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Selective Synthesis and Characterization of CdSe Nanorods and Fractal Nanocrystals

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CdSe nanorods and dendritic fractals were synthesized through a novel controllable solution-phase hydrothermal method. Soluble selenite was employed to provide a highly reactive Se source in the synthesis. Both morphologies and phases of the CdSe products could be successfully controlled by choosing appropriate complexing agents to adjust the dynamics of the reaction process. Reaction temperature and Cd/Se ratio in raw materials were also important parameters influencing the morphologies and phases of the products. The phase structures, morphologies, and optical properties of the CdSe products were investigated by XRD, TEM, HRTEM, and UV–vis and photoluminescence spectroscopies. The formation mechanisms of the nanorods and fractals were investigated and discussed on the basis of the experimental results.

Introduction

During the past decades, CdSe has been extensively investigated because of its novel optical and electrical properties,[1−3] which are of interest for, for example, photovoltaic devices,[4] electroluminesence (EL),[5] and bioattachment applications.[6,7] Morphologies and structures are found to have great influence on their properties, and great attention has been paid to the core/shell structures,[8] shape control synthesis of CdSe,[9,10] and its solid−solid structural transitions[11].

Lots of synthetic methods for preparing CdSe have been reported, including MBE[12] (molecular beam epitaxy), MOCVD[13] (metalorganic vapor chemical deposition), OMVPE[14] (organometallic vapor phase epitaxy), solvothermal methods,[15−17] and hydrothermal methods.[18−20] Recently, Alivisatos[10] et al. have developed a controllable synthetic method which uses $Cd(CH_3)_2$ reacting with Se in a hot TOPO medium[21] at about 300 °C. It can selectively get very fine CdSe nanorods with different sizes and CdSe nanocrystals of other shapes (arrow, teardrop, and tetrapod). Chen[22] et al. synthesized CdSe nanorods through a surfactant (CTAB) based method in a colloid system, which uses $CdCl_2$ and Na_2Se as raw materials.

Very recently, pattern formation in nonequilibrium growth has also been an area of intense study.[23] Variable related phenomena have been found and investigated in chemical systems, especially fractal patterns,[24,25] which have shown a

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new nonlinearly scientific world and may provide us a geometry method to describe the nature morphology. Basic theories, formation of models, mathematical analysis, and computer simulations have been active topics in both physical and chemical science.[26,27]

In this paper, we report a convenient and controllable synthetic method based on a complex reaction in an aqueous system, which can produce both high quality CdSe nanorods and fractals at low temperatures (100 −180 °C). Na_2SeO_3, $Cd(NO_3)_2$, and the reductant $N_2H_4 \cdot H_2O$ are used as reactants in this hydrothermal method. By using appropriate complexing agents as controlling reagents and adjusting the reaction temperature, both morphologies and structural phases (zinc blende or wurtzite structures) of products can be easily controlled. Because of high yield, simple reaction apparatus, and low reaction temperature, this novel method will have a good prospect in future large-scale application and surely can be used to synthesize other II−VI nanometer-sized nanocrystals.

Experimental Section

I. Materials. All chemicals used in this work, such as cadmium nitrate ($Cd(NO_3)_2 \cdot 4H_2O$), sodium selenite (Na_2SeO_3, highly toxic, but does not need any post-treatment after reaction with the excess $N_2H_4 \cdot H_2O$ in the system), ammonia ($NH_3 \cdot H_2O$), EDTA, and hydrazine hydrate ($N_2H_4 \cdot H_2O$, 50%) were A. R. regents from the Beijing Chemical Factory, China.

II. Synthesis of CdSe Nanorods and Fractals. $Cd(NO_3)_2 \cdot 4H_2O$ (3.08 g, 0.01 mol) was put into a Teflon-lined autoclave of 100 mL capacity and dissolved in water. An appropriate amount of $NH_3 \cdot H_2O$ was added into the solution until the disappearance of the initially produced white precipitate to convert Cd^{2+} into $Cd(NH_3)_4{}^{2+}$. After 5 min, 0.86 g (0.005 mol) of Na_2SeO_3 and 10 mL of hydrazine hydrate ($N_2H_4 \cdot H_2O$) were added into the autoclave, and finally, the system formed a colorless and transparent solution. The autoclave was filled with deionized water up to 70% of the total volume, sealed, and heated at 100−180 °C for about 2 h. After the heating treatment, the autoclave was allowed to cool to room temperature naturally. Black product was obtained and collected by filtration, washed with deionized water and absolute ethanol, and then dried at 60 °C. The yield of the product is about 95% on the basis of the calculation of Na_2SeO_3.

III. Controlled Synthesis of CdSe Nanocrystals with Wurtzite and Zinc Blende Structure. CdSe products obtained in section II are wurtzite structures. To synthesize CdSe nanocrystals with the zinc blende structure, 3.08 g of $Cd(NO_3)_2 \cdot 4H_2O$ (0.01 mol) was added into 50 mL of EDTA solution, which was made by dissolving 3.72 g of EDTA (0.01mol) in 50 mL of 1 M NaOH solution. The system was heated until a colorless and transparent solution was formed. A 0.86 g portion (0.005 mol) of Na_2SeO_3 and 10 mL of hydrazine hydrate ($N_2H_4 \cdot H_2O$) were added later. The final solution was then transferred into a Teflon-lined autoclave of 100 mL capacity. After heating at 100 °C for 2 h, zinc blende structure CdSe nanocrystals were produced. The yield was about 90% on the basis of the calculation of Se.

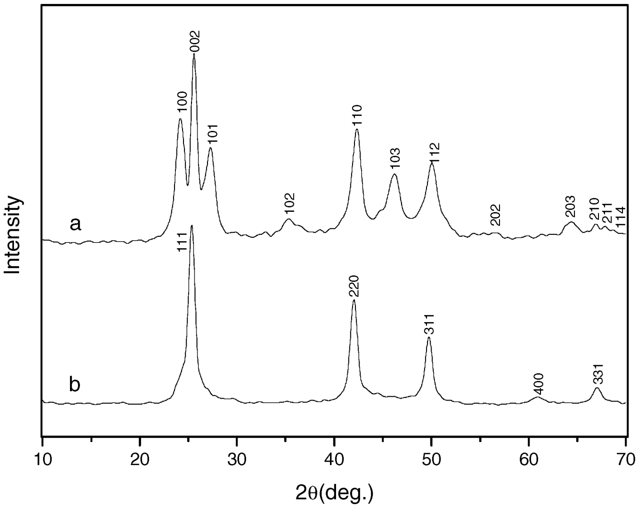

Figure 1. XRD patterns of CdSe nanocrystals: (a) wurtzite CdSe (using $NH_3 \cdot H_2O$ as complexing agent at 100−180 °C); (b) zinc blende CdSe (using EDTA as complexing agent at 100 °C).

IV. Characterization of Samples. XRD was performed on a Bruker D-8 Advance X-ray diffractomater with Cu Kα radiation ($\lambda = 1.5418$ Å). The 2θ range used was from 10° to 70° in steps of 0.02° with a count time of 1 s. The size and morphology of CdSe nanocrystals were measured by using a Hitachi Model H-800 transmission electron microscope, with a tungsten filament at an accelerating voltage of 200 kV. Structural information for the nanocrystals was measured by high-resolution transmission electron microscopy (HRTEM) on a JEOL JEM-2010F transmission electron microscope operated at 200 kV. Optical diffuse reflectance of the samples was recorded on a Shimadzu UV-2100S spectrophotometer on the basis of the procedure described in the literature.[28,29] Photoluminescence experiments were conducted in air on a Perkin-Elmer LS-50B fluorescence spectrophotometer. The samples were placed in quartz cuvettes. The wavelength of excitation was shorter than the onset of absorption of the particular sample. Raman shifts were recorded on a Perkin-Elmer spectrum GX/FT-Raman spectrometer with the excitation wavelength of 1064 nm.

Results and Discussion

XRD Studies. Figure 1a shows the XRD pattern of wurtzite CdSe obtained using $NH_3 \cdot H_2O$ as complexing agent in the experiments, which indicates that the products are pure phases with lattice parameters of $a = 4.299$ Å and $c = 7.01$ Å (JCPDS 77-2307). Although wurtzite CdSe is the thermodynamically favored form, zinc blende phase CdSe has been obtained through the same method by using EDTA as a complexing agent under a strong alkaline environment at 100 °C (in our experiments, pH = 14 was chosen). Figure 1b shows that zinc blende CdSe is also a pure phase, with a calculated lattice parameter of $a = 6.077$ Å (JCPDS 19-0191).

The mechanism for the formation of zinc blende CdSe is still under investigation. Compared to $NH_3 \cdot H_2O$, the strong chelation between Cd^{2+} and EDTA must be a reason for the formation of zinc blende CdSe. The transformation from zinc

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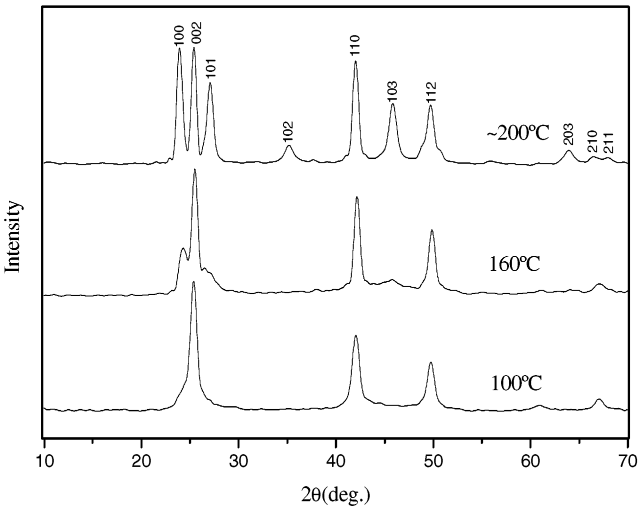

Figure 2. Evolution of XRD patterns of CdSe samples (using EDTA as complexing agent) under different reaction temperatures (100, 160, ~200 °C).

blende CdSe to wurtzite CdSe has been observed with the evolution of reaction temperatures (100, 160, ~200 °C) through the XRD patterns (Figure 2). The characteristic wurtzite peaks (100, 101) appearing at 160 °C indicate the formation of wurtzite CdSe in the products. When the temperature is increased to ~200 °C, all the products can be thought to have the wurtzite structure as evidenced from XRD results.

Morphologies of Samples. Transmission electron microscopy (TEM) allows the direct imaging of nanocrystals and provides more information on the quality of individual particles. High magnification imaging with lattice contrast allows the determination of the structure of an individual nanocrystal.

Figure 3a−c shows the TEM images of a series of branchlike fractals of CdSe nanocrystals obtained at 100 °C using $NH_3{\cdot}H_2O$ as complexing agent. The size of a prototypical cluster is about 1−2 μm. With careful observation, the branches can be found to be composed of small nanorods with diameters of 20−30 nm. When the reaction temperature is raised to 180 °C, well-crystallized CdSe nanorods with diameters of 40−60 nm are produced instead of fractals. Figure 3d,e shows that these CdSe nanorods are well-dispersed with lengths ranging from 200 to 600 nm (average length ~400 nm). The inset electron diffraction (ED) pattern of an individual CdSe nanorod indicates that these nanorods are single-crystallized with wurtzite structure.

In the experiments, complexing agents and the Cd/Se ratio of raw materials are found to play important roles in controlling morphology. Figure 3f shows the spherical CdSe nanocrystals produced through the same method without using any complexing agent at 180 °C. The average diameters of them are about 60 nm. Compared to the fractals and nanorods, these nanocrystals are very easy to aggregate, and they form large clusters because of their spherical shape. Figure 3g shows that the morphology of the CdSe product is an irregular branchlike shape (180 °C) when the Cd/Se ratio of raw materials was adjusted to 1:1. No nanorods or regular branches were found from 100 to 180 °C in our experiments.

Formation of Nanorods. Crystalline whisker or fiber growth at high temperature can usually be explained by the widely known vapor−liquid−solid (VLS)[30] and the vapor−solid (VS) mechanism.[31] A hydrothermal liquid−solid (LS) whisker or fiber growth mechanism[32] was proposed by Masahiro et al. Buhro proposed a solution−liquid−solid (SLS) mechanism[33] for the growth of III−V semiconductor fibers in organic solution. In these mechanisms, the effect of nucleation and growth is the critical factor for the synthesis of different morphology products. Wurtzite CdSe is an anisotropic material with a unique *c*-axis, and nanorods usually can be obtained under the condition of fast growth rate.[9,10] To obtain rodlike CdSe nanocrystals, a high concentration of CdSe monomers (single CdSe molecule before its nucleation and growth) in the reaction solution is needed to enhance the nucleation and growth rate.

Using a complex reaction to control the nucleation and growth is a simple but effective way. By using different complex compounds with different formation constants, different environments for nucleation and growth of products will be created and will affect the morphology of the precipitations. It might be possible to form rodlike (or other morphologies) nanocrystals with the use of an appropriate complexing agent. In our system, $NH_3{\cdot}H_2O$ is found to be an appropriate and very cheap controlling reagent in the formation of CdSe nanocrystals.

The reaction to form CdSe nanocrystals can be formulated as follows:

$$2Cd(NO_3)_2 + 2Na_2SeO_3 + 3N_2H_4 \xrightarrow{100-180\ ^\circ C,\ NH_3\cdot H_2O} 2CdSe(\downarrow) + 3N_2(\uparrow) + 4NaNO_3 + 6H_2O$$

In this reaction, Na_2SeO_3 will first be reduced to Se by hydrazine.[34,35] The newly produced Se with high reactivity will be reduced further by $N_2H_4{\cdot}H_2O$ or disproportionate in the alkaline solution (pH ≈ 11) to generate Se^{2-}. Se^{2-} will immediately react with $Cd(NH_3)_4{}^{2+}$ and produce CdSe product.

The complexing agent ($NH_3{\cdot}H_2O$) plays an important role in the formation of CdSe nanocrystals. In the present reaction system, it helps to form a stable, transparent, and colorless solution by forming $Cd(NH_3)_4{}^{2+}$ to avoid $CdSeO_3$ precipitation before reacting. The uniformity of the solution will provide a good environment for the growth of high quality CdSe nanocrystals. The reaction would not happen unless the solution was heated to about 100 °C, and this provided us a good opportunity to conduct different pretreatments to control the reaction products. Second, it causes a competition between the precipitation and complex reactions. The

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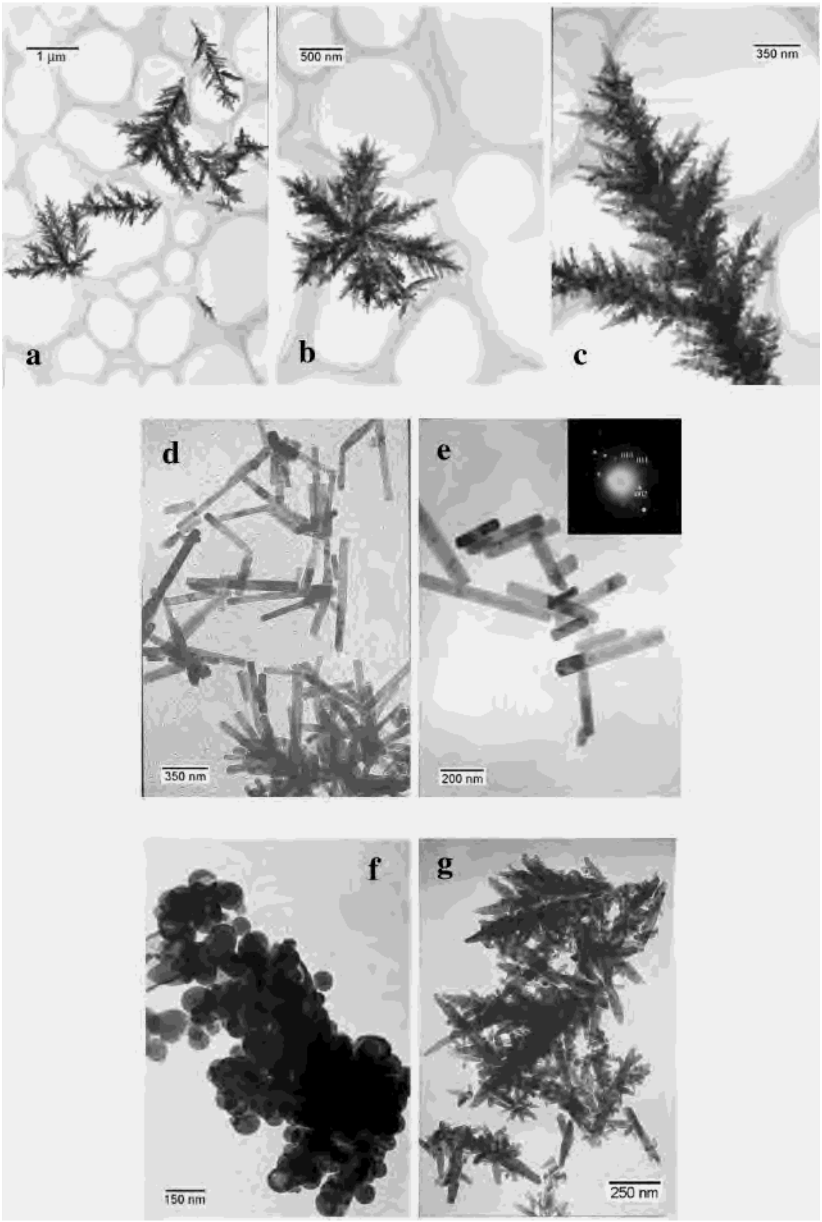

Figure 3. TEM images of CdSe fractals, nanorods, and other morphologies under different magnifications: (a−c) dendritic CdSe fractals at 100 °C (in $NH_3{\cdot}H_2O$ complexation system); (d,e) CdSe nanorods at 180 °C (in $NH_3{\cdot}H_2O$ complexation system); (f) CdSe spheres (without using any complexing agent); (g) irregular branchlike CdSe nanocrystals (Cd/Se ratio of raw materials was 1:1).

dynamics of the whole reaction would be affected, and the nucleation, and thus the growth, of CdSe could be adjusted. Finally, it can favor the formation of pure CdSe nanocrystals but inhibit the production of $Cd(OH)_2$ in the final product without the need of any further treatment. Surely, the existence of $Cd(OH)_2$ in the reaction system will have influences on the resultant morphologies of CdSe. In a word, the use of $NH_3{\cdot}H_2O$ not only can adjust the reaction dynamics but also can provide a relative “clean” reaction environment, which will increase the formation opportunity for rodlike CdSe nanocrystals.

In our reaction, the reason that Na_2SeO_3 was used instead of Se powder is that it can dissolve easily in water and be reduced to highly reactive Se quickly by hydrazine hydrate upon heating. These highly reactive ultrafine Se particles produced in situ form Se^{2-} much easier than commercial Se powders do. A high concentration of CdSe monomer will be formed and thus will favor the growth of rodlike CdSe nanocrystals. At relatively high reaction temperature (180 °C), the moving rate and moving range of CdSe monomers are both increased, so large nuclei in smaller quantity will be formed in the solution, which results in the formation of CdSe nanorods with relatively large sizes. In the experiments, the reaction was usually completed in 2 h. The fact that no CdSe products would be obtained if commercial Se powder was used as reactant instead of Na_2SeO_3 is evidence for the mechanism we described.

Formation of Fractals. Diffusion-limited aggregation (DLA)[26] and nucleation-limited aggregation (NLA) models[27] are usually used to interpret various fractal phenomena. At the lower reaction temperature of 100 °C, dendritic CdSe fractals are produced instead of CdSe nanorods. At this time, the possible mechanism may be described in the following way: With the moving rate and moving range of CdSe

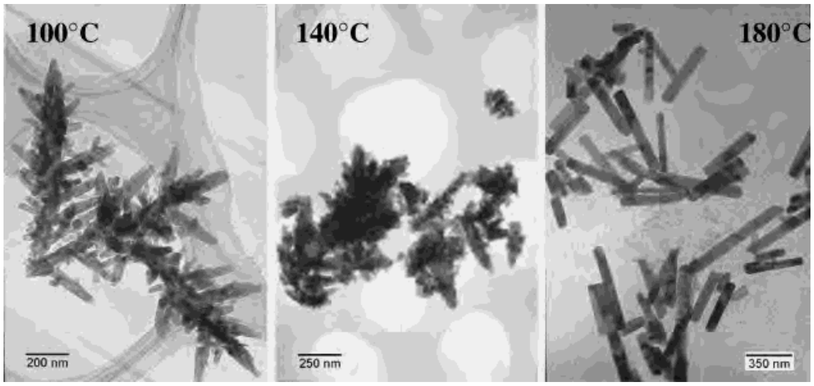

Figure 4. Evolution from CdSe fractals to nanorods based on reaction temperatures (100, 140, and 180 °C).

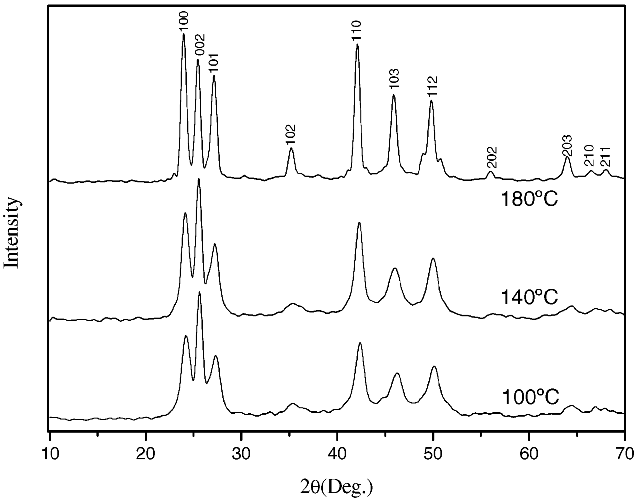

Figure 5. XRD patterns of CdSe nanocrystals under different reaction temperatures (100, 140, and 180 °C).

monomers decreasing, more nuclei will be formed (with respect to 180 °C) in the solution during the nucleation process. These nuclei grow themselves to form thin CdSe nanorods with the coming of CdSe monomers, and at the same time, these random moving nuclei accumulate with each other to form fractal structures, just like that described in the DLA model.

By adjusting the reaction temperatures, the evolution from CdSe fractals to nanorods was found in our experiments. Figure 4a−c shows the changes of CdSe morphologies under different reaction temperatures (100, 140, and 180 °C). At 140 °C, CdSe with transitional morphology between branch-shaped fractals and uniform nanorods was produced, and only CdSe nanorods were obtained at 180 °C. This change can also be reflected from the XRD patterns (Figure 5). The relative intensities of the XRD peaks (100, 101) can be found to have changes at 180 °C, which indicates the different orientation of CdSe nanocrystals.

HRTEM was employed to further investigate the obtained CdSe fractals. Figure 6 gives the HRTEM images of a typical fractal tip (a) and two crossed branches (c) (partial enlarged detail in the black frame of b). Both of them show clear lattice fringes, which indicate that these branches are single crystals. The interplane distances in Figure 6a,c are calculated as 0.35 and 0.32 nm, respectively, corresponding to (002) and (101) crystal planes of wurtzite CdSe. The angles between the (101) lattice fringes and the long axes of different branches are all found to be about 60°, which is very close to the angle (62°) between the (002) and (101) crystal planes in wurtzite CdSe. This angular relationship is consistent with the direction of (002) lattice fringes in Figure 6a, implying that all the fractal branches in Figure 6 grow along the same direction. By combining the (002) and (101) fringe images in Figure 6, we could judge that these branches grow along the [210] direction. This means that the growth of the fractals corresponds to the preferential stacking of (100) planes of hexagonal wurtzite CdSe.

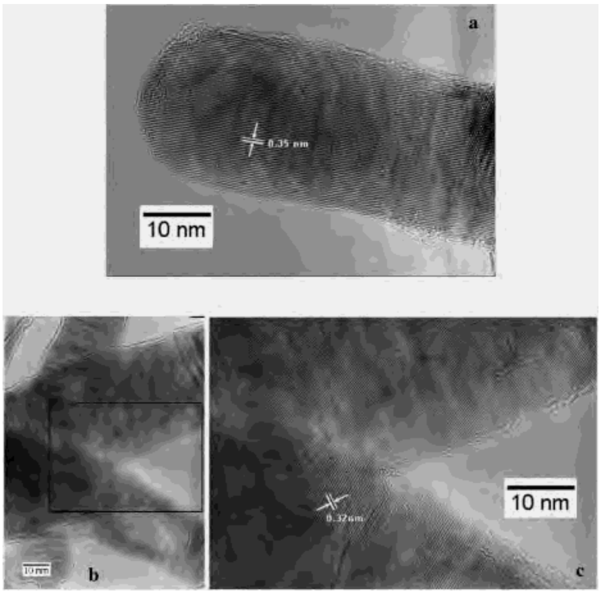

Figure 6. HRTEM images of CdSe fractals: (a) a typical fractal tip; (b) crossed branches; (c) partial enlarged detail of two crossed branches in the black frame of b.

It is generally accepted that fractal aggregation occurs at situations far from thermodynamic equilibrium and usually forms rough crystallites with weak anisotropy because of its high driving force and random association.[25] However, with closer inspection of Figure 3a−c, these dendritic CdSe fractals could be found to be constructed by lots of well-crystallized thin CdSe nanorods grown from several thick main branches, which shows a low driving force with strong anisotropy. In our system, the fractal aggregation may not be completely random. Both the strongly correlated orientations of CdSe nanocrystals and the usual nucleation process cause the formation of thin CdSe nanorods composed of

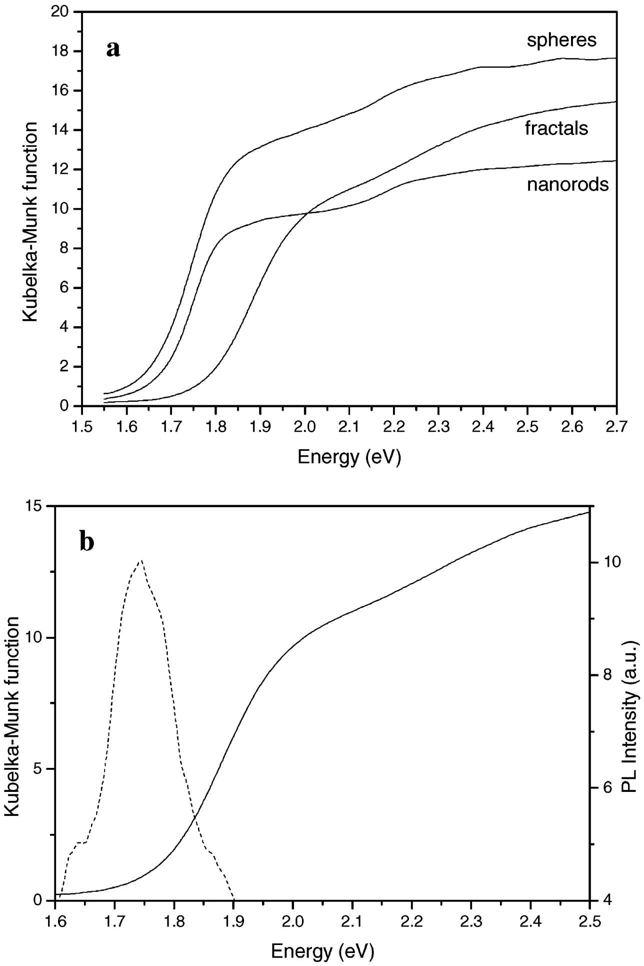

Figure 7. (a) UV−vis absorbance of CdSe fractals, nanorods and spheres. (b) Photoluminescence spectrum (- - -) of CdSe fractals (the corresponding absorption spectrum is also included).

fractals. This phenomenon is similar to that described in ref 24. If certain additives (for example, appropriate surfactants) were used to prevent the aggregation of CdSe nuclei, small CdSe nanorods instead of fractals might be obtained. According to the evolution from CdSe fractals to nanorods with the rising reaction temperature, the correlated orientations of CdSe nanocrystals seem to become stronger (prefer to form nanorods), accompanying the weakness of the nucleation-controlled aggregation process to form fractals.

Optical Properties. The optical diffuse reflectance spectra can be used to estimate the band gap of the sample. The spectra of CdSe nanorods, fractals, and spheres are given in Figure 7a. Because the individual particle size is much less than the thickness of the sample layer, an ideal diffuse reflectance with constant scattering coefficient could be expected. The Kubelka−Munk function,[36] which is the ratio between the absorption and scattering factors, is used for the absorbance plotting, which shows a clear absorption edge at about 1.78 eV (fractals), 1.68 eV (nanorods), and 1.65 eV (spheres), respectively. The slightly smaller band gap values of these samples compared with that of bulk CdSe (1.74 eV as reported in the literature) might be due to experimental errors. Because the particle sizes are much larger than the diameter of the Bohr exciton in bulk CdSe (54 Å), no strong quantum confinement effect is observed, but the blue shift of fractals with respect to nanorods and spheres still can be observed (about 0.1 eV). The shift could be attributed to the smaller dimension of the fractal CdSe nanocrystals than those of other samples.

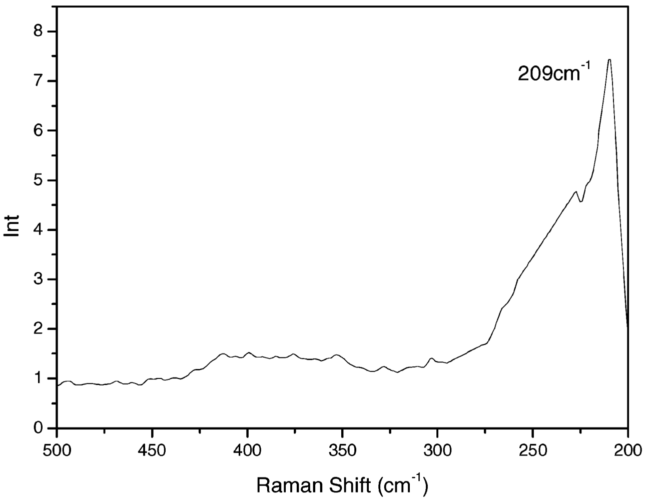

Figure 8. FT-Raman spectrum of CdSe fractals.

Figure 7b shows the photoluminescence spectrum (- - -) of CdSe fractals, which shows a narrow peak with an emission maximum at 1.73 eV ($\lambda_{\mathrm{exc}} = 520$ nm). The small red shift (0.05 eV) of the photoluminescence peak with respect to the corresponding absorption spectrum (—) is caused by the Stokes shift, which is attributed to emission from a "dark exciton".[37]

FT-Raman. Figure 8 shows the FT-Raman spectrum of CdSe fractals, which shows a strong peak at 209 cm^{-1}, whereas strong fluorescence background was found in that of CdSe nanorods and spheres. The peak at 209 cm^{-1} is the characteristic vibration of Cd−Se−Cd.

Conclusion

Choosing soluble selenite as a highly reactive selenium source and using a complex reaction to control the morphologies of the products proved successful in the syntheses of both rodlike and fractal CdSe nanocrystals. This novel method can surely be carried out to synthesize other high quality selenides, which may be difficult to obtain through conventional methods, and it will have potential applications in future large scale synthesis because of its high yield, simple reaction apparatus, and low reaction temperature.

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Supporting Information Available: EDX results. This material is available free of charge via the Internet at http://pubs.acs.org.

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