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LETTER

# Synthesis and optical characteristic of ZnO nanorod

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ZnO is a wide band gap semiconductor with an energy gap of 3.37 eV at room temperature. It is a versatile material and has been used considerably for its catalytic, electrical, optoelectronic and photochemical properties [1, 2]. ZnO has large exciton binding energy (60 meV) which allows UV lasing action to occur even at room temperature and ZnO with oxygen vacancies (ZnO:Zn) exhibits an efficient green emission. ZnO semiconductor used as photocatalytic degradation materials of environmental pollutants has been extensively studied because of its advantage in non-toxic nature, low cost and high reactivity. However, such photocatalytic degradation only proceeds under UV irradiation because of its wide band-gap and can only absorb UV light. Therefore, ZnO-based materials capable of visible-light photocatalysis are required [3]. To change the optical absorption properties and improve the visible-light photocatalysis, several approaches based on $TiO_2$ photocatalysts have been applied such as implanting transition metal ions into a $TiO_2$ powder or film to produce a red shift of the absorption spectra, treating $TiO_2$ photocatalysts by applying hydrogen plasma technology to create a new absorption band in the visible-light region through the formation of oxygen vacancies, surface sensitization of a semiconductor $TiO_2$ photocatalyst to extend the spectral response into the visible region and so on. Among the above approaches, some are effective to produce visible absorption with special facility; and some are not effective. Recently, one-dimensional ZnO nanomaterials such as nanorods and nanowires have been intensively investigated for its remarkable properties. Among them, most of the literature reported the photoluminescence properties with UV emission and little are dedicated to fabricate nanorods with visible absorption.

In literature study, many methods have been used to fabricate 1D ZnO nanorods. In the solution hydrothermal method, always alkali solution of $Zn(OH)_4^{2-}$or $Zn(NH_3)_4^{2-}$ was used as precursors [4]. In this paper, precipitate of $ZnCl_2$ and ammonia solution was used as precursors to hydrothermally synthesize ZnO nanorod and CTAB was used as surfactant and modifying agent. The absorption spectra of the as-synthesized ZnO nanorod showed red shift comparing with bulk ZnO powders. The reason for visible-light absorption was discussed.

An aqueous solution of 0.5 M $ZnCl_2$ was mixed with diluted ammonia solution slowly under stirring until pH = 6.7. After the reaction completed, the precipitate was washed and dried at 60 °C to obtain precursor. Appropriate amount of the precursor powder (0.98 g) was dispersed in 20 mL distilled water. Then 20 mL CTAB (0.1 M) was added and the pH value is adjusted by diluted ammonia or NaOH solution. The mixture was transferred into a Teflon-lined autoclave of 60 mL and pretreated by ultrasonic water bath for 30 min. After that, the autoclave was sealed and hydrothermally heated at 180 °C for 12–24 h. The obtained product was washed with distilled water and ethanol and dried.

Powder X-ray diffraction (XRD) was performed on a Bruker D8-advance X-ray diffractometer with Cu Kα ($\lambda$ = 1.54178 Å) radiation. The size and morphology of

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the product were determined using a Hitachi model H-800 transmission electron microscope (TEM) performed at 200 kv. UV-Visible absorption spectra were recorded using a 760 CRT UV-Vis double-beam spectrophotometer with a scanning wavelength range 200–800 nm.

XRD patterns of the as-prepared precursor in Fig. 1 shows that the precursor is crystalline and the diffraction peaks are consistent with the compound $ZnCl_2{\cdot}4Zn(OH)_2$ (JCPDS card No. 7–115). XRD patterns of the as-obtained nanorods are shown in Fig. 2. All the peaks of the nanorods prepared under different conditions can be indexed to the wurtzite ZnO (JCPDS card No. 36–1451, a = 3.249 Å and c = 5.206 Å) with high crystallinity. No characteristic peak of impurities such as $Zn(OH)_2$ or $ZnCl_2$ was detected. The precursor $ZnCl_2{\cdot}4Zn(OH)_2$ crystals all decomposed and grew into ZnO single crystals.

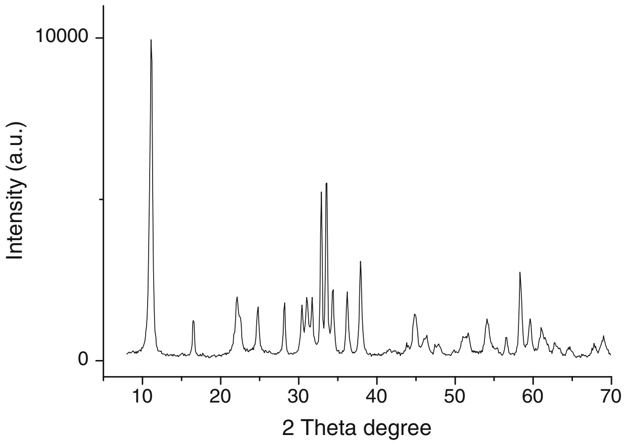

**Fig. 1** XRD patterns of the as-prepared precursor

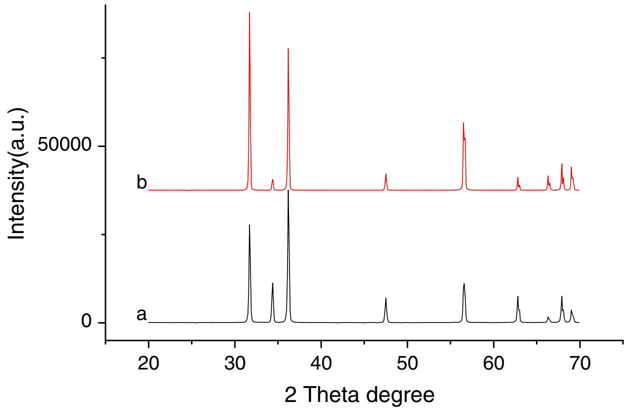

**Fig. 2** XRD patterns of ZnO nanorod prepared (**a**) in the absence of CTAB, reaction time 12 h (**b**) in the presence of CTAB, reaction time 24 h

Figure 3 shows the TEM images of the as-obtained ZnO nanorod synthesized under different conditions. Images of Fig. 3a show that the obtained samples are relatively straight and uniform with diameters between 60 and 100 nm and length between 600 and 800 nm. The aspect ratio of a corresponding nanorod is about 10. A typical selected-area electron diffraction (SAED) is shown in the inset of Fig. 3a. The ED reveals that the obtained ZnO nanorods exhibit a single-crystal structure with wurtzite type, which is in agreement with the XRD patterns.

From the appearance of the TEM images, nanosize holes are observed on the surface of the nanorods (Fig. 3b). The average diameter of the holes is about 5 nm. High-resolution TEM images (Fig. 3e) show that the holes are defects on the rod surface, which may be formed when the crystals grew. We think the microstructure is caused by the oriented aggregation of the ZnO nanocrystals, which is observed in the formation of $Co_3O_4$ nanoparticles by hydrothermal method [5]. From the viewpoint of crystal growth, oriented aggregation different from Ostwald ripening is investigated as one of the important crystal growth mechanism [5]. In the experiments by Penn and Banfield, they observed that anatase and iron oxide nanoparticles with sizes of a few nm can coalesce under hydrothermal conditions in a way they call ‘‘oriented attachment’’ [6]. In the so formed aggregates, contact areas between the adjacent particles lead to defects in the finally formed bulk crystals [6]. And the defects may be the good reason for the strong optical absorption in visible region discussed in the latter parts.

When the initial pH was adjusted to 10 by NaOH solution, with the increase of basicity, spindle shape nanorod was obtained (Fig. 3c). Though the nanorod does not exhibit well-defined border, the SAED pattern in the inset shows good single-crystal structure. These nanorods are a good evidence of ‘‘oriented attachment’’ growth. From the TEM images, one can even observe the nanoparticles are just in the process of ‘‘oriented attachment’’. The individual particles are aligned like a wall, where the second layer of bricks just started to be put on the first. During the formation process, CTAB may act as a transporter of the particles and a modifier that leads to the oriented growth of ZnO nanorods [7]. For the reaction system in the absence of CTAB ($NH_3{\cdot}H_2O$ as solvent, pH 9), large blocks of ZnO nanorod (Fig. 3d) were obtained with the diameter and length 300 nm and 2.5 μm, respectively. The morphology of the nanorods was not well controlled, however, microstructure of holes was also

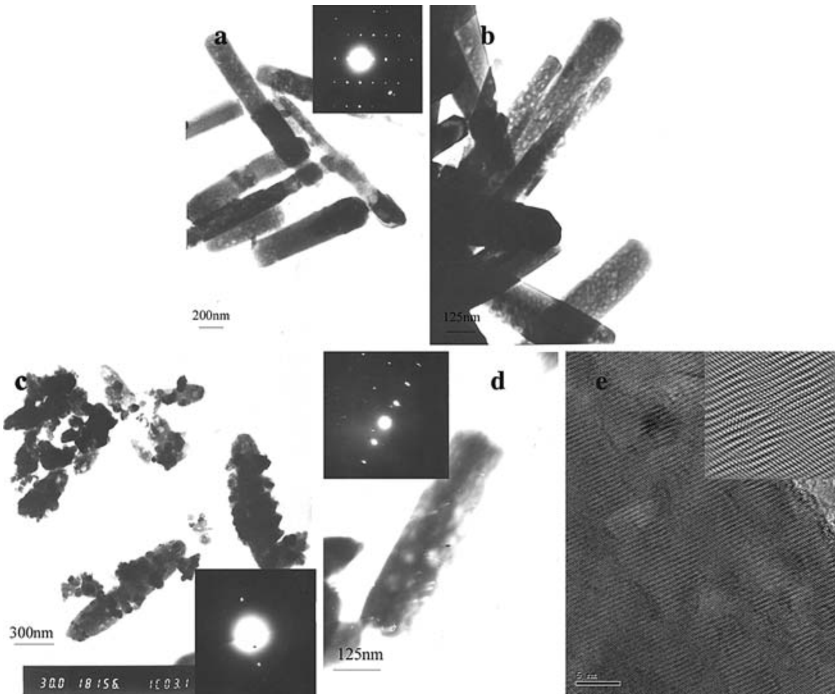

**Fig. 3** TEM images of ZnO nanorod prepared (**a**) and (**b**) in the presence of CTAB, reaction time 24 h, pH 9 (**c**) in the presence of CTAB, reaction time 12 h, pH 10 (**d**) in the absence of CTAB, reaction time 12 h (**e**) high-resolution TEM images of (**b**)

observed on the surface of the nanorod. The growth direction of the rod is [100] (Fig. 3d) different from the system in the presence of CTAB.

The UV-Vis absorption spectra of the ZnO nanorods at room temperature are shown in Fig. 4. The absorption spectrum shows a well-defined exciton band at 381 nm and red-shifted relative to the bulk exciton absorption (373 nm) [8]. From the spectra curves, one can see there is absorption almost in the whole violet and visible region. The band edge absorption begin with the wavelength at ~800 nm suggests that more absorption states or defect energy bands exist in the samples which agrees well with the discussion on the formation mechanism of the nanorods.

In summary, through the hydrothermal method with $ZnCl_2 \cdot Zn(OH)_2$ compound as precursors, ZnO nanorods have been prepared. Microstructures of holes with diameters about 5 nm were observed on the surface of the nanorod in spite of different pH conditions. “Oriented attachment” of the nanoparticles will lead to defects in the nanorod, which in turn is the reason for the red-shifted absorption examined by UV-Vis absorption spectrum. This study will provide new approaches to change the optical absorption properties and improve visible-light photocatalysis. The significant optical properties of this material may be very interesting for further application on catalyst and chemical sensors.

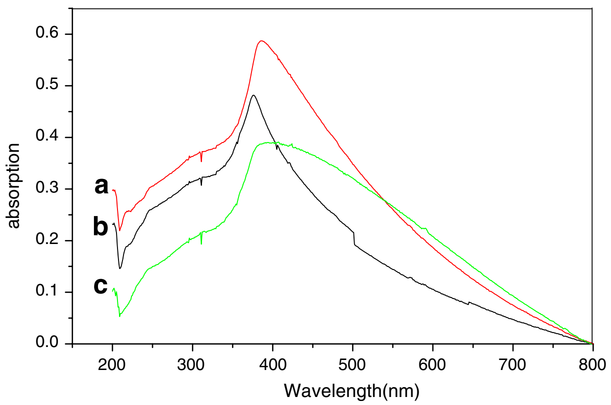

**Fig. 4** UV-Vis absorption spectra of ZnO nanorod prepared in the system of (**a**) in the presence of CTAB, reaction time 12 h, pH 10 (**b**) in the presence of CTAB, reaction time 24 h, pH 9 (**c**) in the absence of CTAB, reaction time 12 h

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