RAPID COMMUNICATION

Microwave-assisted aqueous synthesis of ultralong ZnO nanowires: photoluminescence and photovoltaic performance for dye-sensitized solar cell

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Abstract Ultralong ZnO nanowires were successfully prepared on a large scale by a microwave-assisted aqueous route without using any surfactant or template at relatively low temperature of 120°C. The obtained nanowires were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), and energy-dispersive X-ray spectrum (EDX). The growth mechanism and photoluminescence of the one-dimensional nanostructure, and photovoltaic performances for dye-sensitized solar cell (DSSC) of the nanowires were discussed in detail.

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1 Introduction

Low-dimensional nanomaterials, such as nanorods, nanobelts, nanowires, and nanotubes, have attracted much attention in the development of novel optical, electronic, magnetic, and catalytic materials [1, 2]. As an important II–VI semiconducting material, zinc oxide nanostructures have been extensively examined for their potential applications in ultraviolet laser, sensors, photocatalysts, solar cells, field emission, and so on, due to their unique optical, acoustic, and electronic properties [3–6]. It is also well known for its wide band gap (3.37 eV) and high excitation binding energy at room temperature (60 meV) [7].

Over the past few years, several methods have been developed to prepare one-dimensional ZnO nanostructures, such as chemical vapor deposition (CVD), hydrothermal/solvothermal route, template-assisted method, and thermal evaporation [8–11]. Wang's research group has successfully prepared a variety of nanostructures of ZnO, including nanowires, nanorings, nanobelts, nanoribbons, and nanonails, by a vapor–liquid–solid (VLS) process [12–15]. However, most of these routes have employed high temperature or expensive organic precursor, which are unfavorable for large-scale production. Recently, microwave-assisted heating treatment has received increasing attention as a promising method for the preparation of nanostructures. The main advantages of microwave heating are rapid volumetric heating, fast reaction rate, short reaction time, high reaction selectivity, and energy saving [16, 17].

In this paper, a large scale preparation of ZnO nanowires was reported. The nanowires were prepared by a microwave-assisted aqueous route without using any surfactant or template at relatively low temperature of 120°C. A possible growth mechanism was proposed. And room-temperature photoluminescence and photovoltaic performance for dye-sensitized solar cell (DSSC) of the nanowires were discussed in detail.

2 Experimental section

All of reagents involved in the experiments were of analytical grade and utilized as received without further purification. In a typical synthesis, zinc nitrate hexahydrate $(Zn(NO_3)_2 \cdot 6H_2O$, 5 mmol) was dissolved into 40 mL distilled water under magnetic stirring. Then, potassium hydroxide aqueous solution (KOH, 4 mol/L) was added into the above Zn-containing solution dropwise under stirring at

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Fig. 1 XRD pattern of the as-obtained ZnO nanowires
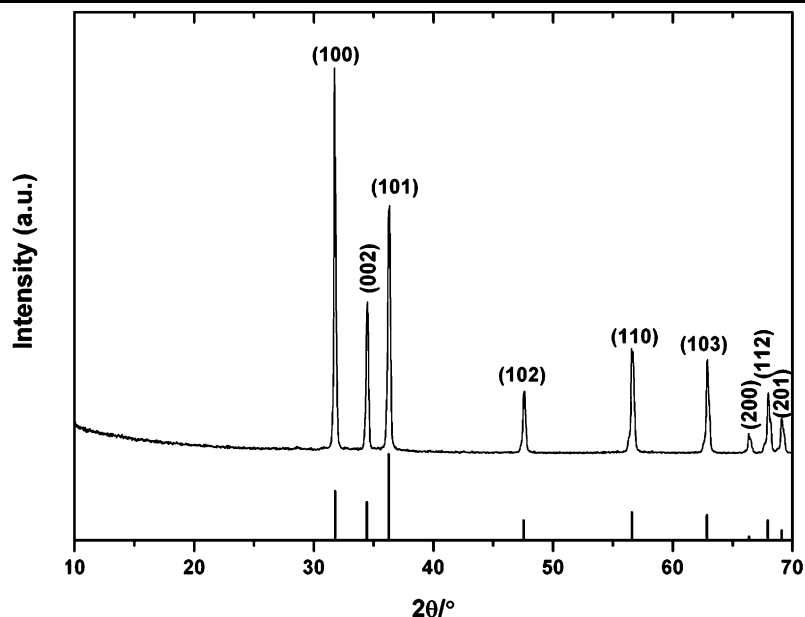
room temperature till a transparent solution was obtained. The resulting solution (PH ≈ 12) was then loaded into a Teflon-lined autoclave specially used for microwave treatment. The sealed autoclave was heated to 120°C by microwave heating and maintained at this temperature for 4 h. The microwave oven used was a focused single-mode microwave synthesis system and could operate at 0–100% of full power (900 W). After cooling to room temperature naturally, the white precipitate was collected from the solution by centrifugation, washed by distilled water and absolute ethanol for several times, dried in vacuum to obtain ZnO nanocrystals, and kept for further characterization.

The phase purity of the as-obtained products was characterized by X-ray diffraction (XRD) on a Rigaku-D Max 2400 diffractometer equipped with graphite monochromatized CuKα radiation ($\lambda = 0.15406$ nm). The size and morphology of the nanowires was determined at 20 kV by a JEOL-5600LV scanning electron microscope (SEM) and at 200 kV by a Hitachi H-800 transmission electron microscope (TEM) and a HRTEM JEM-2010FEF. Energy-dispersive X-ray (EDX) microanalysis of the samples was performed during SEM measurements. Room-temperature photoluminescence (PL) spectrum was recorded using a continuous-wave He–Cd laser as the excitation source (325 nm).

Dye-sensitized solar cell (DSSC) was prepared using the ZnO nanowires as active material as reported [18]. The porous ZnO film was deposited on In–Sn-oxide-coated glass substrates by doctor blade technique. The sample (1.0 g) was ground with 4 mL of deionized water and polyethylene glycol (0.4 g, molecular weight: 20,000). Then the slurry was spread on the surface of conducting substrate using an adhesive tape as spacer. The film was calcined in air

at 400°C for half an hour. The resulting film was dipped into a 0.4 mmol/L ethanol solution of Eosin-Y dye for a day, rinsed with ethanol to remove excess dye, and dried at room temperature. The gel electrolyte was fabricated as below: 4 mL of tetraethylorthosilicate (TEOS), 0.4 mL of glacial acetic acid, 0.3 mL of PEG, and 0.5 mL of distilled water were mixed together and sonicated for 0.5 h. Then 7 mL of redox electrolyte containing 0.03 g NaI, 0.003 g I_2, 0.15 g ethylene carbonate:propylene carbonate 1:1 in 25 mL of acetone was added into the above mixture and sonicated for additional 10 min. The as-prepared ZnO film electrode was immersed in the resulting gel electrolyte for several minutes. The ZnO electrode coated with gel electrolyte was then pressed onto a Pt sheet, which was used as counter electrode. I–V characteristic of the cell was tested with a 100 mW tungsten lamp as the light source. For comparison, the photovoltaic performance for DSSC of commercially ZnO powder with average particle size of 2 μm was also examined.

3 Results and discussion

The crystal structure of the resulting ZnO was investigated by XRD measurements. The XRD pattern displayed in Fig. 1 shows that all the diffraction peaks can be indexed as the pure hexagonal phase ZnO with the lattice parameters $a = 3.248$ Å and $c = 5.208$ Å (Space group: $P63mc$(186)), which are very close to the reported data (JCPDS File No.: 36-1451). No reflection peaks from other impurities were detected. The abnormal intensity of the diffraction peak at $2\theta = 31.75°$ (100) suggests that the oxide was preferentially oriented with their (100) planes parallel to the supporting substrate.

Fig. 2 Morphology of the ZnO naowires prepared by microwaved-assisted aqueous route: (**a**) FESEM image; (**b**) TEM image of a typical individual nanowire and the corresponding SAED pattern; (**c**) HRTEM image; (**d**) EDX spectrum of the nanowire
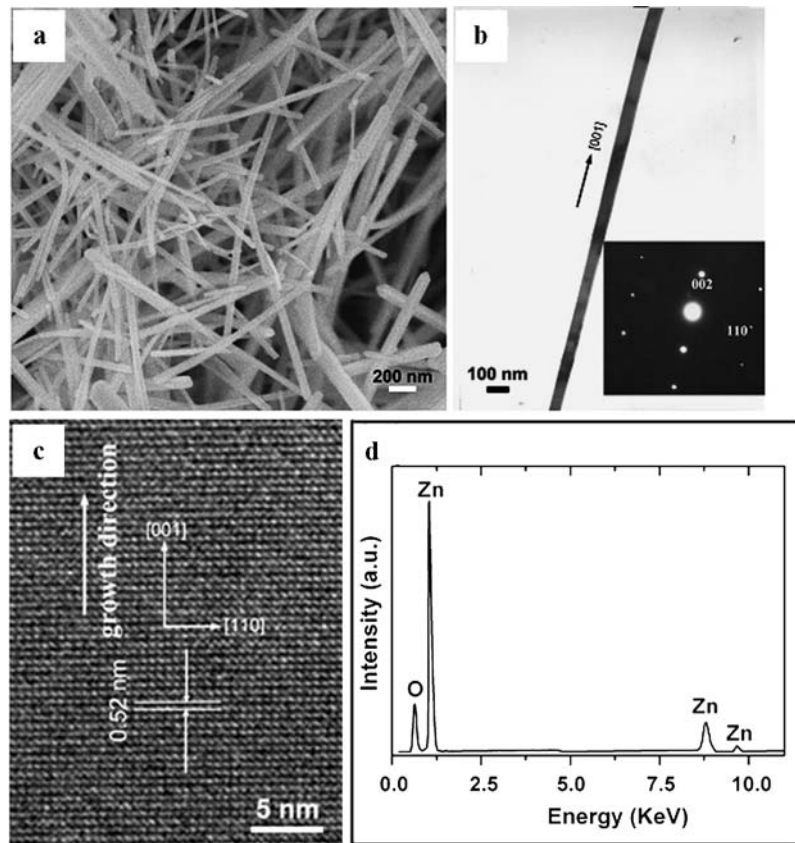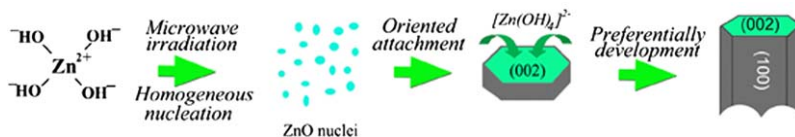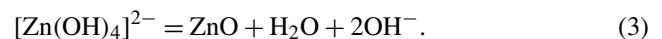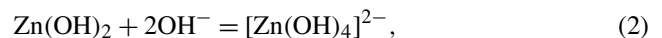

Fig. 3 Schematic representation of the formation of ZnO nanowires

The SEM image of the as-prepared ZnO was shown in Fig. 2a. As shown in the image, large quantities of uniform wire-like nanostructures were observed, and the mean diameter of the nanowires is about 80 nm with lengths up to tens of micrometers. Figure 2b exhibits a representative TEM image and the corresponding selected area electron diffraction (SAED) pattern. According to the features of the SAED pattern, the preferential growth direction of the ZnO nanowires is along [001] direction (*c*-axis), marked with an arrow in Fig. 2b. The HRTEM image displayed in Fig. 2c clearly shows a well-resolved lattice spacing of 0.52 nm corresponding to the *d* spacing of the wurtzite ZnO (001) crystal plane also indicating the preferential growth of the nanowires along *c*-axis. Furthermore, the SAED pattern and HRTEM image also reveal that the resulting nanowires are single-crystalline in nature. The composition of the nanowires was examined with EDX microanalysis. The typical EDX spectrum exhibited in Fig. 2d suggests that the nanowires are composed of Zn and O elements. Together with the XRD data and the morphology observations, all these results confirm that the ultralong single-crystalline

ZnO nanowires can be fabricated on a large scale by the microwave-assisted aqueous synthesis route.

The growth of ZnO nanowires in alkaline solution can be simply described by the following reactions:

$$Zn^{2+} + 2OH^- = Zn(OH)_2, \tag{1}$$

$$Zn(OH)_2 + 2OH^- = [Zn(OH)_4]^{2-}, \tag{2}$$

$$[Zn(OH)_4]^{2-} = ZnO + H_2O + 2OH^-. \tag{3}$$

At the initial stage of the reaction, a large quantity of homogeneous ZnO nuclei formed by hydrolysis (2) and condensation (3) during a very short crystallization time under the microwave irradiation, which is crucial to the further growth of a uniform one-dimensional nanostructure. The possible growth mechanism of ZnO nanowires was interpreted as Fig. 3. Firstly, ZnO seeds and nanoplates or nanorods were formed by dehydration of $[Zn(OH)_4]^{2-}$ and subsequent crystal growth process relating to the anisotropic crystal structure of ZnO. Due to the surface energy of the (100) planes is much lower than that of (002), the [001] di-

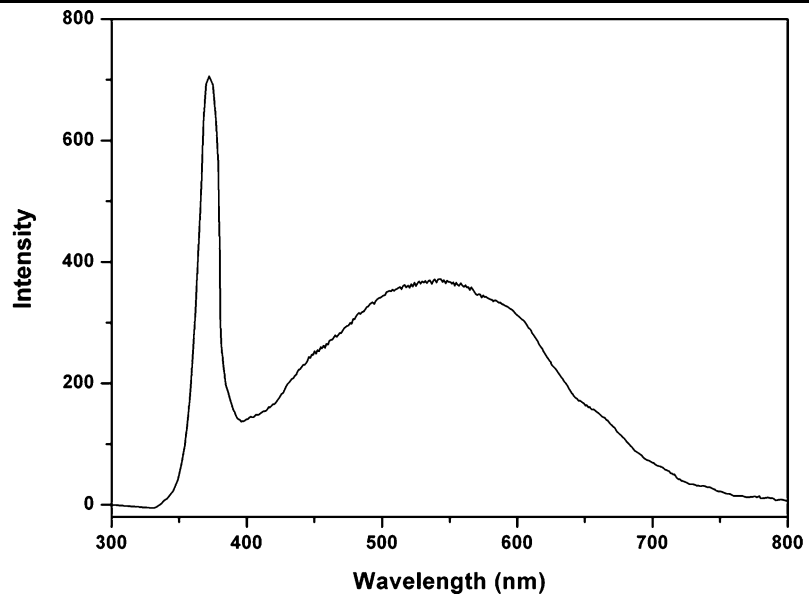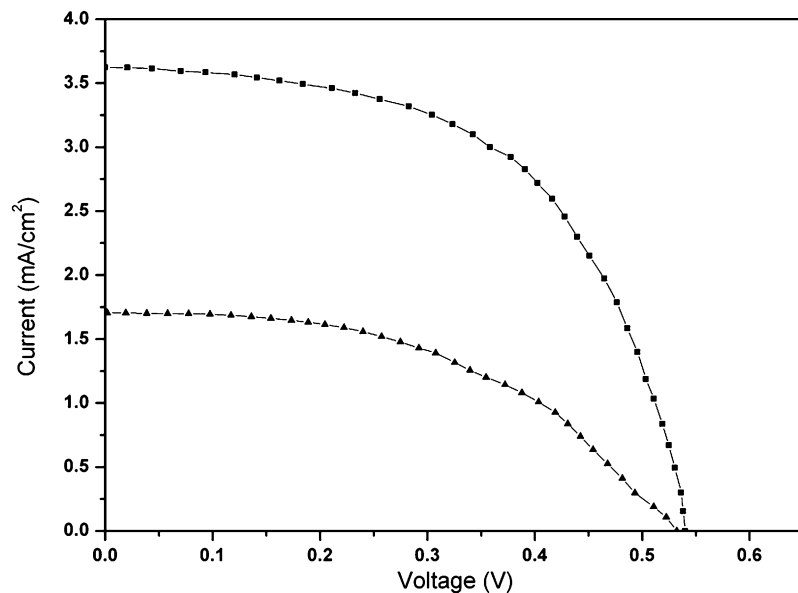**Fig. 4** Room-temperature PL spectrum of the resulting ZnO nanowires

Fig. 5 Current-voltage characteristics of dye-sensitized solar cells using the as-prepared nanowires (■: Cell-a) and commercial ZnO powder (▲: Cell-b)

rection have the highest growth rate [19, 20]. For thermodynamic stability of growth habit, ZnO prefers to grow into one-dimensional nanostructure along c-axis by the oriented-attachment process. And the surface of the nanowires are mainly (100) and (002) planes, which is consistent with the XRD results. Therefore, the whole formation process of the nanowires can be interpreted in three steps:

(1) rapid homogeneous nucleation of ZnO under microwave irradiation;
(2) oriented attachment of ZnO nuclei along c-axis; and
(3) further preferentially development of the one-dimensional nanostructures to obtain the ZnO nanowires, which was ascribed to the high surface free energy of the (001) plane.

The room temperature photoluminescence (PL) spectrum of the nanowires was measured (Fig. 4). It is can be clearly seen that the resulting ZnO nanowires display an intensive ultraviolet emission at 375 nm and a relatively weak and broad green light emission at about 540 nm. As it is well known, the ultraviolet emission is attributed to the near-band-edge emission of the wide band-gap ZnO, which are somewhat blueshifted as compared to that the bulk ZnO. Moreover, the broad band at 540 nm corresponds to the deep level emission due to oxygen vacancies. We consider that the rapid microwave heating might enhance the deep level emission.

The photovoltaic performance for DSSC of the nanowires was examined. Figure 5 shows the I–V characteristics of DSSC using the nanowires (Cell-a) and commercially ZnO

powder (Cell-b), respectively. It can be obviously observed that the open circuit voltage is the same for the two cells, whereas the short-circuit current, fill factor, and power conversion efficiency for Cell-a is much higher than for Cell-b, which might attributed to the nanocrystalline nature and unique synthetic route of the nanowires. Further study is on the way to understand the influence of growth condition on the photovoltaic performance for DSSC.

4 Conclusions

In summary, the ultralong single-crystalline ZnO nanowires were successfully prepared by the microwave-assisted aqueous route without any surfactant and template at relatively lower temperature. A variety of techniques were used to characterize the resulting oxide nanostructure. A possible growth mechanism was proposed. A room-temperature photoluminescence and a photovoltaic performance for dye-sensitized solar cell (DSSC) of the nanowires were discussed in detail. Due to the advantages of microwave heating, homogeneous and better crystalline nanostructures could be synthesized within a few minutes. As a promising heating method, a further wide application to preparation and control of nanostructures is expected.

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