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Ultrasonic-assisted synthesis and photocatalytic performance of ZnO nanoplates and microflowers

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ABSTRACT

Nanoplates, multi-layered nanorod petal flowers and microflowers of nanoneedles with pyramid tips of hexagonal ZnO nanostructures were ultrasonically synthesized in the solutions containing zinc nitrate hexahydrate, ammonium hydroxide and cetyltrimethyl ammonium bromide (CTAB) with pH adjusting to 7–10. The as-synthesized wurtzite hexagonal ZnO was detected by X-ray diffraction (XRD). Fourier transform infrared (FTIR) spectroscopy revealed the standard peak of zinc oxide at 507–518 cm^{-1}, and Raman spectroscopy at 437 cm^{-1}. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to characterize the products with the morphologies of nanoplates, multi-layered nanorod petal flowers and microflowers of nanoneedles with pyramid tips at the pH of 7, 8-9, and 10, respectively. In addition, the photocatalytic degradation of methylene blue (MB) under UV radiation by the hexagonal ZnO nanoplates is the highest at 97.54%.

1. Introduction

In recent years, controlled morphologies of one-, two- and three-dimensional (1D, 2D and 3D) inorganic micro- and nanostructure materials have been potential applications in photonics, nanoelectronics, catalysis, information storages, biosensors, drug-delivery carriers, biomedical diagnosis, light weight fillers, acoustic insulators and chemical reactors. Thus they have been attracted interest a number of scientists and engineers. The properties and performance of micro- and nanostructure materials are largely influenced by the morphologies comparing with their bulk counterparts [1–3].

ZnO with direct band gap of 3.37 eV and large exciton binding energy of 60 meV at room temperature is one of II–VI semiconducting materials having a variety of applications: solar cells, optoelectronic devices, varistors, ultraviolet laser, field-effect transistors, photodetectors, gas sensors, photocatalysts in functional devices and UV-light emitters, including biosafety and biocompatible material for biomedical applications [4–7]. The different physical and chemical synthetic methods such as hydrothermal reaction [1,5], thermal evaporation [8,9], chemical vapor deposition (CVD) [10–12], electrochemical deposition [13,14] and microwave-assisted synthesis [15,16] have been used to control morphology of ZnO nanostructures: star-shape [1], rods [4,11], dumb-bells [4], nanosheets [5], triangular shape [6], flowers [7], tetrapod [8], hexagonal columnar [12], nanotubes [13,14], nanosheet-assembled flowers [15,16] and hexagonal pyramids [15,16].

High frequency ultrasonic wave was used to synthesize inorganic micro- and nano-structure materials such as AMO_4 (A = Ca, Sr and Ba and M = Mo and W) [17,18], CdS [19], Mn_2O_3 [20], $LiMn_2O_4$ [20], TiO_2 [21] and Fe_2O_3 [22]. During ultrasonic processing, propagation of pressure wave and implosive collapse of bubbles in liquid medium are intense enough to induce formation and growth. These bubbles generate localized hot spots having extreme high temperature (>5000 K) and pressure (>20 MPa) with very high cooling rate (10^{10} $K \cdot s^{-1}$). This method has the advantage used to prepare inorganic materials with unique morphology and unusual properties owing to the rapid reaction rate, controllable reaction and ability to form materials with uniform shape, narrow size distribution and high purity [23,24].

In this research, nanoplates and flowers containing multi-layered petals and nanoneedles with pyramid tips of ZnO nanostructures were

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synthesized by ultrasonic-assisted solution synthesis. The structure, morphologies, formation mechanism and photocatalytic properties were investigated and discussed in this report.

2. Experimental procedure

The different morphologies of ZnO nanostructures were synthesized by the ultrasonic-assisted solution method using zinc nitrate hexahydrate, ammonium hydroxide and cetyltrimethyl ammonium bromide (CTAB) as starting materials. All chemicals were purchased from Sigma-Aldrich Corporation and used without further purification.

Typically, 0.005 mol of zinc nitrate hexahydrate was dissolved in 100 ml deionized water. Ammonium hydroxide aqueous solution was dropped in Zn^{2+} solutions until reaching at the pH 7, 8, 9 and 10 with continuous stirring. Following the pH adjusting, each 10 ml 0.01 M CTAB was added to the precursor solutions with constant stirring for 30 min. Subsequently, the resultant solutions were ultrasonically vibrated at 80 °C for 5 h. In the end, white precipitates were synthesized, filtered, washed with methanol several times to remove ionic impurities and dried at ambient temperature.

Phase and crystalline degree of the products were analyzed by an X-ray diffractometer (XRD, Philips X'Pert MPD) with Cu K_α radiation in the 2θ range of 15°–60°. The morphology investigation was carried out by a field emission scanning electron microscope (FE-SEM, JEOL JSM-6335F) operating at 35 kV and a transmission electron microscope (TEM, JEOL JEM-2010) operating at 200 kV. A Fourier transform infrared spectrometer (FTIR, Bruker Tensor 27) was carried out at room temperature in the range of 400–4000 cm^{-1}. ZnO samples were diluted by 40 times KBr for FTIR testing. A Raman spectrometer (T64000 HORIBA Jobin Yvon) was operated using a 50 mW and 514.5 nm wavelength Ar green laser.

Methylene blue (MB) was used as probe molecules to determine photocatalytic activity. The photocatalysis was conducted through solutions under UV radiation at room temperature. The photocatalytic system contained 200 mg photocatalyst dispersed in each 200 ml 1×10^{-5} M MB aqueous solution. Prior to irradiation, the suspension was magnetically stirred in the dark for 30 min to establish an adsorption/desorption equilibrium of MB on the photocatalytic surface. During photocatalysis, approximately 5 ml solution was sampled every 20/40 min. The aqueous solutions were spun to precipitate the suspended catalytic particles. The residual concentrations of the MB solutions containing in liquid cuvettes were determined by a UV–visible spectrophotometer (Perkin Elmer Lambda 25) with de-ionized water as a reference. The MB degradation was calculated by the following

$$\text{Decolorization efficiency } (\%) = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

C_o is the initial MB concentration and C_t is the residual MB concentration after photocatalysis for a period of time (t).

3. Results and discussion

The samples synthesized in the solutions with the pH 7, 8, 9 and 10 by sonochemical process for 5 h was characterized by XRD over the 2θ range of 15°–60°, as the results shown in Fig. 1. The XRD patterns revealed five peaks at 2θ of 32.0°, 34.5°, 36.5°, 47.8° and 56.5° specified as the (100), (002), (101), (102) and (110) planes of wurtzite hexagonal close-packed ZnO structure (JCPDS no. 36-1451) [25], respectively. No other diffraction peaks originated from impurities were detected, indicating the successful synthesis of high purified ZnO crystal. Note that all diffraction intensities of the highest basicity (pH = 10) were higher than those of others which revealed the synthesis of ZnO with the highest crystalline degree.

Hexagonal ZnO belongs to C_{6v}^4 space group with two formula units per primitive cell and all atoms occupy the 2b sites of C_{3v} symmetry.

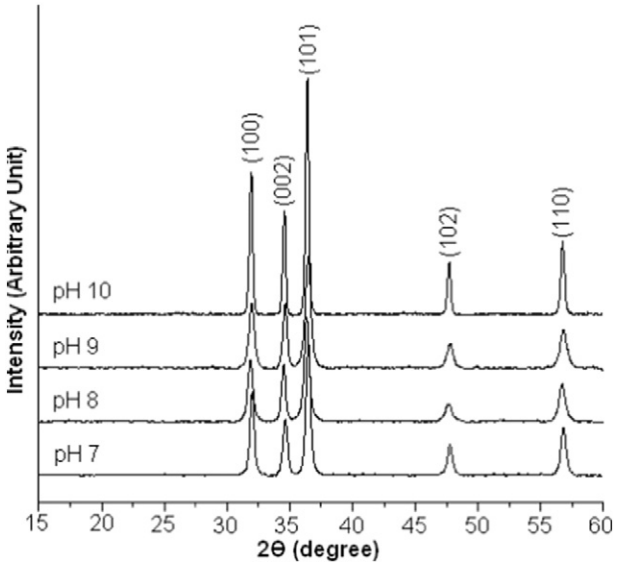

Fig. 1. XRD patterns of ZnO synthesized in different precursor solutions with the pH of 7, 8, 9 and 10.

According to the group theory, the single-crystalline ZnO has six optical phonon modes at the center of Brillouin zone [15,16,26,27]:

$$\Gamma = A_1 + 2B_1 + E_1 + 2E_2 \quad (2)$$

Only A_1, E_1 and E_2 are Raman active for wurtzite hexagonal ZnO single crystalline materials. Furthermore, A_1 and E_1 are also infrared (IR) active and are split into longitudinal optical (LO) and transverse optical (TO) components. The nonpolar phonon modes with E_2 symmetry have two frequencies: E_{2H} associated with oxygen atoms and E_{2L} associated with Zn sublattice [5,15,16,26,27]. Fig. 2 shows the Raman spectra of ZnO samples operated by Ar-ion green laser with 514.5 nm excitation wavelength over the wavenumber of 200–800 cm^{-1} range with silicon wafer as reference at room temperature. They show two lower intensity peaks at 330 and 380 cm^{-1} of the $E_{2H} - E_{2L}$ (multi-phonon process) and A_{1TO} modes, respectively. A strong dominant E_{2H} mode at 437 cm^{-1} was specified as the intrinsic characteristic of the Raman-active mode of wurtzite hexagonal ZnO structure. Apparently, suppressed peak at 581 cm^{-1} was assigned to the E_{1L} mode. It was attributed to the impurities and structural defects (oxygen vacancies and Zn interstitials) of the as-synthesized ZnO samples [5,15,16,26,27].

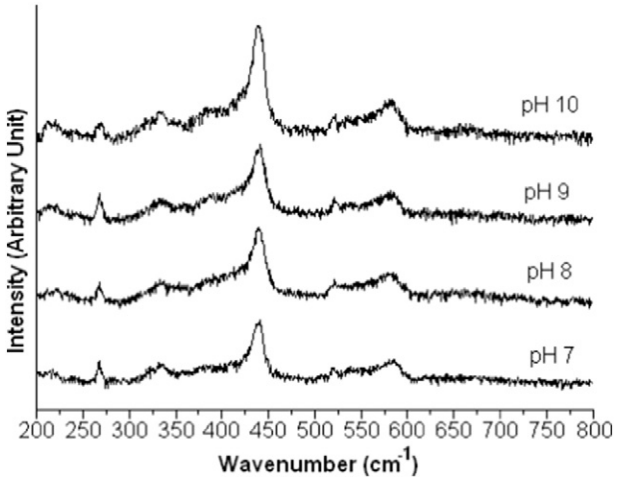

Fig. 2. Raman spectra of ZnO synthesized in different precursor solutions with the pH of 7, 8, 9 and 10.