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A simple low-temperature growth of ZnO nanowhiskers directly from aqueous solution containing $Zn(OH)_4^{2-}$ ions†

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One-dimensional (1D) needle-like ZnO nanowhiskers have been grown directly from aqueous solution containing $Zn(OH)_4^{2-}$ ions produced by zinc chloride and sodium hydroxide, in the presence of sodium dodecyl sulfate (SDS).

Zinc oxide is a versatile material and has been used considerably for its catalytic, electrical, optoelectronic and photochemical properties. In recent years, room temperature UV lasing studies in ZnO epitaxial films, nanorods and nanowires have been reported,[1] which have stimulated intensive interest in the optical properties of ZnO. ZnO has potential uses as light-emitting diodes, field-effect transistors, and ultraviolet nanolasers[2] due to its wide direct-band gap of 3.37 eV and high exciton binding energy of 60 meV. In particular, one-dimensional (1D) ZnO nanostructures have attracted increasing attention owing to their promising application in nanoscale optoelectronic devices.[3]

Many works on the synthesis of 1D ZnO nanomaterials have been reported, including methods such as a conventional sputter deposition technique,[4] chemical vapor deposition (CVD),[5] and thermal evaporation.[6] However, these methods involving special equipment, complex process control or high temperatures are unfavorable for an industrialized process. Recently, a lot of reports on the preparation of 1D ZnO nanostructures through wet chemical techniques have appeared. Perpendicularly orientated ZnO rods have been grown on thin ZnO templates from aqueous solutions of zinc acetate and hexamethylenetetramine (HMT).[7] A similar process to obtain 1D single crystal ZnO nanorods on a ZnO nanostructured substrate by a soft chemical method has been proposed.[8] ZnO nanorods have also been prepared by the cetyltrimethylammonium bromide (CTAB) favored hydrothermal oxidization of zinc metal at 180 °C for 20 h.[9] Reports on the hydrothermal synthesis of ZnO nanorods or whiskers have also been given by other investigators,[10] but a simple process to synthesize ZnO nanorods with different aspect ratios by a one-step, hydrothermal method, without template or substrate, had not been reported until very recently.[3] Encouraged by this recent report, we developed a much simpler and softer process for preparing 1D ZnO nanowhiskers. Following on from this work, we have simplified the devices further, lowered the temperature, shortened the reaction time, and increased the reactant concentration. In addition, the appearance of the as-grown needle-like ZnO nanowhiskers, with one sharp top end and another gradually contracted and layered hexagonal flat end, is of great novelty.

Herein, we describe a simple and novel approach for the low-temperature growth of 1D ZnO nanowhiskers directly from an aqueous solution containing $Zn(OH)_4^{2-}$ ions without a substrate. The experimental procedure was carried out as follows: aqueous solutions of 30 mL of 4 M sodium hydroxide and 5 mL of 0.2 M SDS were, respectively, added dropwise to an aqueous solution of 20 mL of 1 M zinc chloride with 45 mL deionized water under vigorous stirring at 3 °C to get a 100 mL clear solution ($[Zn^{2+}] = 0.2$ M, $[OH^-] = 1.2$ M; molar ratio of $Zn^{2+}/OH^- = 1 : 6$). After a while, the solution was maintained at room temperature under mild continuous stirring for 1.5 h (some white precipitate appeared, which we call *nucleation at room temperature*), and subsequently transferred to a 250 mL ground-glass stoppered conical flask, aging at 85 °C for 5 h. White products were collected, thoroughly washed with deionized water, and dried in air at ambient temperature. An X-ray diffraction (XRD) study was firstly carried out using a Bruker AXS D8 ADVANCE X-ray diffractometer (with Cu–Kα radiation at 40 kV and 40 mA). The as-obtained products were further characterized by field emission scanning electron microscopy (FESEM; JEOL JSM-6700F), and high-resolution transmission electron microscopy (HRTEM; Hitachi H-9000) equipped with ED.

Fig. 1 shows the XRD pattern of the ZnO nanowhiskers. All the diffraction peaks are in good agreement with the JCPDS file of ZnO (JCPDS 36-1451), which can be indexed as the hexagonal wurtzite structure of ZnO. The general morphology of the ZnO nanowhiskers is shown in Fig. 2. In Fig. 2(a), a low-resolution TEM image of the whiskers shows that high-purity whiskers have a straight needle-like shape, with diameters ranging from 80 to 150 nm and an average length of about 4μm (aspect ratio ~ 40 : 1). The definition of the needle-shape comes from the geometrical similarity to a real needle; it gets thinner and thinner along the $+c$ axis, and ultimately leads to a pointed shape at the end of the $+c$ axis, while towards the other end, the diameter gets smaller gradually along the $-c$ axis but there is no pointed tip at the end. The amplified images of the two ends of the whiskers are shown in Fig. 2(b) and Fig. 2(c), respectively. An individual whisker has a sharp top end and another hexagonal flat end. Moreover, we can identify that the hexagonal flat ends are gradually contracted layered structures, which differ from those reported by Lee and coworkers.[5] The impressive layered structure seems to be formed from the stacking of uniform hexagonal ZnO crystals with gradually decreased areas layer upon layer. Fig. 3 shows the HRTEM image of a representative edge of an individual whisker randomly chosen from the sample. The image clearly reveals only the fringes of (002) planes with a lattice spacing of about 0.26 nm, indicating that the ZnO nanowhisker is singly crystalline in nature, which is in accordance with the SAED pattern inserted in Fig. 3. Furthermore, the spacing of 0.26 nm corresponds to the distance

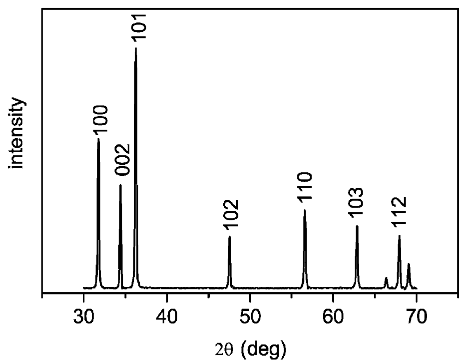

Fig. 1 XRD pattern of the ZnO nanowhiskers obtained directly from aqueous solution.

† Electronic supplementary information (ESI) available: SEM images of ZnO crystals. See http://www.rsc.org/suppdata/cc/b4/b409425e/

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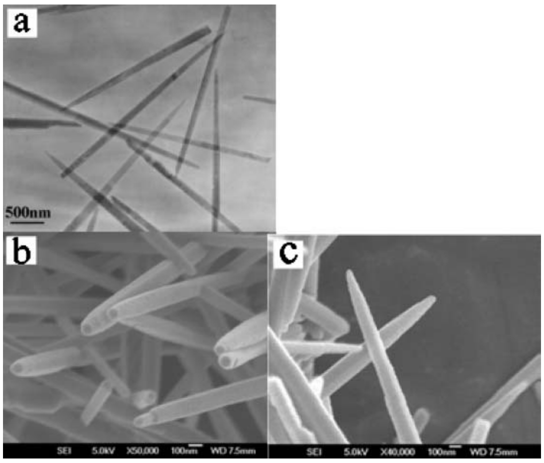

Fig. 2 (a) Low resolution TEM image of ZnO nanowhiskers; (b) enlarged FESEM image of the hexagonal flat ends of ZnO nanowhiskers; (c) enlarged FESEM image of the top ends of ZnO nanowhiskers.

between two adjacent (002) planes, indicating that [0001] is the growth direction of the whiskers.

A detailed account of the crystallization of ZnO under hydrothermal conditions has been given by Zhang *et al.*[11] However, until now, the growth mechanism of ZnO from a solution of $Zn(OH)_4^{2-}$ had not yet been adequately reported. We have performed additional experiments with different molar ratios of Zn^{2+}/OH^- (molar concentration of Zn^{2+} is invariable) under the same conditions as described above. As a result, needle-like nanowhiskers occur only within the range of $Zn^{2+}/OH^- = 1:6–1:7$. Based on numerous experimental results, we found that if the concentration of OH^- ions existing in the solution is too high ($Zn^{2+}/OH^- < 1:7$) or the growth process excludes nucleation at room temperature, bigger flower-like clusters of ZnO will be unexpectedly formed due to the greatly decreased amount of ZnO nuclei[12] (see ESI [1]†). So we infer that the formation of the whiskers in the alkali solution depends greatly on the nucleation frequency of ZnO. It is known that $Zn(OH)_2$ can change to ZnO under basic conditions at room temperature, and a homogeneous solution containing $Zn(OH)_4^{2-}$ ions can be formed only under strongly basic conditions.[13] In our experiment, mixing Zn^{2+} with OH^- at an extremely low temperature (3 °C) produces a clear solution of $Zn(OH)_4^{2-}$ with a relatively low concentration of OH^- ions (the critical molar ratio of $Zn^{2+}/OH^- = 1:6$), which may facilitate the nucleation of ZnO and results in needle-like nanowhiskers. Also, the process of nucleation at room temperature before heating efficiently separates the nucleation from the subsequent growth stage, which may also provide a moderate nucleation frequency for the formation of the whiskers.

In addition, the effects of the surfactant SDS on the shape of the ZnO crystals have also been investigated. Results show that the addition of 0.01 M SDS into the solution obviously increases the aspect ratio of the whiskers (see ESI [2]†). Further work on this is under way.

In summary, we have demonstrated a simple and novel low-temperature route to synthesize 1D ZnO nanowhiskers directly from an aqueous solution containing $Zn(OH)_4^{2-}$ ions on a large scale. Controlling the nucleation frequency of ZnO plays a crucial role in the formation of the nanowhiskers. The surfactant SDS promotes thinner and longer whiskers in the strongly basic solution. Moreover, we can control the morphology and particle size closely by varying the experimental conditions *via* the simple solution route. Related work will be reported later.

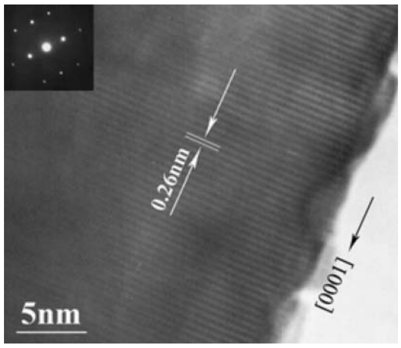

Fig. 3 HRTEM and inserted SAED images of an individual ZnO nanowhisker.

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