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ORIGINAL ARTICLE

Synthesis and magnetic properties of hexagonally packed ZnO nanorods

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Abstract Large-scale uniform aligned ZnO nanorods with a hexagonal tip were successfully synthesized via a facile process at low temperature of (~140 °C) without using any additives and substrate. The process is based on a simple reaction of zinc powder and de-ionized water. The results reveal that the as-prepared ZnO products have an average length of 10 μm and a diameter in the range of 50–260 nm, possessing a single crystal wurtzite structure. The structure and morphology of the ZnO products are characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectrometer (EDX). The possible formation mechanism of nanorods is proposed in brief. The optical properties of grown products were characterized by room-temperature. The magnetic property was tested with a vibrating sample magnetometer at room temperature and revealed a high hysteresis loop indicating a strong ferromagnetic nature of as synthesized ZnO nanorods. The yield producing nanorods with this method includes ease, flexibility, fast being low cost and ineffective on environment free.

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1. Introduction

ZnO is a versatile semiconductor material with excellent properties and potential applications in electronics, photoelectronics, sensors and catalysts due to its wide band gap and high exciton binding energy (Klingshrin, 2007; Xu et al., 2002, 2004). The optical and electronic properties of ZnO crystals can be modulated by changing their size and morphology. Thus the control over the size and morphology of the nanometer or micrometer-sized ZnO crystals represents a great challenge to realize the design of novel functional devices. nano structural transition metal oxides like spinel ZnO have emerged from their interesting properties and technological applications in fields like catalysis, coatings, anode electrode, solid-state sensors, energy storage, optoelectronics, photothermal, and magnetism.

Up to now, a large quantity of ZnO nano- and microstructures with various exciting shapes have been successfully synthesized by different techniques (Wie et al., 2005; Pan et al., 2001; Wang,2004, 2007; Yang et al., 2006). The gas phase based processes always involve vacuum environment, high temperature, and complicated controlling process, which may result in poor dispersion, impurity or the decomposition of

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the final product and are unfavorable for low-cost and large-scale production. In contrast, the facile solution-based synthesis approaches become a promising choice to solve the above problems due to their facile manipulation, low cost, and potential for scale-up by increasing the amount of the reactants and keeping the same molar concentration. Due to the low growth temperature, the convenience and simplicity in fabrication process, hydrothermal treatment, as a typical solution approach, has been extensively explored for growing ZnO single crystals with a variety of morphologies, including rods, tubes, disks, flowers, dumbbells, or other nano- and micro-structures by self assembly of nano scaled building blocks (Park et al., 2002; Koh and Loh, 2005; Muller et al., 2003; Yang and Chen, 2004). But most of the pathways in solution approach suggested for the synthesis of ZnO involve environmentally malignant chemicals which are toxic and not easily degraded in the environment. Organic solvents are practically problematic because many are toxic which makes the nanomaterials useless for practical applications. Environmental friendly chemical synthesis requires alternative solvents such as ionic liquids, liquid and water. Water is particularly attractive because it is inexpensive, environmentally benign and bestowed with many virtues especially under supercritical conditions (Lyu et al., 2002). In our preliminary studies reported earlier, we have obtained nanorods by varying the parameters of the reaction (Shah and Al-Marzouki, 2010). Encouraged by the results, the present studies have been carried out keeping the time and temperature constant.

In this paper, we report a simple route to fabricate aligned hexagonal ZnO nanorods without any templates, or substrates or surfactants at a low temperature of ~140 °C. The crystallinity, morphology, and structure of the samples are examined by various techniques. Furthermore, the possible formation mechanism of the growth is discussed in detail. To the best of our knowledge, the synthesis of nanorods with a hexagonal tip without organics, catalyst and toxic solvents has not been reported so far. From the viewpoint of material design, preparation of ZnO nanosrods with high surface area and narrow size distribution can provide effective nanorods as catalysts and magnetic materials in its applications. With the above consideration in mind, this study focuses mainly on the synthesis of ZnO nanorods by hydrothermal method at relatively low temperature. Material characteristics including crystal structure, morphology, optical and magnetic properties were investigated in detail, too. The reported method besides being organics free is economical, fast, environmentally benign and free of pollution, which will make it suitable for large scale production.

2. Experimental

2.1. Materials

Zinc powder AR grade (Ranbaxy > 5 μg) was used as a source of zinc and was cleaned by ultra-sonication in acetone and water for 10 min in each solvent. A closed cylindrical Teflon lined stainless steel chamber was used for the synthesis. De-ionized water was prepared in the laboratory, which has been used throughout the synthesis.

2.1.1. Synthesis

In synthesis, taken 4 mg of zinc metal powder was taken with 40 ml of de-ionized water in a Teflon-lined stainless steel chamber with 50 ml capacity. The prepared reaction mixture was kept at 140 °C in an oven for 6 h. After the desired time, the system was allowed to cool down naturally and the resulting mixture was centrifuged. The zinc foils, collected from the reactions vessels, were washed with de-ionized water several times and finally dried in air.

2.1.1.1. Preparation of ZnO nanorods. All the chemical reagents used in the present experiments were of analytically pure grade without further purification. The synthesis of zinc oxide (ZnO) nanorods was handled with a hydrothermal technique. In a typical synthesis, 0.025 mol of zinc metal powder was dissolved in 100 ml deionized water and then a solution containing 2 mol NaOH was slowly added with magnetic stirring at room temperature. The resulting precipitate was filtrated with distilled water and dried at 80 °C for 24 h, after that annealing at 400 °C for 2 h in a furnace. The annealing powders were dissolved again in water to get a solution. The homogeneous solution was transferred into a 100 ml Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 120 °C for 30 h, and then allowed to cool to room temperature naturally. Subsequently, the resulting precipitate was collected by filtration treatment. After being washed with deionized water several times, the products were dried at 80 °C under vacuum for 5 h.

2.1.2. Instrumental analyses

The phase structure of as synthesized ZnO was performed using X-ray diffraction (Philips PW1370) with Cu Kα (λ = 1.54056), operating at 35 kV and a scanning rate of 0.02°/s. The morphology, size and microstructure of the synthesized products were characterized by field emission scanning electron microscopy (FESEM) using a JEOL JSM 6330F instrument, operating at an accelerating voltage 10 kV, equipped with Energy dispersive spectroscopy (EDS). Transmission electron microscopy (TEM) measurements were carried out using a JEOL JEM-2000 FX electron microscope, operating at an accelerating voltage 130 kV. The chemical structure of the prepared particles was performed by using a Fourier transform infrared (FTIR) Raman spectrometer (Nicolet, USA), laser source of 0–2 W and an exposure power of 0.7 W was used for measuring the ultraviolet absorption spectra in the region of 200–4000 cm^{-1} frequency range. The sample was mixed with KBr pellets and pressed in the form of pellets for FTIR spectral measurements. The thermal stability of prepared sample was investigated using Thermogravimetric measurements non-isothermally with a Perkin Elmer TGS-2 instrument. The measurements were conducted at heating rates of 10 °C/min in air atmosphere in the temperature range of 20–800 °C. The magnetic properties of as prepared ZnO nanorods were investigated using a vibrating sample magnetometer (VSM, Model TM-VSM1230-HS) at room temperature and magnetic susceptibility measured at different temperatures.

2.1.3. Characterization of samples

Phase structure and the purity of the as prepared samples were characterized by powder X-ray diffraction (XRD) taken on a Philips (X'Pert PRO PW-3710) diffractometer with 2θ ranging from 10° to 60°, using Cu Kα (λ = 0.15141 nm) radiation operated at 40 kV and 30 mA. The morphology of the products was carried out using Field Emission Scanning Electron

Microscope (FEI SEM, NNL 200, Japan), coupled with energy dispersive X-ray spectrometer EDX (Gensis).

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3. Results and discussion

3.1. Morphology examinations

Fig. 1(a,b) show the low-magnification FESEM images of the nanorods and confirms that the nanorods are grown in a very high density over the whole foil substrate. The nanorods are hexagonal in shape and possessing smooth and clean surfaces throughout their lengths. The typical diameters of the as-grown nanorods are ~50–260 nm with length in micrometers. The nanorods are exhibiting hexagonal surfaces and facets throughout their lengths which confirm that the nanorods are well-crystalline and possessing wurtzite hexagonal phase.

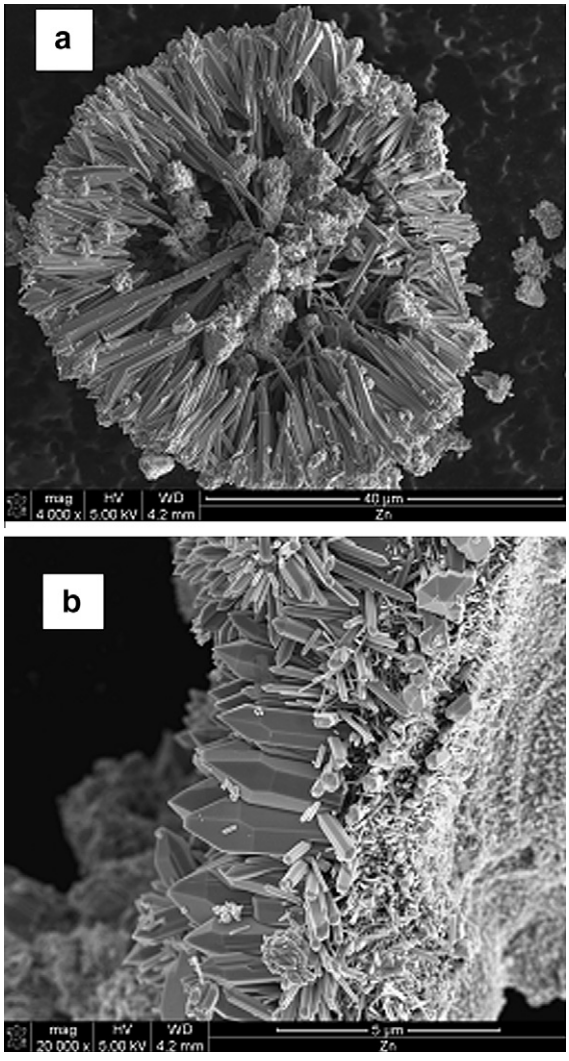

Figure 1 Typical (a and b) low FESEM images of nanorods obtained by the reaction of zinc metal powder with water at 140 °C for 6 h.

3.2. Composition of sample

EDX analysis was performed as shown in inset in Fig. 2. It is confirmed from the EDX analysis that the grown nanorods are composed of zinc and oxygen only. The molecular ratio of Zn:O of the grown nanorods, calculated from EDX and quantitative analysis data, is close to that of bulk.

3.3. Structural information

The XRD patterns of the as-prepared samples synthesized at 140 °C shown in Fig. 3 reveal diffraction peaks of (1 0 0), (0 0 2), (1 0 1), (1 0 2) and (1 1 0), which are characteristic of the pure ZnO with the wurtzite hexagonal phase. All the peaks in the pattern can be indexed to hexagonal wurtzite structure with space group $P6_3mc$ and lattice constants $a = 0.3249$ nm, $c = 0.5206$ nm, (JCPDS card No. 36–1451). No diffraction peaks arising from any impurity can be detected in the pattern and confirms that the grown products are pure ZnO. The fact that no discernible peak was identified in the low range of $2\theta = 1$–$10°$ has ruled out the existence of the amorphous structure. The results indicate that the hydrothermal method is a fast and cheap route for the fabrication of single phase ZnO nanorods at relatively low temperature. One of the most often used approaches in estimating the average particle size from the X-ray data is the utilization of the Debye–Scherer formula (Klingshrin, 2007; Wang et al., 2007):

$$D = \frac{k\lambda}{\beta \cos\theta} \tag{1}$$

where k is a constant which is taken to be 0.89, λ is the wavelength of the X-rays used (1.54056), β is the full width at half maximum of the peak and θ is the Bragg diffraction angle.

The average diameter of the ZnO nanrods calculated from X-ray patterns by using the Scherer formula was 22 nm.

However, the lattice parameter (a) of synthesized cubic ZnO has been calculated from X-ray data using the formula (Dornheim et al., 2003; Martin et al., 2003):

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \tag{2}$$

where d is the lattice spacing and h, k, and l are the miller indices of the plane. The strongest reflection peak (3 1 1) at $2\theta = 36.48°$, was used to estimate the lattice expansion of the ZnO nanorods. The computed values of lattice parameter (a) of synthesized cubic ZnO is found to be 8.084 . It is interesting to note that a small lattice contraction along the (3 1 1) was detected in the cubic ZnO which can be ascribed to large aspect ratio and high surface area. To confirm the above fact we estimated the specific surface area of the cubical face centered ZnO along the strongest reflection peak (3 1 1) using the formula:

$$S_a = \frac{6a^3 N_a}{8DM_w} \tag{3}$$

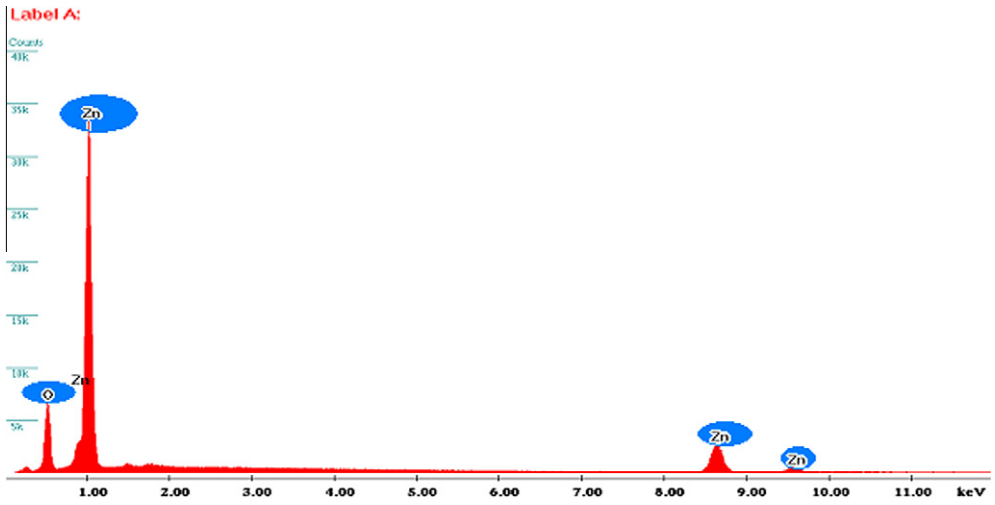

Figure 2 The EDX analysis confirming the existence of all elements involved in sample preparation.

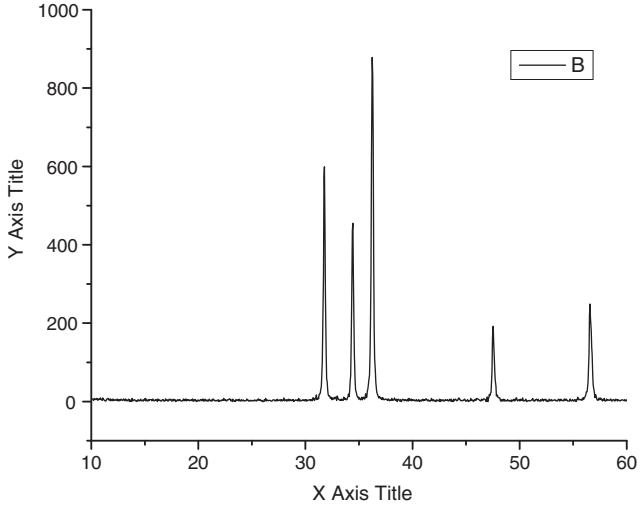

Figure 3 Typical XRD pattern of as-grown ZnO nanorods.

where M_w is the molecular weight of ZnO and N_a is Avogadro's constant.

The estimated values of specific surface area are 81.6 m^2/g. These results show that the high surface area of ZnO nanorods again produce the lattice contraction along the (3 1 1) plane.

The surface morphology of the synthesized ZnO nanorods was examined by field emission scanning electron microscopy (FESEM) images. FESEM examinations reveal a large amount of ZnO nanorods formed with a straight structure and several dozens of nanometers in diameter as shown in Fig. 1(a,b), observed a typical low-magnification, medium-magnification, and high-magnification FESEM images indicates that the as-synthesized ZnO consists of a large quantity of 1D nanostructures and the overall morphology of ZnO nanorods. The straight uniform nanorods were randomly oriented with a length about 7 μm. The nanorods have mean diameters of 22 nm and given good agreement with the results obtained from X-ray above.

These results are in good agreement with those reported in the literature.

3.4. The formation mechanism

The formation of ZnO nanorods on zinc powder in the presence of water can be explained by various chemical reactions. As initially, zinc does not react with water molecules but at 140 °C and under pressure in Teflon-lined stainless chamber, zinc reacted with water and forms a protective zinc hydroxide ($Zn(OH)_2$) layer with dissolved hydroxide ions onto the surfaces of zinc. As the concentration of Zn^{2+} and OH^- ions exceeds a critical value, the precipitation of ZnO nuclei starts. $Zn(OH)_2$ can be transformed into ZnO crystals via the simple chemical reactions mentioned below:

$$Zn(OH)_2 \xrightarrow{\Delta} ZnO + H_2O \quad (4)$$

The formed ZnO nuclei are the building blocks for the formation of the final products. Even though a plausible growth process for the formation of ZnO hexagonal-shaped ZnO nanorods is described here but more studies are needed to clearly explain the growth process for the formation of these nanorods. The zinc oxide nuclei formed are the building blocks for the formation of final products. Due to crystal habits of ZnO, the nuclei have a hexagonal shape. In the wurtzite hexagonal phase, ZnO has polar and nonpolar faces. In polar ZnO crystals, the zinc and oxygen atoms are arranged alternately along the *c*-axis and the top surfaces are zinc terminated (0 0 0 1) and are catalytically active while the bottom surfaces are O-terminated (0 0 0 1) and are chemically inert. The zinc metal on reaction with water slowly gives out hydrogen (g) and the liberated oxygen reacts with the metal to give oxides as shown in the above reaction. Zn reacts with oxygen and forms ZnO nuclei, which further serve as seeds for ZnO nanorods growth. The growth of nanorods could be occurring at the small oxide nuclei that may be present on the metal surfaces (Kamalasanan and Chandra, 1996; Tonto et al., 2008).

Due to the high temperature and high pressure in the autoclave under the hydrothermal condition, a completely different reaction mechanism and formation sequence may be rationalized. Steam is generated under high temperatures to produce a hydrostatic pressure which in turn imposes a profound effect on the ultimate microstructure of the oxides thus prepared. This autogenous hydrostatic pressure can be as high as 6 bars

under a hydrothermal temperature of 140 °C. Therefore, it can be said that in this aqueous system in the sealed autoclave, the temperature has a much higher impact on reaction rate, the morphology, as well as the reaction mechanism.

3.4.1. Magnetic properties

The magnetic properties loop provides a relation between the magnetization and the applied field were measured for the ZnO nanorods at room temperature using a vibrating magnetometer. High applied field conditions were used to assure that saturation magnetization was achieved and measured (Xu et al., 2002; Pan et al., 2001). The magnetization curve of as synthesized ZnO nanorods obtained at room temperature is depicted in Fig. 4a. From Fig. 4a, it is seen the curve is typical for a soft magnetic material and indicates a hysteresis loop for the ferromagnetic behavior of the ZnO nanorods. The magnetic behavior of ZnO nanorods is induced by a cooperative spin transition that takes place at room temperature, which is related to a random cation distribution. Clearly seen are high hysteresis, irreversible changes of the magnetization as well as a shifted shape, indicating high remanent magnetization (M_r) of about 0.521 emu/g. The saturated magnetization values (M_s) of ZnO nanorods is found to be 1.28 emu/g and is lower than M_s and is found to be 2.8 emu/g of the bulk phase of ZnO (Yang and Chen, 2004; Lyu et al., 2002). The coercivity (H_c) value of the randomly oriented ZnO of about 22 nm nanorods is 0.713 kOe. These values indicate that the as synthesized ZnO has high magneto-crystalline anisotropy and good domain structure (Wang et al., 2007).

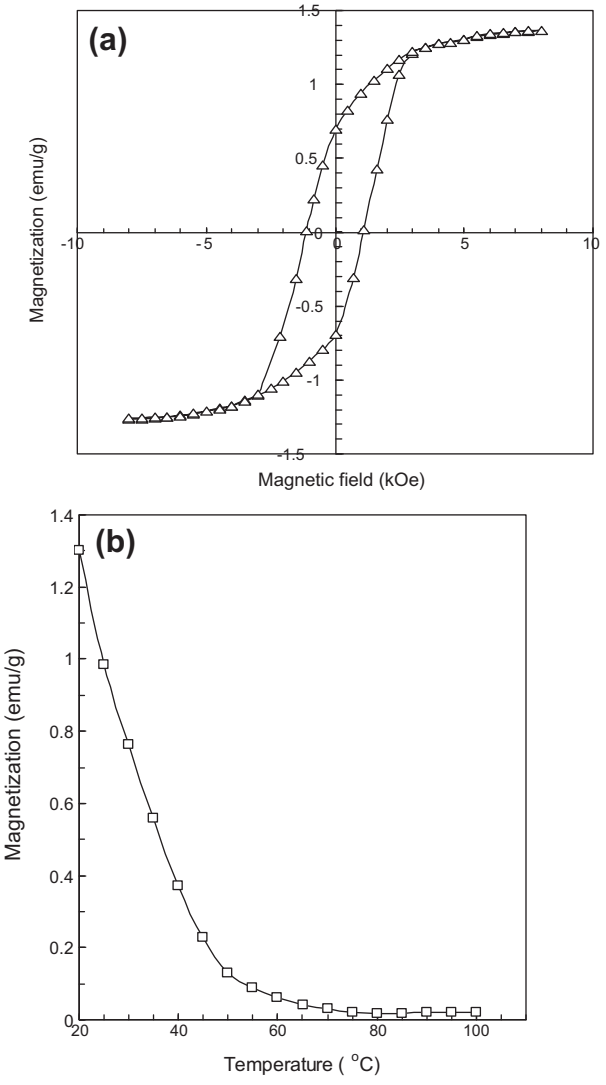

Figure 4 (a) Magnetization loop of as prepared ZnO nanorods and (b) zero-field-cooling and field-cooling curves measured at 100 Oe field with various temperature of the as-synthesized ZnO nanorods.

It is well known that the squareness ratio (SQR) is an important assessment of the quality of magnetic materials and is given by Park et al. (2002):

$$SQR = \frac{M_r}{M_s} \tag{5}$$

The estimated value of SQR is about 0.407. The high value of SQR, suggest that the as synthesized ZnO nanorods have the properties of a recording medium and are very useful for technological applications.The experimental magnetic moment (η_B) is computed from the saturation magnetization data using the following formula (Lyu et al., 2002; Shah and Al-Marzouki, 2010):

$$\eta_B = \frac{M_w M_s}{5585} \tag{6}$$

The magnetic moment per ion for the ZnO nanorods was estimated to be 4.87 B. This value is slightly higher than that of bulk crystalline ZnO (4.14 B) Koh and Loh (2005). The slight increase in the magnetic moment and the ferromagnetic behavior of the ZnO nanorods can be explained as follows. Magnetic properties of oxides depend on the way electron spins are paired. Also, it has zero net magnetization due to the complete compensation of sub lattice magnetizations (Lyu et al., 2002). Hence the change from an antiferromagnetic state for bulk ZnO to a weakly ferromagnetic state for ZnO nanorods can be ascribed to the uncompensated surface spins and finite size effects (Lyu et al., 2002; Kamalasanan and Chandra, 1996). Magnetically active Zn^{2+} ions that are localized in the hexagonal (A) sites have a permanent moment (3.25 B). Due to the small size of ZnO nanorods it is possible that some minor amount of switching of the two ion charge states between the two sites takes place (Muller et al., 2003). In addition, that is probably a part of Zn^{2+} with B and A sites due to local electron hopping. As a consequence of such a partly inverted structure, the antiferromagnetic interactions between cobalt ions on the A sites do not annihilate (Wang, 2004). So, the magnetic behavior is induced by a cooperative spin transition that takes place at room temperature, which is related to random ion distribution.

The temperature-dependent magnetization was measured in a 100 Oe field with the zero-field cooling (ZFC) procedures for the ZnO nanorods. On cooling, the ZFC magnetization begins to drop and deviates from FC magnetization at blocking temperature (TB). This study indicates that superparamagnetic behavior is blocked at 80 °C for as synthesized ZnO nanorods. These low blocking temperatures are consistent with the low magneto-crystalline anisotropy of the fcc structure.

4. Conclusion

In summary, aligned ZnO nanorods with hexagonal tip were prepared by water in a simple reaction of Zn powder and water at 140 °C without any substrates. This method is found to be a mild, convenient and efficient route to prepare ZnO nanostructures without the template or crystal seeds. It may be extended to fabricate other metal oxide nanomaterials. Successfully synthesized a hexagonal structure of ZnO nanorods in length at relatively low temperature, by a hydrothermal method which is a very simple, low cost and environmentally friendly. This convenient synthetic route can be readily extended to other technologically important metal oxides.

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