Synthesis and Optical Properties of CdSe and CdSe/CdS Nanoparticles

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This paper described the optical properties of CdSe and CdSe/CdS nanoparticles, synthesized by the microemulsion method followed by refluxing in toluene/methanol (60:1). Both optical spectroscopy and structural characterization (XPS, XRD, and HRTEM) suggested the core/shell structure of CdSe/CdS samples. Most notable in this work was that capping CdSe nanoparticles with CdS materials yielded a strong narrow band-edge luminescence, indicating a successful passivation by removing surface deep trap luminescence. Proper surface modification with cadmium ions resulted in the further enhancement of the photoluminescence quantum yields of the CdSe and CdSe/CdS nanoparticles. The XPS data confirmed the elemental composition of the CdSe and CdSe/CdS nanoparticles. The CdSe and CdS diffraction patterns exhibited peak positions corresponding to those of their bulk wurtzite crystal structures.

Introduction

Control of particle size and surface structure continues to be of interest in the investigation of semiconductor nanoparticles.[1,2] Because of the high surface-to-volume ratio of nanoparticles, the surface properties have significant effects on their structural and optical properties.[3] Modifying the surfaces of nanoparticles with various organic and inorganic species is expected to remove their surface defects and influence their optical properties. Organic capping of nanocrystallites with surfactants would give rise to a barrier to aggregation and electronic passivation of the crystallites. Typically, CdSe nanocrystals with trioctylphosphine oxide already have a quantum yield of ~10% at room temperature.[4] Most recently, the trend in semiconductor nanoparticles synthetic research has been expanded beyond studies of isolated nanoparticles to include investigations of the properties of core/shell type structures, such as CdSe/ZnS,[5] CdSe/CdS,[6] CdSe/ZnSe,[7] CdS/Cd(OH)$_2$,[8] and CdS/

HgS/CdS.[9] Inorganic capping by shell materials with a wider band gap has been shown to improve the luminescence quantum yield significantly, enhance the photostability, and decrease fluorescence lifetimes related to tailoring of relative band gap positions between the two materials.[5b,c,6b]

Several strategies had been developed to prepare CdSe/ZnS, CdSe/CdS, and CdSe/ZnSe core/shell type nanoparticles during the past several years.[5–9] By using the advantage of the synthesis of high-quality nearly monodisperse CdSe nanocrystallites, highly luminescent CdSe/CdS and CdSe/ZnS core/shell nanocrystallites were synthesized recently by the epitaxial encasing.[5b,c,6b] CdSe/CdS and CdSe/ZnS nanoparticles synthesized by the inverse micelle technique or colloid chemistry also exhibited enhanced band-edge luminescence and increased photoluminescence quantum yield.[5a,6a] Here, we provided a useful and experimentally easy way to synthesize CdSe and CdSe/CdS core/shell type nanoparticles. The optical properties of CdSe and CdSe/CdS nanoparticles could be controlled by refluxing the samples in toluene/methanol (60:1) solution. The fluorescence efficiency of CdSe and CdSe/CdS nanoparticles could be further improved by proper surface modification with cadmium ions.

Experimental Section

Chemicals. Cadmium chloride, sodium sulfide, toluene, thiophenol, triethylamine, pyridine, and methanol were all of the highest quality commercially available. Sodium dodecyl-

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benzenesulfonic acid (NaDBS) was purified by recrystallization in isopropyl alcohol. NaHSe solution was prepared from the reaction between selenium and sodium borohydride in water according to the ref 10.

Synthesis of CdSe and CdSe/CdS Nanoparticles. In a typical procedure, 100 mL of mixed solution containing 5.0×10^{-3} M NaDBS and 5.0×10^{-4} M $CdCl_2$ was prepared. The pH value of the mixture was adjusted to 9.1 using sodium hydroxide. Afterward, 50 mL toluene was added, followed by stirring for 20 min in order a white microemulsion. The microemulsion was then purged with high-purity N_2 for about 30 min in a flask. To this microemulsion was added 5 mL of 0.01 M NaHSe solution drop by drop with the use of a syringe. The resulting solution was allowed to stir for 5 min and 20 mL of 0.2 M $CdCl_2$ was added followed by stirring for 10 min to ensure complete extraction. Finally, the red organic solution was extracted from the water phase and dried with $CaCl_2$.

In the CdSe/CdS nanoparticles preparation, a 400-mL microemulsion was prepared as described above and divided into two portions: 120 and 280 mL. In the first 120-mL portion, 3.75 mL of 0.01 M NaHSe was added. Afterward, this solution was added to the second 280-mL portion. Then 8.75 mL of 0.01 M Na_2S was added very slowly over about 5 h with the use of a syringe, after which 0.2 M $CdCl_2$ was added to destroy the emulsion. The resulting orange red organic phase with water phase was extracted and dried with $CaCl_2$.

The CdSe and CdSe/CdS solutions were further refluxed in toluene/methanol (60:1) mixed solution. Any residual precipitate, probably resulting from the aggregated large particles, was removed by filtering. The resulting solution was totally clear and stable over a time period of months at room temperature. Evaporation of the organic solvent with a rotavapor at 40−45 °C yielded the powder samples, which were stored in dark and dryness. The powder samples can be redissolved in hydrocarbon solvents (such as, toluene, $CHCl_3$, and DMF) to give an optically homogeneous solution.

Synthesis of Thiophenol-Capped CdSe and CdSe/CdS Nanoparticles. The CdSe (or CdSe/CdS) powder samples (0.2 g) were transferred to a flask. A total of 10 mL of $CHCl_3$ was added to this flask. After which, 0.5 mL of thiophenol and 0.3 mL of triethylamine was added with stirring. The solution became turbid and was stirred for 5 h. The resulting nanoparticles were isolated from solvents and unreacted reagents by centrifugation. The final powder was then obtained after washing four times with toluene. For X-ray diffraction measurements, the powder samples were placed on quartz plates. These isolated nanoparticles were readily soluble in pyridine. For X-ray photoelectron spectroscopy experiments, the pyridine solution containing thiophenol-capped nanoparticles was evaporated on a clean single-crystal silicon substrate to formation a thin cast film of nanoparticles.

Characterization. UV−vis spectra were obtained using a Shimadzu 3100 UV−vis−near-IR recording spectrophotometer. The fluorescence experiments were taken on a Shimadzu RF-5301 PC spectrofluorophotometer. All measurements were carried out at room temperature under ambient atmosphere.

X-ray photoelectron spectroscopy (XPS) was performed using a VG ESCALAB MKII spectrometer with an Al Kα monochromatized X-ray source. X-ray powder diffraction (XRD) patterns were recorded using a SIEMENS D5005 X-ray diffractometer with Cu Kα radiation.

High-resolution transmission electron microscopy (HRTEM) measurements were carried on a CM200 FEG electron microscope operating at 300 kV. Samples for transmission electron microscopy were prepared as follows: the nanoparticle-containing toluene solution was dropped on the surface of water, which dispersed to be a layer of film immediately. Carbon-coated copper grids were allowed to float on the organic film for 1 min. Care was taken to avoid deposition of the film on both sides of the grid, after which these grids were allowed to dry under ambient conditions.
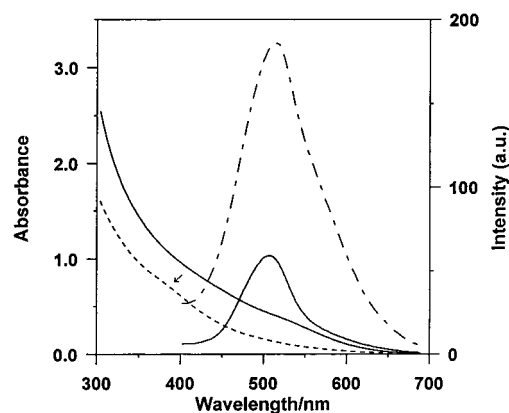

Figure 1. The UV−vis (left) and photoluminescence (right) spectra of CdSe (−) and CdSe/CdS (- - -) nanoparticles dispersed in toluene. λ_{exc} = 380 nm.

Results and Discussion

The UV−vis spectra of the CdSe and CdSe/CdS nanoparticles before reflux had no character (Figure 1), caused by the broad particle size distribution. The photoluminescence spectrum of CdSe showed an emission with maximum at 510 nm, corresponding to electron−hole radiative recombination from trap states lying 0.2−1.0 eV below the exciton level. To improve the fluorescence efficiency of these CdSe nanoparticles, experiments were attempted that involved the growth of a semiconductor layer with larger band gap. Previous studies by Brus and co-workers[5a] on the growth of ZnS on CdSe in inverse micelle revealed that ZnS layers could eliminate the surface traps efficiently, as the broad trap emission was eliminated and replaced by narrow band-edge emission with a high quantum yield. In our experiments, the addition of S^{2-} to CdSe microemulsion did not result in a dramatic enhancement in the emission intensity in the 450−650 nm region, but rather an accentuation of the CdSe defect emission in this region. This observed result was similar to ones proposed for Cd_xZn_yS particles in DHP vesicles and polynucleotides solution.[11,12] One possibility was that many small islandlike clusters of CdS on the surface of CdSe particles were formed, which yielded more surface defects at the ill-defined interface of CdSe and CdS.[12] From the absorption spectrum of CdSe/CdS, we found an observable band under 400 nm, which may be a reflection of the very small CdS clusters.

Therefore, a main challenge of this work was to improve the quality of these particles. In previous studies, size-selective precipitation was often chosen to narrow the size distribution, while reflux was often used to improve crystallization of semiconductor nanoparticles.[4] As can be observed in Figure 2, after one size-selective precipitation, the absorption spectrum of CdSe nanoparticles showed an obvious band around 530 nm. In addition, the photoluminescence showed a narrow band around 533 nm and a broad low energy with an emission maximum of ∼650 nm corresponding to band-edge luminescence and the recombination of trapped charge carriers, respectively. Unfortunately, the photoluminescence quantum yield of CdSe nanoparticle

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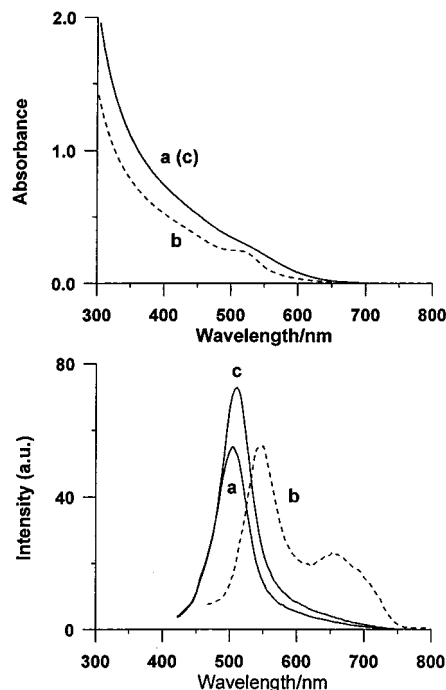(12) Bigham, S. R.; Coffer, J. L. *J. Phys. Chem.* **1992**, *96*, 10581.

Figure 2. The UV−vis (top) and photoluminescence (bottom) spectra of (a) CdSe nanoparticles, (b) CdSe nanoparticles after one step size-selective precipitation; (c) CdSe nanoparticles after reflux in toluene for 2.0 h. λ_{exc} = 400 nm. The absorption spectra of a and c were overlapping.
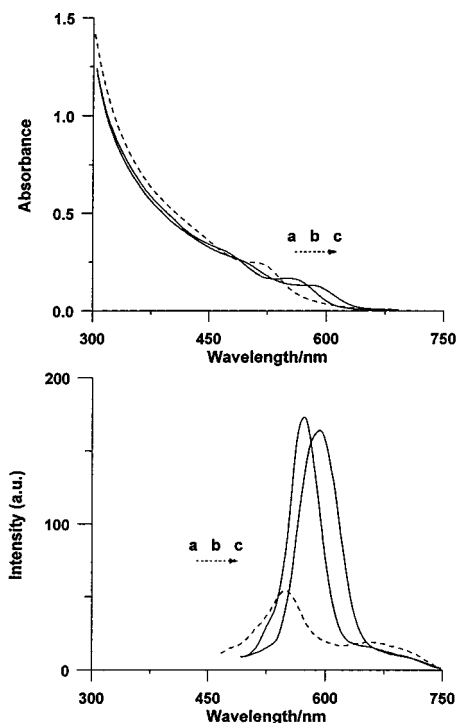

Figure 3. The UV−vis (top) and fluorescence (bottom) spectra of the CdSe solutions after reflux in toluene/methanol (60:1) for (a) 0 h (corresponding to one size-selective precipitation with methanol), (b) 1.0 h, and (c) 3.5 h. λ_{exc} = 450 nm.

solution was very low (<1%). From Figure 2, it was also found that the absorption and photoluminescence spectra did not change under reflux in toluene.

Under reflux in toluene/methanol (60:1), we found optical properties of the CdSe solution (Figure 3) could be changed to a well-resolved character. By comparing curve b with curve a, it was found that the absorption
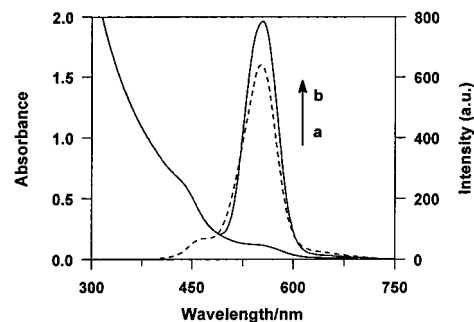

Figure 4. The UV−vis (left) and photoluminescence spectra (right) of CdSe/CdS nanoparticles after reflux in toluene/methanol (60:1). λ_{exc} = (a) 380 and (b) 470 nm.

onset of CdSe nanoparticle solution was red-shifted obviously after reflux in toluene/methanol. The absorption spectrum (curve b) showed a well-resolved $1s_e−1s_h$ transition at ∼560 nm and a second weaker transition at ∼468 nm, corresponding to that same transition with the hole in the spin−orbit−split valence band.[13] The fluorescence of the CdSe nanoparticle solution was red-shifted accordingly. At the same time, the band-edge fluorescence intensity could be enhanced. The results suggested that both surface structure and the size of the CdSe nanoparticles changed under reflux in toluene/methanol. In addition, the absorption onset and the fluorescence of the CdSe solution could be tuned by prolonging the refluxing time.

Figure 4 shows the UV−vis and fluorescence spectra of CdSe/CdS nanoparticles after reflux in toluene/methanol (60:1) for 3.0 h. The absorption spectrum showed two separate absorption edges at 612 and 480 nm, corresponding to those of CdSe and CdS, respectively. The photoluminescence of CdSe/CdS exhibited a narrow band (fwhm ≤ 60 nm) centered around 560 nm corresponding to that reported for the $1s_e−1s_h$ excitonic state of CdSe,[13] as well as a small shoulder around 465 nm. Another important result of the present work was that the PL intensity of CdSe/CdS enhanced significantly compared that of CdSe, which indicated that the CdSe was capped and passivated with CdS successfully, implying a CdSe/CdS core/shell structrure.[5−8] In addition, we found the photoluminescence excitation of CdSe/CdS had similar tracks to the absorption spectrum, which is evidence for the efficient transfer of excitations of energies to the CdSe. The results indicated again the removal of surface defects by CdS capping. By comparing with Figure 1, the fluorescence of CdSe/CdS changed significantly from the defect emission to band-edge emission, which strongly indicates a structural change on the surface of CdSe nanoparticles. The possible reason may be that many, small islandlike clusters of CdS with a structure locally coherent with the CdSe formed in the preparation as indicated by Figure 1. Under reflux in toluene/methanol, those CdS islands coalesced to form a continuous shell on the CdSe surface, resulting in filling the surface traps and increasing the band-edge luminescence. The PL quan-

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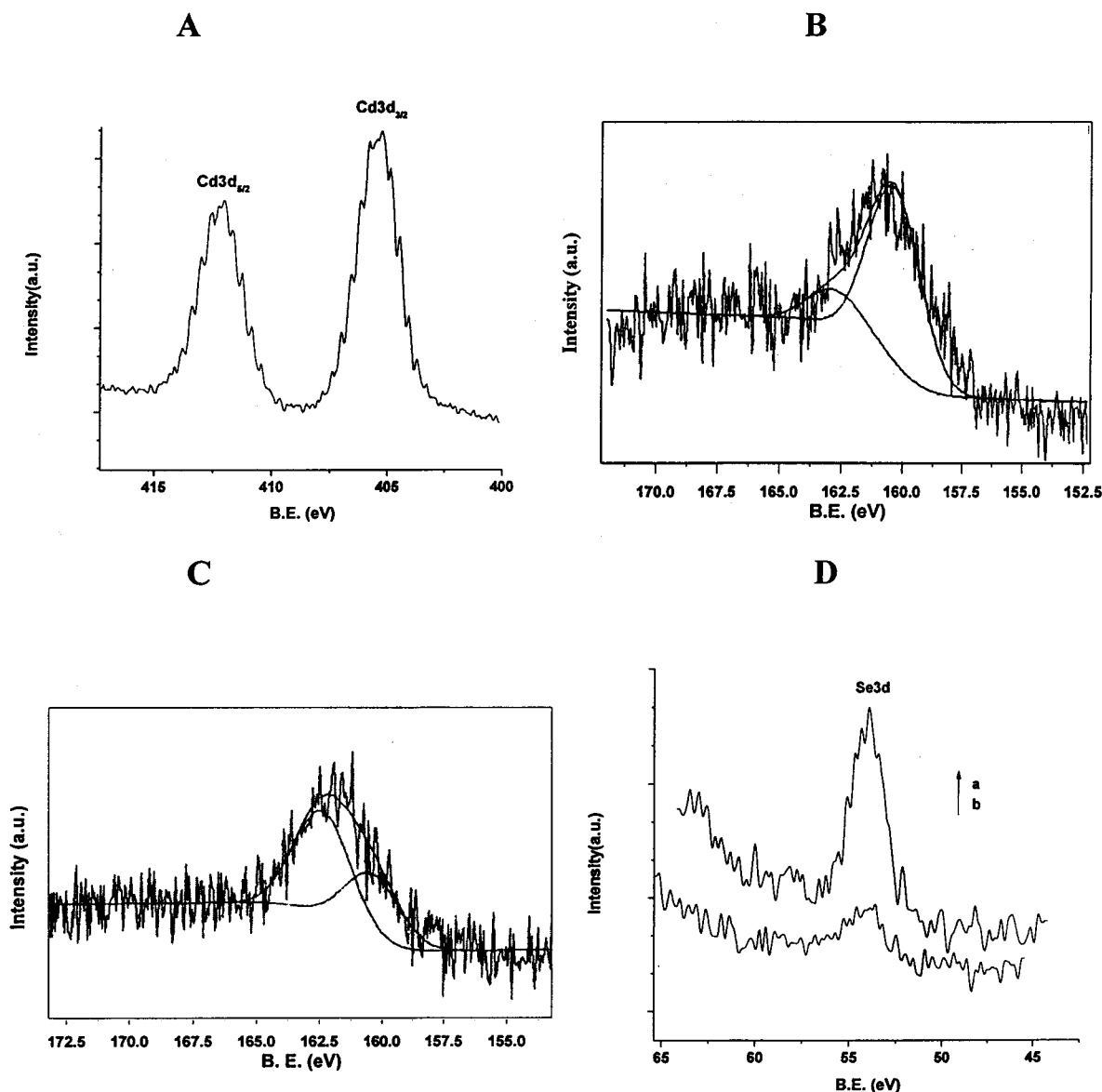
A

B

Cd3d$_{5/2}$

Cd3d$_{3/2}$

Intensity(a.u.)

Intensity (a.u.)

B.E. (eV)

B.E. (eV)

C

D

Se3d

Intensity (a.u.)

Intensity(a.u.)

B. E. (eV)

B.E. (eV)

Figure 5. X-ray photoelectron spectra of thin cast films of thiophenol-capped CdSe and CdSe/CdS nanoparticles: (a) cadmium 3d, (b) sulfur 2p and selenium 3p levels of CdSe samples, (c) sulfur 2p and selenium 3p levels of CdSe/CdS samples, and (d) selenium 3d levels of CdSe and CdSe/CdS samples.

tum yields of our CdSe/CdS nanoparticles were about 10−15% calculated by comparing the integrated emission to that of Rhodamine 6G in methanol at room temperature. In general, the typical core/shell nanocrystalites prepared by epitaxial growth should have 20−80% quantum yields with an excitation around its excitation peak, which were higher than those of our samples.[5b,c,6b] The possible reason was the formation of grain boundaries as the CdS islands coalesce could then be responsible for the relatively lower quantum yields than those of the typical core/shell nanocrystals prepared by epitaxial growth.[5b,c,6b] It was also worth mentioning that an obvious band around 465 nm could be observed upon high-energy excitation. The spectral shape was similar to that of the CdSe/CdS colloidal solution, in which the emission maximum, centered around 470 nm, was assigned to separately nucleated CdS.[6a] Since this band did not appear in the PL spectra of CdSe (Figure 3), we also assigned tentatively the emission around 465 nm to separately nucleated CdS particles.

Although organic capping of nanocrystallites with dodecylbenzenesulfonic acid gives rise to a barrier to aggregation and electronic passivation of the crystallites,[4] the presence of surfactants shell on the surface of nanoparticles makes the structural characterization difficulty. For the CdSe particles capped with surfactants, it was difficult to observe the existence of selenium by XPS. Also, the XRD patterns of the CdSe particles capped with surfactants looked ill-defined. Therefore, it was necessary to replace the surfactants with small molecule. Here, thiophenol was selected because of the strong interaction between thiols and the cadmium on the surface of nanoparticles.

The elemental composition of the CdSe and CdSe/CdS samples was analyzed by XPS, which had proved to be a useful tool to investigate the chemical nature of the cluster surface.[14] Unique information about the amount and chemical state of the sulfur and selenium had been

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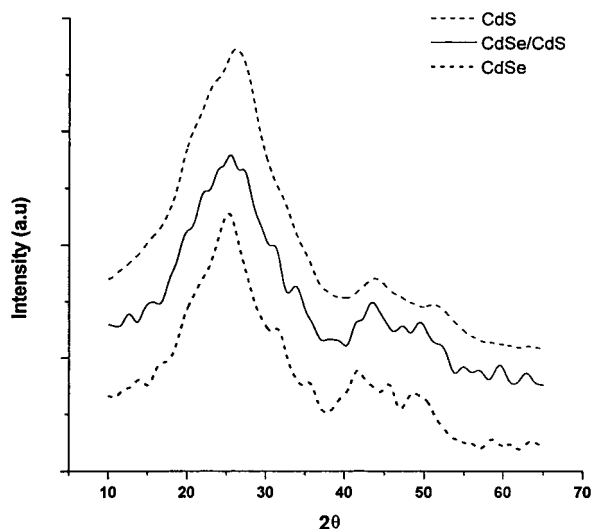
Figure 6. X-ray powder diffraction patterns of CdS nanoparticles of 3.7 nm (top), CdSe/CdS nanoparticles of 5.1 nm (middle), and CdSe nanoparticles of 3.8 nm (bottom). All the nanoparticles were capped with thiophenol molecules.

achieved by applying this technique. As could be seen in Figure 5, the appearances of $Cd3d_{5/2}$ at 405.3 eV, S2p at 163 eV, and Se3p at 160.7 eV in both the thiophenol-capped CdSe and CdSe/CdS samples confirmed the existence of cadmium, selenium, and sulfur. For the CdSe samples, the atomic ratio of S/Se was determined to be 0.207:1 by dividing the integrated peak areas by the electronic core level sensitivity factors for each element. For the CdSe sample, the S2p at 63 eV only originated from the thiophenol molecules. It was worth mentioning that the absence of the peak centered at 168 eV illustrated that the surfactants were replaced by thiophenol completely. After the surfactants were replaced, the Se spectrum centered at 160.7 ($Se3p_{3/2}$) and 53.4 eV (Se3d) could be observed clearly. However, the atomic ratio of S/Se of CdSe/CdS samples was determined to be 4.07/1. The first reason could be that the S2p spectrum reflected the information of both the CdS part and thiophenol molecules. Moreover, the core/shell structure of CdSe/CdS, indicated by the optical characterization, made the electrons originating from Se atoms have a lower probability of escaping the nanoparticle and being detected.[5a,6b] Consistent with this, the Se3d signals of CdSe/CdS nanoparticles (Figure 5d) were much weaker than that of the CdSe nanoparticles. The XPS results then confirmed the elemental composition of the CdSe and CdSe/CdS nanoparticles and were also consistent with the core/shell structure model for the CdSe/CdS samples.

Figure 6 showed the XRD patterns of thiophenol-capped CdSe, CdS, and CdSe/CdS nanoparticles. The CdSe and CdS diffraction patterns exhibited peak positions corresponding to those of their bulk wurtzite crystal structures. In the case of the CdSe/CdS nanoparticles, the powder diffraction patterns showed roughly the same peak widths and shifted in the peak position toward CdS values. The trend indicated no qualitative difference in structure between the CdSe nanoparticles and the CdSe/CdS composite particles, which was similar to that of the CdSe/CdS and CdS/ZnS nanocrystals prepared by the epitaxial encasing.[5b,c,6b] First, it was notable here that the peak width was close to that of CdSe. If the mixture of CdSe and CdS samples was detected, both the CdS and CdSe components should contribute to the X-ray. The peak width should then be broad and could fit as a sum of the two components.[5a] Second, the CdSe/CdS composite peaks were at larger angles, and probably have some contribution from CdS fragments. These results, as well as the optical spectroscopy, then indicated that CdS grows on the CdSe surface with basically coherent layer structures.

High-resolution transmission electron microscopy (HRTEM) could give a wealth of information on the size and structure of the materials.[4,5c,6b,9,15] Figure 7 showed the HRTEM images of CdSe and CdSe/CdS nanoparticles, in which well-resolved lattice fringes could be found. The CdSe and CdSe/CdS nanoparticles had average sizes of 3.8 and 5 nm, respectively. The diameter of the CdSe/CdS particles was larger than that of the CdSe nanoparticles, which also implied a core/shell structure. CdSe nanoparticles were slightly prolate with an average aspect ratio 1.15. This particle shape was similar to that of CdSe nanocrystals generated in the coordinating solvent trioctylphosphine (TOP)[4] and CdS nanocrystals synthesized using phosphatidylcholine vesicles.[15] The lattice spacing of CdSe was measured carefully as 3.22 Å, which was consistent with the lattice spacing between {101} planes for hexagonal CdSe. A corresponding d spacing for cubic CdSe did not exist. From Figure 7b, it was found that the CdSe/CdS core/shell nanoparticles contained some defects or dislocations, which might be caused by the stacking faults at the surfaces and the grain boundaries during the CdS shell formation.[6b,9] Most recently, a well-defined interface between CdSe core and ZnS (or CdS) shell in some high-quality CdSe/ZnS (or CdSe/CdS) nanocrystals prepared by epitaxial growth was observed by HRTEM measurements.[5c,6b] This might explain the lower PL quantum yields of our CdSe/CdS nanoparticles compared to those of the core/shell nanocrystallites prepared by epitaxial growth.[5b,c,6b]

The fluorescence of semiconductor nanoparticles strongly depended on the surface chemistry.[5,6,16] Under reflux in toluene/methanol (60:1), the enhancement of the fluorescence (Figure 3) implied structural changes on the surface of the CdSe nanoparticles. In the preparation of CdSe nanoparticles, excess cadmium ions together with dodecylbenzenesulfonic acid could also be extracted to the organic phase, which could be verified by treatment of the toluene solution with H_2S gas, obtained by adding excess cadmium ions directly to destroy the microemulsion. Under reflux in toluene/methanol, excess cadmium ions would complex on the surface of CdSe, resulting in removing the surface traps. In our case, we refluxed the CdSe or CdSe/CdS nanoparticles again by adding NaDBS, $Cd(Ac)_2$ (cadmium acetate), and $Cd(DBS)_2$ (cadmium dodecylbenzenesulfonic acid). From the UV–vis absorption spectra, we found that the addition of $Cd(Ac)_2$, NaDBS, and $Cd(DBS)_2$ only changed slightly the absorption edge, while the PL intensity (Figure 8) was further enhanced

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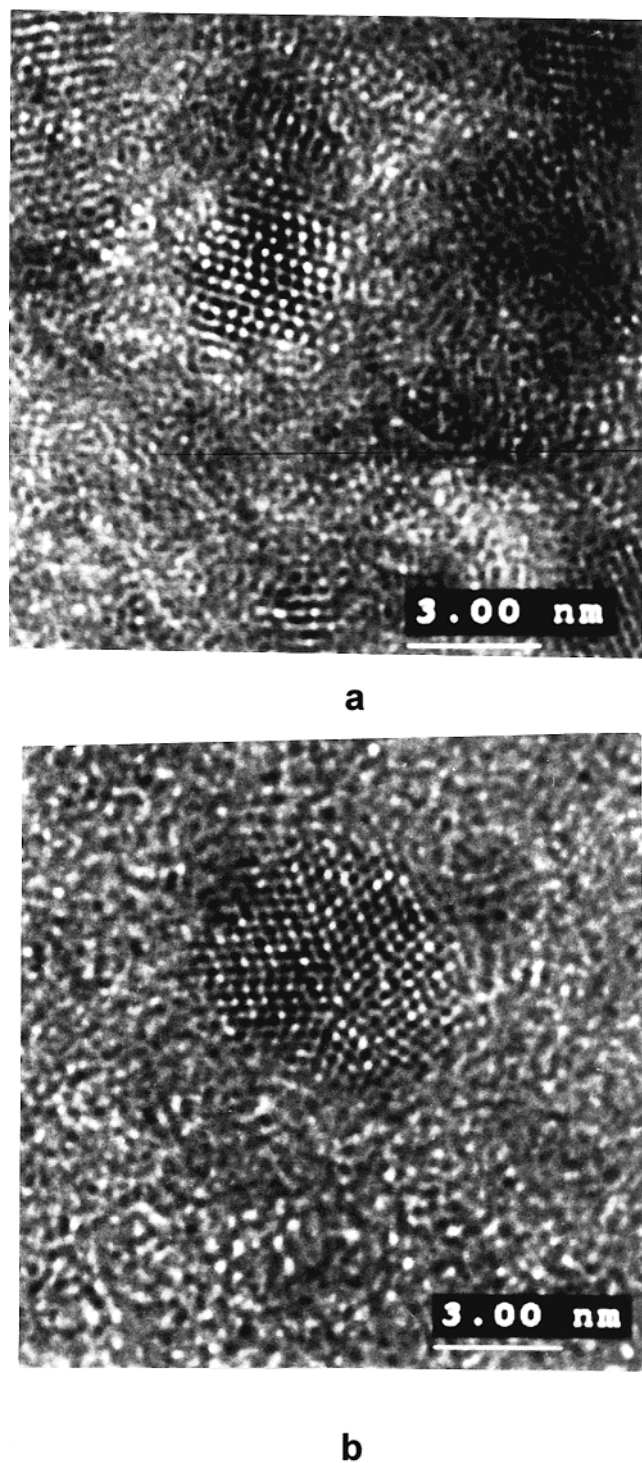(16) Gao, M.; Kirstein, S.; Möhwald, H. *J. Phys. Chem. B* **1998**, *102*, 8360.

a

b

Figure 7. High-resolution TEM of (a) CdSe nanoparticles and (b) CdSe/CdS nanoparticles after reflux in toluene/methanol (60:1) for 3.0 h.

Figure 8. Fluorescence spectra of CdSe refluxed in toluene/methanol mixture for 1.5 h (a) and fluorescence spectra of these CdSe nanoparticles by further surface modification with (b) NaDBS, (c) $Cd(DBS)_2$, and (d) $Cd(Ac)_2$. $\lambda_{exc} = 468$ nm.

Figure 9. Fluorescence spectra of CdSe nanoparticles (- - -) refluxed in toluene/methanol for 0, 1.0, and 3.0 h, same as Figure 3. After that, these CdSe nanoparticles were refluxed again in the presence of $Cd(DBS)_2$ for 1.5 h, which fluorescence spectra (—) were also shown. $\lambda_{exc} = 440$ nm.

obviously in the presence of $Cd(Ac)_2$ and $Cd(DBS)_2$. This illustrates that the additional modification on the surface of the particles took place rather than a change of the size of the nanoparticles. The addition of NaDBS did not enhance the PL intensity, which illustrated that the additional surface modification was caused by the cadmium ions instead of NaDBS. Under reflux, the additional cadmium ions bound to the surface of CdSe and CdSe/CdS nanoparticles, which removed the anion defects and yielded in higher surface coverage with CdS shell for the CdSe/CdS nanoparticles. The fluores-
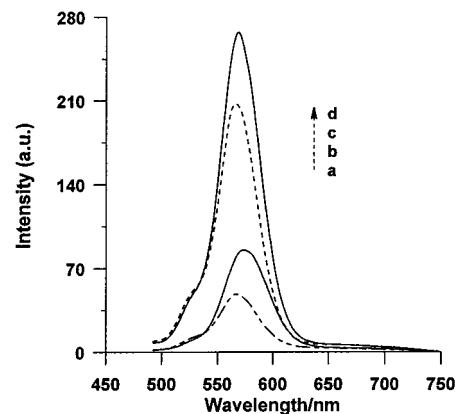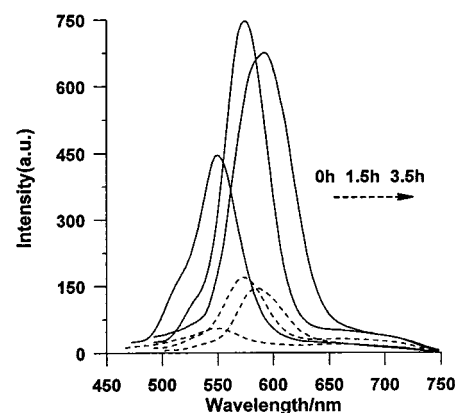
cence intensity was therefore enhanced significantly (Figure 9). For the CdSe/CdS nanoparticles, the photoluminescence quantum yield in the best case was estimated to 25–30%.

The following mechanisms can therefore be suggested during the reflux of the CdSe in toluene/methanol mixed solution: (1) The presence of methanol leads to increased average polarity of the solvent and reduces the energetic barrier to flocculation. The large particles experience the greatest attraction forces and have a higher probability of overcoming the reduced barrier to precipitate, corresponding to the size-selective precipitation.[4] (2) Refluxing under the reduced barrier would give the excess cadmium ions a chance to complex on the surface of the particles, resulting in improving the fluorescence efficiency. (3) For the CdSe/CdS nanoparticles, refluxing under the reduced barrier would help the small CdS islandlike clusters to coalesce as a continuous shell on the CdSe surface and remove surface traps, thus resulting in the appearance of the strong band-edge emission. It was worth mentioning that this process is different from the size-selective precipitation. Size-selective precipitation with methanol was a useful way to further narrow the size distribution of semiconductor nanoparticles.[4] However, size-selective precipitation should be a physical separation and did not affect the particle's quality. In our experiments, we

found that the above-mentioned results were absent from the samples treated only by the size-selective precipitation (Figure 2). In addition, the residual precipitation after reflux could not be redispersed in toluene, chloroform, and hexane, which was also different from the size-selective precipitation.

Conclusion

CdSe and CdSe/CdS nanoparticles had been synthesized by the microemulsion method, which was easy to process and low technique at low cost. Both optical spectroscopy and structural characterization (XPS, XRD, and HRTEM) suggested the core/shell structure of CdSe/CdS samples. Capping CdSe nanoparticles with CdS materials yielded a strong narrow band-edge luminescence, indicating a successful passivation by removing surface defects. Proper surface modification with cadmium ions resulted in the further enhancement of the photoluminescence quantum yields of the CdSe and CdSe/CdS nanoparticles. For the structural characterization, thiophenol was successfully used to replace the surfactant molecules on surface of nanoparticles. The XPS data confirmed the elemental composition of the CdSe and CdSe/CdS samples. The CdSe and CdS diffraction patterns exhibited peak positions corresponding to those of their bulk wurtzite crystal structures. This work may provide a useful method for controlling the surface structure and the size of semiconductor nanoparticles.