One-step Synthesis of Single-crystalline CdSe Nanorods via γ-Ray Irradiation

Qingchun Zhao,* Wenming Chen, and Qingren Zhu
Department of Material Science and Techonolgy, Anhui Institute of Architecture & Industry,
Hefei 230022 Anhui, P. R. China

(Received March 18, 2004; CL-040304)

High aspect ratio single-crystalline CdSe micrometer rods with a uniform and smooth surface texture are synthesized via γ-ray irradiation at 170 °C. The length of the rods and the diameter of the CdSe micrometer rods are about tens micron and 240–300 nm, respectively.

One-dimensional (1D) nanostructures, such as nanowires, nanorods, 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.[1] 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.[2–4] 1D nanostructures are also ideal systems for investigating the dependence of electrical transport, optical properties, and mechanical properties on size and dimensionality.[5]

1D nanostructured materials, including metals and alloys,[6–8] oxides,[9,10] semiconductors,[11,12] inorganic salts,[13] have been successfully synthesized via chemical vapor deposition,[14] templates,[15] hydrothermal,[16] wet chemistry,[6–8] laser ablation,[17] self-assembled process.[18] CdSe nanorods[19] came to be exciting materials because of some important properties: up to 100% polarized luminescence.[20] In this communication, we report single-crystalline CdSe nanorods that have been synthesized via γ-ray irradiation. This method for the synthesis of rod-like CdSe particles is simple, inexpensive, and without an extremely dangerous organomrtallic.

To prepare CdSe micrometer rods $CdCl_2$ (0.00025 mol), Na_2SeO_4 (0.00025 mol), and isopropyl alcohol (0.025 mol) were dissolved in water. 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 and irradiated by γ rays with 110 Gy/min, heating at 170 °C for 48 h. The system was then allowed to cool to room temperature. The final product was collected by filtration, and washed with deionied water to remove any possible ionic remnants, and then dried at 60 °C.

Salts of Cd^{2+} and $SeO_4{}^{2-}$ ions were chosen as the source of Cd^{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 follows:

$$H_2O \xrightarrow{\gamma\ \text{irradiation}} H_3O^+{}_{aq},\ OH,\ H,\ H_2O_2,\ H_2,\ e^-{}_a \qquad (1)$$

In the presence of isopropyl alcohol, some oxidative radicals such as OH were scavenged in solution owing to the following reaction:

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

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 follows:

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

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

$$Cd^{2+} + Se^{2-} \rightarrow CdSe \qquad (5)$$

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 Eqs 3 and 4, which could react with Cd^{2+} ions in solution to produce CdSe nanoparticles in Eq 5. It is impossible to produce comparable rod-like CdSe particles without the irradiation of γ-rays under otherwise the same conditions and even a temperature higher than 170 °C.

The concentration of $Cd^{2+}$and $SeO_4{}^{2-}$ was found to play a significant role in the formation and growth of the CdSe nanoparticles. Figure 1 is a typical SEM image of the products, clearly showing that CdSe possesses micrometer-sized rod structures. Examining numerous SEM images of the sample prepared at 170 °C for 48 h, most of the particles are micrometer rods with a uniform and smooth surface texture. The products were further characterized by transmission electron microscopy (TEM). A typical TEM image is shown in Figure 2a, indicating that the micrometer-sized CdSe micrometer rods are indeed observed. The length of the rods is about several hundreds micron and the rods can be seen by microscopy. This result is agreement with that ob-

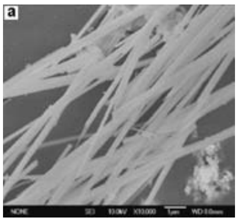

Figure 1. SEM images of CdSe micrometer rods.

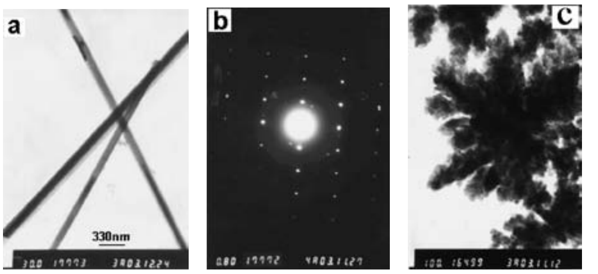

Figure 2. TEM images of CdSe nanoparticles.

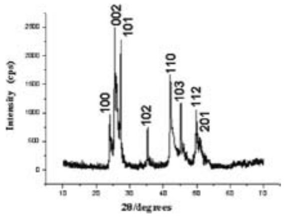

Figure 3. XRD patterns of products.

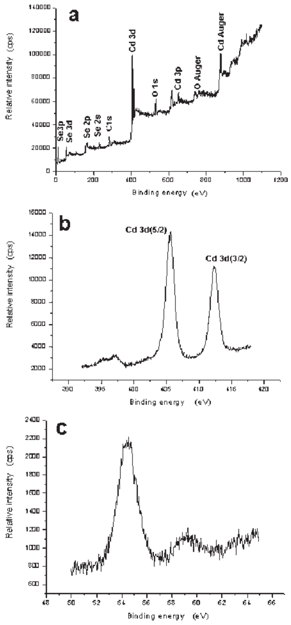

Figure 4. XPS spectra of an as-grown CdSe micrometer rods: (a) survey spectrum; (b) Cd (3d) binding energy spectrum; (c) Se (3d) binding energy spectrum.

served from the SEM. Electron diffraction patterns (Figure 2b) taken from a single CdSe micrometer rods reveal the single-crystalline nature of the sample, and can be indexed as the *c* axis of the hexagonal CdSe, which is consistent with the XRD results present below. Figure 2c shows a TEM image of the product obtained by irradiating the solution containing $0.02\,\mathrm{mol\,L^{-1}}$ of $CdCl_2$ and $0.02\,\mathrm{mol\,L^{-1}}$ of Na_2SeO_4 at 170 °C for 48 h. The obtained products are the dendritic structures of the CdSe clusters. It indicates that well-defined CdSe micrometer rods can be obtained under the presented experimental conditions. We believe that the excess of Cd^{2+} in the solution may be favorable for the aggregation and growth into the dendritic structures of the CdSe clusters.

If the reaction took place at room temperature, the spherical particles can be obtained.[21] The growth of such anisotropic structure should require a relatively high chemical potential.

X-ray diffraction (XRD) analysis is used to examine the crystal structure of the products. The XRD pattern of the as-synthesized CdSe nanostructures is shown in Figure 3. From this figure, it is clear that the obtained product is pure-phase wurtzite crystal structure with lattice parameters close to the reported data (JCPDS 5-0596), and is preferentially oriented in the *c* axis direction.

The composition of the products is analyzed by X-ray photoelectron spectroscopy (XPS) and the typical survey spectrum of the CdSe nanostructure was shown in Figure 4a. The two strong peaks at about 54 and 405 eV show the presence of the Se and Cd. Meanwhile, the spectra also reveal the existence of C and O due to the gaseous molecules absorbed from the surface of the products. Figure 4b is the spectrum for Se 3d (54.00 eV) core, which shows that no elemental selenium or SeO_2 was observed in the produced CdSe nanostructure. The close-up spectrum of Cd was shown in Figure 4c and the obtained value of the binding energy for Cd $2d_{5/2}$ is 405.05 eV. Peak areas of the measured Zn and Se cores were used to calculate the Cd/Se ratio for the CdSe nanocrystallites. Molar ratio of the Cd/Se is about 0.972:1. This result shows that the γ-ray irradiation reductive CdSe nanocrystallites are close to stoichiometric.

References

1 G. R. Patzke, F. Krumeich, and R. Nesper, *Angew. Chem., Int. Ed.*, **41**, 2447 (2002).
2 X. F. Duan, Y. Huang, Y. Cui, J. F. Wang, and C. M. Lieber, *Nature*, **409**, 66 (2001).
3 W. Wong, E. Sheehan, and P. Lieber, *Science*, **277**, 1971 (1997).
4 M. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, and P. Yang, *Science*, **292**, 1897 (2001).
5 P. Yang, Y. Wu, and R. Fan, *Int. J. Nanosci.*, **1**, 1 (2002).
6 M. P. Zach, K. H. Ng, and R. M. Penner, *Science*, **290**, 2120 (2000).
7 B. Mayers, B. Gates, Y. Yin, and Y. Xia, *Adv. Mater.*, **13**, 1380 (2001).
8 C. J. Murphy and N. R. Jana, *Adv. Mater.*, **14**, 80 (2002).
9 M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, and P. Yang, *Science*, **292**, 1897 (2001).
10 X. Wang and Y. Li, *J. Am. Chem. Soc.*, **124**, 2880 (2002).
11 W. U. Huynh, J. J. Dittmer, and A. P. Alivisatos, *Science*, **295**, 2425 (2002).
12 V. F. Puntes, K. M. Krishnan, and A. P. Alivisatos, *Science*, **291**, 2115 (2001).
13 D. B. Kuang, A. W. Xu, Y. P. Fang, H. D. Ou, and H. Q. Liu, *J. Cryst. Growth*, **244**, 379 (2002).
14 Z. W. Pan, Z. R. Dai, and Z. L. Wang, *Appl. Phys. Lett.*, **80**, 309 (2002).
15 F. Gao, Q. Lu, X. Liu, Y. Yan, and D. Zhao, *Nano Lett.*, **1**, 743 (2001).
16 W. Xun, X. M. Sun, D. P. Yu, B. S. Zou, and Y. D. Li, *Adv. Mater.*, **15**, 1442 (2003).
17 A. M. Morales and C. M. Lieber, *Science*, **279**, 208 (1998).
18 K. K. Caswell, J. N. Wilson, U. H. F. Bunz, and C. J. Murphy, *J. Am. Chem. Soc.*, **125**, 13914 (2003).
19 X. Peng, L. Manna, W. Yang, J. Wickham, E. Scher, A. Kadavanich, and A. P. Alivisatos, *Nature*, **404**, 59 (2000).
20 X. Chen, A. Nazzal, D. Goorskey, M. Xiao, Z. A. Peng, and X. Peng, *Phys. Rev. B*, **64**, 245304 (2001).
21 Q. Yang, K. Tang, F. Wang, C. Wang, and Y. Qian, *Mater. Lett.*, **57**, 3508 (2003).

Published on the web (Advance View) December 22, 2004; DOI 10.1246/cl.2005.120