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Article

Synthesis of CdSe, ZnSe, and $Zn_xCd_{1-x}Se$ Nanocrystals and Their Silica Sheathed Core/Shell Structures

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Uniform $Zn_xCd_{1-x}Se$ nanocrystals have been prepared at the artificially designed water–oil interface using Na_2SeO_3, $Cd(NO_3)_2$, and $Zn(NO_3)_2$ as precursors. The chemical composition and band gap of the $Zn_xCd_{1-x}Se$ nanocrystals can be adjusted via different combinations of source material. The coating of a SiO_2 shell could transform the hydrophobic particles into hydrophilic particles. An advantage of this method is that a water phase could be added to the oleic acid (OLEA) synthesis system, which could be extended to make the synthesis of various nanocrystals more simple and flexible.

Introduction

Semiconductor nanocrystals are of great interest, recently, for both fundamental research and technical applications because of their quantum confinement effect. Among them, CdSe nanocrystals with uniform shape and size have been deeply and systematically researched not only because their synthesis was a milestone in the history of colloid nanocrystals[1] but also because of their unique properties in superlattices,[2] core/shell structures,[3] light-emitting diodes,[4] solar cells,[5] photoluminescence,[6] and biological labels.[7] Among these applications, mostly CdSe-based nanoparticles used for biological diagnosis have been reported since the pioneering research in 1998. Compared with the conventional dyes, CdSe-based colloidal nanoparticles render higher photostability; their emission is narrow ensuring no cross-coupling of signals, and numerous colors can be excited by a single source allowing for multiplex detection. Therefore, it is a great challenge for the chemists to prepare uniform CdSe nanocrystals and solve the problem of toxicity, biocompatibility, and water solubility.[8]

In the past decades, various chemical routes were reported to synthesize CdSe nanocrystals,[1,9−11] including the pyrolysis of single molecular organometallic compounds and the solvothermal treatment of elemental Se and organometallic Cd in the TOPO/TOP/HAD system. Our lab has also established a simple hydrothermal approach to fabricate CdE (E = S, Se, Te) materials.[12]

Now, we develop this reaction to a water−oil heterogeneous system and successfully prepare uniform $Zn_xCd_{1-x}Se$

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nanocrystals at the artificially designed water−oil interface using Na_2SeO_3, $Cd(NO_3)_2$, and $Zn(NO_3)_2$ as precursors. This method was based on our previous investigation[12] and partly inspired by the recent research of oleic acid (OLEA) synthesis system.[13] Because of the special reaction system, normal inorganic compounds can be used as precursors, which greatly decreases the cost of synthesis, and a relatively low temperature (180 °C) is adopted to manipulate the reaction. The band gap of the as-synthesized $Zn_xCd_{1-x}Se$ nanocrystals can be tuned by changing the composition. Meanwhile, a subsequent silica-encapsulation process has been introduced to give these nanocrystals hydrophilic surfaces, which are favorable for biological applications.

Experimental Section

Materials. All reagents used in this work, including $Na_2SeO_3\cdot 5H_2O$, $Cd(NO_3)_2\cdot 4H_2O$, $Zn(NO_3)_2\cdot 6H_2O$, NaOH, oleic acid, $N_2H_4\cdot H_2O$, *n*-octanol, and *n*-hexane, were AR grade reagents (>99.99%) from the Beijing Chemical Factory, China, and were used directly without any treatment.

Synthesis of CdSe Nanocrystals. $Na_2SeO_3\cdot 5H_2O$ (100 mg), NaOH (800 mg), and $N_2H_4\cdot H_2O$ (3 mL) were dissolved in deionized water (5 mL) to form a transparent solution, A, at room temperature. $Cd(NO_3)_2\cdot 4H_2O$ (308 mg) was added to *n*-octanol (5 mL), which was heated to 60 °C in air, forming a clear solution, B. After solution A was transferred to an autoclave, oleic acid (15 mL) was added to completely cover it. Then, solution B was added to the autoclave, which was sealed and heated to 160 °C for 24 h.

After the reaction, the autoclave was cooled to room-temperature naturally, and the black liquid products were covered with a sticky substance, which might be sodium oleate. The products were dissolved in *n*-hexane (40 mL), and ethanol (20 mL) was added to precipitate the nanoparticles by centrifugation. Finally, the CdSe nanocrystals were redispersed in *n*-hexane to form a deep red transparent solution.

Synthesis of ZnSe Nanocrystals or $Zn_xCd_{1-x}Se$ Nanocrystals. The method was similar to the one described above except that solution B was prepared by dissolving $Zn(NO_3)_2\cdot 6H_2O$ (298 mg) or mixture of $Zn(NO_3)_2\cdot 6H_2O$ and $Cd(NO_3)_2\cdot 4H_2O$ (total of 1 mmol) in *n*-octanol. The ZnSe nanocrystals were dispersed in *n*-hexane to form a yellowish green transparent solution.

Synthesis of $Zn_xCd_{1-x}Se/SiO_2$ Core/Shell Structures. In a typical process, the water-in-oil microemulsions were prepared by mixing 30 mL of a *n*-hexane solution of CdSe or ZnSe with 3 mL of Triton X-100, 3 mL of hexanol, 0.2 mL of TEOS, and 0.9 mL of deionized water. Then, 0.1 mL of aqueous ammonia was added to catalyze the silica-polymerization reaction. After the microemulsions were stirred at room temperature for 24 h, the particles were isolated by adding acetone; then, they were centrifuged and washed with ethanol several times to remove the surfactant. Finally, the products were redispersed in deionized water.

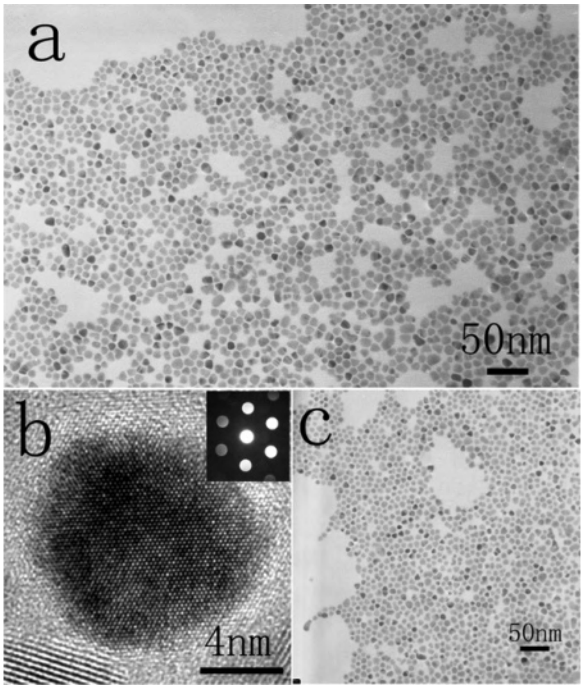

Figure 1. TEM images of (a and b) CdSe and (c) ZnSe nanocrystals.

Characterization. The samples was characterized by a Bruker D8 Advance X-ray diffractmeter (XRD) with Cu Kα radiation ($\lambda = 1.5418$ Å). The size and morphology of the nanoparticles were obtained by a JEOL JEM-1200EX transmission electron microscope (TEM) and a JEOL JEM-2010F high-resolution transmission electron microscope (HRTEM). Energy dispersive spectroscopy (EDS) and microbeam electron diffraction (MBD) were also measured using the TEM and HRTEM. The electronic absorption spectra were obtained on a Hitachi U-3010 UV−vis spectrometer.

Results and Discussion

Figure 1a and c shows the TEM images of the CdSe and ZnSe nanocrystals, respectively. Both samples consist of nearly uniform spherical nanocrystals. Figure 1b is the HRTEM image of an isolated 10 nm CdSe nanoparticle. The lattice fringes in the image correspond to a group of atomic planes within the particle, indicating that the particle is a single crystal. The distance between two adjacent planes is 0.187 nm, corresponding to (200) lattice planes in the wurtzite CdSe. The inset of Figure 1b shows the microbeam electron diffraction pattern, which is formed by a finely focused electron beam passing through the specimen surface. According to the calculation, the six bright dots could be indexed to six equivalent lattice planes of the (200) plane. This illustrates that the electron beam irradiates the particle just along its *c* axis. An EDS analysis has been taken for the CdSe nanocrystals (Figure 2). Only Cd and Se were detected, indicating that the nanocrystals were highly pure.

XRD measuremenst of CdSe and ZnSe nanoparticles were also made (Figure 3). The position of all diffraction peaks match well with the standard powder diffraction data (Joint Committee for Powder Diffraction Studies (JCPDS) No. 080459 for CdSe and 800021 for ZnSe) The average particle

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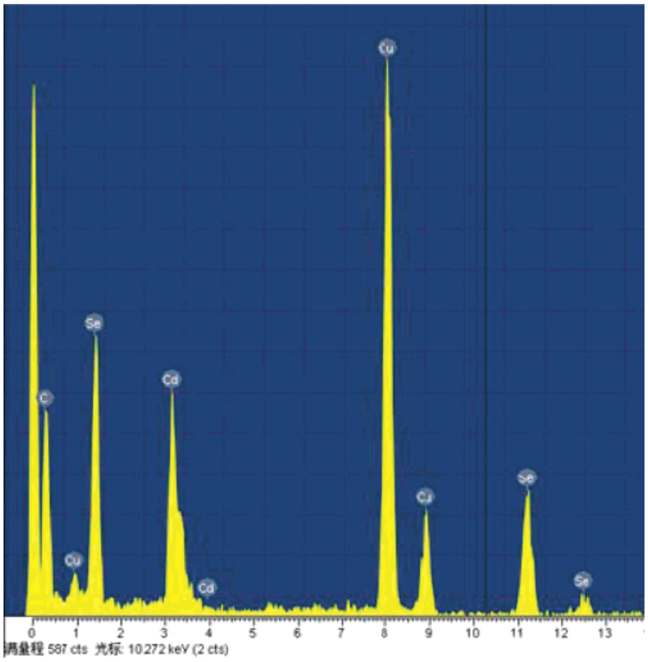

Figure 2. EDS spectrum of CdSe nanocrystals.

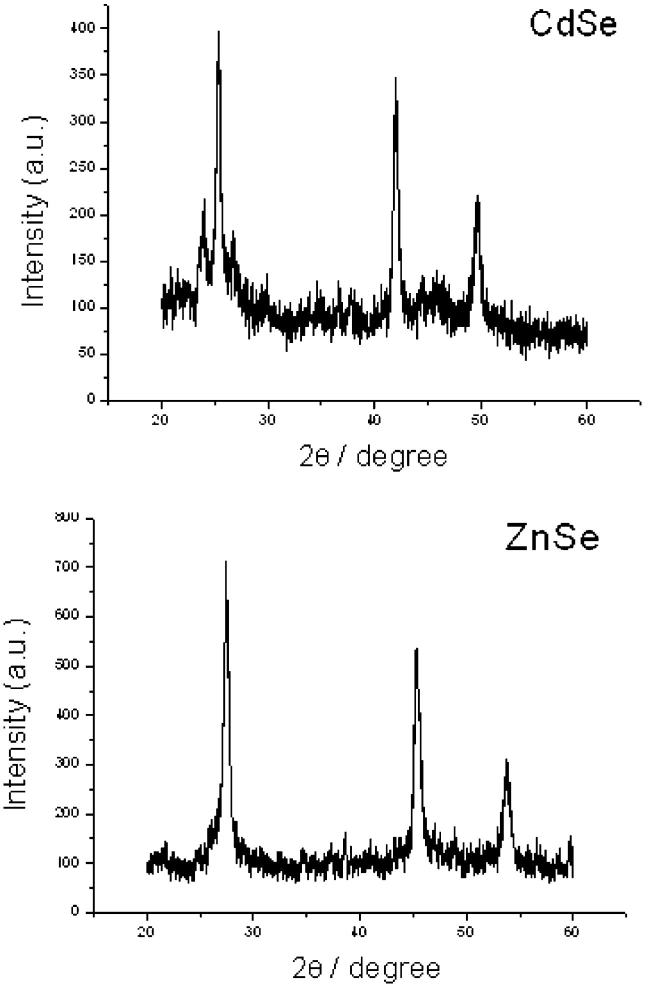

Figure 3. XRD patterns of CdSe and ZnSe nanocrystals.

diameter estimated from Scherrer's formula is consistent with that determined by statistical analysis of the TEM images, which also indicates that each particle is a single crystal.

Several experimental parameters, including the amount of oleic acid and *n*-octanol, reaction time, and reaction temperature, were tested to obtain optimal results. First, more than 10 mL of oleic acid gives better results. In the specially designed interface reaction and the 3.5 cm inner diameter autoclave, oleic acid is used not only for the capping the nanocrystals but also for preventing premature contact of the Cd and Se sources under lower temperature, which would greatly decrease the yield of nanocrystals. Second, the amount of *n*-octanol was found to have a small effect on the final product because it only helps in the solvation of the metal salts and it acts, partly, as a cosurfactant in the water−oil system. Therefore, 5 mL of *n*-octanol is enough for the preparation. Third, to ensure the phase formation of nanocrystal, the reaction time should be at least 12 h. An extension of the reaction time will not increase the size of nanocrystal. Fourth, the reaction temperature will affect the size of nanocrystal to some extent. Generally, the size decreases with the decreasing reaction temperature. The relative UV absorption spectra, which strongly confirm our conclusion, will be discussed below.

For semiconductor nanocrystals, the band gap (E_g) is an important value for electron transportation. Generally, the band gap of semiconductor nanocrystals could be modulated by controlling the particle size, which has been widely reported. Here, we try another way, forming the nanocrystal alloy to adjust the band gap between the value for CdSe and ZnSe (the bulk powder E_g for CdSe is 1.74 eV, and that for ZnSe is 2.67 eV).

With this thought, we started the synthesis with different combinations of metal nitrate. Fortunately, about 10 nm nanocrystals also formed in this situation. EDS analysis showed that the Zn and Cd elements coexist in the naonparticles (Figure 4). The corresponding nanoparticles were well-dispersed in *n*-hexane, forming transparent solutions. (Figure 5a) The room-temperature electronic absorption spectra of these $Zn_xCd_{1-x}Se$ nanocrystals in *n*-hexane are shown in Figure 5b. The band gap was determined by the derivative spectrum and the formula $(\alpha h\nu)^2 = B(h\nu - E_g)$. For 10 nm CdSe and ZnSe nanocrystals, the E_g values are 1.81 and 2.82 eV, respectively, which are slightly larger than the bulk materials mentioned above. The shapes and positions of the absorption spectra matches well with the literature report.[1] Maybe the size is just at the value where particles began to exhibit quantum effects; the absorption peak was not very clear but could be determined from the derivative spectrum and the direct band-gap calculation. The photoluminescence spectra of CdSe, ZnSe, and $Zn_{0.44}Cd_{0.56}Se$ were shown in Supporting Information Figure S1. The PL peaks located at 701, 460, and 550 nm are close to their corresponding absorption edge, which seem right with the previous report.

The chemical composition was then estimated according to the Vegard formula [$E_g(AxBy) = xE_g(A) + yE_g(B)$]. The corresponding results are listed in Table 1, from which we can learn that the composition of the final products was not same as the designed composition. It is obvious that the Cd−Se bond is easier to form than the Zn−Se bond in our

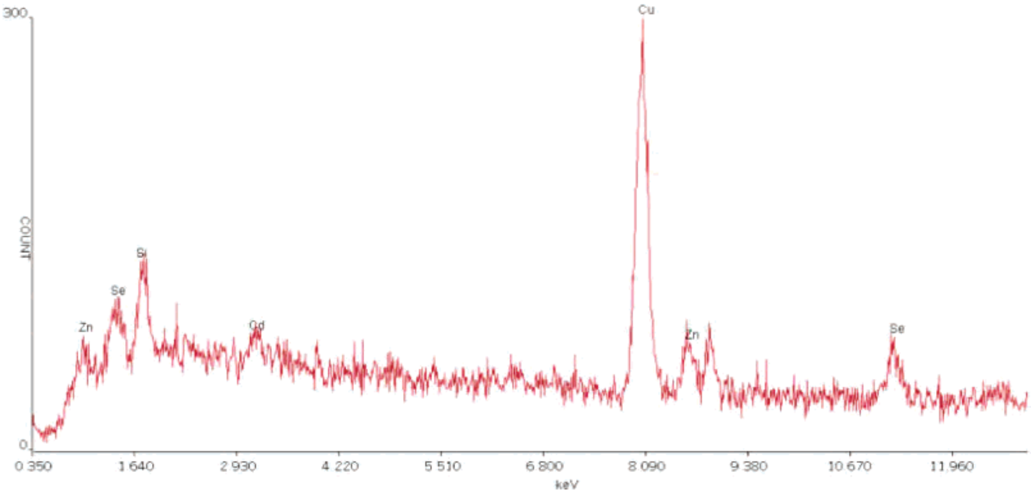

Figure 4. EDS spectrum of $Zn_xCd_{1-x}Se$ nanocrystals.

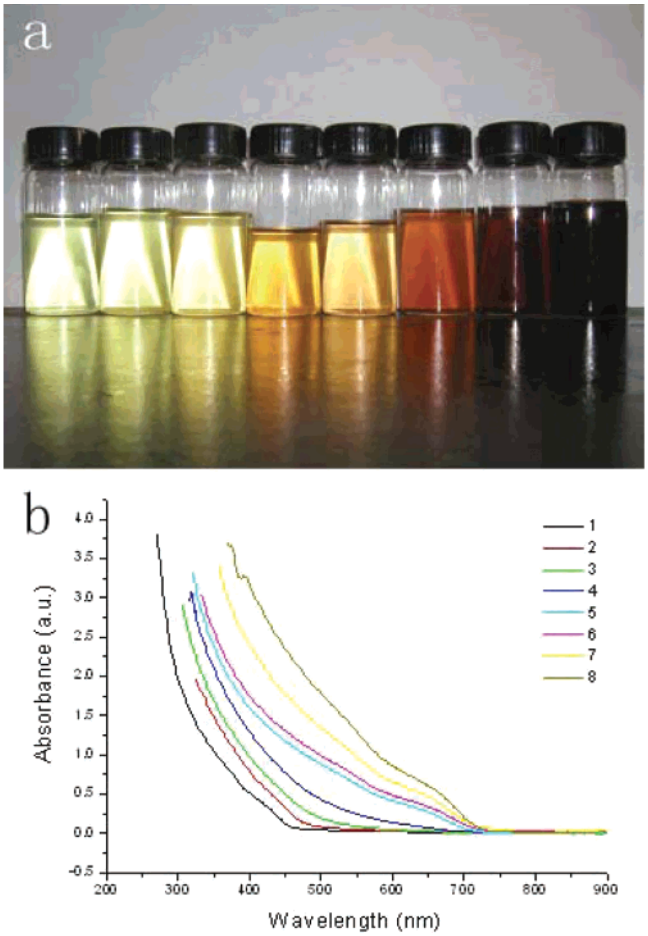

Figure 5. (a) Transparent *n*-hexane solutions of $Zn_xCd_{1-x}Se$ nanocrystals. From left to right, these samples are ZnSe, $Zn_{0.83}Cd_{0.17}Se$, $Zn_{0.76}Cd_{0.24}Se$, $Zn_{0.44}Cd_{0.56}Se$, $Zn_{0.65}Cd_{0.35}Se$, $Zn_{0.07}Cd_{0.93}Se$, $Zn_{0.02}Cd_{0.98}Se$, and CdSe. (b) Electronic absorption spectra of $Zn_xCd_{1-x}Se$ nanocrystals. Samples 1−8 correspond to those listed in Table 1.

Table 1. Band Gap of $Zn_xCd_{1-x}Se$ Nanocrystals with Various Chemical Compositions

sample	source material	E_g (eV)	chemical composition
1	$Zn(NO_3)_2$ 1 mmol	2.82	ZnSe
2	$Zn(NO_3)_2$ 0.975 mmol + $Cd(NO_3)_2$ 0.025 mmol	2.65	$Zn_{0.83}Cd_{0.17}Se$
3	$Zn(NO_3)_2$ 0.9 mmol + $Cd(NO_3)_2$ 0.1 mmol	2.47	$Zn_{0.65}Cd_{0.35}Se$
4	$Zn(NO_3)_2$ 0.8 mmol + $Cd(NO_3)_2$ 0.2 mmol	2.26	$Zn_{0.44}Cd_{0.56}Se$
5	$Zn(NO_3)_2$ 0.7 mmol + $Cd(NO_3)_2$ 0.3 mmol	1.89	$Zn_{0.07}Cd_{0.93}Se$
6	$Zn(NO_3)_2$ 0.6 mmol + $Cd(NO_3)_2$ 0.4 mmol	1.87	$Zn_{0.05}Cd_{0.95}Se$
7	$Zn(NO_3)_2$ 0.2 mmol + $Cd(NO_3)_2$ 0.8 mmol	1.84	$Zn_{0.02}Cd_{0.98}Se$
8	$Cd(NO_3)_2$ 1 mmol	1.82	CdSe

reaction, which makes it complicated. Nevertheless, it is believed that, with careful adjustments, $Zn_xCd_{1-x}Se$ nanocrystals with a specific E_g value can be prepared.[14]

In addition to the band-gap tuning by composition, variation of E_g caused by size was also observed in our synthesis. As mentioned above, decreasing the temperature will make the nanocrystals smaller. The electronic absorption spectra of CdSe and ZnSe nanocrystals prepared under different temperature are shown in Figure 6, and the corresponding band gaps are listed in Table 2. The band gap has a small change, which should be caused by the slight change of particle size resulting from the different reaction temperatures.

When Na_2SeSO_3 substituted for Na_2SeO_3 in a very similar synthesis under 160 °C, the final product are much smaller nanocrystals with an average diameter of 3−5 nm. Figure 7a reveals its TEM image, and Figure 7b shows the UV spectra of nanocrystals prepared with Na_2SeSO_3 and Na_2SeO_3 precursors. The band gaps are calculated to be 2.41 and 1.82 eV, respectively. Obviously, the change in size is responsible for the variation in the band gap. Although the morphology of these smaller CdSe nanocrystals is not uniform enough now, it confirms that this method may also be useful in the preparation of nanocrystal with smaller dimensions.

For the potential biological application of the CdSe nanoparticles, it is necessary to modify the surface to make these particles water-soluble and biocompatible[7,15] because the nanoparticle was hydrophobic and toxic. Traditionally, the CdSe nanoparticles were capped with the TOPO/TOP mixtures, and these hydrophobic particles became water-soluble after an exchange of the surface ligands with thiolate

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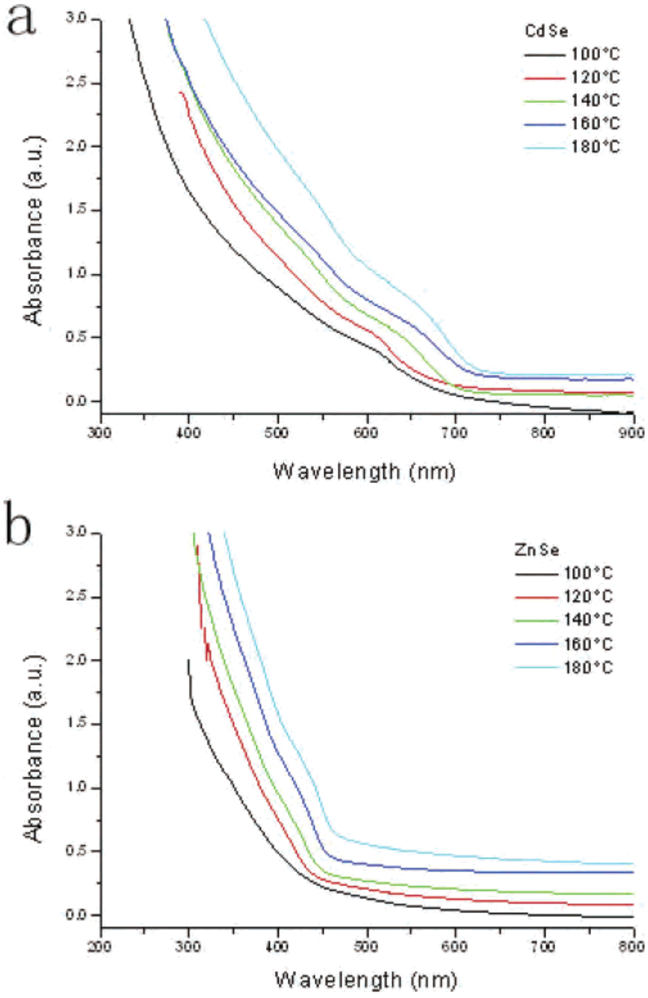

Figure 6. Electronic absorption spectra of (a) CdSe and (b) ZnSe nanocrystals prepared at different temperatures.

Table 2. Band Gaps of CdSe and ZnSe Nanocrystals Prepared at Different Temperatures

temp (°C)	E_g (eV) of CdSe	Eg (eV) of ZnSe
100	2.0	3.01
120	1.98	2.99
140	1.86	2.90
160	1.82	2.82
180	1.79	2.77

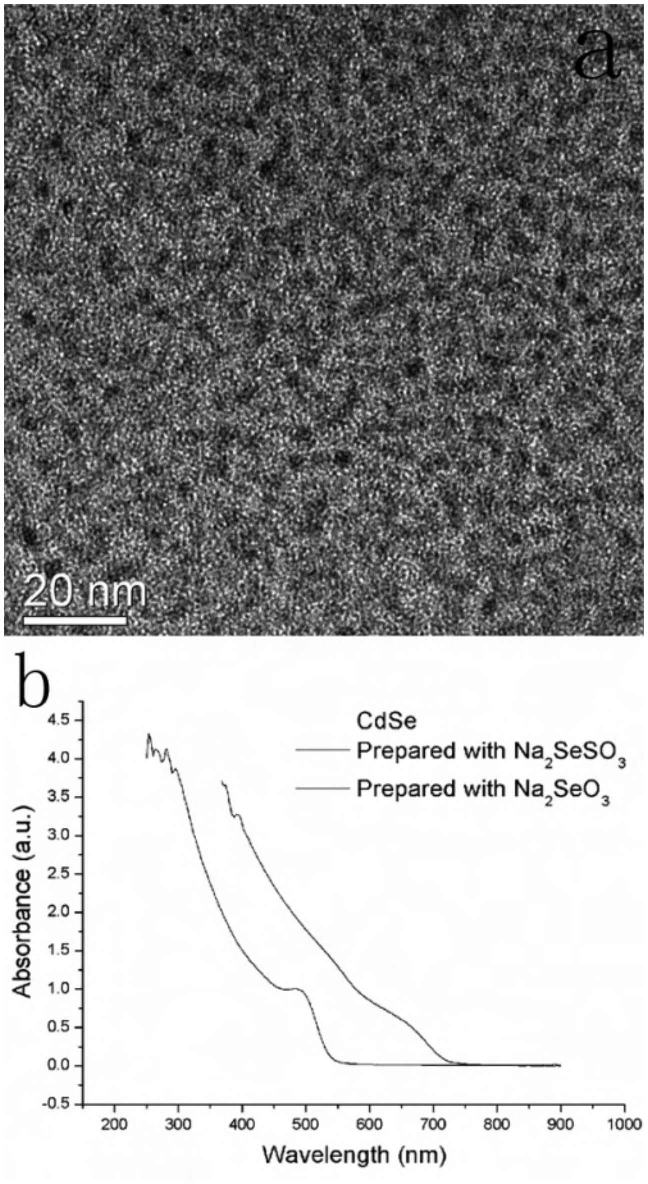

Figure 7. (a) TEM image of CdSe nanocrystals prepared with Na_2SeSO_3 as a precursor. (b) Comparison of the UV absorption spectra with different Se precursors.

or after they were coated with a silica shell. Here, the CdSe particles were stabilized by oleic acid, which is different from many previous reports. The silica-coating method was selected for the polarity transformation because silica surfaces are biocompatible and can be easily functionalized for bioconjugation purposes. A silica shell was coated around the CdSe and ZnSe nanoparticles in a water-in-oil microemulsion in reference to the classic Stober method. As shown in Figure 8, the size of the ZnSe/SiO_2 core structure is about 40 nm, and they could be well dispersed in alcohol and water. After the particles were coated with silica, the electronic absorption spectra were also measured, (Figure 9), and they suggested that the conversion will not change the intrinsic properties of these semiconductor particles.

Conclusions

In conclusion, we designed a water−oil interface reaction to fabricate CdSe, ZnSe, and $Zn_xCd_{1-x}Se$ nanocrystals with inorganic compounds: metal nitrate and sodium selenite. The chemical composition and band gap of the $Zn_xCd_{1-x}Se$ nanocrystals can be adjusted (from 1.81 to 2.82 eV) via different combinations of the source material. These hydrophobic nanocrystals were transformed into the hydrophilic particles by being coated with a SiO_2 shell in a microemulsion solution, which allow applications in biological detecting.

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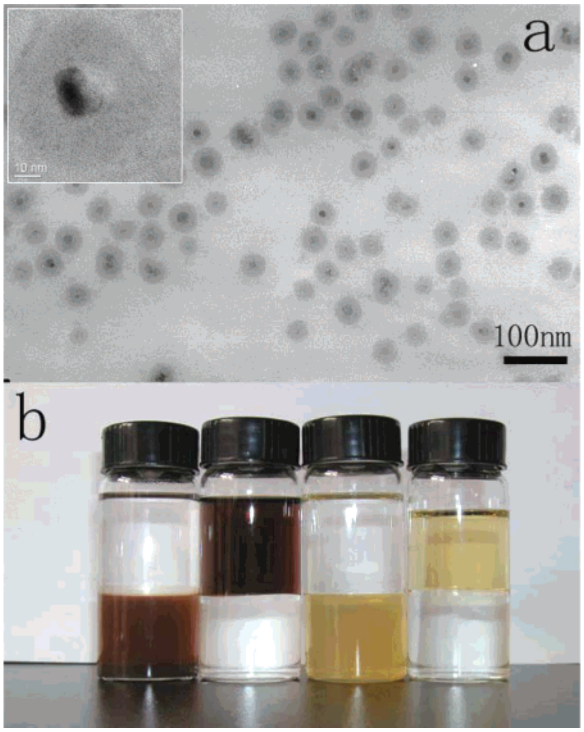

Figure 8. (a) TEM image of silica-sheathed ZnSe nanocrystals. The inset is an HRTEM image of a single particle. (b) The upper layer is *n*-hexane and the bottom layer is deionized water. From left to right, the bottles contain $CdSe/SiO_2$ in water, CdSe in hexane, $ZnSe/SiO_2$ in water, and ZnSe in hexane.

The method applied here was an important improvement for the OLEA synthesis system because the introduction of water-soluble inorganic precursors will make the manufacture of nanocrystals more flexible and abundant. The artificial water−oil interface is also suitable for the preparation of other uniform nanoparticles, such as oxide, chalcogenide, and rare-earth fluorides.

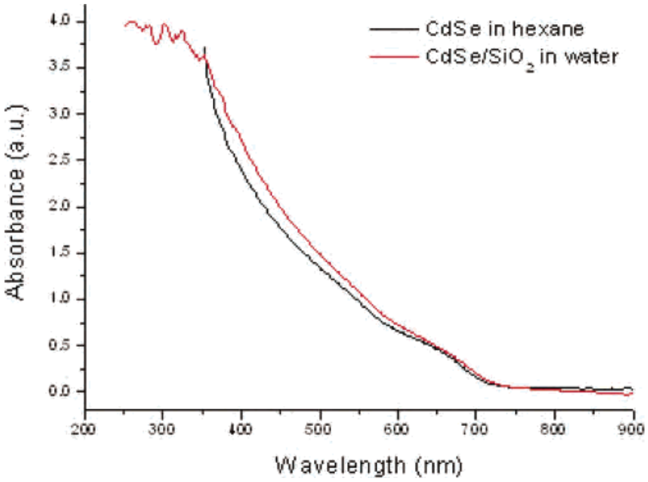

Figure 9. Electronic absorption spectra of CdSe in hexane and $CdSe/SiO_2$ in water after coating.

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Supporting Information Available: UV absorption and photoluminescence spectra of CdSe, $Zn_{0.44}Cd_{0.56}Se$, and ZnSe nanocrystals. This material is available free of charge via the Internet at http://pubs.acs.org.

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