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Article

An Effective Oxidation Route to Blue Emission CdSe Quantum Dots

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Nearly monodisperse CdSe quantum dots with blue emission are obtained through an oxidation approach, in which CdSe particles can be etched into smaller ones. During the oxidation process, CdSe with yellow emission (546 nm) can be rapidly oxidized to blue emission (466 nm) due to its incompletely crystallized structure. Further oxidation results in the slow blue-shift of the photoluminescence peak to 433nm. The quantum fluorescence efficiency of CdSe with blue emission is about 10%, and surface-trap emission becomes evident when the PL peak of CdSe reaches the blue−violet region, since the surface atom ratio increases. This oxidation route offers a simple and mild way to get extremely small CdSe quantum dots.

Introduction

Semiconductor quantum dots are of great interest for both fundamental research and technical applications because of their unique, novel properties which are caused by the quantum confinement effect.[1] Their size-tunable optical properties, stability, and narrow emission bandwidths have made them attractive materials in applications such as light-emitting diodes (LED)[2–6] and biological labeling.[7–12] Among these semiconductor materials, II−IV groups semiconductor quantum dots, especially CdSe quantum dots, have been deeply and systematically researched due to the well-established synthetic technique, and they also offer a unique opportunity to observe the evolution of their physical properties with size.[13–17] CdSe bulk material has a suitable band gap (1.74 eV) and a rather large exciton Bohr radius (5.6 nm). When the crystal radius is smaller than its Bohr radius, the size quantization effect becomes visible; its optical spectrum blue-shifts as the crystal radius decreases. Therefore, with tunable sizes, CdSe quantum dots' photoluminescence (PL) emission can range from red to blue. Although the optical tuning range of CdSe quantum dots spans the whole visible region of the spectrum, CdSe with blue emission (460−470 nm)[6] or even shorter-wavelength emission are difficult to obtain, as it requires the quantum dots to be smaller than 2 nm. The synthesis of such small CdSe quantum dots with high quality and good quantum efficiency is hard by employing the traditional direct synthesis approaches.[18–20]

Herein, we present a two-step synthetic method to get small CdSe quantum dots with blue emission through a photo-oxidation process. The two steps are as follows: first, synthesis of CdSe quantum dots materials at room temperature; second, the oxidation process, in which rather large CdSe particles can be reduced to smaller ones. In the

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oxidation section, sunlight was utilized as the catalyst and oxygen in the ambient air was used as the oxidant. Although the blue shift of the photoluminescence by oxidation of CdSe quantum dots has been previously reported,[21-24] the fluorescence often quenches at the end of the oxidation process. The fluorescence quenching phenomenon has been used as a fluorescent probe to detect oxygen species or other special ions.[23,24] However, in this study, the photoluminescence of CdSe can be effectively controlled in the blue region without fluorescence quenching under mild oxidation conditions. Along with the oxidation process, the emission peak of the CdSe can be continuously shifted to the violet region, up to 433 nm.

Experimental Section

Materials. All reagents used in this work, including Se powder, Na_2SO_3, NaOH, oleic acid (OA), $Cd(Ac)_2 \cdot 2H_2O$, H_2O_2 (30%), ethanol, and *n*-hexane, were A.R. reagents (>99.99%) from the Beijing Chemical Factory, China. The selenium source Na_2SeSO_3 solution was prepared by refluxing 5 mmol selenium powder and 5 mmol Na_2SO_3 in 50 mL distilled water for 1 h.

Synthesis. The synthesis of CdSe materials in the first step was performed at room temperature using $Cd(Ac)_2 \cdot 2H_2O$ and Na_2SeSO_3 as the reactants passed through a positive microemulsion method.[25] In a typical synthesis, 300 mg NaOH and 4.0 mL OA were dissolved in the solution of 8 mL deionized water and 15 mL C_2H_5OH to form a transparent solution, 133 mg $Cd(Ac)_2 \cdot 2H_2O$ dissolved in 5 mL deionized water was added to this solution by stirring, and then 5 mL Na_2SeSO_3 solution (0.1mol/L) was added. The solution changed from white to yellow after about 5 s, and was kept stirring for about 20 min. After reaction, 20 mL *n*-hexane was added to extract the OA-capped CdSe quantum dots to the oil phase, and ethanol was added subsequently to precipitate the nanocrystals by centrifugation. Finally, the CdSe quantum dots were redispersed in *n*-hexane to form a yellow transparent solution. In the second photo-oxidation process, the solution with CdSe quantum dots was just laid in the sunshine in a bottle and exposed to the air. The desired products were obtained by taking the solution out of the sun at different times. For the H_2O_2 oxidation process, 0.5 mL H_2O_2 (10%) was added to the 10 mL CdSe solution which has a CdSe monomer concentration of about 0.1 mol/L; then, the solution was laid in a dark environment, and aliquot solutions were taken at different times to monitor the oxidation process.

Characterization. The samples was characterized by a Bruker D8 Advance X-ray diffractmeter (XRD) with Cu Kα radiation (λ = 1.5418 Å) and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai G2 F20 S-Twin working at 200 kV). Raman spectra were recorded with an RM 2000 microscopic confocal Raman spectrometer (Renishaw PLC, England) employing a 633 nm laser beam. The electronic absorption spectra were obtained on a Hitachi U-3010 UV–visible spectrometer. Luminescence spectra were recorded with a Hitachi F-4500 fluorescence spectrophotometer.
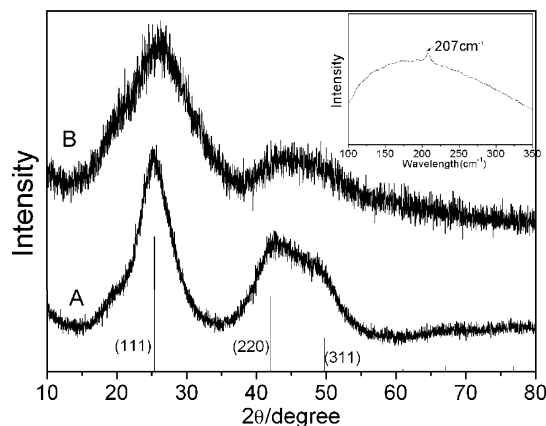
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Figure 1. The XRD pattern of CdSe samples before (A) and after (B) oxidation. Inset is the Raman spectrum of the sample after the oxidation.

Results and Discussion

Figure 1 displays the XRD pattern of the samples before and after oxidation. Since the sample was synthesized at room temperature, the crystallization was not so good, and the diffraction peaks were not distinguished well. The deep valley at around 35.1° 2θ angle indicates that the samples are zinc blende structure. Thus, we can identify the main diffraction peaks as (111), (220), and (311) crystal plane (JCPDF no 19–0191). The broader peak in the (111) crystal plane after oxidation indicates a smaller-size product than the sample before oxidation. The onset of Figure 1 is the Raman spectrum of the sample after oxidation. The characteristic vibration peak at 207 cm^{-1} for the formation of the Cd−Se bond is observed though the peak intensity is weak because of the high-intensity photoluminescence background of CdSe;[26,27] this reveals that the oxidation product is still CdSe.

Figure 2a shows the UV–vis absorption and photoluminescence (PL) spectrum of CdSe samples before (A) and after (B) oxidation, in which one can see that the peaks have an evident blue shift in both UV–vis absorption and PL spectra. After the oxidation, the PL peaks shift from 546 to 466 nm, which means that the PL emission has changed from yellow to blue. Figure 2b shows the photograph of this color change when the samples were excited by ultraviolet lamp (λ_{ex} = 365 nm).

According to the quantum confinement effect, the blue shift of the spectrum is influenced by the decrease in the nanocrystal size. In a classical spherical model in which the carriers are confined by a potential that becomes infinite at the surface, the energy band gap can be expressed as follows:[28]

$$E_8(\text{dot}) = h^2/8m_{\text{eff}}a^2 + E_g(\text{bulk}) \qquad (1)$$

For CdSe quantum dots, m_{eff} in the formula is the effective mass of the electron which has the value of 0.13 m_e (m_e is rest mass of the electron),[26] and *h* is Planck's constant, and

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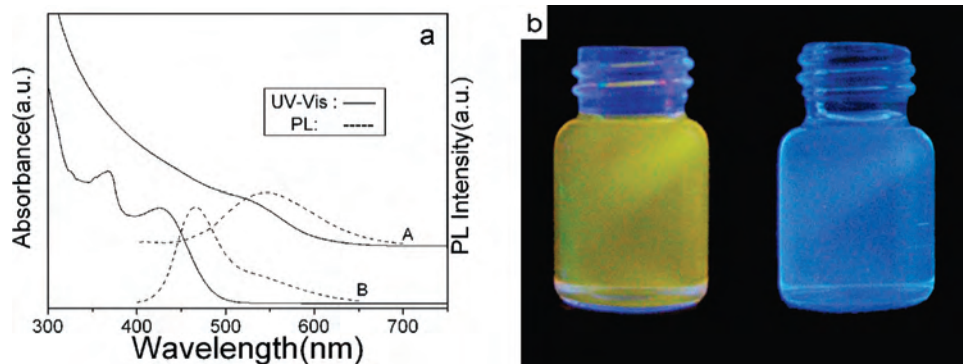(28) Nirmal, M.; Brus, L. *Acc. Chem. Res.* **1999**, *32*, 407.

Figure 2. (a) UV–vis spectra and photoluminescence (PL) spectra (λ_{ex} = 365 nm) of CdSe samples before (A) and after (B) oxidation. The UV–vis and PL spectra of sample B were measured when the oxidation process had gone for 10 days. (b) The photograph of the CdSe samples excited by the UV lamp before (left) and after (right) oxidation.
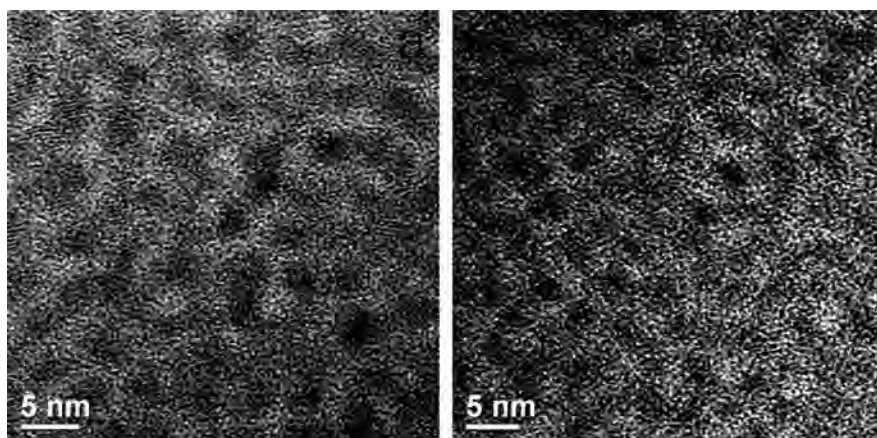

Figure 3. (a) TEM images of CdSe materials before oxidation. (b) TEM images of CdSe with blue emission after oxidation.

a is the diameter of the particle. When we use the first peak wavelength (441 nm) from our UV–vis spectrum data, we can obtain 2.817 eV of E_g(dot) for CdSe, which means that the energy band gap shifted 1.077 eV from its bulk material (1.74 eV). A higher energy of 1.077 eV requires the product CdSe with a size of 1.65 nm in diameter according to eq 1. Figure 3b shows the TEM images of the CdSe quantum dots with blue emission. It can be seen that the sizes of the CdSe quantum dots are about 1.7 nm, which matches the calculated value well. By using the Scherror equation, the diameter of the sample after the oxidation from the XRD pattern is about 1.65 nm. The results shown here indicate that this oxidation method is an effective way to get small CdSe quantum dots with blue emission.

The change of the PL peak over the whole oxidation process is shown in Figure 4, where it can be seen that the shift of the PL peak in the oxidation process is irregular. An extra peak at about 480 nm appeared quickly when the oxidation started, then as the oxidation went along the intensity of the peak at 480 nm was enhanced while the peak at 550 nm slowly weakened. However, the blue-shifted effect of the PL peak at wavelengths shorter than 480 nm was not so visible. It took much more time to shift from 480 to 466 nm than from 550 to 480 nm. Also, the blue shift of the PL peak from 466 nm to the violet region took time, which can be reflected by the captions in Figure 4. Meanwhile, the quantum fluorescence efficiency increases from 2.5−3% to
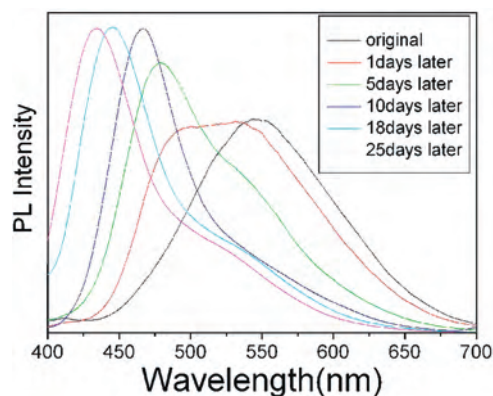

Figure 4. The evolution of the PL spectrum over the whole oxidation process. The peaks are at (from right to left): 546 nm, 478 nm, 466 nm, 445 nm, and 433 nm.

about 10%[29] when the emission peak shifted from 546 to 466 nm; it can slowly increase to 12−14% as the emission peak shifted to 433 nm.

At the first stage of the oxidation until the PL peak reached 466 nm, there was some red precipitate produced in the reaction, while in the further oxidation stage when the PL peak shifted in the blue−violet region, little white precipitate was produced. By EDX characterization, we found that the red precipitate was Se (Figure 5a). The XRD spectrum of the white precipitate is shown in Figure 5b; the result infers that the white precipitate product was $CdSeO_3$, which is in
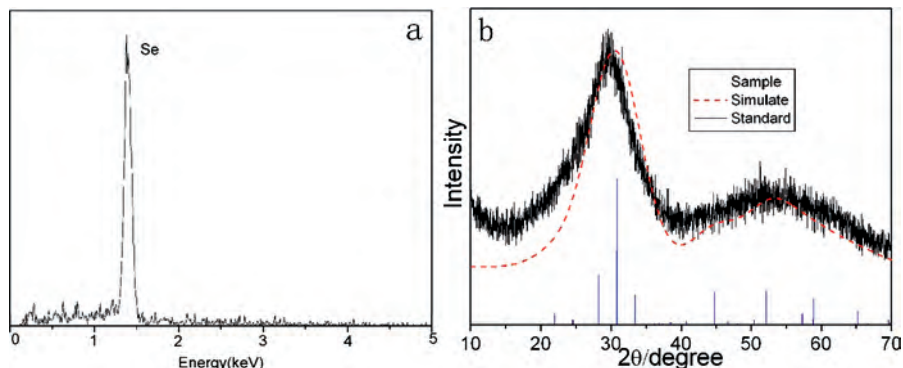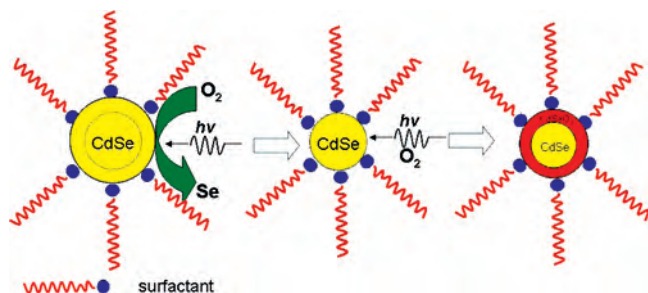
Figure 5. (a) EDS spectrum of red precipitate during the oxidation process. (b) XRD spectrum of the white precipitate after the complete oxidation of CdSe. The standard pattern corresponds to $CdSeO_3$ (JCPDF No 82–1207). The dashed line is the simulation of $CdSeO_3$ with 2 nm using the Scherror equation.

Scheme 1. Mechanism of the Oxidation Process

agreement with some results in the literature.[22] In this mild oxidative condition, the oxidation process can be effectively stopped by preventing the sample from oxidating or just removing the sample from the direct sunshine; the CdSe quantum dots can remain in *n*-hexane solution during the whole oxidation process.

The irregular PL peak shift in the oxidation process may be caused by the poorly crystallized structure. Generally, crystallization requires energy. In a crystal growth process, after the nucleation, the material that grows on the nucleus will be in a quasi-amorphous state before complete crystallization; this could happen in a state where the core of the entity becomes crystalline and is covered by a somewhat amorphous shell.[30,31] The crystallization of this amorphous shell can finish quickly at a high reaction temperature, sometimes with surface reconstruction. When the reaction was operated at room temperature here, there was an insufficient energy supply for complete crystallization of the
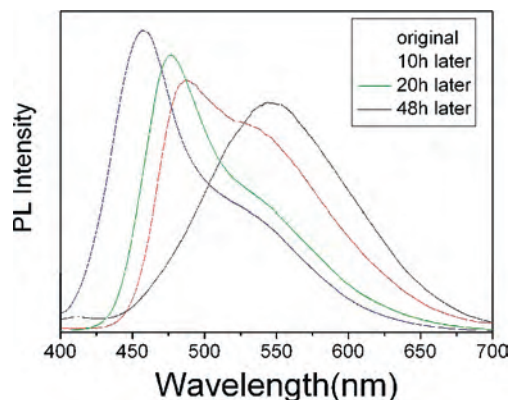

Figure 6. Evolution of the PL spectrum using H_2O_2 as the oxidant. The peaks are located at (from right to left): 546 nm, --, 478 nm, 458 nm.

CdSe quantum dots; then, the CdSe materials obtained in the first synthesis step remain in the state in which the entity core was covered by a quasi-amorphous shell. The quasi-amorphous shell had a relative relaxed structure, while the particle within the entity core had a strong binding force between the atoms. The size of the entity core depends on the temperature,[32] and is about 1.7 nm in this work. Thus, we can describe the oxidation process as in Scheme 1. At the first stage of the oxidation, the periphery of the particles seemed to be easily corroded off until the entity core had a relaxed structure. This corresponds to the rapidly rising peak (in PL spectra) at about 480 nm instead of a gradual blue shift of the emission from yellow, green, to blue. The oxidation at the entity core was more difficult in this mild oxidative condition; this slowed down the oxidative rate at the entity core resulting in narrowing of the crystal size distribution, since the crystals remained at the size of the entity core. This can be reflected by the narrower fwhm (full width at half-maximum) of the PL peak after oxidation in Figures 2a and 4. The quantum efficiency increases at this time, possibly because the disappearance of the amorphous shell decreases the quenching of the fluorescence. The CdSe particles could be further oxidized within the entity core even though the oxidative rate was low, which resulted in the continued blue shift of the PL peak in the blue–violet region as shown in Figure 4.

A broad tail at 525 nm in the PL spectrum in Figure 4 exists all the time even when the emission peak shifted to the blue–violet region, which we consider to be caused by the surface-trap emission due to the increasing surface atom ratio. Surface atoms usually have fewer adjacent coordinate atoms and more dangling bonds and can be treated as defects

(29) The fluorescence quantum yield (QY) of CdSe quantum dots is determined from the integrated fluorescence intensities of the quantum dots and the reference (quinine aqueous solution whose quantum efficiency is 55%). The quantum yield of the sample (QY_s) was calculated using the following equation: $QY_s = (F_s \times A_r \times QY_r)/(F_r \times A_s)$ where F_s and F_r are the integrated fluorescence emissions of the sample and the reference, respectively, A_s and A_r are the absorbances at the excitation wavelength ($\lambda_{ex} = 365nm$) of the sample and the reference, respectively, and QY_s and QY_r are the quantum yields of the sample and the reference, respectively.
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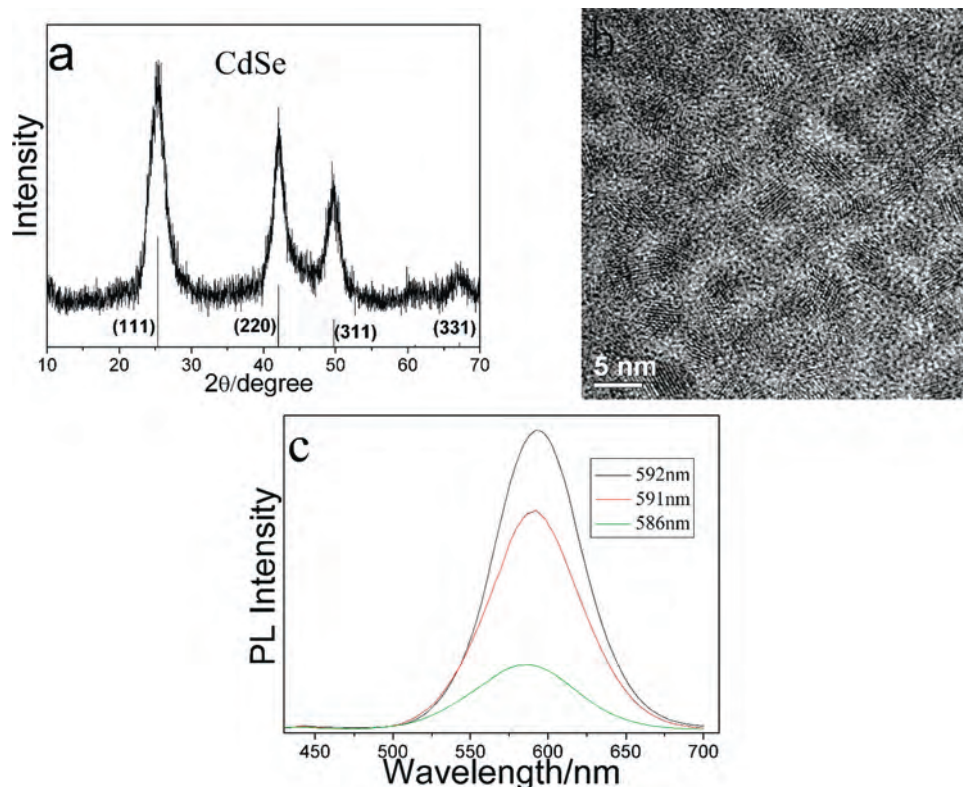
Figure 7. XRD pattern (a) and TEM image (b) of the CdSe nanoparticles after the "hot liquid annealing" process. (c) The PL evolution of these well-crystallized nanoparticles using H_2O_2 as the oxidant. The figure can reflect the PL evolution during the oxidation process.

as compared to the bulk atoms. These defects induce additional electronic states in the band gap, and may also influence the spacing of the energy levels and optical properties of the nanocrystals. The surface-trap emission of CdSe is rarely observed, since there is seldom a report about CdSe quantum dots with blue emission. The tail of the PL peak in Figure 4 proves that, when the size of the CdSe nanoparticle is small enough to have blue emission or the shorter-wavelength emission, the surface-trap emission will become evident. Surface-trap emission remaining at 525 nm means that the additional surface-state energy may have the constant energy spacing from the covalent band energy. The phenomenon of surface-trap emission hints that the application of CdSe quantum dots as emitting LEDs in the blue−violet region has to be accompanied by some matching materials that can saturate the dangling bonds on the small CdSe surfaces.

When a more active oxidant, H_2O_2, was introduced into the oxidation process, the oxidative rate was faster. The change of the PL spectrum with H_2O_2 as oxidant is shown in Figure 6. It can be seen that Figure 6 is similar to Figure 4: a rapidly rising peak at 480 nm at the first stage, then the slow blue shift of the PL peak in the blue−violet region, which indicates that the processes of these two types of oxidation are similar. However, the oxidation process using H_2O_2 as oxidant is not easy to control, it often leads to complete oxidation of the CdSe material, leaving mainly white precipitate in the bottle.

Generally, in a traditional one-pot method, the synthesis of CdSe quantum dots often operates at high temperature between 250 to 350 °C using an "injection technology". The

nucleation and growth of the crystal are fast at this high temperature. Also, the size of the nucleus increases as the reaction temperature increases, because the melting point of the extremely small crystal is relative to the size of the crystal.[32,33] The diameter of the CdSe crystal right after the nucleation, for example, at 250 °C is about 1.75 nm as determined by an in situ method reported by Peng;[34] the PL peak at this time is around 500 nm. The subsequent growth of the CdSe crystal, however, resulted in the red shift of the PL peak to green, yellow, and red as the size of the crystal increases. CdSe nanocrystals with blue emission are difficult to get. Therefore, the oxidative etching method becomes an effective way to get smaller CdSe nanocrystals. The mild oxidative condition presented here enables the slow etching of the nanocrystal without sharp corrosion of the structures or the complete oxidation of the nanocrystals, which can also lead to the remaining fluorescence during the whole oxidation process. Second, the structure of the sample, which stays in a state in which the entity core iss covered by a quasi-amorphous shell, is suitable for this photo-oxidation process. When a "hot liquid annealing" technique is used to improve the crystallization of the nanoparticles synthesized at room temperature, which is to transfer the crude solution to the autoclave and maintain at 120 °C for 6 h, the CdSe products can be well-crystallized. At the same time, the fluorescence is shifted to orange with the emission peak at 592 nm. While these well-crystallized nanoparticles seem insensitive to the photo-oxidation process, the fluorescence of these nanopar-

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ticles stays almost the same when they are laid under the direct irradiation for about 1 month. These well-crystallized nanoparticles can be oxidized by H_2O_2; however, the oxidation process meets the same problem of easily completed oxidation of the nanoparticles after the fluorescence is slightly blue-shifted. The XRD and TEM of these well-crystallized nanoparticles and the PL evolution of the oxidation process are shown in Figure 7.

Conclusion

In summary, an oxidation approach is used to obtain small CdSe quantum dots with blue emission (466 nm). The quantum fluorescence efficiency of CdSe with blue emission is about 10%, and the reduced oxidation rate at around 480 nm has been the focus of the size distribution. As the oxidation process goes on, the emission spectrum of the CdSe can be adjusted in the blue−violet region by controlling the oxidation process. Compared to the direct synthesis process, this oxidation method offers an effective approach to obtain extremely small CdSe quantum dots in a simple and mild condition, and it also provides the opportunity to learn the optical properties of these small nanocrystals.

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