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Low-Temperature Elemental-Direct-Reaction Route to II−VI Semiconductor Nanocrystalline ZnSe and CdSe

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Semiconductor compounds have attracted more and more attention during the past few years due to their novel optical and transport properties and their many potential applications.[1−4] The nanoscale II−VI semiconductor compounds, such as the direct band gap materials ZnSe and CdSe, have been thoroughly investigated and widely used.[5−8] Lots of methods of synthesizing them have been developed, including molecular beam epitaxy (MBE),[7] metalorganic chemical vapor deposition (MOCVD),[8] organometallic vapor phase epitaxy (OMVPE),[9] and some other methods.[10,11] But these methods often use toxic metalorganic reagents as precursors and need a special device.

Solvothermal synthetic methods have been developed by using organic solvents such as pyridine at 180 °C.[12−15] The syntheses were accomplished at a relatively low temperature and pressure in a closed system and could be easily controlled, but the organic solvent is usually harmful to the environment and not appropriate for use on a large scale.

The most straightforward way to synthesize ZnSe and CdSe is the direct combination of elemental metal and selenium at very high temperature. In this communication, we report a novel hydrothermal elemental direct reaction to produce nanocrystalline ZnSe and CdSe using only water as the reaction medium. During the reaction the pH does not change and the solution stays neutral. This method provides us a new idea and greatly decreases the direct reaction temperature of elemental Zn (or Cd) and Se. The reaction mechanism is very interesting and will be helpful to the design of other nanocrystalline semiconductors.

Appropriate amounts of metal powder (99.99%, Zn or Cd) and selenium powder (99.95%) were put into a Teflon-lined autoclave of 100 mL capacity. Then the autoclave was filled with deionized water up to 70% of the total capacity. The autoclave was sealed into a stainless steel tank and kept at 180 °C for 24 h without shaking or stirring. The autoclave was then allowed to cool to room temperature naturally. The precipitate was collected and washed with 1 M HCl and 1 M NaOH solutions to eliminate unreacted Se, metal, and other impurities. The sample was filtered off, washed, and dried in a vacuum at 80 °C for 3 h, giving black CdSe or yellow-greenish ZnSe in yields of about 50−60%.

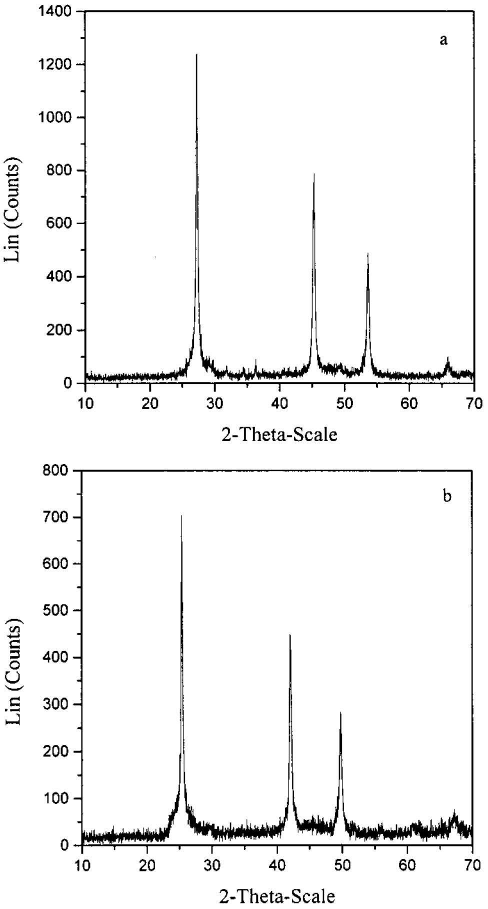

Figure 1. The XRD patterns of ZnSe and CdSe.

X-ray power diffraction (XRD) was carried out on a Bruker D-8 Advance X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). Transmission electron microscopy (TEM) images and energy-dispersive X-ray analysis (EDX) were taken with a Hitachi model H-800 transmission electron microscope, with a tungsten filament, using an accelerating voltage of 200 kV. Raman shifts were recorded on a Perkin-Elmer spectrum GX/FT-Raman spectrometer.

In our elemental-direct-reaction route, the reaction process can be described simply as follows:

$$\mathrm{Zn(Cd)} + \mathrm{Se} \xrightarrow{\mathrm{H_2O,\ 180\ ^\circ C}} \mathrm{ZnSe(CdSe)} \qquad \text{(a)}$$

Plots a and b of Figure 1 show the XRD patterns of ZnSe and CdSe, respectively. In Figure 1a, the peaks can be indexed as cubic zinc blende phase ZnSe with a lattice parameter $a =$

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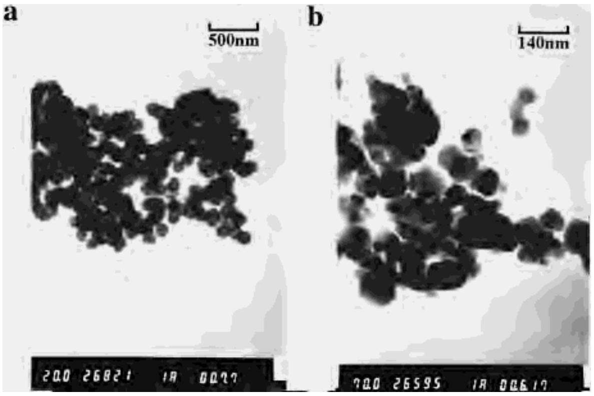

Figure 2. TEM micrographs of nanocrystalline ZnSe and CdSe.

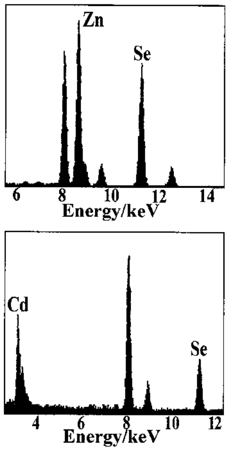

Figure 3. EDX results of nanocrystalline ZnSe and CdSe.

5.66876 Å, which is close to the reported data (JCPDS card, No. 37-1463, $a = 5.66882$ Å). Although wurtzite phase is the thermodynamically favored bulk form of CdSe, it is very interesting that the product obtained here has a cubic phase structure (Figure 1b) with a lattice parameter $a = 6.07676$ Å (JCPDS card, No. 19-0191, $a = 6.0700$ Å).

TEM micrographs of ZnSe and CdSe nanocrystallites are given in Figure 2. Both are well-dispersed particles with an average size of about 70−100 nm. The uniform nanoparticles of ZnSe (Figure 2a) are found to be composed of many fine particles through careful observation. Figure 3 shows the EDX results of the two samples, which indicate that the particles are composed of the elements Zn(Cd) and Se (other peaks arise from the Cu grid).

Raman spectroscopy (Figure 4) was also used to characterize the two metal selenides. The strong peaks at 250 and 235 cm^{-1} are the characteristic vibrations of nanocrystalline ZnSe and CdSe, respectively.[16]

After reaction, the solution remained neutral (pH = 7), as it was before the reaction. When the temperature was lowered to 160 °C, the reaction terminated with only the mixture of metal oxide (or metal hydroxide) and unreacted Se.

During the reaction, Zn or Cd powder can first react with water and generate metal oxide (or metal hydroxide) and H_2.[17] At a temperature of about 180 °C, selenium can partially dissolve in water[18] and the dissolved ones may be reduced by the H_2 to produce Se^{2-}. So a possible mechanism to produce ZnSe or CdSe should be

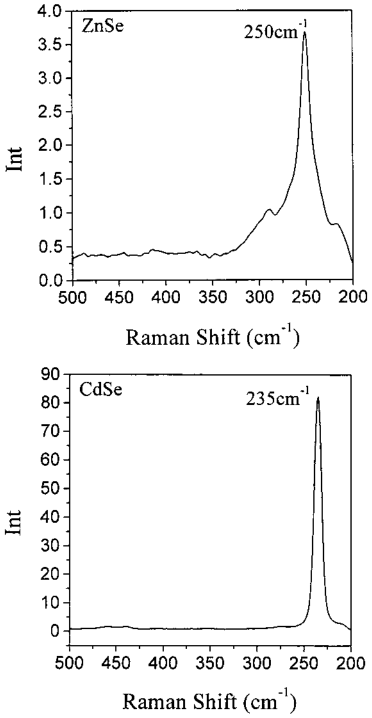

Figure 4. FT-Raman spectra of nanocrystalline ZnSe and CdSe.

$$3Zn + 6H_2O \rightarrow 3Zn(OH)_2 + 3H_2 \tag{1}$$

$$3Se \xleftrightarrow{H_2O,\ 180\ ^\circ C} 3Se(sol) \tag{2}$$

$$3Zn(OH)_2 + 3Se(sol) + 3H_2 \rightarrow 3ZnSe + 6H_2O \tag{3}$$

$$3Zn + 3Se \xrightarrow{H_2O,\ 180\ ^\circ C} 3ZnSe \tag{4}$$

The K_{sp} of ZnSe is very small (10^{-31}), which could be the driving force of the whole reaction 4. From the above reactions we can see that all of the $Zn(OH)_2$ generated in step 1 is all consumed to form the product (step 3), and this can explain why the system stays neutral after reaction. When the reaction temperature is decreased to 160 °C, Se does not have enough solubility in water and the metal selenides cannot be obtained.

Additional experiments have been also performed to investigate the reaction mechanism. When ZnO (or $Zn(OH)_2$) and Se powder were put into an autoclave with water as reaction medium and kept at 180 °C for the same reaction time, no ZnSe product was produced. This shows that the hydrogen generated in the system plays an important role in the elemental direct reaction.

On the basis of the mechanism discussed above, this method should be also applicable to other selenides (for example, the II−V semiconductor selenides), and the relative work is in progress.

In summary, a novel hydrothermal elemental-direct-reaction method to produce ZnSe and CdSe nanocrystallites has been successfully established. This method is very simple and convenient and greatly decreases the direct reaction temperature of elemental Zn (Cd) and Se. It provides us a new idea and thus is expected to be applicable to fabricate other nanosized semiconductor compounds.

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