One-step Preparation of ZnSe Nanorod Aggregates

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(Received July 18, 2006; CL-060801; E-mail: qczhao@ustc.edu)

ZnSe semiconductor aggregations were prepared via γ-ray irradiation method. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the products clearly show that ZnSe possesses an aggregation structure, and these aggregations were found to form through the aggregation of ZnSe nanorods. The length and the diameter of the ZnSe nanorods are about 500–1000 and 30–60 nm, respectively. Electron diffraction patterns of an individual ZnSe nanorod and X-ray diffraction (XRD) analysis were used to examine the crystal structure of the products. The obtained product is pure-phase hexagonal system ZnSe. The composition of the products was analyzed by X-ray photoelectron spectroscopy (XPS). Effect of the pH value on product morphology was investigated.

The synthesis of inorganic materials with dimensions on the nanometer scale has greatly improved in the last 10 years.[1–7] One-dimensional (1D) nanostructures, such as nanorods, nanowires, nanoribbons, and nanotubes, are known to have many fascinating physical properties and are of great importance in both basic scientific research and potential technological applications.[8] Many unique and interesting properties have been proposed or demonstrated for nanoscale 1D materials, such as superior mechanic toughness, higher luminescence efficiency, enhancement of thermoelectric figure of merit, and lowered lasing threshold.[9–11] 1D nanostructures are also ideal systems for investigating the dependence of electrical transport, optical and mechanical properties on size and dimensionality.[12]

As an important II–VI semiconductor with a room temperature bulk band gap of 2.67 eV (460 nm), ZnSe has long been a material of choice for blue diode lasers and photovoltaic solar cells. In the past few years, ZnSe nanowires were prepared by laser ablation of ZnSe powder,[13] thermal evaporation in the presence of Au catalyst via the vapor–liquid–solid mechanism,[14] metallorganic chemical vapor deposition,[15] a thermochemical method,[16] laser-assisted catalytic growth,[17] and an atomic layer deposition process.[18] In addition, solvothermal processes have also been used to synthesize ZnSe nanorods,[19,20] nanowires,[21] nanoparticles,[22–24] and precursor.[25]

Herein, we report a method developed to prepare monodispersed ZnSe semiconductor nanorod aggregations. These aggregations were found to form through the aggregation of ZnSe nanorods, which were prepared via γ-ray irradiation. Se^{2-} was easily obtained in solution without added other reductive via γ-ray irradiation method at room temperature. Our study may provide a new method for direct growth of nanorod aggregations and related materials, and this method may offer a path for growth 3D nanostructured materials.

To prepare ZnSe nanorod aggregations, Na_2ZnO_2 (0.25 mmol), Na_2SeO_4 (0.25 mmol), and isopropyl alcohol (0.025 mol) were dissolved in water, and then pH of the solution was rapidly adjusted to a designed value using 10% NaOH solution. Water was added to the solution until final volume is 25 mL. After the solution transferred into a 50-mL autoclave and was bubbled with N_2 for 20 min to eliminate oxygen, it was sealed, irradiated in the field of a 2.22×10^{15} Bq ^{60}Co γ-ray source with 110 Gy/min and heated at 170 °C for 48 h. The system was then allowed to cool to room temperature. The final product was collected by filtration, washed with deionized water to remove any possible ionic remnants, and then dried at 60 °C.

Salts of ZnO_2^{2-} and SeO_4^{2-} ions were chosen as the source of Zn^{2+} and Se^{2-} ions, respectively. When solution was irradiated by γ-rays, sets of reactions could sequentially occur in the reaction system. In the procedures, several products were initially generated by the radiolysis in aqueous solution as follow:

$$H_2O \xrightarrow{\gamma\text{-rays irradiation}} H_3O^+(aq), \cdot OH, H\cdot, H_2O_2, H_2, e^-(aq) \quad (1)$$

In the presence of isopropyl alcohol, some oxidative radicals such as $\cdot$OH were scavenged in solution by the following reaction:

$$\cdot OH + CH_3CH(OH)CH_3 \rightarrow H_2O + (CH_3)_2(OH)C\cdot \quad (2)$$

Meanwhile, because of the produced reductive radicals (such as hydrated electron), the reductive atmosphere of the system was maintained, and several reactions sequentially occurred as follow:

$$SeO_4^{2-} + 6e^-(aq) + 8H_3O^+(aq) \rightarrow Se + 12H_2O \quad (3)$$

$$Se + 2e^-(aq) \rightarrow Se^{2-} \quad (4)$$

$$ZnO_2^{2-} + Se^{2-} + 4H_3O^+(aq) \rightarrow ZnSe + 6H_2O \quad (5)$$

The homogeneously dispersed SeO_4^{2-} reacted with the reductive particles (such as hydrated electron) to form elemental Se and further reduced to produce Se^{2-} ions in equations (3) and (4), which could react with ZnO_2^{2-} ions in solution to produce ZnSe nanoparticles in equation (5).

The product morphology was determined by scanning electron microscopy (SEM). Figure 1a is a typical SEM image of the products, clearly showing that ZnSe possesses an aggregation structure. Examining numerous SEM images of the sample prepared at 170 °C for 48 h, and the value pH is 14, all the particles are aggregations. It indicates that well-defined ZnSe aggregation nanostructures can be obtained under the present experimental conditions. The growth of the aggregations is rather unique. The individual ZnSe aggregation has three-dimensional (3D) structure. A higher magnification SEM image can clearly show their structure, as demonstrated in Figure 1b. The length and the diameter of the ZnSe nanorods are about 500–1000 and 30–60 nm, respectively.

The products were further characterized by transmission electron microscopy (TEM). A typical TEM image is shown in

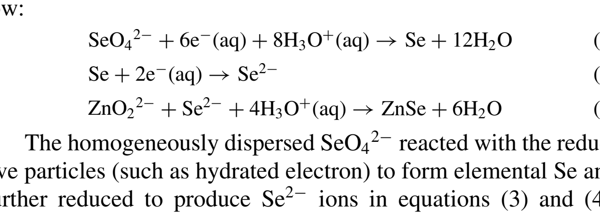

Figure 1. (a) SEM images of ZnSe nanostructures, (b) the high-magnification image of products.

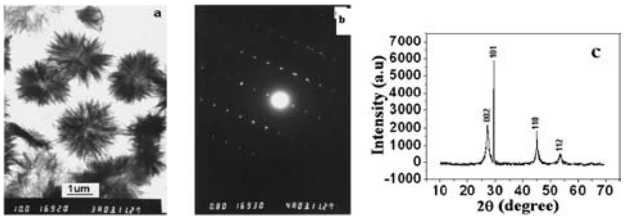

Figure 2. (a) TEM images of ZnSe nanostructures, (b) electron diffraction patterns of a individual ZnSe nanorod, (c) XRD patterns of products.

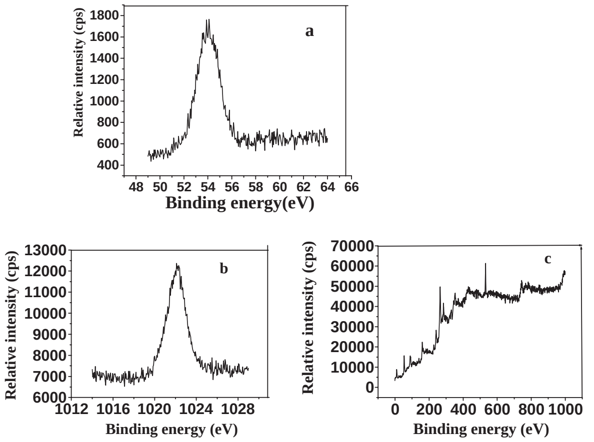

Figure 3. XPS spectra of an as-grown aggregations: (a) Se (3d) binding energy spectrum, (b) Zn (2p) binding energy spectrum, (c) survey spectrum.

Figure 2a, indicating that the ZnSe aggregations are indeed observed. This result is agreement with that observed from the SEM. Electron diffraction patterns (Figure 2b) taken from a single ZnSe nanorod reveal the single-crystalline nature of the sample, and can be indexed as the *c* axis of the hexagonal ZnSe, The ED pattern can be indexed as a hexagonal phase with lattice constants of $a = 0.401$ nm and $c = 0.651$ nm, which is consistent with the XRD results present below. X-ray diffraction (XRD) analysis was used to examine the crystal structure of the products.

The XRD pattern of the as-synthesized ZnSe nanostructures is shown in Figure 2c. From this figure, it is clear that the obtained product is pure-phase hexagonal system ZnSe. Which are consistent with the ideal values of wurtzite ZnSe (JCPDS Card: 5-115).

The composition of the products was analyzed by X-ray photoelectron spectroscopy (XPS), and the typical survey spectrum of the ZnSe nanostructure was shown in Figure 3c. The two strong peaks at about 54 and 1022 eV show the presence of the Se and Zn. Meanwhile, the spectra also reveal the existence of C and O due to the gaseous molecules absorbed from the surface of the products. Figure 3b is the spectrum for Se 3d (54.00 eV) core, which shows that no elemental selenium or SeO_2 was observed in the produced ZnSe nanostructure. The close-up spectrum of Zn was shown in Figure 3c, and the obtained value of the binding energy for $Zn_{2p}{}^{3}$ is 1022.20 eV. Peak areas of the measured Zn and Se cores were used to calculate the Zn/Se ratio for the ZnSe nanocrystallites. Molar ratio of the Zn/Se is about 0.912:1. This result shows that the γ-ray irradiation reductive ZnSe nanocrystallites are close to stoichiometric.

Hydrothermal methods have been shown to be effective in the preparation of nanowires, nanorods, and nanotubes.[26,27] The influence of chemical potential on the shape evolution of nanocrystals has been elucidated by Peng and Peng,[28] and in the case of one-dimensional nanostructure growth it would be advantageous to have a higher chemical potential, which is mainly determined by the pH value of the solution in our adopted reaction system.

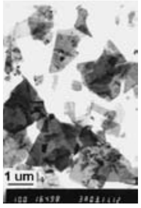

Figure 4. TEM image of the product prepared in the pH range of 10–11.

The influence of γ-ray irradiation on the formation of ZnSe nanorod aggregations was investigated; the control experiment was performed. The experiment was carried out keeping other reaction conditions as same without γ-ray irradiation; results show that ZnSe can not be obtained without reductive atmosphere of the system.

In order to investigate the influence of pH value on the formation of ZnSe nanorod aggregations, the control experiment was performed. The pH value of the solution is maintained between 10 and 11, the experiment was carried out keeping other reaction conditions as same. The pH value of the solution is not change after the solution was irradiated by γ-rays, only irregular flakes were obtained, as shown in Figure 4. This indicated that the pH value of the solution play important roles in the formation of well-defined ZnSe nanorods aggregations.

In summary, we have presented a simple hydrothermal process for preparing unusual ZnSe aggregation nanostructures via γ-ray irradiation. A possible mechanism for the formation has been proposed. However, the exact mechanism for the formation of ZnSe nanorod aggregations is still not fully understood, and further studies are needed to explain the observed phenomena. The experimental results (SEM, TEM) clearly show that the ZnSe nanostructures prepared in the present study is aggregations, consisting of ZnSe nanorods. Our study may provide a new method for direct growth of nanorods and related materials, and this method may offer a path for growth 3D nanostructured materials.

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