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Hydrothermal Synthesis of Ultralong and Single-Crystalline $Cd(OH)_2$ Nanowires Using Alkali Salts as Mineralizers

Bo Tang,* Linhai Zhuo, Jiechao Ge, Jinye Niu, and Zhiqiang Shi

College of Chemistry, Chemical Engineering and Materials Science, Shandong Normal University, Jinan 250014, China

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Ultralong and single-crystalline $Cd(OH)_2$ nanowires were fabricated by a hydrothermal method using alkali salts as mineralizers. The morphology and size of the final products strongly depend on the effects of the alkali salts (e.g., KCl, KNO_3, and K_2SO_4 or NaCl, $NaNO_3$, and Na_2SO_4). When the salt is absent, only nanoparticles are observed in TEM images of the products. The 1D nanostructure growth method presented herein offers an excellent tool for the design of other advanced materials with anisotropic properties. In addition, the $Cd(OH)_2$ nanowires might act as a template or precursor that is potentially converted into 1D cadmium oxide through dehydration or into 1D nanostructures of other functional materials (e.g., CdS, CdSe).

One-dimensional (1D) nanoscale materials have stimulated great interest recently both because of their unique electronic, optical, and mechanical properties and because of their potential application in nanodevices.[1−7] Many attempts have been made to synthesize one-dimensional nanostructured materials.[1−10] Of the methods used in 1D nanostructure synthesis, hydrothermal processes have emerged as powerful tools for the fabrication of anisotropic nanomaterials with some significant advantages, such as controllable particle size and low-temperature, cost-effective, and less-complicated techniques. Under hydrothermal conditions, many starting materials can undergo quite unexpected reactions, which are often accompanied by the formation of nanoscopic morphologies that are not accessible by classical routes. In recent years, 1D nanomaterials such as $Ln(OH)_3$,[11,12] $CdWO_4$,[13] MoO_3,[14] $Dy(OH)_3$,[15] and others have been successfully synthesized using hydrothermal methods. $Cd(OH)_2$ is an important precursor that is potentially converted into cadmium oxide through dehydration or into other functional materials (e.g., CdS, CdSe) by reaction with appropriate elements or compounds. In this communication, we report a facile hydrothermal method for the direct growth of ultralong and single-crystalline $Cd(OH)_2$ nanowires using alkali salts as mineralizers.

In a typical procedure, $Cd(NO_3)_2{\cdot}2H_2O$ (0.001 mol) was dissolved in deionized water (20 mL), and then 3.00 mL of 5.0% KOH was rapidly added to the solution under stirring vigorously. A white precipitate appeared immediately. After the mixture had been stirred for about 10 min, the precipitate was washed with deionized water by centrifugation five times and then transferred into a 20-mL Teflon-lined autoclave that was filled with deionized water up to 80% of the total volume. Before the autoclave was sealed, 0.30 g of $NaNO_3$ was added to the system and agitated to be soluble. The system was heated at 250 °C for about 12 h and then cooled to room temperature. The final products were collected by centrifugation, washed with distilled water and ehanol, and then vacuum-dried at room temperature for 12 h.

Phase identification of the sample was carried out using a Rigaku D/Max-rB X-ray powder diffraction (XRD) instrument with Cu $K\alpha_1$ radiation ($\lambda = 1.5406$ Å). Figure 1 shows a typical XRD pattern of the $Cd(OH)_2$ nanowires. The average $Cd(OH)_2$ lattice constants obtained by refinement of the XRD data are $a = 3.4947$ Å and $c = 4.7106$ Å, which are consistent with the values for bulk $Cd(OH)_2$ (JCPDS31-228).

* To whom correspondence should be addressed. E-mail: tangb@sdnu.edu.cn.

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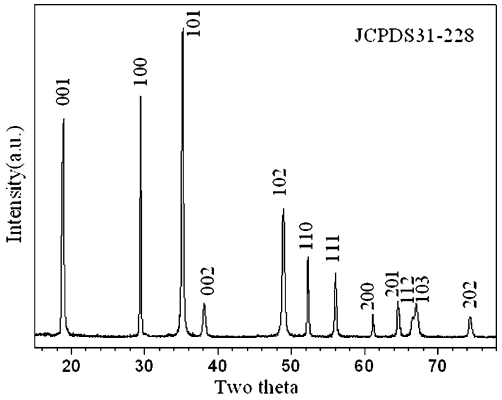

Figure 1. X-ray diffraction pattern of the as-prepared $Cd(OH)_2$ nanowires.

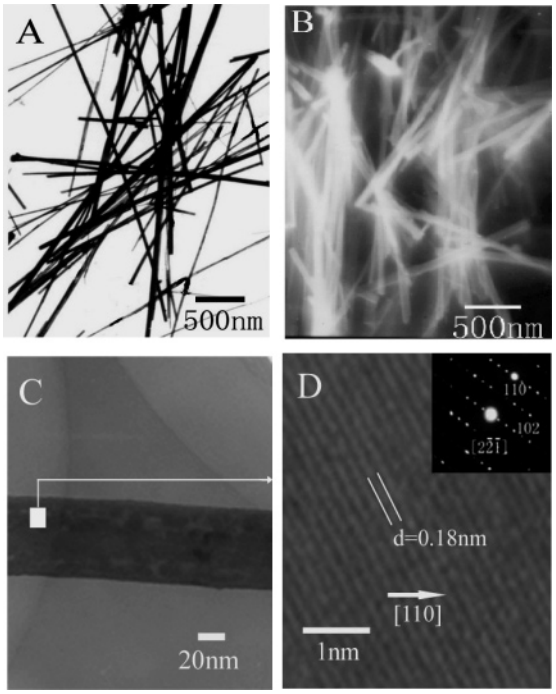

Figure 2. (A) TEM image of $Cd(OH)_2$ nanowires. (B) SEM image of $Cd(OH)_2$ nanowires. (C) TEM image of a single $Cd(OH)_2$ nanowire. (D) HRTEM image of the rim part of the nanowire wall with clearly resovled lattice fringes. The inset in Figure 2D is the SAED pattern recorded from the same nanowire.

The morphology of the samples was characterized using a Hitachi H-800 transmission electron microscope (TEM) and a JEOLJEM-2010F high-resolution transmission electron microscope (HRTEM). Typical images of the nanowires are shown in Figure 2. The average diameter of these uniform nanowires was about 70 nm, and the length of the nanowires reached several hundreds of microns. As can be seen from Figure 2A and C, the surfaces of these nanowires are smooth. The morphology of the sample was further examined by scanning electron microscope (SEM; Figure 2B). Both the size and morphology determined by SEM are similar to the TEM results. Figure 2D shows an HRTEM image of a selected area from a single $Cd(OH)_2$ nanowire in Figure 2C. The HRTEM image of the nanowire shows a fringe spacing (ca. 0.18 nm) that agrees well with the separation between the (1 0 2) lattice planes of hexagonal $Cd(OH)_2$. The nanowires grew along the [1 1 0] direction. A selected area electron diffraction (SAED) pattern indicating the single-crystalline nature of the sample is shown in Figure 2D; it was obtained by focusing the electron beam along the [2 $\bar{2}$ $\bar{1}$] direction. The clear lattice fringes together with the SAED pattern confirm that these nanowires are single-crystalline.

The morphology of the white precipitate before being subjected to the hydrothermal process was shown to be aggregates of nanoparticles together with a small quantity of nanoneedles, which indicates that the subsequent hydrothermal process involves a process of recrystallization. Control experiments were carried out to investigate the influence of pH in our system. If excess hydroxyl ions were present in the system, no nanowires could be obtained. Another experiment was also performed in which KOH was used as the mineralizer nanowires could not be obtained in this case either. In the experiments, the morphology and size of the $Cd(OH)_2$ was found to depend strongly on the effects of the alkali salts. When the salt is absent, only nanoparticles are observed in the TEM images of the products. Thus, the presence of the salts is one of the important factors influencing the recrystallization process and the growth of the $Cd(OH)_2$ nanowires. One effect of these salts is to increase the chemical potential of the solution, and higher chemical potential conditions would be advantageous for one-dimensional nanostructure growth.[11] Moreover, the addition of salts can significantly decrease the viscosity of the solution, which increases the mobility of the components in the system and allows atoms, ions, or molecules to adopt appropriate positions in developing crystal lattices.[16] Thus, the addition of salts can provide a favorable environment for the growth of nanowires in our system.

In summary, high-aspect-ratio, single-crystalline $Cd(OH)_2$ nanowires have been synthesized by a facile hydrothermal method. The 1D nanostructure growth method presented herein offers an excellent tool for the design of other advanced materials with anisotropic properties. In addition, the $Cd(OH)_2$ nanowires might act as precursors or templates that are potentially converted into 1D cadmium oxide through dehydration[11] or into 1D nanostructures of other functional materials (e.g., CdS, CdSe) by reaction with appropriate elements or compounds according to the method of template-directed synthesis though which single-crystalline nanowires of Ag_2Se have been synthesized by templating against nanowires of trigonal Se.[17]

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