Wet synthesis and characterization of MSe (M = Cd, Hg) nanocrystallites at room temperature

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(Received 3 December 2001; accepted 21 February 2002)

Semiconductor selenides of MSe (M = Cd, Hg) nanocrystalline powders were synthesized through the reactions between metal chlorides and sodium selenosulfate in the ammoniacal aqueous solution at room temperature for 6–10 h. The samples were characterized by x-ray powder diffraction, transmission electron microscopy, electron diffraction, x-ray photoelectron spectroscopy, and elemental analysis. The average diameters of CdSe and HgSe nanocrystallites are 4 and 8 nm, respectively. The storage and an interesting phase transition under hydrothermal conditions have been presented. The absorption spectrum of the as-prepared samples exhibits obvious blue shift due to the size confinement.

I. INTRODUCTION

The synthesis and characterization of nanostructured materials have attracted much attention over the last several years due to their unconventional properties. Particularly, semiconductor nanoparticles exhibit novel catalytic, optoelectronic, and electrical properties. The different properties between the nanocrystallites and bulk material are mainly caused by the surface effects and size effects (quantum size effects). For example, being an important semiconductor, bulk CdSe has an optical band gap at 716 nm, but the optical absorption edge of CdSe nanocrystallites with 1.2–11.5-nm diameter has a considerable blue shift.5

Cadmium and mercury selenides belong to the II–VI group semiconductors, which have been conventionally prepared by elemental reactions.5 This method is important and widely used to prepare II–VI chalcogenides. Meanwhile, other techniques such as chemical solution deposition and ionic reaction,7–9 the molecular precursor method,10–12 gas–liquid precipitation,13 and electrochemical,14,15 sonochemical,16,17 γ-irradiation,18 and solvothermal19 methods have been employed to synthesize the selenides. In contrast, the solution reaction growth technique appears to be the cheapest and most convenient approach to prepare the selenides20,21 because it does not involve complex instrumentation and growth rate is easily controllable. Recently, the solution technique has attracted considerable interest to the materials chemistry community on the research of II–VI semiconductor nanocrystallites.22

Selenosulfate and selenourea are the main selenium sources to afford Se2− ions for the preparation of selenides through reactive solution growth. However, selenourea is expensive and not readily available. Thus, selenosulfate is a better Se2− source for solution preparation of selenides. Kitaev’s group first employed selenosulfate as Se2− source to synthesize selenides through a chemical solution deposition route in the CdCl2–NH4OH–NaSeSO3–KOH system.7 Thereafter, other groups also prepared selenides using selenosulfate as Se2− source. For example, Skyllas-Kazacos et al.23 used selenosulfate to synthesize selenides through electroreduction deposition in aqueous solution. Pramanik et al.24 has also prepared several semiconducting films of selenides from selenosulfate by the solution technique. In our work, we synthesized MSe (M = Cd, Hg) nanocrystalline powders with high quality from metal chlorides and sodium selenosulfate in the ammoniacal aqueous solution at room temperature for 6–10 h. In the route, the synthesis of MSe nanocrystallites is referred to that reported by Kitaev, but the route is KOH free in ammoniacal solution.

II. EXPERIMENTAL

A. Reagents and preparation of the initial solutions

The analytical purity reagents of CdCl2 · 2H2O, HgCl2, Se, Na2SO3, concentration ammonia (solution), and solvents were used in the experiments.

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A typical experiment includes two steps: the preparation of initial solutions and the synthesis of MSe. A 1.26 g amount of sodium sulfite was dissolved in a conical flask. Then, 0.79 g elemental selenium was added into the flask in the presence of ammonia (concentration ammonia solution), forming a solution of sodium selenosulfate (Na₂ SeSO₃, 60–100 mM) at pH 10–11 for about 2 h. Meanwhile, 100 mM cadmium chloride and mercury chloride aqueous solutions were prepared in other two conical flasks (with cover). Thereafter, concentration ammonia solution was added into the two chloride aqueous solutions drop by drop, and with the dripping of the ammonia solution, white colloid precipitates were formed from the colorless solutions. Then, the ammonia solution was continuously added until the white precipitates were dissolved to form two kinds of metal complexes. In the process, the vessels were covered and the prepared solutions were employed to synthesize MSe.

B. Synthesis of MSe powders

While stirring, sodium selenosulfate solution was slowly dropped into the prepared cadmium chloride and mercury chloride ammoniacal aqueous solutions (the feedstock of metal chlorides were a little excessive to the stoichiometric amount) and then the two containers were covered. Precipitates with scarlet and gray were gradually produced from the two colorless mixture solutions after the solutions were stored at room temperature for 6–10 h (reaction time). Then the precipitates were collected by a vacuum filter and washed with concentration ammoniacal solution, distilled water, and absolute alcohol to dissolve and remove the impurities (including metal salts and byproducts). Vacuum dried at room temperature for 4 h, the final powders were obtained.

C. Characterization of products

Powder x-ray diffraction (XRD) was carried out on a China Dandong x-ray diffractometer with graphite-monochromatized Cu Kα (λ = 1.54178 Å) radiation. The scanning rate of 0.05°/s was applied to record the patterns in the 2θ range of 10° to 70°. The crystal size was estimated upon the half width of the diffraction peaks using Debye–Scherrer’s equation. The morphology and the size of the products were observed by transmission electron microscopy, carried on a Hitachi H-800 transmission electron microscope. Meanwhile, selected area electron diffraction (ED) was also conducted. High-resolution transmission electron microscopy (HRTEM) was taken on a JEOL-2010 transmission electron microscope (Japan). Samples were prepared by placing a drop of dilute alcohol suspension of CdSe crystallites dispersed using a supersonic disperser on to an amorphous carbon-coated copper grid and then wicking away the solution. X-ray photoelectron spectroscopy (XPS) was recorded on a VG-ESCALAB MKII x-ray photoelectron spectrometer (England), by using nonmonochromatized Mg Kα (hν = 1253.6 eV) x-ray as the excitation source with an energy resolution of 1.0 eV. Binding energies were calibrated to the internal standard C 1s peak. Element analysis was done by ICP-AES, which was carried out on an Atomscan Advantage spectrometer (Thermo Jarrell Ash Corporation, USA). UV–visible–infrared absorption spectra of the samples (dispersed in ethanol) were recorded on a Shimadzu UV-365 recording spectrophotometer, using 1-cm quartz cuvettes, scanning from 400 to 900 nm at room temperature with ethanol as the reference.

III. RESULTS AND DISCUSSION

A. Characteristics of MSe

The as-prepared samples were identified by XRD, illustrated in Fig. 1. It shows the three strong peaks ([111], (220), and (311)) of CdSe [in Fig. 1(a)], which could be indexed as the cubic CdSe with lattice constant a = 6.075 Å. The result is in good agreement with the reported data for cubic CdSe (JCPDS Card File, 19-191, a = 6.077 Å). The XRD pattern shown in Fig. 1(b) demonstrates the formation of cubic HgSe powders with lattice constants a = 6.088 Å, according to the literature. The as-prepared samples were identified by XRD, illustrated in Fig. 1. It shows the three strong peaks ([111], (220), and (311)) of CdSe [in Fig. 1(a)], which could be indexed as the cubic CdSe with lattice constant a = 6.075 Å. The result is in good agreement with the reported data for cubic CdSe (JCPDS Card File, 19-191, a = 6.077 Å). The XRD pattern shown in Fig. 1(b) demonstrates the formation of cubic HgSe powders with lattice constants a = 6.088 Å, according to the literature.
(JCPDS Card File, 8-469, \(a = 6.085\) Å). By means of XRD analysis, no impurities are detected. The three prominent lattice planes of these materials seen by XRD show MSe are crystalline rather than amorphous which would yield only a very broad single nearest neighbor peak near the (111) line. The broadened peaks in the pattern are due to the small average dimension of the polycrystallites. From Debye–Scherrer’s equation, the average size of the nanocrystallites is 3.8 nm for CdSe and 8.2 nm for HgSe, respectively.

Figure 2 shows that the morphologies of both CdSe [Fig. 2(a)] and HgSe [Fig. 2(b)] samples are nearly spherical particles. The average size of CdSe is about 4 nm, and the size of HgSe is 10 nm. The aggregation in the samples could be observed from the TEM images, and the size of the samples is slightly larger than that calculated from Debye–Scherrer’s equation. The HRTEM image for the CdSe nanocrystallites [Fig. 2(a), below] shows that the most easily observed lattice fringe is 3.50 Å, which is agreement with the theoretical value (3.51 Å) for the (111) plane. Selected area ED patterns [inserts in Figs. 2(a) and 2(b), respectively] confirm the XRD results illustrated in Figs. 1(a) and 1(b). It could be observed that the relative intensity between ED and XRD is comparable. The broadening width of rings implies that the selenide crystallites have small dimensions.

The survey XPS of CdSe reveals that there are very little contaminated oxygen and carbon absorbed in the sample. The close-up Cd 3d core level spectrum gives 405.05 eV of binding energy for Cd 3d_{5/2}, which is near the literature value for CdSe. The binding energy of Se 3d is 54.15 eV, which demonstrates that no elemental selenium or selenium dioxide is contained in the product. XPS analysis also confirms the formation of HgSe in the route. The spectra show the binding energies of Hg 4f_{7/2} and Se 3d are 100.00 and 54.00 eV, respectively. No obvious peaks indicating N, element Hg, or oxides are observed.

Peak areas of the Cd 3d, Hg 4f, and Se 3d cores are measured and used to determine the chemical composition of the samples. Quantification from Cd 3d and Se 3d peak areas gives a molar ratio of 0.923:1 for Cd:Se, and it also similarly gives a molar ratio of 1.089:1 for Hg:Se. A direct elemental analysis method is employed by ICP-AES, and it gives the molar ratios of Cd:Se and Hg:Se as 1.000:0.935 and 1.000:1.042, respectively. The results reveal the obtained crystallites are stoichiometric.

### B. Precipitation of MSe and storage

In the present experiments the reaction system is KOH free, but the overall chemical reaction of the precipitation of CdSe powders could be expressed as the following equation in basic ammoniacal conditions referring to Kitaev’s work:

\[
\text{[Cd(NH}_3\text{)}_4\text{]}^{2+} + \text{SeSO}_3^{2−} + 2\text{OH}^− \rightarrow \text{CdSe} + \text{SO}_4^{2−} + 4\text{NH}_3 + \text{H}_2\text{O}.
\]

In solution, the [Cd(NH_3)_x]^{2+} complexes dominated, but [Cd(NH_3)_x]^{2+} complexes (where \(x = 0–3\)) could not be excluded, because according to free energy calculations the [Cd(NH_3)_x]^{2+} may also exist. Compared with

![FIG. 2. (a) Transmission electron microscope (TEM) images for CdSe nanocrystallites (upper part), the corresponding selected area electron diffraction (ED) pattern (inset), and the high-resolution TEM images (lower part). (b) TEM images for HgSe and the corresponding ED pattern (inset).](image-url)
[Cd(NH$_3$)$_4$]$^{2+}$, although the concentration of [Cd(NH$_3$)$_4$]$^{2+}$ is much smaller, these complexes could also react with SeSO$_3^{2-}$ and finally form CdSe nanocrystallites:

\[
[Cd(NH$_3$)$_4$]$^{2+}$ + SeSO$_3^{2-}$ + 2OH$^-$ → CdSe + SO$_4^{2-}$ + xNH$_3$ + H$_2$O \quad (x = 0 \sim 3) .
\] (2)

Metal chlorides are controlled to slightly excessive amounts, which is used to prevent elemental selenium from precipitating into the products. In the process, the flasks are covered. When the cover is removed, ammonia volatilizes away from the vessel and carbon dioxide is absorbed into solution, CdCO$_3$ could emerge mixing with the product [Fig. 1(c)]. Meanwhile, Cd(OH)$_2$ could also form due to the basic solution. To obtain products in high quality, the pH of the solution should also be controlled to confine the formation of Cd(OH)$_2$. The reviewed and studied effects of the pH value of the solution on the deposition of CdSe films$^{20,26}$ could be referred for consideration in the present experiments. Also, the byproduced metal salts from the excessive metal chlorides may also be dissolved and washed by ammoniacal solution after reaction.

HgSe nanocrystallites were precipitated as well by this route. The similar formation of HgSe has been discussed for the films presented in recently reported literature$^{21}$ in which Hg(NO$_3$)$_2$ was employed. Although HgCl$_2$ used in the present route is different from Hg(NO$_3$)$_2$, the two processes are comparable.

The storage of the as-prepared products was investigated, and the results are listed in Table I. The scarlet CdSe changed into red brown when the dried CdSe nanocrystallites were stored at room temperature for a certain period (more than 3 months). The changed color of CdSe may result from the absorption or/and the oxidation of the samples. To investigate the status of the stored CdSe particles, XRD [Figs. 1(d)–1(g)] and XPS (Fig. 3) were used to characterize the particles. The XRD pattern [Fig. 1(d), asterisk used for SeO$_2$] gives some extra peaks besides the three CdSe characteristic peaks, and it shows the existence of some amount of oxides. Also, the existence of oxides could be implied from XPS analysis. The peak broadening in Cd 3d and Se 3d spectra indicates that cadmium and selenium have more than one elemental environment, which implies the existence of oxides. Figure 3 gives the close-up spectrum of Se, which illustrates two values of 53.75 eV for Se$^{2-}$ in CdSe and 59.50 eV for Se in SeO$_2$ and confirms the above proposal. In contrast, when the purified crystalline CdSe powders were stored in water, ethanol, and cyclohexane, the oxidation of the powders was not detected and the change in color was not easily observed although the aggregation was not avoided. The condition for HgSe nanocrystallites was similar.

The crystalline structural transition was studied when the as-prepared cubic CdSe nanocrystallites were treated at 120–200 °C under hydrothermal conditions (listed in Table I). At 120 °C, no obvious change could be observed in XRD pattern [Fig. 1(e)], except that the three cubic peaks become a little bit sharp. While the CdSe particles were treated at 160 °C, there are some extra peaks emerging in the pattern [Fig. 1(f)], which indicates a change in the crystalline structure from cubic to a hexagonal. It is interesting that the transition temperature under hydrothermal treating conditions is lower than that under Ar atmospheric thermal annealing in Ref. 8. The different structural transition temperature may be due to the effect of pressure under hydrothermal conditions. Meanwhile, the XRD spectral linewidth decreases with the increasing treating temperature [at 200 °C, Fig. 1(g)], indicating an increase in the crystallite size with increasing temperature (Fig. 4).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Storage state and treatment</th>
<th>Temp. and time</th>
<th>Property and status</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe</td>
<td>Dry air</td>
<td>Room temp. &gt;3 months</td>
<td>Aggregation and oxidation on surface, a,b red brown, cubic</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td></td>
<td>Aggregation, scarlet, cubic phase, ~4 nm</td>
</tr>
<tr>
<td></td>
<td>Enthanol</td>
<td></td>
<td>Brown, cubic phase, c spherical particles, ~6 nm</td>
</tr>
<tr>
<td></td>
<td>Cyclohexane</td>
<td></td>
<td>Brown, cubic and hexagonal (little) phases, d spherical particles, ~8 nm</td>
</tr>
<tr>
<td>HgSe</td>
<td>Dry air</td>
<td>Room temp. &gt;3 months</td>
<td>Aggregation and oxidation on surface, dark gray, cubic</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td></td>
<td>Aggregation, gray, cubic phase, ~10 nm</td>
</tr>
<tr>
<td></td>
<td>Enthanol</td>
<td></td>
<td>Brown, hexagonal and cubic phases, e spherical particles, f ~12 nm</td>
</tr>
</tbody>
</table>

a Figure 1(d).

b Figure 3.

1 Figure 1(e).

e Figure 1(f).

f Figure 1(g).

1 Figure 4.
C. Optical properties of MSe

To get some effective information of the optical properties, UV–visible–infrared absorption spectra were used to characterize the samples. Figure 5 shows the absorption spectra of the samples, dispersed in ethanol. The as-prepared CdSe absorption edge [Fig. 5(a)] considerably shifts from its 716-nm bulk band gap. The blue shift in the spectrum is due to the dimensional effect (for CdSe, smaller than 12 nm). Treating CdSe particles at 120–200 °C for 2–6 h under hydrothermal conditions resulted in different shift in optical spectra [Figs. 5(b)–5(d)]. All the shifts in the spectra are due to the dimension of the CdSe particles approaching the Bohr radius of excitons. The result approximately agrees with the reported value in literature.5 As for HgSe nanocrystallites [in Fig. 5(c)], the absorption edge is at about 720 nm.

IV. CONCLUSION

In summary, a simple wet method has been used to synthesize CdSe and HgSe nanocrystalline semiconductors through the reactions between the metal chloride and fresh sodium selenosulfate in an ammoniacal aqueous solution at room temperature for 6–10 h. Structural features, morphologies, chemical composition, and storage have been investigated using various techniques. The as-prepared nanocrystallites are easily oxidized in air due to the surface effects. An interesting structure transition of CdSe nanoparticles is also illustrated under hydrothermal conditions. The study of the storage and stability may be one of the important aspects on the potential applications. Meanwhile, the as-prepared samples in quantum size exhibiting quantum confinement have been discussed.

ACKNOWLEDGMENTS

Financial support of this work by the National Science Foundation of China and the 973 Projects of China is gratefully acknowledged. We are indebted to Prof. G.E. Zhou,
Shuyuan Zhang, Dr. X.M. Liu, and Z.W. Chen for their help with the XRD and TEM analyses, and to Prof. M.R. Ji and J.X. Wu for obtaining the XPS results and the valuable comments. We express our gratitude to Prof. Shuyu Chen and Zitai Song for their assistance with optical analysis and to Dr. Z.H. Han for his valuable comments.

REFERENCES