is the lattice parameter of the as-prepared $\text{CdSe}_{1-x}\text{S}_x$) [17], the chemical composition value of x is calculated to be 0.8. Thus the chemical formula of $\text{CdSe}_{1-x}\text{S}_x$ can be now expressed as $\text{CdSe}_{0.2}\text{S}_{0.8}$. Obviously, the diffraction peaks for $\text{CdSe}_{0.2}\text{S}_{0.8}$ nanocrystals have been broadened, indicating the formation of ultrafine nanocrystals. The average particle size calculated from Scherer's formula was 4.5 nm. In fact, wurtzite and zinc blende structure have similar lattice structures, both of them own the same tetragonally positioned first nearest neighbors and nearly identical secondary nearest neighbors [40]. Therefore, XRD pattern is hard to discriminate zinc blende structure from wurtzite structure in the as-prepared CdSeS nanocrystals. The existence of the wurtzite structure could not be excluded in this broadened XRD pattern. However, the XRD pattern exhibits standard shape of zinc blende structure, which was considered to be the final phase of the as-prepared $\text{CdSe}_{0.2}\text{S}_{0.8}$ nanocrystals and the evidence for the calculation of their lattice parameter. High resolution transmission electron microscopy (HRTEM) images of these CdSeS nanocrystals in the following section will prove that this hypothesis is correct.

1.2. Morphology and microstructure

The microstructure and morphology of the as-prepared $\text{CdSe}_{0.2}\text{S}_{0.8}$ nanocrystals are exhibited in Figure 2 (c) shows a low magnification TEM image of the $\text{CdSe}_{0.2}\text{S}_{0.8}$ nanocrystals. It can be seen from Figure 2 (c) that glycerin forms a network frame, which hosts the $\text{CdSe}_{0.2}\text{S}_{0.8}$ nanocrystals on branches. Some aggregation of the $\text{CdSe}_{0.2}\text{S}_{0.8}$ nanocrystals on the network frame can be observed in Figure 2 (c) due to the high viscosity of the glycerin.

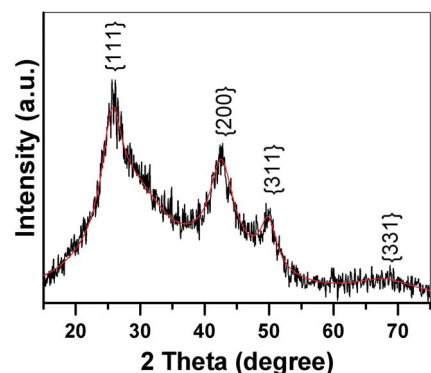


Figure 1. XRD pattern of as-prepared $\text{CdSe}_{0.2}\text{S}_{0.8}$ nanocrystals. doi:10.1371/journal.pone.0077253.g001

Figure 2 (a) (b) and (d) show the HRTEM images of as-prepared $\text{CdSe}_{0.2}\text{S}_{0.8}$ nanocrystals using glycerin as the stabilizing agent. They clearly confirm the well order crystal structure of $\text{CdSe}_{0.2}\text{S}_{0.8}$ nanocrystals. The lattice fringes are clearly seen in these nanocrystals, which are assigned to {111} and {200} lattice planes in zinc blende structure. The HRTEM images of individual nanocrystals further confirm the cubic structure feature of the as-prepared $\text{CdSe}_{0.2}\text{S}_{0.8}$ nanocrystals using the glycerin as the stabilizing agent, being in good agreement with the XRD results. Lattice disorder and stacking faults are clearly seen in these particles, as being shown in Figure 2 (a) & (b). The particles are homogeneously distributed, ranging from 3 nm to 6 nm. The polymer with higher viscosity would induce big stress upon the surface of the nanocrystals, which could easily cause the formation of the defects and twin structures in the CdSeS nanocrystals. However, individual $\text{CdSe}_{0.2}\text{S}_{0.8}$ nanocrystals could be still discriminated each other on these HRTEM images. Some particles are well separated; exhibiting monodispersive size distribution, as being shown in Figure 2.

1.3. UV-vis spectra

Figure 3 shows the tunable UV – Vis absorption spectra of $\text{CdSe}_{0.2}\text{S}_{0.8}$ nanocrystals upon different particle size, which was controlled by temperature and period of heat treatment. With control of the particle size of the $\text{CdSe}_{0.2}\text{S}_{0.8}$ nanocrystals, the color of the $\text{CdSe}_{0.2}\text{S}_{0.8}$ QDs could be tuned. The absorption spectrum showed a slight broadening caused by the size increase during the growth of the $\text{CdSe}_{0.2}\text{S}_{0.8}$ nanocrystals, as being shown in Figure 3. The particle size increases with the temperature and period of heat treatment of the solution, inducing the absorption peaks red shift to longer wavelength side, as being shown in Figure 3.

There are two absorption peaks locating at 335 nm and 358 nm respectively for the $\text{CdSe}_{0.2}\text{S}_{0.8}$ nanocrystals which were heat treated at 140°C for 5 minutes (Figure 3 (a)). The two peaks red shift to 356 nm and 388 nm for the $\text{CdSe}_{0.2}\text{S}_{0.8}$ nanocrystals which were heat treated at 180°C for 5 minutes (Figure 3 (b)). These absorption peaks keep shifting to the longer wavelength side when $\text{CdSe}_{0.2}\text{S}_{0.8}$ nanocrystals were heat treated at higher temperature or for longer period; until it reaches at 432 nm after $\text{CdSe}_{0.2}\text{S}_{0.8}$ nanocrystals were heat treated at 260°C for 5 hours (Figure 3 (k)). This kind of red shift was caused by well-known quantum confinement effect. The higher is the heat treatment temperature, the larger is the particle size and thus smaller the band gap energies of the $\text{CdSe}_{0.2}\text{S}_{0.8}$ nanocrystals, which leads to the red shift of the absorption peaks of the quantum dots.

XRD results and HRTEM images demonstrate that the as-prepared $\text{CdSe}_{0.2}\text{S}_{0.8}$ nanocrystals were in zinc blende structure when glycerin was used as the stabilizing precursor. The band gap energy of CdSe is 1.714 eV [41], while that of cubic CdS is 2.50 eV. The band gap energy of bulk $\text{CdSe}_{0.2}\text{S}_{0.8}$ should be located somewhere between 1.714 to 2.50 eV. However, when size of $\text{CdSe}_{0.2}\text{S}_{0.8}$ nanocrystals is smaller than its Bohr radius, the band gap will be enlarged due to quantum confinement effect. Therefore the UV visible absorption peaks didn't move to the conventional wavelength region within 500~650 nm for pure CdSe nanocrystals due to the enlargement of its band gap by finer particle size. Instead the absorption peaks of our $\text{CdSe}_{0.2}\text{S}_{0.8}$ nanocrystals are located within the wavelength range of 335 nm~432 nm, which shouldn't reflect ultra-small particle size of CdSe nanocrystals, but actually is corresponding to the tunable band gap energies of $\text{CdSe}_{0.2}\text{S}_{0.8}$ nanocrystals being caused by the chemical composition. These kinds of $\text{CdSe}_{0.2}\text{S}_{0.8}$ being produced using glycerin as the stabilizing agent are water soluble.

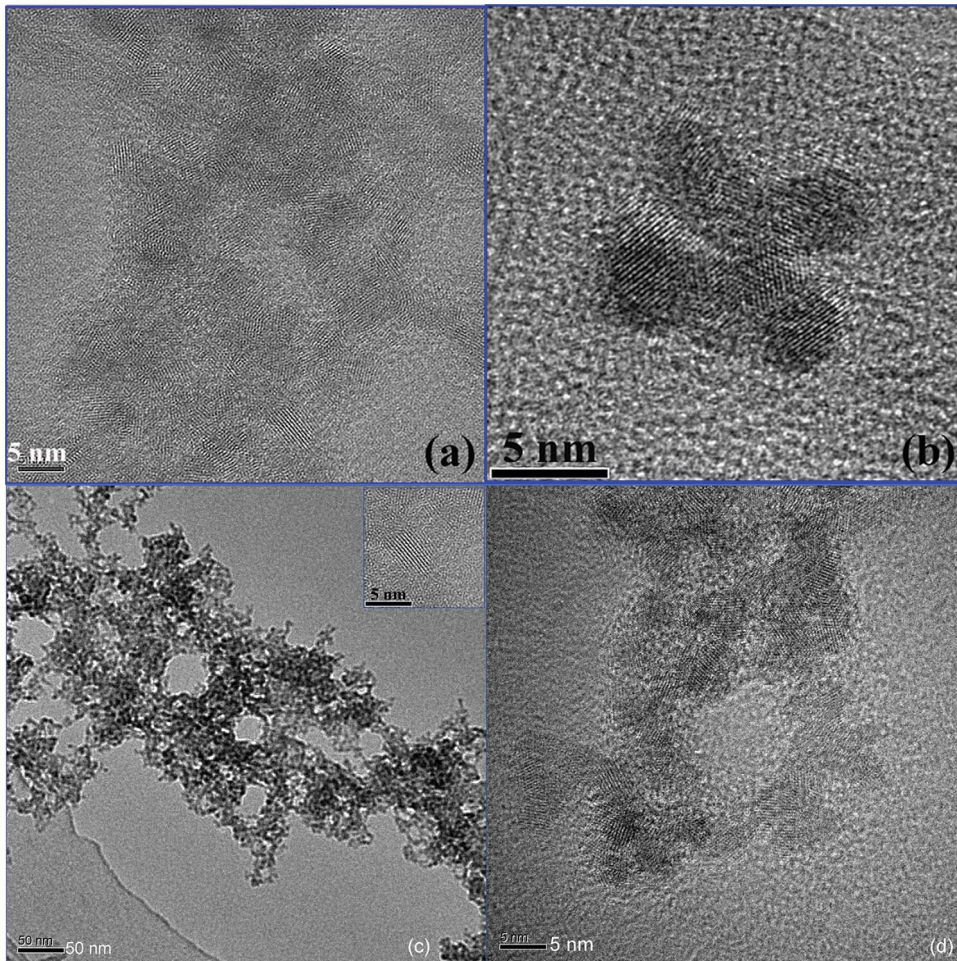


Figure 2. TEM and HRTEM images of as-prepared CdSe_{0.2}S_{0.8} nanocrystals.
doi:10.1371/journal.pone.0077253.g002

Series CdSe_{1-x}S_x nanocrystals were intentionally fabricated using Na₂SeO₃ and Na₂S solution as the Se-S sources. The experimental process was the same as the above CdSe_{0.2}S_{0.8} nanocrystals except that MPA was replaced by Na₂S to provide S source. The atomic ratio of Na₂SeO₃: Na₂S was set to be 0:1 ($x = 1$), 0.25:0.75 ($x = 0.75$), 0.5:0.5 ($x = 0.5$), 0.75:0.25 ($x = 0.25$)

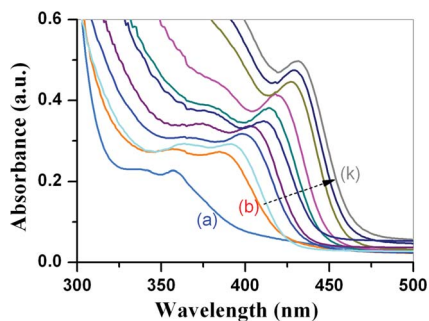


Figure 3. Tunable UV-Vis absorption spectra of CdSe_{0.2}S_{0.8} nanocrystals upon particle size, the solution containing CdSe_{0.2}S_{0.8} nanocrystals was heat treated at (a) 140°C for 5 min, (b) 180°C for 5 min, (c) 220°C for 5 min, ... (j) 260°C for 4 hs; (k) 260°C for 5 h.
doi:10.1371/journal.pone.0077253.g003

and 1:0 ($x = 0$). Se-S mixed precursor was dropped into Cd precursor very slowly at a temperature of 260°C. All the specimens were heat treated at this temperature for 5 minutes. The UV visible absorption spectra of the as-prepared CdSe_{1-x}S_x nanocrystals are demonstrated in Figure 4, where it can be seen that the absorption peaks red shift to longer wavelength side with the concentration of Se. There is an absorption peak locating at 290 nm for CdS ($x = 1$) nanocrystals, this peak red shifts to 368 nm and 401 nm for the composition of $x = 0.75$ and $x = 0.5$ respectively, as being shown in Figure 4 (a) ~ (c). The absorption peak further red shifts to 461 nm as well as 558 nm for the composition of $x = 0.75$ and $x = 1$ respectively, as being shown in Figure 4 (d) ~ (e). The band gap energies of CdSe_{1-x}S_x nanocrystals red shift to longer wavelength side when the concentration of Se sources increased, driving the absorption peak approaching to that of pure CdSe nanocrystals. In other words, the more S source is contained in the CdSe_{1-x}S_x nanocrystals, the larger is its band gap energy and the shorter wavelength is the absorption peak for the CdSe_{1-x}S_x nanocrystals. Therefore chemical composition provides us an additional degree to tune the band gap energies of ternary semiconductor nanocrystals except the traditional quantum size effect. Of course this paper is not the first one to tune the band gap energies of semiconductor nanocrystals by chemical composition, but it is the first one for fabrication of water soluble CdSe_{1-x}S_x nanocrystals. It

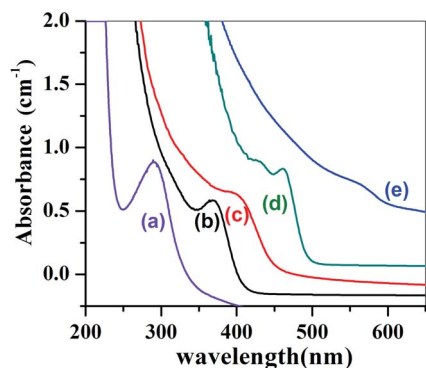


Figure 4. The UV absorption of CdSe_{1-x}S_x nanocrystals in different Se/S ratio, (a) x = 1, (b) x = 0.75, (c) x = 0.5, (d) x = 0.25 and (e) x = 0.

doi:10.1371/journal.pone.0077253.g004

is a facile green and environment friendly way to synthesize CdSe_{1-x}S_x nanocrystals with very low cost.

1.4. Photoluminescence spectra

Figure 5 shows the photoluminescence spectra of as-prepared CdSe_{0.2}S_{0.8} nanocrystals which were heat treated at different temperatures. The coexistence of CdS nanocrystals and CdSe nanocrystals at 80°C, represented by a narrow PL signal at 464 nm and a broad PL signal at 528 nm, respectively, was observed in Figure 5a (80°C). The narrow PL signal at 464 nm was correlated to the emission peak of the CdS nanocrystals by PLE measurements and thus proving the origin of the blue luminescence, while the broaden signal at 528 nm was corresponding to the emission spectrum of CdSe nanocrystals (Figure 5a). This result indicates that single phase CdSe_{0.2}S_{0.8} was not formed at the beginning of the reaction (80°C), instead a mixture of CdS and CdSe were the initial products. The other possibility is the coexistence of smaller and larger particles with two size distribution centers.

This possibility for the appearance of two emission peaks in Figure 5 (a) is the equilibrium between smaller and larger particles being related to the two peaks at 464 nm and 528 nm respectively. The small CdSe_{0.2}S_{0.8} nanoparticles act as growth material or even as nuclei for the larger NCs after raising the temperature from 80°C to 260°C. Transmission electron microscopy (TEM) observation of the above-mentioned equilibrium confirmed the existence of spherical particles with two mean diameters of 3.2 nm

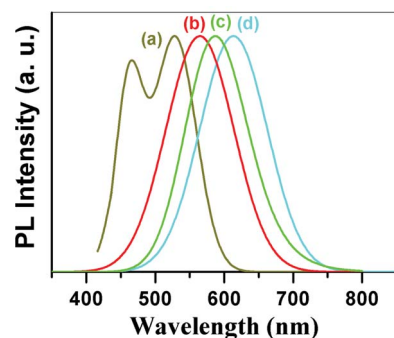


Figure 5. Tunable photoluminescence spectra of CdSeS nanocrystals with particle size. CdSeS nano-specimens were heat treated at (a) 80°C, (b) 180°C, (c) 220°C, (d) 260°C, all for 5 minutes. doi:10.1371/journal.pone.0077253.g005

and 5 nm (Figure 2 (c) & (d)), which is consistent with the values calculated from the spectroscopic data according to Yu et al. [42]. The larger particles exhibited a broad size distribution, whereas the smaller particles showed an unexpected narrow size distribution. This can be concluded from the FWHM of the corresponding PL spectra.

The clear evidence that small cubic CdSe_{0.2}S_{0.8} nanocrystals differ significantly from conventional NCs can be seen by raising the reaction temperature from 80°C to 260°C (Figure 4). Subsequently, the narrow peak of the small cubic NCs decreases without showing any red shift while the broad peak shifts to longer wavelength side, indicating that the growth of NCs was at the cost of smaller particles. The transition from two emission peaks to one peak accompanying with the disappearance of the first small emission peak in the photoluminescence spectra was observed in Figure 5 (a) and (b) when the heat treatment temperature of the specimen rises from 80°C to 180°C. This transition may also implicate the formation of single phase CdSe_{0.2}S_{0.8} nanocrystals, which should be able to trig only one emission peak. The broad peak at 528 nm red shifts to 563 nm when the temperature of the heat treatment for the suspension solution of CdSe_{0.2}S_{0.8} nanocrystals was raised from 80°C to 180°C (Figure 5 b), which further shifts to 586 nm after the heat treatment of the specimen at higher temperature (220°C) for 5 minute (Figure 5c). Finally the PL emission peak red shifts to 614.5 nm when the specimen was heat treated at 260°C for 5min, as being shown in Figure 5 (d). This single PL emission peak should reflect the electron transition from the valence band to conduction band in single phase CdSe_{0.2}S_{0.8} nanocrystals instead of mixture of CdSe and CdS nanocrystals. This result is in good agreement with the formula of CdSe_{0.2}S_{0.8} compound being drawn from XRD pattern. Similar results have been reported by Kasuya et al. [43], Chen [44] and Riehle et al. [37] who studied the transformation of magic size CdSe clusters into CdSe NCs by UV-vis absorption spectroscopy and photoluminescence spectra. Again the big resolved quantum confinement based on photoluminescence spectra is due to the larger particle size of cubic CdSe_{0.2}S_{0.8} nanocrystals instead of ultrasmall particle size for pure CdSe nanocrystals. This point differs significantly from the results being observed by Riehle et al. [37], who assigned the strong quantum confine effect in PL spectra to ultra small particle size of pure CdSe nanocrystals, which were also fabricated using MPA as the surface activation agent. Actually the S ions inside MPA molecule may release additional S sources, which would combine with Se source to react with Cd precursor together, thus CdSeS instead of pure CdSe nanocrystals could be formed.

The PL quantum yield efficiency of CdSeS nanocrystals was found to develop with a time constant of 5 days from zero to terminal saturation value of approximate 49%, which was maintained constant within the remaining time of several months.

Materials and Methods

First of all, a stock solution of Se-S precursor was prepared by dissolving 0.0154 g Na₂SeO₃ powder in 2 mL distilled water, afterwards 20 mL glycerin was put into the above solution. Then 1.0078 g glucose powder dissolving in 2 mL distilled water together with 1mL 3-mercaptopropionic acid (MPA) was added into above solution at 80°C. Glucose was used as reduction agent to produce Se source, while MPA plays both roles of surface activating agent and providing the source of S. The mixture solution was heated up to 260°C for 20 minutes, the color of the solution changes from limpidity, yellow, orange, red to dark red at different temperatures of heat treatment. The colorful suspension

comes from the formation of Se nanoparticles, which was reduced from Na_2SeO_3 by glucose. Afterwards the red suspension solution was cooling down to room temperature. In order to fabricate homogeneous CdSeS nanocrystals, a transparent Se precursor is necessary. Therefore the red suspension solution was heated up to 220°C again, the Se nanoparticles were dissolved in the solution. However, after the precursor solution was cooling down to room temperature, a few black suspended colloids could be observed in the limpidity solution. In this case, 10 mL more distilled water was added into the suspension solution, which was heated up to 260°C once more. At this point, the black suspended colloids disappeared and the suspension becomes colorless transparent solution after cooling down to room temperature. The clear solution was stored as Se-S precursor.

0.0211 g $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ powder and 0.2166 g polyethylene glycol were dissolved together in 15 mL distilled water in a three neck flask at 60°C, afterwards 0.1 mL MPA and 10 mL 1 M NaOH were added into the above solution, which was used as the stock solution of Cd precursor. The Cd stock solution was maintained at 80°C, into which the stock solution of Se-S precursor was injected slowly. Immediately CdSeS nanocrystals were formed, the solution turned into transparent yellow one. 5 mL of the specimen was taken out and put in a small glass bottle for optical and microstructure measurement. The remaining suspension keeps heating at 120°C, 180°C and 260°C, respectively. At each temperature point, 5 mL colloid suspension solution was taken out from the flask for optical measurement. There was no evaporation but some refluxing in the reaction solution. The above process was carried out under ambient atmosphere. The colloid dispersion solution exhibits excellent stability, nanoparticles didn't deposit onto the bottom of the bottle or the color of the solution didn't change for several months. The glycerin and MPA formed a macromolecule frame network, on which nanocrystals were pinned up making the dispersion solution of CdSeS nanocrystals extremely stable. The as-prepared products were characterized by using various methods. The sample for the X-ray diffraction (XRD) was prepared by centrifugation of the solution

with distilled water at 12000 rpm for 30 min. The structural characterization of the CdSeS nanocrystals was monitored by Rigaku powder X-ray diffraction machine. The microstructure feature of the CdSeS nanocrystals was performed upon a JEOL 2100F high resolution transmission electronic microscopy (HRTEM). UV-vis absorption spectra for the suspension solution of CdSeS nanocrystals has been recorded by a Phoenix 1900PC UV-Vis-NIR Spectrophotometer and fluorescence spectrum by USB 4000 spectroscopy made by Ocean optics.

Conclusion

In summary, we have demonstrated a phosphine-free protocol for synthesizing water soluble CdSeS nanocrystals. It employed glycerin to facilitate Cd $(\text{CH}_3\text{COO})_2$ powder dissolution in water at room temperature; phosphine-free Na_2SeO_3 precursor in polyethylene glycol and MPA as Se-S sources have been successfully applied toward the synthesis of CdSeS nanocrystals in zinc blende structure. Glucose was used as reduction agent to produce Se source, XRD pattern and HRTEM images confirmed the formation of cubic $\text{CdSe}_{0.2}\text{S}_{0.8}$ nanocrystals, whose UV-Vis absorption peaks locate within the range of 335 nm~432 nm. This shouldn't reflect ultra-small particle size of pure CdSe nanocrystals, but actually is corresponding to the quantum confinement effect of cubic $\text{CdSe}_{0.2}\text{S}_{0.8}$ nanocrystals. Tunable band gap energies of series water soluble $\text{CdSe}_{1-x}\text{S}_x$ have been achieved through chemical composition upon atomic ratio of Se/S sources, which come from the Na_2SeO_3 and Na_2S solution. The corresponding PL spectra revealed band-edge luminescence for $\text{CdSe}_{0.2}\text{S}_{0.8}$ QDs of all size range, whose PLE peaks cover from 464 nm to 614.5 nm; no deep trap luminescence was detected.

Author Contributions

Conceived and designed the experiments: GT. Performed the experiments: FJ. Analyzed the data: GT FJ. Contributed reagents/materials/analysis tools: GT. Wrote the paper: GT.

References

- Brus LE (1986) Relates the band gap to particle size of a spherical quantum dot. *J. Phys. Chem.* 90: 2555–2560.
- Herron N, Calabrese JC, Farneth WE, Wang Y (1993) Crystal structure and optical properties of $\text{Cd}_{32}\text{S}_{14}(\text{SC}_6\text{H}_5)_{36}$. *DMF*₄, a cluster with a 15 Angstrom CdS core. *Science* 259:1426–1428.
- Krätschmer W, Lamb D, Postropoulos K, Huffman DR (1990) Solid C60: a new form of carbon. *Nature* 347:354–358.
- Murray CB, Norris DJ, Bawendi MG (1993) Synthesis and characterization of nearly monodisperse CdE (E = sulfur, selenium, tellurium) semiconductor nanocrystallites. *J. Am. Chem. Soc.* 115: 8706–8715.
- Colvin VL, Schlamp MC, Alivisatos AP (1994) Light-emitting diodes made from cadmium selenide nanocrystals and a semiconducting polymer. *Nature* 370: 354–357.
- Rizzo A, Li Y, Kudara S, Della SF, Tanella M, et al. (2007) Blue light emitting diodes based on fluorescent CdSe/ZnS nanocrystals. *Appl. Phys. Lett.* 90: 051106–051109.
- Caruge JM, Halpert JE, Wood V, Bulovic V, Bawendi MG (2008) Colloidal quantum-dot light-emitting diodes with metal-oxide charge transport layers. *Nature Photon* 2: 247–250.
- Steckel JS, Snee PT, Coe-Sullivan SA, Zimmer JP, Halpert JE, et al. (2006) Color-saturated green-emitting QD-LEDs. *Angew. Chem. Int. Ed.* 45: 5796–5799.
- Huynh WU, Dittmer JJ, Alivisatos AP (2002) Hybrid nanorod-polymer solar cells. *Science* 295: 2425–2427.
- Gur I, Fromer NA, Geier ML, Alivisatos AP (2005) Air-stable all-inorganic nanocrystal solar cells processed from solution. *Science*. 310: 462–465.
- Bruchez M, Moronne M, Gin P, Weiss S, Alivisatos AP (1998) Semiconductor nanocrystals as fluorescent biological labels. *Science* 281: 2013–2016.
- Alivisatos P (2004) The use of nanocrystals in biological detection. *Nature Biotechnol.* 22: 47–52.
- Bailey RE, Nie S (2003) Alloyed semiconductor quantum dots: tuning the optical properties without changing the particle size. *J. Am. Chem. Soc.* 125: 7100–7106.
- Jiang W, Singhal A, Zheng J, Wang C, Chan W. C W (2006) Design and characterization of lysine cross-linked mercapto-acid biocompatible quantum dots. *Chem. Mater.* 18: 4845–4845.
- Ratcliffe CI, Yu K, Ripmeester JA, Zaman MB, Badarau C, et al. (2006) Solid state NMR studies of photoluminescent cadmium chalcogenide nanoparticles. *Phys. Chem. Chem. Phys.* 8: 3510–3519.
- Jang E, Jun S, Pu L (2003) High quality CdSeS nanocrystals synthesized by facile single injection process and their electroluminescence. *Chem. Commun.* 19: 2964–2965.
- Swafford LA, Weigand LA, Bowers MJ, McBride JR, Rapaport JL, et al. (2006) Homogeneously alloyed $\text{CdS}_x\text{Se}_{1-x}$ nanocrystals: synthesis, characterization, and composition/size-dependent band gap. *J. Am. Chem. Soc.* 128:12299–12306.
- Al-Salim N, Young AG, Tilley RD, McQuillan AJ, Xia J (2007) Synthesis of CdSeS nanocrystals in coordinating and noncoordinating solvents: solvent's role in evolution of the optical and structural properties. *Chem. Mater.* 19: 5185–5193.
- Zhong X, Han M, Dong Z, White TJ, Knoll W (2003) Composition-Tunable $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ nanocrystals with high luminescence and stability. *J. Am. Chem. Soc.* 125: 8589–8594.
- Zhong X, Feng Y, Knoll W, Han M (2003) Alloyed $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ nanocrystals with highly narrow luminescence spectral width. *J. Am. Chem. Soc.* 125: 13559–13563.
- Zhong X, Zhang Z, Liu S., Han M, Knoll W (2004) Embryonic nuclei-induced alloying process for the reproducible synthesis of blue-emitting $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ nanocrystals with long-time thermal stability in size distribution and emission wavelength. *J. Phys. Chem. B* 108: 15552–15559.

22. Zhong X, Liu S, Zhang Z, Li B, Zheng W, Knoll W (2004) Synthesis of high-quality CdS, ZnS, and $Zn_xCd_{1-x}S$ nanocrystals using metal salts and elemental sulfur. *J. Mater. Chem.* 14:2790–2794.
23. Ouyang J, Ripmeester JA, Wu X, Kingston D, Yu K, et al. (2007) Upconversion Luminescence of colloidal CdS and ZnCdS semiconductor quantum dots. *J. Phys. Chem. C* 111: 16261–16266.
24. Liu TY, Li M, Ouyang J, Zaman MB, Wang R, et al. (2009) Non-Injection and low-temperature approach to colloidal photoluminescent PbS nanocrystals with narrow bandwidth. *J. Phys. Chem. C* 113: 2301–2308.
25. Ouyang J, Ratcliffe CI, Kingston D, Wilkinson B, Kuijper J, et al. (2008) Gradiently alloyed $Zn_xCd_{1-x}S$ colloidal photoluminescent quantum dots synthesized via a noninjection one-pot approach. *J. Phys. Chem. C* 112: 4908–4919.
26. Ouyang J, Vincent M, Kingston D, Descours P, Boivineau T, et al. (2009) Noninjection, one-pot synthesis of photoluminescent colloidal homogeneously alloyed CdSeS quantum dots. *J. Phys. Chem. C* 113: 5193–5200.
27. Peng ZA, Peng X (2001) Formation of high-quality CdTe, CdSe, and CdS nanocrystals using CdO as precursor. *J. Am. Chem. Soc.* 123:183–184.
28. Yang YA, Wu H, Williams KR, Cao YC (2005) Synthesis of CdSe and CdTe nanocrystals without precursor injection. *Angew. Chem. Int. Ed.* 44: 6712–6715.
29. Yu WW, Peng X (2002) Formation of high-quality CdS and other II–VI semiconductor nanocrystals in noncoordinating solvents: tunable reactivity of onomers. *Angew. Chem. Int. Ed.* 41: 2368–2371.
30. Cao YC, Wang J (2004) One-Pot Synthesis of high-quality zinc-blende CdS nanocrystals. *J. Am. Chem. Soc.* 126: 14336–14337.
31. Al-Salim N, Young AG, Tilley RD, McQuillan AJ, Xia J (2007) Synthesis of CdSeS nanocrystals in coordinating and noncoordinating solvents: solvent's role in evolution of the optical and structural properties. *Chem Mater.* 19: 5185–5193.
32. Peng XG, Manna L, Yang WD, Wickham J, Scher E, et al. (2000) Shape control of CdSe nanocrystals. *Nature* 404: 59–61.
33. Li JJ, Wang YA, Guo W, Keay JC, Mishima TD, et al. (2003) Large-scale synthesis of nearly monodisperse CdSe/CdS core/shell nanocrystals using air-stable reagents via successive ion layer adsorption and reaction. *J. Am. Chem. Soc.* 125: 12567–12575.
34. Ma XD, Qian XF, Yin J, Zhu ZK (2002) Preparation and characterization of polyvinyl alcohol/selenide nanocomposites at room temperature. *J. Mater. Chem.* 12: 663–666.
35. Khanna PK, Gokhale RR, Subbarao VS, Singh N, Jun KW, Das BK (2005) Synthesis and optical properties of CdS/PVA nanocomposites. *Mater. Chem. Phys.* 94: 454–459.
36. Wei Y, Yang J, Lin AWH, Ying JY (2010) Highly reactive Se precursor for the phosphine-free synthesis of metal selenide nanocrystals. *Chem. of Mater.* 22: 5672–5677.
37. Riehle FS, Bienert R, Thomann R, Urban GA, Krueger M (2009) Blue luminescence and superstructures from magic size clusters of CdSe. *Nano Letts.* 9: 514–518.
38. Yang YJ, Xiang JW (2005) Template-free synthesis of CuS nanorods with a simple aqueous reaction at ambient conditions. *Appl. Phys. A: Mater. Sci. Proc.* 81: 1351–1353.
39. Sedaghat Z, Tagavina N, Marandi M (2006) Thermal control of the size and crystalline phase of CdS nanoparticles. *Nanotechnology* 17: 3812–3814.
40. Stampfl APJ, Hoffman Ph, Schaff O, Bradshaw AM (1997) Valence-band structure of cubic CdS as determined by angle-resolved photoemission. *Phys. Rev. B.* 55: 9679–9684.
41. Kale RB, Lokhande CD (2005) Band gap shift, structural characterization and phase transformation of CdSe thin films from nanocrystalline cubic to nanorod hexagonal on air annealing. *Semicond. Sci. Technol.* 20: 1–9.
42. Yu WW, Qu L, Guo W, Peng X (2003) Experimental determination of the extinction coefficient of CdTe, CdSe, and CdS nanocrystals. *Chem. Mater.* 15: 2854–2860.
43. Kasuya A, Sivamohan R, Barnakov YA, Dmitruk IM, Nirasawa T, et al. (2004) Ultra-stable nanoparticles of CdSe revealed from mass spectrometry. *Nature Mater.* 3: 99–102.
44. Chen X, Hutchison JL, Dobson PJ, Wakefield G (2010) Tuning the internal structures of CdSeS nanoparticles by using different selenium and sulphur precursors. *Mater. Sci. Eng. B* 166:14–18.