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Article

Large-Scale Synthesis of Perpendicular Side-Faceted One-Dimensional ZnO Nanocrystals

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A novel route to the rational fabrication of narrow one-dimensional ZnO nanocrystals with perpendicular side facets is demonstrated in alcoholic solutions. The synthesis involves no-template or no-substrate solution method, which still allows the oriented growth of ZnO nanostructures at large-scale, low-cost, and moderate temperatures. The management consists of monitoring of the nucleation, growth, and aging processes by means of chemical and solvent control of the interfacial free energy. It enables the control of the size of nano-, meso-, and microcrystallites with various aspects from cubes to rods, wires, and belts.

Introduction

In recent years, a broad range of applications, ranging from photonic crystals,[1] photodetectors,[2] photodiodes,[3] light-emitting diodes,[4] varistors,[5] and gas sensors,[6] to solar cells,[7] which is based on ZnO nanomaterials, have been reported because of its excellent chemical and thermal stability and its specific optoelectronic and electrical properties of being a II−VI semiconductor with a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV. One-dimensional nanostructures are the ideal system for studying the transport process in 1D confined objects, which are of benefit not only for understanding the fundamental phenomena in low-dimensional systems but also for developing new generation nanodivices with high performance.[8,9] The synthesis of one-dimensional ZnO nanostructures has attracted considerable interest because of their promising applications in optics, optoelectronics, catalysis, and piezoelectricity.[9,10] One-dimensional ZnO nanostructures have been successfully fabricated by chemical vapor deposition (CVD),[11] thermal evaporation,[9] molecular beam epitaxy (MBE),[12] and a high-temperature vapor transport process[13] using high temperatures or special equipment. In addition, the preparation of one-dimensional ZnO nanostructures via wet chemical techniques, which include microemulsion hydrothermal synthesis,[14] direct deposition in aqueous solution,[15] surfactant-assisted hydrothermal orientation growth,[16,17] and alcohol-solution refluxing,[18,19] has been reported with low growth temperatures and good feasibility for scale-up.

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As the recent research has suggested, in addition to size and dimension, the cross-section also has a shape-effect on the properties of nanomaterials:[20] one-dimensional ZnO nanostructures with rectangular cross-sections have been tailored by the thermal evaporation method[9,21] and wet chemical methods.[17] Unfortunately, for the thermal evaporation method, ZnO nanobelts with a uniformly narrow width have been obtained only rarely in the published works. Moreover, for the wet chemical methods, the cross-section control needs organic compounds as templates, and the resulting ZnO nanostructures have widths over 50 nm, and the growth processes have been simply attributed to template help or are considered to be attachment-driven.[17] Stimulated by our early work,[19,22] our strategy to design one-dimensional ZnO nanostructures with perpendicular side facets and various shapess from cubes to rods, narrow wires (with a diameter range down to 15 nm), mesocrystallites, and microcrystallites is based entirely on a wet chemical bottom-up approach, without template, that was synthesized from theoretical modeling and experimental monitoring of the alcohol−oxide interfacial thermodynamics and kinetics of nucleation, growth, and aging. Furthermore, this technique has already been successfully demonstrated by the fabrication of large one-dimensional growth of other kinds of one-dimensional nanomaterials in our further work.

Experimental Section

The synthesis was conducted by the solvothermal decomposition of a Zn(II) hydroxy complex with reagent grade chemicals. Experimental autoclaves, with 160 a mL Teflon inside liner, were transfused with an alcoholic solution of zinc chloride ($ZnCl_2$, 99.99%, Aldrich), zinc acetate dihydrate, ($(C_2H_3O_2)_2Zn$, 98+%, Aldrich), sodium hydroxide (NaOH, 97%, Aldrich), methanol (CH_3OH, 98%, Aldrich), and ethanol (CH_3CH_2OH, 98%, Aldrich). After the solution was stirred for 30 min, a white slurry appeared. Then the autoclaves were airproofed and heated at a constant temperature for several hours in a regular laboratory oven. After reactions, the clear supernatant solutions were carefully removed, and the white products were washed by ethanol and water several times to remove the unreacted chemicals; then the products were vacuum-dried.

The crystal structure was determined with powder X-ray diffraction (XRD, Philips X′Pert-MPD system, Cu Kα radiation, $\lambda = 1.54056$ Å) at a scanning rate of 0.02°/s for 2θ in the range from 5 to 80°. The morphology and compositional information of the products were obtained with transmission electron microscopy (TEM, JEOL, JEM-2010), high-resolution TEM, selected area electron diffraction, energy-dispersive X-ray spectroscopy (HR-TEM/ED/EDS, HITACHI, H-7500), and field-emission scanning electron microscopy (FE-SEM, JEOL, JSM-6700FSEM).

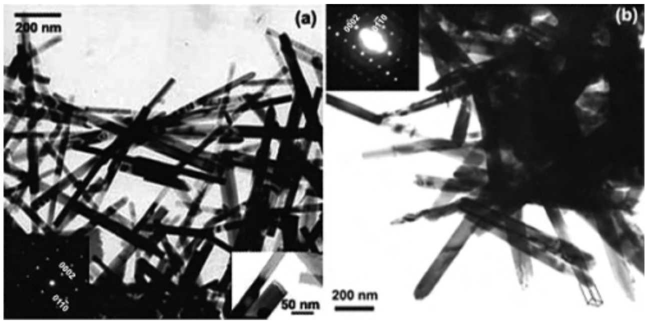

Figure 1. One-dimensional ZnO nanomaterials with different widths and their corresponding electron diffraction (ED) patterns: (a) 25−40 nm width range and (b) 75−90 nm width range.

Result and Discussion

To give an insight into the capability of controlling one-dimensional crystalline ZnO with perpendicular side facets is over the control of the width. Moreover, to reach the low nanometer range, the design of one-dimensional, highly facet-oriented nanostructures, as well as different width and length ranges, in the control of ZnO fabrication, is presented by following similar theoretical concepts. The electronic configuration and ionic strength for the octahedral−tetrahedral equilibrium of the complexes of Zn(II), the inherent diversity of facet energy and the lack of ligand-field stabilization energy, as well as the inability of alcohol to deprotonate divalent metal cations at ambient pressure, require the use of solvothermal conditions and neutralization in basic medium or chemical complexation to generate zinc oxide from zinc salts.[23] The different surface energy of the crystal facets supplies a possibility of fabricating perpendicular side-faceted one-dimensional ZnO nanostrutures.[24,25] Such facts substantially limit the electrostatic control of the interfacial tension and nucleation free energy. Therefore, the easiest way to obtain smaller anisotropic nanoparticles of ZnO is using weaker polarity alcohol solvent, lowering the overall concentration of the reagents, or lowering the temperature.

As expected, without surfactant as template, single-crystalline one-dimensional ZnO nanostructures with perpendicular side facets, typically 25 to 40 nm wide, 15 nm thick, and almost 500 nm to 1 μm long, grew in 20 mL of a methanol solution that contained 0.01 M zinc chloride and 0.1 M sodium hydroxide at 200 °C for 24 h (Figure 1a). In Figure 1b, 75−90 nm wide and 30 nm thick structures were produceded in 20 mL of an ethanol solution containing 0.02 M zinc chloride and 0.15 M sodium hydroxide at 160 °C for 24 h. With same reaction parameters, this perpendicular side-faceted aspect was not observed in the ethanol solvent, which will be discussed later. Well-defined faces (i.e., polar facets (0002) and nonpolar facets {01-10}) and the single crystalline characteristics can be clearly identified by the white pointsg in the image of the electron diffraction (ED) pattern (Figure 1a and b inset). The rectangular cross-section can be confirmed by the enlarged image at the right bottom corner in Figure 1a. The rougher ends with double or triple tips in Figure 1b hinted the growth of a different crystal.

In the enlarged HRTEM images, the smooth edges without an amorphous shell of the one-dimensional ZnO nanostruc-

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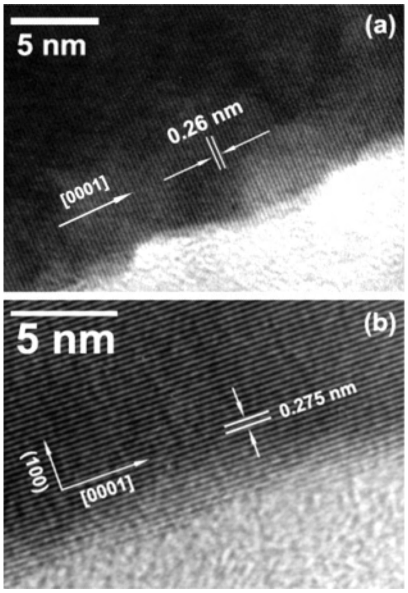

Figure 2. Corresponding HR-TEM images of the ZnO nanostructures in Figure 1a and b, respectively.

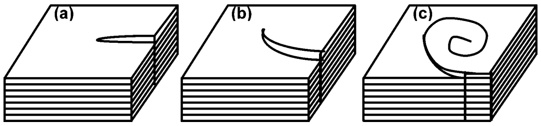

Figure 3. Screw dislocation model: (a) lattice defect and (b and c) propagation of the screw.

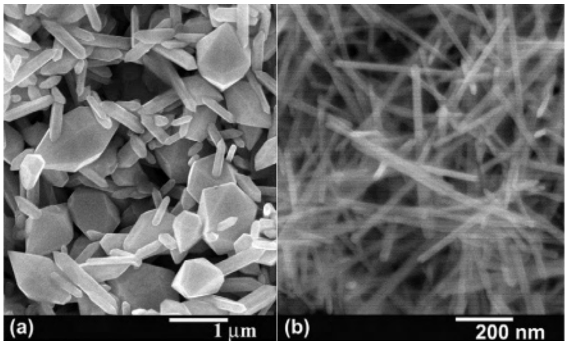

Figure 4. Products from ethanol solution at 200 °C reacted for (a) 24 and (b) 1 h.

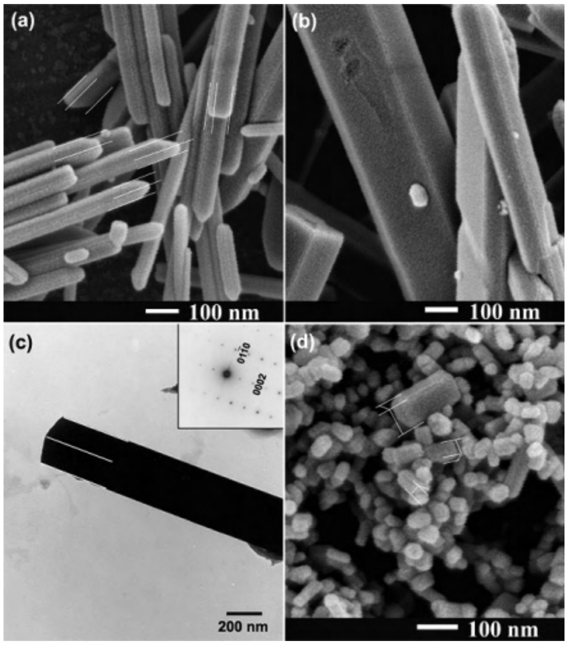

Figure 5. SEM and TEM images of variable ZnO nanostructures with perpendicular side facets (a) formed in ethanol solvent, (b and c) secondary growth in ethanol solvents, and (d) secondary growth from nanoparticles to cubics.

tures agree with the Screw dislocation model very well. The interplanar spacing of the crystalline stripes is 0.26 nm and can be indexed to the (002) plane corresponding with the [0001] growth orientation in Figure 2a, and the 0.275 nm interplanar spacing of the (100) plane shows the {01-10} side facets in Figure 2b. In addition, both HR-TEM images are perfectly consistent with the electron diffraction patterns in the insets of Figure 1a and b on the single-crystalline character, polar growth orientation, and nonpolar side facets.

The fabrication of one-dimensional nanostructures can be separated into two steps: (i) nucleation and (ii) crystal growth. In general, the minimum size of one-dimensional nanostructures is both dependent on nucleation thermodynamics and the growth kinetics (energy stability theory).[26,27] At the nucleation stage, the overall Gibbs free energy of formation of the cluster, ΔG_t, is given as the sum of the decrease in the Gibbs free energy of formation of the cluster lattice, ΔG_l, and the surface excess energy, ΔG_s

$$\Delta G_t = \Delta G_l + \Delta G_s$$

As the positive ΔG_s, under the same ΔG_l condition, the low-energy facets, such as the nonpolar facets {01-10} and polar facets (0002) in zinc oxide crystal, have the preference to be formed first.[24] The selectable formation of different energy facets can be observed under a more moderate reaction condition, for example, in this paper, using lower polarity alcohol solvent as media instead of the water used in solvothermal reactions.

As shown in Figure 3, in the model of Screw dislocation of crystal growth, the kink site (such as lattice defects, etc.) has the highest binding energy and is the most favorable position for the incorporation of a unit molecule from the solution phase, additionally, the angular velocity near the corner of the lattice defects is faster than that at the edge of the crystal. Therefore, the dislocation proceeds in a spiral form in the propagation of the step.[27] The model also suggested that once the smooth facets of the crystals have been formed, spontaneously precipitating molecules stick on these surfaces differently. Thus the extending of the smooth low-energy side-facets, the nonpolar {01-10} facets, can lead the oriented growth of the crystals into one-dimensional forms under a given reaction condition. In fact, our experimental results matched the Screw dislocation theory perfectly with the smoothly perpendicular side facets, the rough tips and planed bottoms, and the uniform width and thickness along the entire length of the one-dimensional ZnO nanostructures. Furthermore, this growth model might discover

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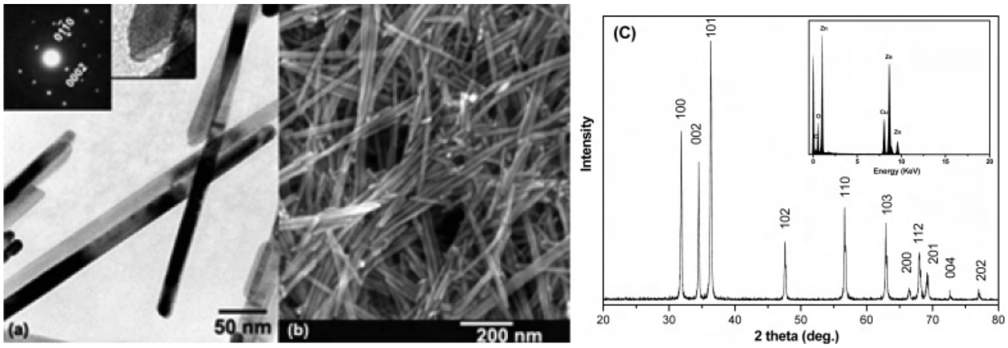

Figure 6. Narrow one-dimensional nanostructures with perpendicular side facets: (a) TEM image of the nanostructures and the corresponding electron diffraction pattern and an enlarged image of a tip, (b) the corresponding FE-SEM image, and (c) the indexed XRD pattern and inset EDX analysis of the products.

the real growth processes in a wide range of fabricated one-dimensional nanomaterials via a solvothermal process.

Generally, the increase in the degree of supersaturation and in the temperature cause an increase in the density of the kink sites and the roughness of the surface. The growth mechanism changes to adhesive growth (i.e., monomers which reach the surface are effectively incorporated into the crystal without surface diffusion).[27] If the polarity of alcohol solvent in our experiments and the resulting white slurry before the solvothermal reaction is considered, the monomer in the reactions should be zinc hydroxide. Therefore, with increased precursor concentration, in Figure 1b, the rougher ends with double or triple tips on the one-dimensional ZnO structures were formed.

The elongated structures characterize the kinetic control reactions. The monomer concentration can be indirectly controlled by changing the reactants to those with different hydrolyzing capabilities, the solvents to those with different polarities, the ratio between the reactants, and the reaction temperatures. For instance, because of the higher polarity, ethanol can supply a higher monomer concentration than methanol at same reaction condition. The higher monomer concentration can supply a higher kinetic energy and chemical potential resulting in a faster reaction rate. Thus, in the 20 mL ethanol solution with 0.01 M zinc chloride and 0.1 M sodium hydroxide after 24 h at 200 °C, only large structures with two sharp ends can be observed (Figure 4a). And the products prepared in a 1 h reaction under same reaction parameters show a uniform aspect, as shown in Figure 4b. The different morphologies shown in Figure 4a and b agree with "1D to 2D ripening" and the further Ostwald ripening and "1D growth" in the early stage, which had been first reported by Peng et al.[28] At the early stage of reaction, high monomer concentrations cause the growth to focus on the *c* axis in the wurtzite structure and lead to the "1D-growth" that produce the uniform one-dimensional structures in Figure 4b. With increasing reaction time, the monomer concentration drops to a certain level, and the equal chemical potential in the bulk solution and the surface atoms of the nanocrystal leads to a diffusion equilibrium at the interface. The monomers diffuse from the stagnant solution of the {0001} facets to the stagnant solution of the other facets. And when the monomer concentration is very low, the Ostwald ripening causes a "defocusing of size distribution" and produces the structures with very different size ranges, as shown in Figure 4a.

By controlling the reactants, the solvents, the reaction temperatures, and time, the morphology of the perpendicular side-faceted one-dimensional ZnO nanostructures can be successfully displayed in a wide aspect range. In Figure 5, image a shows the one-dimensional ZnO nanostructures with main diameters between 50 and 70 nm, which were obtained in an 20 mL ethanol solution containing 0.02 M $ZnCl_2$ and 0.2 M NaOH at 160 °C for 24 h. All the structures reveal their perpendicular side facets with the flat bottoms and rough tips characteristic of Screw dislocation growth. The strict control of the precipitation and dispersion conditions allows the interfacial free energy of the system to be monitored. Therefore, without the requirements of template, membrane, and surfactant to create anisotropic property or to control the growth orientation, the generation of well-defined and facet-oriented nanostructures within variable size and shape is allowed.

With the control of the ion-releasing speed using the low polarity alcohol solvents, micro-sized one-dimensional ZnO structures can be generated by increasing the temperature, concentration of reactants, or secondary growth under the same conditions. As shown in Figure 5b and c, ZnO structures secondarily formed in 20 mL ethanol solutions containing with 0.005 M $ZnCl_2$ and 0.05 M NaOH and 0.01 M $ZnCl_2$ and 0.1 M NaOH at 160 °C for 24 h. After the intial growth in the solution, the supernatant solution (clear) was carefully removed, and then the same precursor solution was injected into the reaction system; the secondary reaction was under the same reaction conditions. This process is named secondary growth in this article. Those materials were observed with their increased widths and thicknesses and their remaining perpendicular side facets. Moreover, they are still single-crystalline structures, confirmed by the homologous electron diffraction pattern. Indeed, if the growth mechanism discussed in our early work is considered seriously,[22] quantized zinc oxide nanoparticles[29] have been used for secondary growth-formed cubes in a 20 mL ethanol

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solution containing 0.005 M zinc chloride and 0.05 M sodium hydroxide (Figure 5d).

To slow the nucleation process, to form smaller perpendicular side-faceted nuclei with higher aspect ratios, zinc acetate had been used instead of zinc chloride as the reactant. As expected, perpendicular side-faceted ZnO nanostructures, typically 15 to 20 nm wide, 5 nm thick, and up to 2 μm long, grew in a 30 mL ethanol solution that contained 0.01 M zinc acetate and 0.1 M sodium hydroxide at 100 °C for 24 h (Figure 6a and b). Well-defined faces, the single-crystalline characteristics, and the rectangular cross-sections can clearly be identified by the electron diffraction (ED) pattern and enlarged image of the tip (Figure 6a inset). In Figure 6c, the corresponding X-ray diffraction (XRD) spectrum of those nanostructures matches well with the Bragg reflections of the typical crystal habit of wurtzite-structured ZnO ($P6_3mc$, $a = 3.249$ Å, $c = 5.206$ Å, JCPDS 36-1451). The energy-dispersive X-ray spectroscopy (EDS) analysis of those nanostructures shows zinc and oxygen as the only detected elements with a ratio close to 1, except the copper from the copper grid, in the Figure 6c inset.

Conclusion

In summary, one-dimensional ZnO nanostructures with perpendicular side facets can be easily synthesized in an approach with more complex architecture over a large scale. Low-polarity alcohol, zinc salts with different hydrolyzing capabilities, and varying reaction parameters have been knowledgeably used to control the reaction kinetic and limit the reaction to follow with the Screw dislocation model. The ultimate goal of such a study is to contribute to the grand challenges of nanotechnology, in other words, the low-cost and large-scale manufacturing of functional nanomaterials for realistic and practical applications.

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