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Hydrothermal synthesis of one-dimensional ZnO nanostructures with different aspect ratios

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1-D ZnO nanorods with different aspect ratios were synthesized by a one-step, hydrothermal method. The ZnO nanorods grow along the [0001] direction to form single crystals. The experimental results reveal that the growth of polar inorganic crystals is sensitive to the reaction solvents.

Studies on one-dimensional (1-D) nanostructures—nanowires, nanorods or nanotubes—have received increasing attention due to their potential use as active components or interconnects in fabricating nanoscale electronic, optical, optoelectronic, electrochemical, and electromechanical devices.[1] Notable examples of 1-D nanostructure applications include light-emitting diodes (LEDs),[2] single-electron transistors,[3] field-effect transistors (FETs),[4] biological and chemical sensors,[5] photodetectors,[6] electron emitters,[7] and ultraviolet nanolasers.[8] A number of methods have been developed to fabricate and assemble 1-D nanostructures, including nanolithographic techniques (*e.g.*, electron beam lithography, proximal probe patterning, and X-ray patterning),[9] and many low cost chemical methods (*e.g.*, vapor–solid, vapor–liquid–solid, solution–solid).

ZnO is of interest in many applications including transparent conductive coatings,[10] electrodes for dye-sensitized solar cells,[11] gas sensors,[12] and electro- and photo-luminescent materials.[13] ZnO exhibits a direct bandgap of 3.37 eV at room temperature with a large exciton binding energy of 60 meV. The strong exciton energy can ensure an efficient exciton emission at room temperature under low excitation energy.[14] The synthesis of 1-D ZnO nanostructures has attracted considerable interest because of their promising applications in nanoscale optoelectronic devices. 1-D ZnO nanostructures have been synthesized by chemical vapor deposition (CVD),[15] thermal evaporation,[16] molecular beam epitaxy (MBE),[17] and high-temperature vapor transport process.[18] All these methods need either high temperatures or special equipment. Recently, a few reports about the preparation of 1-D ZnO nanostructures *via* wet chemical techniques have appeared. These wet chemical methods include microemulsion hydrothermal synthesis,[19] direct deposition in aqueous solution,[20] surfactant-assisted hydrothermal orientation growth,[21] and alcohol solution refluxing.[22,23] However, most wet chemical methods[19–21] fail to produce small diameter (< 50 nm) ZnO nanorods and rod-shape nanoparticles.[23] Stimulated by the alcohol refluxing method, we developed a large-scale, single-step, direct hydrothermal method and have successfully prepared small-diameter single crystalline ZnO nanorods with different aspect ratios.

In a typical procedure, solutions of zinc acetate dihydrate ($Zn(Ac)_2{\cdot}2H_2O$) in methanol, ethanol, and solutions of sodium hydroxide (NaOH) in methanol, ethanol with different concentrations were prepared as stock solutions in advance. 10 mL of 0.1 M of zinc acetate stock solution in methanol was mixed with 20 mL of 0.5 M NaOH solution in methanol to get a clear solution which was transferred to a Teflon-lined stainless steel autoclave and heated at 150 °C for 24 hours. The reaction procedure in ethanol medium is the same. A white precipitate was collected, washed with water and ethanol several times, and dried in air at ambient temperature.

The synthesized product was characterized by X-ray powder diffraction (XRD) (Rigaku Multiflex X-ray diffractometer, with Cu–K_α radiation (λ = 0.154178 nm at 40 kV and 40 mA), transmission electron microscopy (TEM; Philips CM-12, with an accelerating voltage of 100 kV), high-resolution transmission electron microscopy (HRTEM; Topcon EM-002B, with a accelerating voltage of 200 kV).

Fig. 1 shows X-ray diffraction patterns from final products prepared in methanol (**A**) and ethanol (**B**). The diffraction peaks are quite similar to those of bulk ZnO, which can be indexed as the hexagonal wurtzite structure of ZnO. The calculated lattice constants are a_A = 3.2529 Å, c_A = 5.2099 Å and a_B = 3.2522 Å, c_B = 5.2084 Å, respectively, for the methanol and ethanol products. Both lattice parameters are in good agreement with the JCPDS file of ZnO (JCPDS 36-1451).

Fig. 2 shows TEM images of products fabricated in methanol (**A**) and ethanol (**B**). It is found that the diameter of ZnO nanorods prepared in methanol is around 25 nm, the length is around 100 nm (aspect ratio 4 : 1). Fig. 2 (**B**) reveals that the average diameter of ZnO nanorods fabricated in ethanol is around 40 nm, but the length is around 500 nm, (aspect ratio > 10 : 1). The corresponding electron diffraction patterns indicate that short and long nanorods are single crystalline.

The single-crystalline structural details of the short and long nanorods were revealed by HRTEM. Fig. 3 shows HRTEM images of a representative edge of a short nanorod (Fig. 3(**A**)) and the end of a long nanorod (Fig. 3(**B**)). The HRTEM images show that the short and long nanorods are structurally uniform, and the 2D lattice fringes illustrate that the short and long nanorods are single crystalline. Also, there does not appear to be any amorphous ZnO on the surfaces of the nanorods.

Fig. 3(**A**) shows the interplanar spacing of the short ZnO nanorod is about 0.256 nm, which corresponds to the distance between two (0001) planes of hexagonal ZnO, similarly indicating that the short

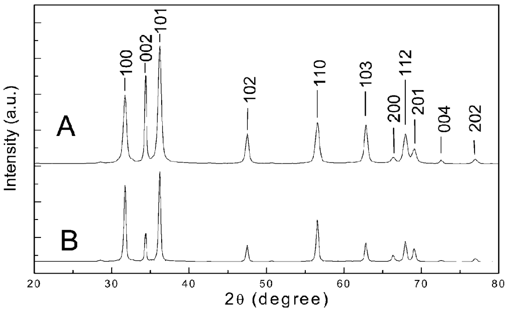

Fig. 1 X-Ray diffraction patterns of final products prepared in methanol (A) and ethanol (B) at 150 °C.

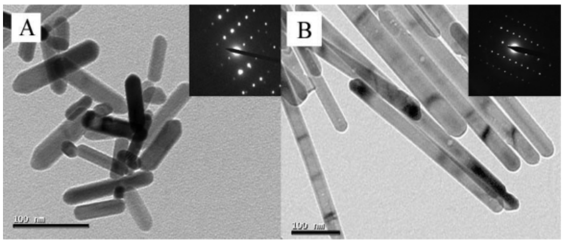

Fig. 2 TEM images of ZnO nanorods prepared in methanol (**A**) and ethanol (**B**) at 150 °C for 24 h; the insets show the corresponding selected area electron diffraction patterns; (scale bar, 100 nm).

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nanorods grow along the [0001] direction. Fig. 3(**B**) shows that the interplanar spacing of long ZnO nanorods is about 0.26 nm, which also corresponds to the distance between two (0001) planes of hexagonal ZnO, indicating preferred growth along the [0001] direction (*c*-axis).

Studies of the growth kinetics and crystallization of ZnO in alcohol–water medium have been reported.[22–25] Besides Ostwald ripening, another growth mechanism, "oriented attachment", has been proposed for the anisotropic growth of ZnO.[22] But in our case, no evidence for oriented attachment of particles was found even at the primary stage of growth. So, 1-D ZnO growth along the *c*-axis under hydrothermal conditions is related to both its intrinsic crystal structure and external factors. ZnO is a polar crystal; its growth habit under hydrothermal condition has been investigated.[26] The overall shape and aspect ratio of crystals are determined by the relative rates of growth of its various faces. In general the growth rate of a face will be controlled by a combination of internal, structurally-related factors (intermolecular bonding preferences or dislocations), and external factors (supersaturation, temperature, solvents and impurities).[27] Among the external factors, the effect of solvents on the nucleation, and growth of crystals has been studied.[24,28] Based on similar observations with SnO_2,[29] we infer that the different aspect ratios of ZnO nanorods result from different growth rates along the *c*-axis in different reaction media, *i.e.*, the growth rate along the *c*-axis in ethanol is higher than that in methanol. This can only be verified with detailed theoretical simulations of interface–solvent interactions using known parameters, *e.g.*, surface energies of different crystal faces, solvent properties that are dependent on the chain length of alcohols. Hence, it is possible that morphologies of polar inorganic nanocrystals can be controlled by the interface–solvent interactions, which in turn, may be specified by choosing a suitable solvent.

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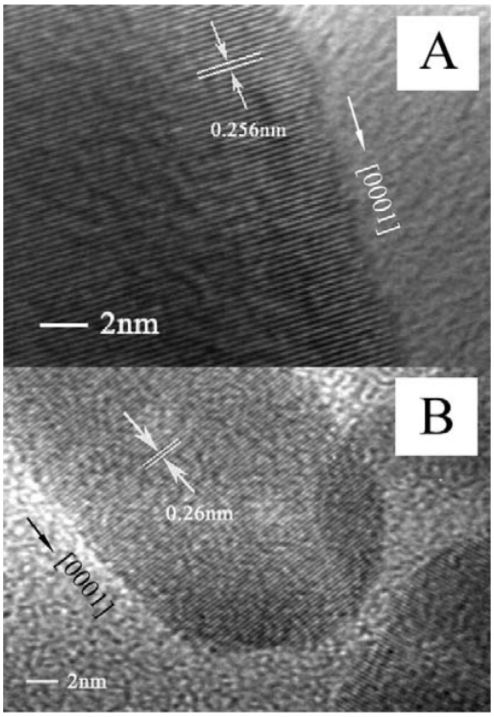

Fig. 3 HRTEM images of the as-prepared ZnO nanorods; (A) the edge of a ZnO nanorod prepared in methanol; (B) the end of one of the ZnO nanorods prepared in ethanol. The results show that the ZnO nanorods grow along the [0001] direction; the lattice spacing (2.56 ± 0.05 Å) corresponds to the distance between two (0001) planes.

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