Inorg. Chem. **2005**, *44*, 7280–7282

Room-Temperature Irradiation Route To Synthesize a Large-Scale Single-Crystalline ZnO Hexangular Prism

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Received June 6, 2005

A large-scale single-crystalline ZnO hexangular prism was successfully synthesized through a simple γ-irradiation method at room temperature and under ambient pressure. The product of a ZnO hexangular prism with a rim of 230 ± 10 nm and a length up to 8.5 μm was well monodisperse and showed a very strong and broad green light emission at around 577 nm. A possible formation process was also proposed.

One-dimensional (1D) semiconductor nanostructures have been extensively studied for their potential applications in manufacturing electronic and optoelectronic devices.[1−3] Zinc oxide (ZnO) is a unique material that exhibits semiconducting, piezoelectric, and pyroelectric multiple properties because of its wide direct band gap (3.37 eV) and a relatively large excitation binding energy (60 meV). Since Yang et al. reported that ZnO 1D materials have possible application as an ideal miniaturized laser light source, many methods have been proposed to synthesize ZnO nanorods or nanowires.[4] For example, the methods of catalytic growth,[5] microemulsion hydrothermal processing,[6−9] high-temperature physical evaporation,[10] high-temperature decomposition, and template-oriented growth etc.,[11−14] are effective to prepare ZnO nanorods.

However, the high-temperature or hydrothermal method is unfavorable to make ZnO nanorods at lower cost (the problems with scale-up and high-energy consumption), and the employment of catalysts or a template brings impurities into the desired products. So, the preparation of ZnO nanorods with high purity and at low cost calls for a simpler, low-temperature, and more tractable route. In this Communication, we report a novel approach to prepare monodisperse and uniform, large-scale, single-crystal ZnO hexangular prisms through a one-step γ-irradiation route at room temperature and under ambient pressure.

In a typical procedure, first, analytically pure 0.72 g of $ZnSO_4 \cdot 7H_2O$ was dissolved into 50 mL of distilled water, 10 mL of 5 M NaOH and 0.8 g of cetyltrimethylammonium bromide (CTAB) were added in succession, and then the mixed solution was intensively stirred for 0.5 h at room temperature. To scavenge oxidative radicals such as hydroxyl radicals ($^{\bullet}$OH) produced during the irradiation, isopropyl alcohol (15 mL) was also added into the system.[15,16] Finally, the mixed transparent solution was placed in the field of a 2.22×10^{15} Bq ^{60}Co γ-ray source with the absorption dose of 100 kGy at the dose rate of 50 Gy/min. After irradiation, the white precipitates were collected, washed with ethanol and distilled water several times, and then dried in the oven at 60 °C.

The composition and the phase of these as-prepared products were determined by X-ray powder diffraction (XRD), using a Philip X'Pert PRO SUPER γA rotation anode with Cu Kα radiation (λ = 1.541 87 Å) at 25 °C. Figure 1 shows the XRD pattern of as-prepared ZnO samples. All of the peaks of the nanorods can be indexed to wurtzite (hexagonal) structured ZnO (JCPDS card No. 05-0664) with cell parameters a = 3.249 Å and c = 5.205 Å. No characteristic peak was observed for other impurities such

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10.1021/ic050909o CCC: $30.25
Published on Web 09/23/2005

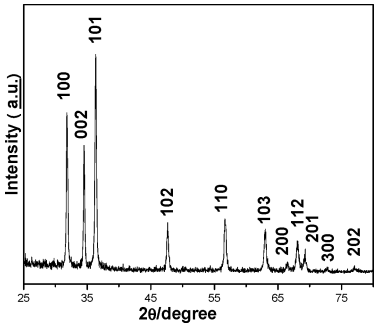

Figure 1. XRD pattern of an as-prepared ZnO hexangular prism.

as $Zn(OH)_2$, etc. A general overview field-emission scanning electron microscope (FESEM; JEOL JSM-6700F SEM) image in Figure 2a shows that the product is completely composed of a hexangular prism with a rim of 230 ± 10 nm and a length up to 8.5 μm. The areas of the rectangle (Figure 2a) are shown enlarged in parts b and c of Figure 2. From these, we can further clearly see that the samples are composed of uniform hexangular prism structure rods with a partly oriented and ordered array in the sections.

Further morphology characterization of the ZnO samples was performed on a transmission electron microscope (TEM; Hitachi model H-800) as shown in Figure 2d, which agrees with the FESEM results. Figure 2e shows a representative high-resolution transmission electron micrograph (HRTEM; JEOL 2010) image of a single rod. The clear lattice fringes further confirm that the product is a single crystal. The fringe spacing is about 0.52 nm, which is close to the separation between the (0001) lattice planes. This means that the axial direction of the as-prepared sample is perpendicular to the normal direction of the (0001) lattice plane of the hexagonal ZnO. Electron diffraction (ED) pattern (inset in Figure 2e) also verifies that the as-prepared products are single crystals of hexagonal ZnO, which is in agreement with the XRD pattern result.

To substantially understand the effect of CTAB on the formation of a ZnO hexangular prism, the experiments according to the change of irradiation time and the condition without CTAB were carried out, respectively. TEM images (JEOL 2011) of ZnO rods, which were prepared in the γ-ray

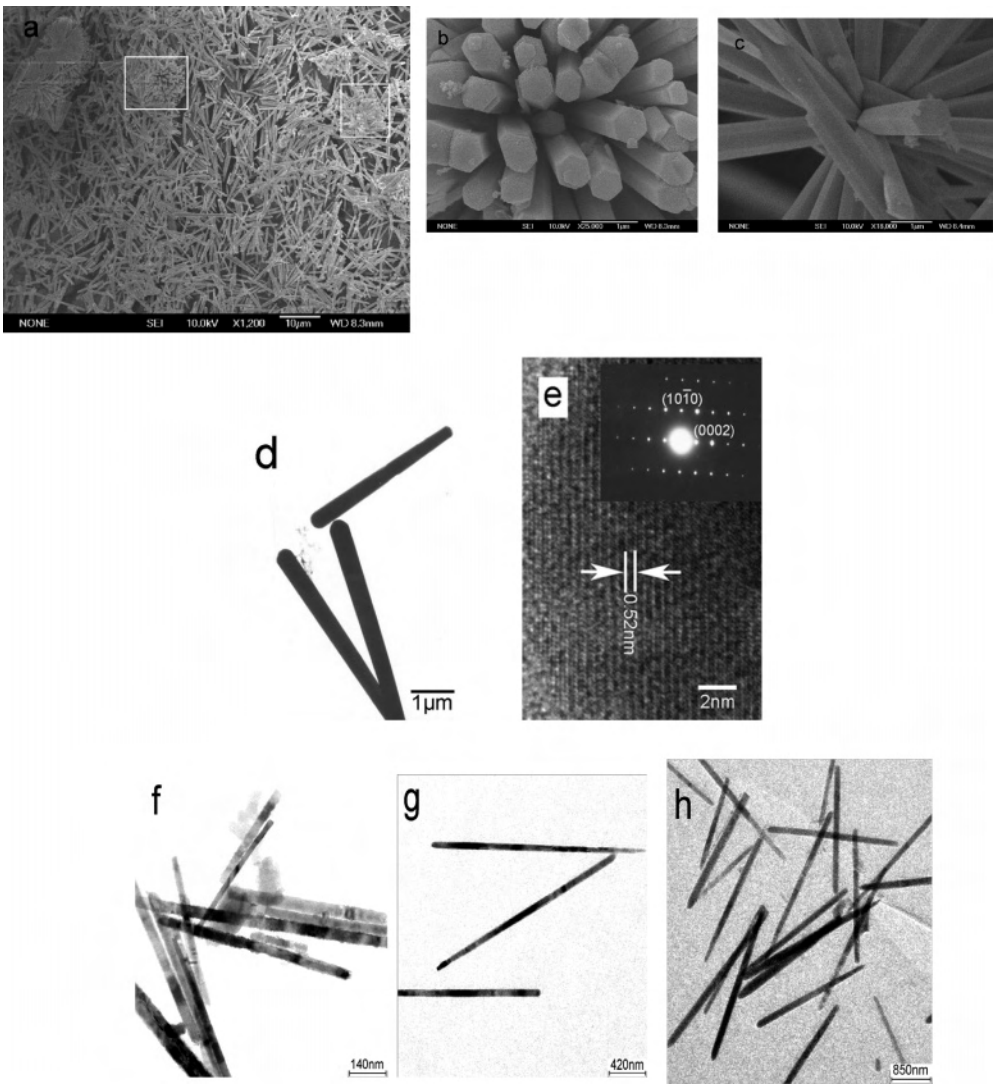

Figure 2. (a) FESEM image of an as-prepared ZnO hexangular prism. The areas of the rectangle are shown enlarged in parts b and c. (d) TEM image and (e) HRTEM image of a ZnO hexangular prism (inset: ED pattern). TEM images of ZnO rods prepared in the γ-ray source at the dose rate of 50 Gy/min after 16, 20, and 22 h are shown in parts f−h, respectively.

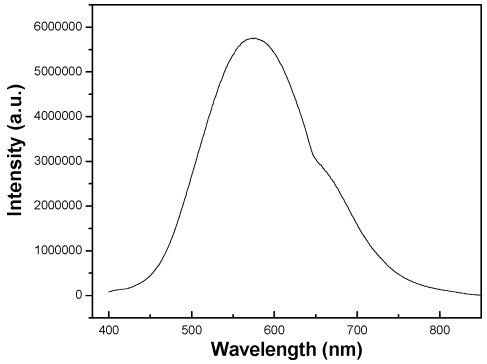

Figure 3. Room-temperature PL spectrum of a ZnO hexangular prism.

source at the dose rate of 50 Gy/min after 16, 20, and 22 h are shown in parts f−h of Figure 2. It has been found that the ZnO rods grow from thinner to thicker with an increase of time in the existence of CTAB. Meanwhile, only a ZnO conglomeration was formed while the solution was irradiated without CTAB. So, the effect of a structure-directing agent of CTAB is evident and necessary.

Room-temperature photoluminescence (PL) of the as-grown products was recorded on a Jobin Yvon−Labram spectrometer with a He−Cd laser, and the PL spectrum of the ZnO hexangular prism is shown in Figure 3, which was obtained with an excitation wavelength of 363 nm. A very strong and broad green light emission at around 577 nm was observed. The green emission peak is commonly referred to as a deep level of trap-state emission. The green transition has been attributed to the singly ionized oxygen vacancy in ZnO, and the emission results from the radiative recombination of a photogenerated hole with an electron occupying the oxygen vacancy.[17] The stronger the intensity of the green luminescence, the more the singly ionized oxygen vacancies. Thus, there is a great fraction of oxygen vacancies in the ZnO hexangular prism.

For the growth process of the as-produced crystals, a possible formation process of ZnO hexangular prisms was suggested as follows. According to the experimental route, first, a Zn^{2+} salt solution reacts with superfluous OH^- to form a transparent $Zn(OH)_4^{2-}$ solution.[18]

$$Zn^{2+} + 2OH^- \leftrightarrow Zn(OH)_2 \quad (1)$$

$$Zn(OH)_2 + 2OH^- \leftrightarrow [Zn(OH)_4]^{2-} \quad (2)$$

Then, the mixed transparent solution with isopropyl alcohol was irradiated by γ-ray. As is understood, lots of species were generated during the radiolysis of the aqueous solution, and at the same time, an oxidative species, e.g., $^{\bullet}OH$, was scavenged by isopropyl alcohol.[15]

$$H_2O \rightsquigarrow e_{aq}^-, H_3O^+, H^{\bullet}, H_2, {}^{\bullet}OH, H_2O_2 \quad (3)$$

Here, the symbol $\rightsquigarrow$ stands for irradiation and e_{aq}^- represents a hydrated electron.

Because the pH value of the solution is alkaline, among the remaining reductive species, e_{aq}^- is predominant. e_{aq}^- (a standard redox potential of −2.77 V[16]) could easily reduce $Zn(OH)_4^{2-}$ into Zn (a standard redox potential of −1.215 V in a basic solution) (eq 4).

$$Zn(OH)_4^{2-} + 2e_{aq}^- \rightarrow Zn + 4OH^- \quad (4)$$

$$2Zn + O_2 \rightarrow 2ZnO \quad (5)$$

The yielded Zn atoms were very active, while when they encountered oxygen (dissolved in the solution and also coming from H_2O_2 dissociation), the oxidative−reductive reaction would take place and produce ZnO (eq 5). CTAB is a kind of cationic surfactant, while in existence with a hydrotropic salt, it can naturally form a rodlike micelle (also a wormlike shape). During the production of ZnO, the structure-directing agent of CTAB in the solution make the ZnO seed crystal grow along a certain orientation to form hexangular prism rods. In the end, the hexangular prism ZnO nanocrystals were obtained.

In summary, monodisperse and uniform ZnO hexangular prisms have been successfully prepared in a CTAB solution system by a simple γ-irradiation method at room temperature and under ambient pressure. To the best our knowledge, this is the first time a ZnO single crystal is synthesized under these mild conditions by γ-ray. The possible growth mechanism has also been proposed. The successful preparation of a ZnO hexangular prism in large scale under mild conditions could be of interest for both applications and fundamental studies.

Acknowledgment. This work was financially supported by grants of the Department of Basic Research, MOST, People's Republic of China, grants-in-aids for special projects of significant basic research (Grant 2003CCA03700), and the National Science Foundation of China.

IC050909O

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