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A simple route towards tubular ZnO

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Thermal treatment of $Zn(NH_3)_4^{2+}$ precursor in ethanol solvent led to the formation of the tubular ZnO which exhibited strong ultraviolet photoluminescence around 385 nm at room temperature; TEM images showed the hollow tubules with ~450 nm in diameter and ~4 μm in length were built up by ZnO polycrystals.

Due to the urgently contemporary requirement in constructing optical and electronic devices towards miniaturization, nanostructured materials are stimulating world-wide research interest. Among such nanostructured materials, tubular materials being used as promising candidates for applications in nanodevices are of great interest. The characteristic tubular structure may open up the possibilities for various new application fields such as catalysis, intramolecular junctions, storage and release systems.[1,2]

Besides the investigations of carbon nanotubes after their discovery by Iijima,[3] a substantial number of studies have been presented detailing the synthesis other tubular materials which possess exceptional mechanical, electrical and optical properties and many synthetic methods have emerged due to this increasing research interest. Tenne and coworkers have prepared MoS_2 nanotubes by high temperature treatment of molecular precursors and a gas-phase reaction between MoO_3 and H_2S protected by argon.[4,5] Afanasiev *et al.* have synthesized molybdenum polysulfide hollow microtubules at room temperature by a solution route.[6] Rao's group has prepared MS_2 (Mo, W, Nb, Ta) nanotubes *via* deoxidation of MS_3 by H_2[7,8] and CdSe nanotubes by a surfactant-assisted method.[9] Moreover, there have been many investigations on tubular oxides such as TiO_2,[10] SiO_2,[11,12] Al_2O_3,[12] MoO_3,[12] ZrO_2[13] and V_2O_5[14–16] produced by template methods. However, it is necessary to prepare tubular materials by simple routes which do not involve complex procedures, sophisticated equipment or rigid experimental conditions.

Nanostructured ZnO with diverse morphologies, especially nanowires or nanorods, has been extensively studied due to its wide bandgap (3.37 eV), large exciton binding energy (60 meV) and promising applications in short-wavelength light-emitting, transparent conductors, piezoelectric materials and room temperature ultraviolet (UV) lasing.[17] However, to our knowledge, no tubular ZnO materials have been prepared by a simple solution route up to now. Here, we present a simple synthesis of tubular ZnO from $Zn(NH_3)_4^{2+}$ precursor decomposition at 180 °C in ethanol. The room temperature photoluminescence of the as-prepared ZnO exhibited strong UV emission at 385 nm.

The preparation was conducted from a mixture of $Zn(NH_3)_4^{2+}$ aqueous solution (adjusting the pH of zinc acetate solution with ammonia to 12) and ethanol (1/11, v/v). The mixture was first transferred into a 25 mL Teflon-lined autoclave under constant stirring, then, the autoclave was maintained at 180 °C for 13 h and cooled down to room temperature naturally. The white precipitate was collected and washed with absolute ethanol and distilled water several times. Finally, ZnO samples were obtained by centrifugation and drying in a vacuum at 60–70 °C. The yield of the tubular ZnO prepared by this method is about 20%.

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The as-prepared tubular ZnO has been structurally characterized by X-ray diffraction (XRD, Rigaku D_{max} 2000, Cu-Kα), indicating a wurtzite structure (hexagonal phase, space group $P6_3mc$) with high crystallinity. A typical XRD pattern is shown in Fig. 1(a) with all diffraction peaks well indexed to hexagonal phase ZnO (JCPDS card No. 36-1451). Compared with the standard diffraction pattern (Fig. 1(b)), the deviation of peak intensities implies preferred growth orientation of the tubular ZnO. The BET specific surface area S_{BET} of tubular ZnO was measured by nitrogen physisorption at 77.5 K using an ASAP 2010 analyzer (Micromeritics. Co. Ltd) and was about 18 $m^2\ g^{-1}$.

The morphology of the as-prepared ZnO was characterized by scanning electron microscopy (SEM, Amary, FE-1910) and transmission electron microscopy (TEM, Hitachi, H-9000NAR). Fig. 2 shows TEM images of the as-prepared tubular ZnO. The image in Fig. 2(a) shows a few tubular ZnO particles coexisting with some very small nanoparticles, while the image in Fig. 2(b) shows a magnified hollow structure of an individual tube marked by the arrow. The outer and inner diameters of the hollow tube with closed ends in Fig. 2(a) are ~450 and ~250 nm, respectively. The average length of the tube is ~4 μm. The wall of the tube of ~100 nm thickness is not smooth due to its build-up by polycrystalline nanoparticles. Fig. 3(a) shows a TEM image of an individual tube with destroyed ends in which the hollow structure is clearly detected. The SEM image in Fig. 3(b) confirmed the tubular morphology.

Room temperature photoluminescence spectra were performed on a Jobin Yvon-Labram Spectrometer with an He–Cd laser focused to *ca.* 1 μm as the excitation source (λ_{ex} = 325 nm). As shown in Fig. 4, the UV emission at 385 nm is assigned to the recombination of excitonic centers,[18] and no defect emission was observed.

In the preparation, when the pH of $ZnAc_2$ solution (0.50 M) is adjusted to 12 with ammonia, $Zn(NH_3)_4^{2+}$ complexes are formed. Thermal treatment of the $Zn(NH_3)_4^{2+}$ precursor in ethanol led to the formation of ZnO according to eqn. (1):

$$Zn(NH_3)_4^{2+} + 2OH^- \rightarrow ZnO + 4NH_3 + H_2O \qquad (1)$$

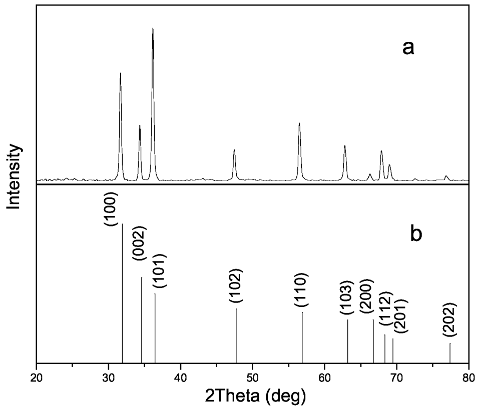

Fig. 1 XRD patterns of (a) tubular ZnO and (b) standard ZnO (JCPDS#36-1451).

Here, NH_3, as a reaction product, plays an important role in the formation of the tubular structure. At the beginning of the reaction, because of the lower temperature and the production of small amounts of NH_3, the ZnO is liable to form small nanoparticles as can be seen from the TEM image in Fig. 1. With increasing temperature, the production of larger amounts of NH_3 and the existence of a gas–liquid equilibrium in the airtight autoclave make the nanoparticles assemble along certain orientations and aggregate into hollow structure. Moreover, the solvent ethanol and the temperature are also important factors for the formation of tubular ZnO. When the temperature is lower than 180 °C, only aggregated nanoparticles are observed and no obvious hollow structures exist. If the solvent is changed to methanol or propanol, no tubular ZnO are found.

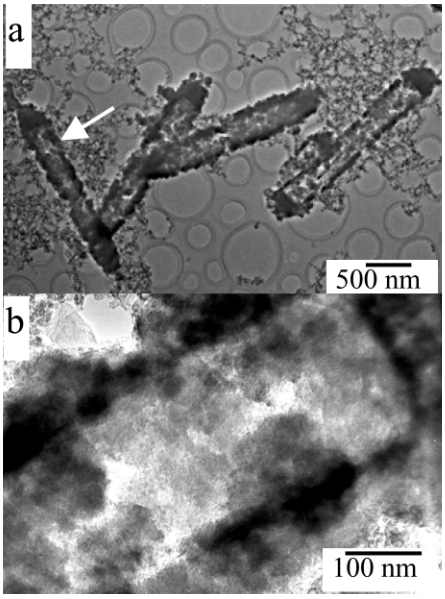

Fig. 2 TEM images of (a) as-prepared tubular ZnO and (b) the magnification of an individual ZnO tube as indicated in (a).

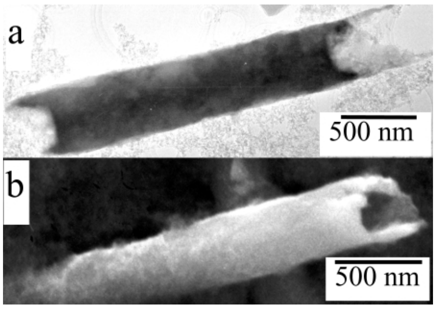

Fig. 3 TEM (a) and SEM (b) images of tubular ZnO with destroyed ends.

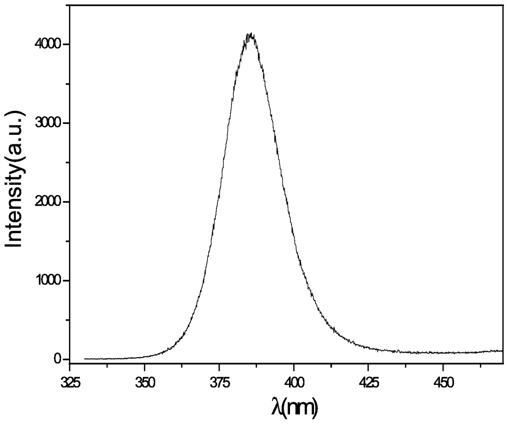

Fig. 4 The room temperature photoluminescent spectrum of tubular ZnO.

In summary, we have succeeded, for the first time, in synthesizing tubular ZnO with ~450 nm width and ~4 μm length by a simple solution route using ethanol as solvent. The room temperature photoluminescent properties of the tubular ZnO composed by ZnO nanoparticles exhibited strong UV emission around 385 nm. It is expected that the novel properties of the tubular ZnO may offer exciting opportunities for potential applications in catalysis, microsize waveguides[19] or optical fibers.[20] Since it is such a simple process, we believe it can also be applied to synthesize other tubular oxides. Further research is under progress in our laboratory.

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