DOI: 10.1002/ejic.200600369

Preparation of ZnO Nanowires in a Neutral Aqueous System: Concentration Effect on the Orientation Attachment Process

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Keywords: Zinc oxide / Orientation attachment / Self-assembly / Nanostructures

ZnO nanowires with diameters in the range of 10 to 30 nm and lengths of ca. several micrometers are prepared with the use of ZnO nanoparticles as building blocks. The length and diameter of the ZnO nanowires can be controlled by the variation of the concentration of the nanoparticles in the orientation attachment process. A plausible mechanism for the concentration-controlled orientation attachment process is suggested.

Introduction

The preparation of nanostructures with control of their size, shape, and crystalline structure has been one of the main objectives in the chemistry of nanomaterials.[1–5] Nanoparticles can be used as building blocks to obtain well-defined assemblies and superstructures, which can lead to novel and unique properties that are not found in the individual components.[6–7] Orientation attachment has attracted increased interest in recent years as a new means for the fabrication and self-organization of nanocrystalline materials.[8] Recent work has shown the universality of the orientation attachment in the formation and growth of nanocrystals.[9–14] To find a facile method that can precisely control the morphology of low dimensional nanostructures through the mastery of the orientation attachment process is still a challenge.

ZnO is an environmentally friendly transparent semiconductor with a large bandgap of 3.37 eV and it exhibits various distinct properties.[15–17] One-dimensional (1D) ZnO is a focused material, which allows it to possess excellent optical properties.[18] Various methods have been successfully utilized to synthesize 1D ZnO.[19–27] For the reported solution method, a basic environment is necessary to induce 1D growth of the ZnO particles in the nanoscale range.[14,24,27–32] Generally, the common formation mechanisms of 1D ZnO involve the vapor–liquid–solid (VLS) growth model,[26] and the Oswald ripening growth model.[27] The VLS process seems to be the most successful for the generation of 1D structures among all of the vapor-based methods. The Oswald ripening phenomenon is a classical crystal-growth method which describes the growth of the crystal in terms of the Gibbs-Thompson equation. The formation of ZnO nanorods on the basis of the orientation attachment process has only recently been demonstrated.[14] Other metal oxide (e.g. TiO_2 and CuO) nanorods have also been prepared by the orientation attachment of nanoparticles.[33–34] In this work, we provide an easy method for the preparation of ZnO nanowires in a neutral aqueous system by the careful control of the orientation attachment of the ZnO nanoparticles. A mechanism for the formation and growth of the low-dimensional nanostructure, which is critical to understand in order to achieve control over the morphology of the nanostructure, and the properties of the structure at the nanoscale level are discussed.

Results and Discussion

Figure 1 shows the SEM image of 1D ZnO obtained by the hydrothermal treatment of ZnO colloidal nanoparticles at a concentration of 0.8 g/L. The ZnO nanowires are several micrometers in length and vary in diameter from 10 to 30 nm. The curvature of the wire implies that there is some flexibility in the backbone of the ZnO nanowires. Figure 1B shows the TEM image of an individual ZnO nanowire with a diameter of ca. 15 nm and a length of ca. 2.3 μm. The inset in Figure 1C displays the selected area electron diffraction (SAED) pattern of an individual ZnO nanowire. The SAED pattern reveals the single-crystalline nature of the ZnO nanowires. Figure 1D shows the HRTEM image of the ZnO nanowire that is shown in Figure 1C. The image indicates that the preferred direction of growth of the ZnO nanowires is [0001]. The morphology of 1D ZnO is strongly dependent on the concentration of the ZnO colloidal nanoparticles. When the concentration of the ZnO nanoparticles is increased to 4 g/L, ZnO nanorods with lengths that vary from 200 to 800 nm and diameters

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Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

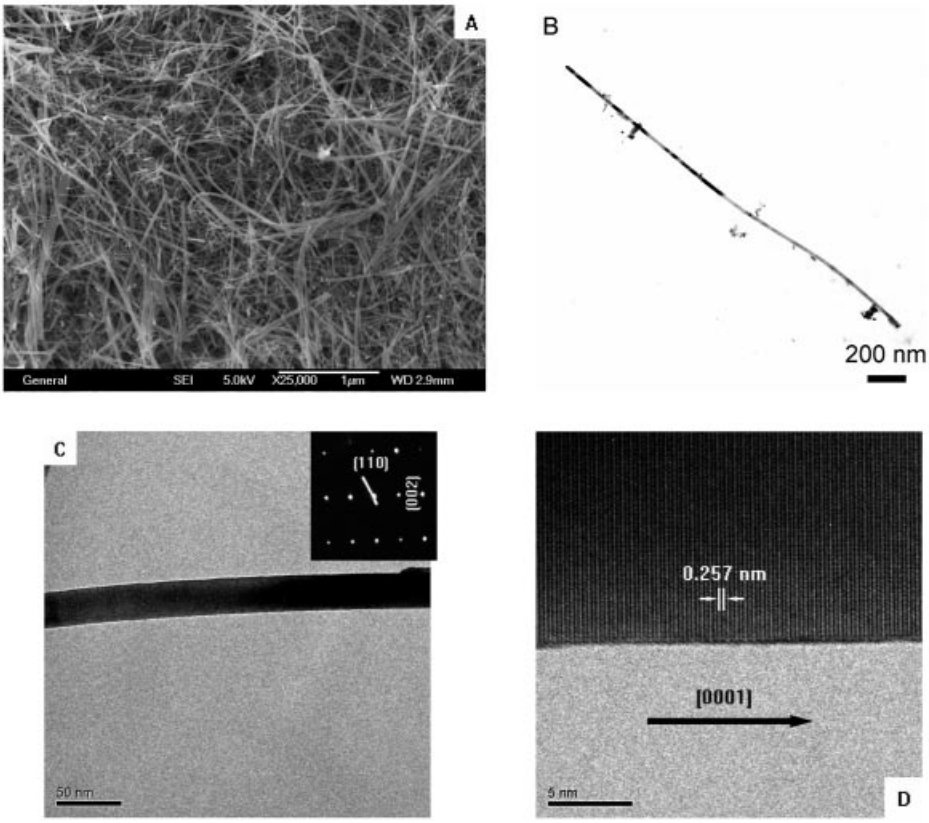


Figure 1. (A) SEM image of ZnO nanowires, (B) and (C) TEM images of ZnO nanowires (inset displays SAED pattern), (D) HRTEM of ZnO nanowires.

that vary from 20 to 40 nm are obtained (see Supporting Information). When the concentration is increased to 16 g/L, ZnO nanorods with smaller aspect ratios are obtained. The diameters of these nanorods vary from 30 to 50 nm and the lengths vary from 60 to 200 nm (see Supporting Information). The narrow distribution of the diameter of the ZnO nanowires is also indicated by the X-ray diffraction (XRD) line broadening. Figure 2 shows the XRD patterns for 1D ZnO obtained at different concentrations of the nanoparticles. All diffraction peaks can be well-indexed to hexagonal phase zinc oxide (JCPDC card No. 36–1451). The diameters estimated from the Debey-Scherrer formula on the basis of the full width of the peak at half-maximum height are 21.0 nm, 28.9 nm, and 48.2 nm obtained by the hydrothermal treatment of 0.8 g/L, 4.0 g/L, and 16.0 g/L ZnO colloidal nanoparticles, respectively. These values are consistent with the SEM observation.

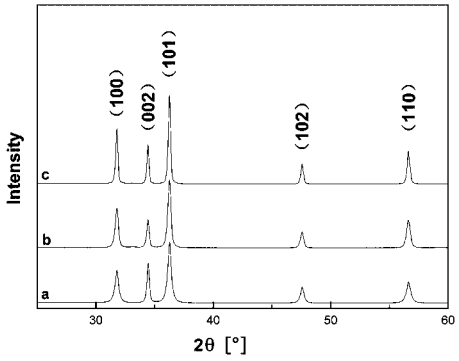


Figure 2. XRD patterns for 1D ZnO obtained by the hydrothermal treatment of (a) 0.8, (b) 4.0, and (c) 16.0 g/L ZnO colloids.

The orientation attachment of the ZnO nanoparticles in the preparation of the ZnO nanowires is observed after 1 h of hydrothermal treatment. Two primary nanoparticles attach to each other along the *c*-axis as shown in Figure 3A and Figure 3B. The nanoparticles may attach to each other along other axes as demonstrated by Pacholski and coworkers,[14] although we did not observe such a phenomenon. The orientation attachment is fundamentally driven by the high surface-energy (3.5 nm) of the ZnO nanoparticles. However, a decrease in the high surface-energy is observed upon the formation of 1D ZnO because there is a reduction in the surface-to-volume ratio. An important characteristic of ZnO is its polar surface. The oppositely charged ions produce positively charged Zn-(001) and negatively charged O-(00–1) polar surfaces, which results in a normal dipole moment and spontaneous polarization along the *c*-axis.[20] The electric dipole moments along the *c*-axis favor the orientation attachment in this direction. According to the model proposed by Penn,[35] the stability constant for the particle encounter complex (K_{os}) can be used to estimate the rate of crystal growth by the orientation attachment. High values of K_{os} tend to favor the orientation attachment process. In a previous report,[14] a high concentration of the ZnO colloid was necessary to form

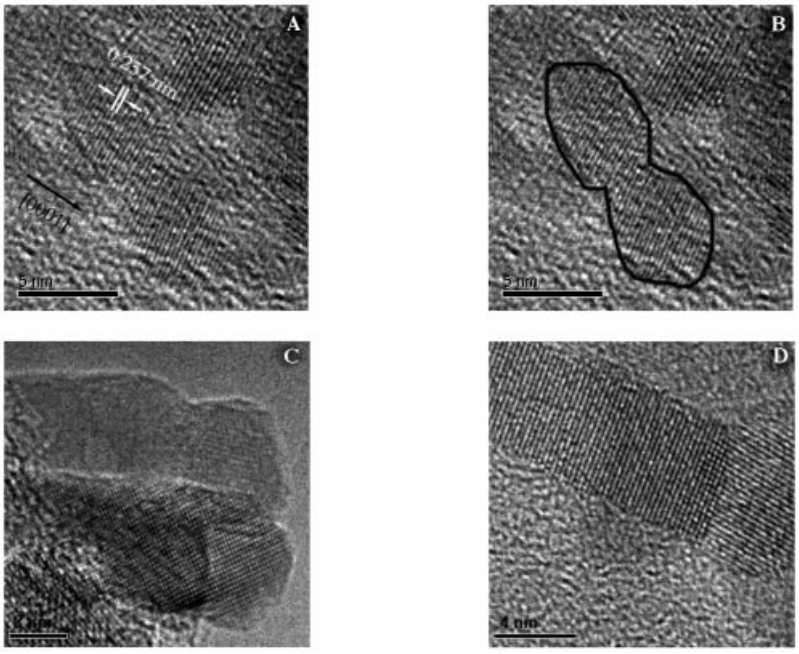
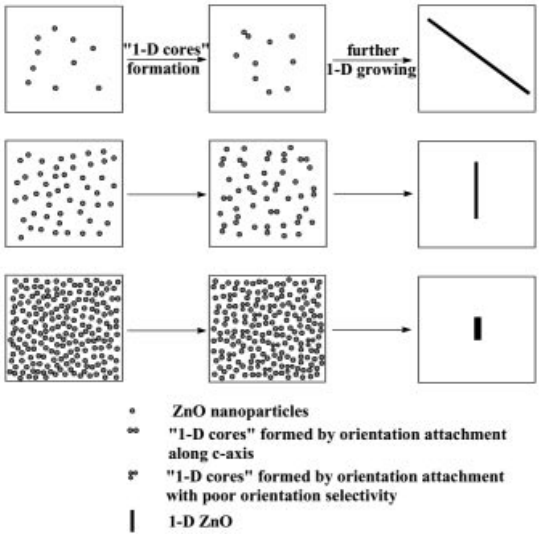


Figure 3. (A) and (B) HRTEM images of the orientation attachment of two ZnO nanoparticles, (C) and (D) HRTEM images of the fusion of "1D cores" and primary nanoparticles.

nanorods in a basic ethanol/water environment. Because ZnO nanoparticles are highly charged in the basic environment, an increase in the surface potential was observed. As the surface potential increased, the stability constant decreased. This means that the orientation attachment process was relatively slow in basic environments and a higher concentration of the nanoparticles was needed to accelerate it. In the neutral aqueous system we report here, the electrostatic repulsion from stabilizers such as OH^- is avoided, which results in an overcompensation of the electric-dipole attractions between the nanoparticles. In other words, the value of K_{os} is much larger in neutral aqueous solutions than it is in basic alcoholic solutions, which allows the orientation attachment of the nanoparticles to occur under much lower concentrations. Our results confirm that orientation attachment can occur at relatively low concentrations of the nanoparticles; in fact, this was found to occur at concentrations as low as 0.8 g/L (0.01 M), which is 10 times lower than the reported value.[14] However, there is also a critical concentration that must be met in order to produce 1D ZnO in neutral aqueous systems. If the concentration of the ZnO nanoparticles is less than 0.4 g/L, the orientation attachment of the ZnO nanoparticles is completely inhibited, and only ZnO nanoparticles that are larger in size relative to the starting nanoparticles are obtained.

Adjustments in the orientation attachment process can be realized by the variation of the concentration of the ZnO nanoparticles in the neutral aqueous system. At a certain concentration, there is a possibility that two primary particles collide and merge into a "1D (nanorod) core". These "1D cores" can continue to grow into nanorods or nanowires. Figure 3C and Figure 3D show that individual nanoparticles and "1D cores" can fuse together by the orientation attachment process, which results in additional 1D growth of the "1D cores". On the basis of our observations, we can speculate that the length of the nanowires can be influenced by the alteration of the number of viable "1D cores". The number of initially merged "1D cores" is related to the concentration of the nanoparticles. Large amounts of "1D cores" form when the concentration is high, whereas only small amounts of "1D cores" form when the concentration is low. In a certain colloidal stock, the number of ZnO nanoparticles is constant. If the number of "1D cores" was reduced, a greater share of nanoparticles would be available for continued 1D growth. It is understandable that fewer "1D cores" will result



Scheme 1. Simplified illustration of the concentration-controlled orientation attachment process.

in an increase of the length of the nanorods. At the same time, if the concentration is high, the orientation attachment will occur with poor orientation selectivity and continued growth will result in ZnO nanorods with large diameters and small aspect ratios. Scheme 1 shows a simplified illustration of the concentration-controlled orientation attachment process. The irregular surface of the 1D ZnO nanostructures can be smoothed and should follow the conventional mechanism of dissolution and growth (Oswald ripening), which finally results in a single crystalline nanowire.

Conclusions

In summary, ZnO nanowires have been obtained with the use of ZnO nanoparticles as building blocks by the concentration-controlled orientation attachment process in a neutral aqueous system. The concentration of the nanoparticles is found to influence the orientation attachment process, and therefore, the continued growth of the ZnO nanowires can be controlled. Our results suggest that the orientation attachment process is similar to the conventional crystal growth process if the nanoparticle colloid is viewed as an ion in solution.

Experimental Section

Physical Methods: Powder X-ray diffraction (XRD) analysis was performed with a Rigaku D/MAX 2500/PC diffractometer with graphite-filtered Cu-K_α radiation. XRD data were collected over 25–60° with a step interval of 0.02° and a preset time of 1.2 s per step at room temperature. Scanning electron microscope (SEM) was performed with a JSM-6700F electron microscope. High resolution transmission electron microscope (HRTEM) was performed with a JEM-3010 electron microscope. The ZnO nanowires will break into shorter ZnO nanorods under strong ultrasonic treatment. If samples are to be observed by HRTEM, prolonged ultrasonic treatment of the samples should be avoided.

Preparation of ZnO Nanoparticles: ZnO nanoparticles are prepared by a conventional sol-gel method.[36–37] In a typical synthesis, zinc acetate dehydrate (2.195 g) is dissolved in ethanol (100 mL) and heated at reflux for 2 h. The solution is then cooled to room temperature and lithium hydroxide hydrate (0.588 g) is added. The suspension is then placed in an ultrasonic bath in order to solubilize the weakly soluble powder. After 30 min, the suspension is filtered through a glass fiber (0.1 μm) frit to remove the insoluble solids and then cyclohexane (300 mL) is added into the as-obtained ZnO colloids to precipitate the ZnO nanoparticles.

Preparation of 1D ZnO: Different amounts of ZnO nanoparticles (0.02 g, 0.10 g, 0.40 g) were dissolved in distilled water (25 mL) and then transferred to a 40-mL Teflon-lined stainless steel autoclave and heated at 160 °C for 12 h. The obtained precipitates were washed with distilled water and then dried at 60 °C for 2 h.

Supporting Information (see footnote on the first page of this article): SEM images of 1D ZnO obtained by hydrothermal treatment of 4.0 g/L and 16.0 g/L ZnO colloidal nanoparticles and TEM image of ZnO nanoparticles.

Acknowledgments

This research was supported by the National Natural Science Foundation of China (No. 20371019 and 20121103).

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Received: April 25, 2006
Published Online: August 28, 2006

