Desalination and Water Treatment
www.deswater.com

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doi: 10/5004/dwt.2011.2159

26 (2011) 297–300
February

Preparation and characterization of mesoporous ZnO by polystyrene microemulsion

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Received 7 July 2010; Accepted 7 January 2011

ABSTRACT

A simple route to synthesize mesoporous ZnO nanoparticle was reported by using polystyrene microemulsion system composed of cetyltrimethylammonium bromide/styrene/zinc nitrate/ammonium persulfate. The samples were characterized by thermogravimetry and differential thermal analysis (TG-DTA), X-ray diffraction, scanning electron microscope and mercury porosimeter. Experimental results showed that the specific surface area and pore volume of the synthesized mesoporous zinc oxide were 11.013 m^2/g and 0.1551 cm^3/g, respectively. On the basis of the experimental results, the possible mechanism of pore formation was proposed. Moreover, the photocatalytic activities of the synthesized ZnO were also evaluated in the photodegradation of methylene blue in aqueous solutions under UV irradiation, and all of the synthesized ZnO exhibited high photocatalytic activities.

Keywords: ZnO; mesoporous materials; microemulsion; polystyrene

1. Introduction

Nano-ZnO known as an important inorganic functional material has attracted researchers' high attention for a long time due to its broad application prospects in the sensor, photoelectric conversion device, photocatalytic and photoelectric materials, etc. [1,2]. In the past several years, various approaches, including thermal decomposition [3], homogeneous precipitation [4], hydrothermal method [5], sol-gel technology [6], mechanochemical synthesis [7], microwave [8], organometallic synthesis [9] and microemulsion [10], have been used to prepare ZnO nanostructures with different morphologies and dimensions. However, due to the special characteristics of the large specific surface area, high porosity and narrow pore size distribution, mesoporous ZnO nonmaterial has been attracting increasing attention because of its great potential application in electron, optics, catalysis, solar energy conversion and other optoelectronic devices. Liu et al. prepared ZnO porous thin films by sol-gel method using PEG as template [11], and similar result was also reported by Sun et al. [12]. Wagner et al. prepared ordered mesoporous ZnO by a two-step structure replication method [13]. However, to the best of our knowledge, few efforts have been made to synthesize ordered, pore-uniform mesoporous ZnO nanoparticles through microemulsion method.

In this paper, we provide a new method to synthesize mesoporous ZnO by using polystyrene microemulsion as template, which is composed of cetyltrimethylammonium bromide (CTAB)/styrene (ST)/zinc nitrate/ammonium persulfate (AP). The specific surface area, pore volume, microstructure and morphologies of the mesoporous ZnO were investigated. The possible mechanism of pore formation was proposed and the photocatalytic activities of the as-prepared ZnO were also evaluated.

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Compared with the traditionally synthetic methods, the present work provides a simple, convenient and low energy route for the preparation of mesoporous ZnO nanoparticles with high photocatalytic activities.

2. Experimental

2.1. Materials and methods

All the chemicals (analytical grade reagents) were purchased from Tianjin Chemical Reagent Company and used without further purification. Deionized water was used throughout this study.

The procedure for the preparation of polystyrene microemulsion was adopted from the literature [14,15] and was used without any other treatment. In a typical procedure, 2.0 g CTAB was firstly mixed with 2.0 g ST and then 100 ml zinc nitrate solution (0.1 mol/l) was slowly added into the mixture under vigorous stirring at room temperature. Then, 0.02 g AP (initiator) was added into the above solution, and the mixture was kept stirring for 6 h at 60°C. After that, the semitransparent polystyrene microemulsion was obtained and subsequently cooled to room temperature. Appropriate ammonia was slowly added into the polystyrene microemulsion by drops under the vigorous stirring. Keep stirring for 5 h and then aged another 24 h, ZnO precursor was obtained by filtration and dried under vacuum. At last, the precursor was transformed to ordered mesoporous ZnO by calcination. The photocatalytic activities of the mesoporous ZnO obtained at different calcination temperature were investigated by degrading the methylene blue (MB). The detailed photocatalytic process was reported in our previous study [16].

2.2. Characterization

TG-DTA analysis of the precursor was carried out by thermal analyzer (TG-DTA Instruments, Netzsch STA449C, Germany). The crystal structures of the mesoporous ZnO were examined by X-ray diffraction (XRD, DX-2000, China). The morphologies of the nanoparticles were observed using scanning electron microscopy (SEM, JSM-63901, Japan) and transmission electron microscopy (TEM, JEM-2100, Japan). The pore size distribution of the synthesized ZnO was determined by mercury porosimeter (Quantachrome Pore Master-33, USA) employing mercury as the adsorbent.

3. Results and discussions

3.1. TG-DTA analysis of the ZnO precursor

Fig. 1 shows the TG-DTA curves of the ZnO precursor in nitrogen atmosphere, by which the thermal behaviors of the precursor can be well understood. The first endothermic peak appearing at around 110°C is attributed to the loss of adsorbed water. The secondly sharp endothermic peak appearing at around 226°C accompanied with obvious weight loss (41%) is ascribed to the vaporization of polystyrene. The last endothermic peak appearing at around 322°C accompanied with the weight loss is due to the decomposition and crystallization of the precursor.

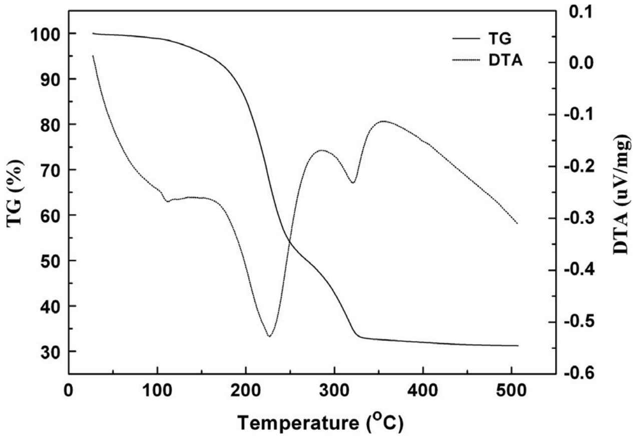

Fig. 1. TG-DTA curves of the ZnO precursor.

3.2. XRD patterns of the mesoporous ZnO

XRD patterns of the mesoporous ZnO prepared at different calcination temperature are shown in Fig. 2. It can be seen that the diffraction peaks match well with the JCPDS card No 36-1451, which corresponds to the hexagonal wurtzite structure of ZnO. In addition, no impure phase is detected in the XRD patterns when the

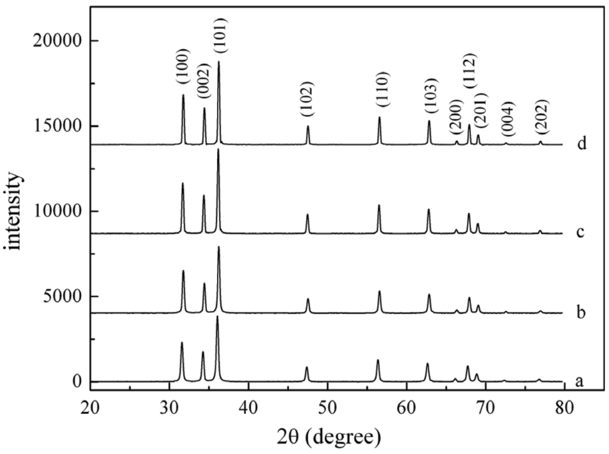

Fig. 2. XRD patterns of ZnO calcined at different temperature (a) 400°C, (b) 500°C, (c) 600°C, (d) 700°C.

calcination temperature varies from 400 °C to 700 °C. According to the Debye–Scherrer formula, the average crystal sizes of the mesoporous ZnO calcined at 400, 500, 600 and 700 °C are 34.9, 40.3, 46.7 and 49.2 nm, respectively, which indicates that the crystallinity and average crystal sizes of the as-prepared ZnO increase with the increasing of the calcination temperature [17].

3.3. Porosity analysis

As shown in Fig. 3, the structural characteristics of the mesoporous ZnO calcined at 500 °C are analyzed by the mercury intrusion method. The pore size distribution, specific surface area and pore volume of the synthesized sample are calculated by Washburn equation. It can be seen that the pore size of the synthesized sample ranges from 21 to 78 nm with a uniform pore size distribution centered at about 40.2 nm, as proved by the pore size distribution inserted in Fig. 3. Additional information can also be found in Fig. 3 that the specific surface area and pore volume of the synthesized ZnO are 11.013 m^2/g and 0.1551 cm^3/g, respectively. The possible mechanism of pore formation is suggested as follows: In polystyrene microemulsion, a number of CTAB-containing polystyrene micelles homogeneously distribute in water phase. When ammonia is slowly added into the polystyrene microemulsion, the inorganic precursors begin to appear and subsequently polymerize into the surface of polystyrene micelles due to the vigorous stirring and electrostatic attraction. The growing inorganic polymers may bind several micelles through aging and then self-assemble into a certain shape precursor [18]. Finally, mesoporous ZnO can be obtained by the volatilization and decomposition of polystyrene through calcination.

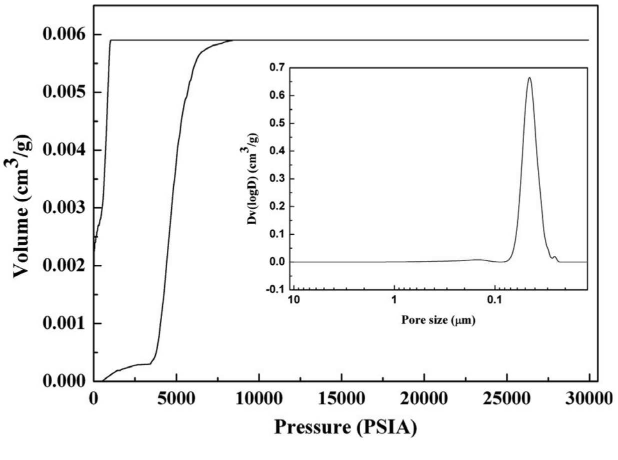

Fig. 3. Images of mercury intrusion and pore size distribution (inset) of ZnO particle calcined at 500 °C.

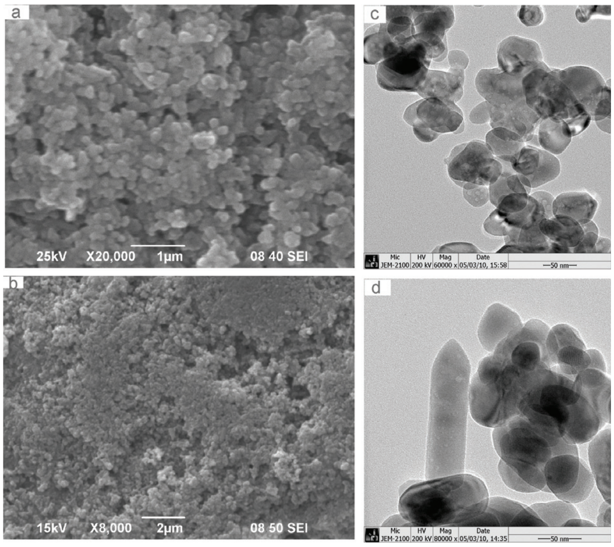

Fig. 4. SEM (a, b) and TEM (c, d) images of ZnO calcined at different temperature (a) 500 °C, (b) 600 °C, (c) 500 °C, (d) 600 °C.

3.4. Morphologies

Fig. 4 shows the SEM and TEM images of the mesoporous ZnO calcined at different temperature. It can be seen from the SEM images that the average diameter and aggregation of the ZnO nanoparticles increase with the increasing of the calcination temperature. The TEM images of Fig. 4 shows that there are a lot of pores with relatively regular dimension in ZnO nanoparticles. By image analysis, the average diameter of ZnO nanoparticle obtained at 500 °C is about 45 nm, which is consistent with that calculated according to Debye–Scherrer formula. Moreover, the pore volume and the numbers of pore decrease with the increasing of the calcination temperature by comparing Fig. 4c with Fig. 4d. This may be contributed to the fact that the increasing temperature results in pore collapse and consequently decreases the pore volume, the numbers of pore and the specific surface area.

3.5. Photocatalytic evaluation

It is well known that the calcination temperature has a significant effect on the photocatalytic activities of the synthesized ZnO, which has been reported in previous study [19]. As shown in Fig. 5, the effect of calcination temperature on the photocatalytic decolorization of MB was investigated. It can be seen that the photocatalytic activities of the synthesized ZnO increase with the increasing of the calcination temperature firstly and then decreases at higher calcination temperature. When the calcination temperature is lower than 500 °C, the increasing temperature leads to the improvement of the crystallinity

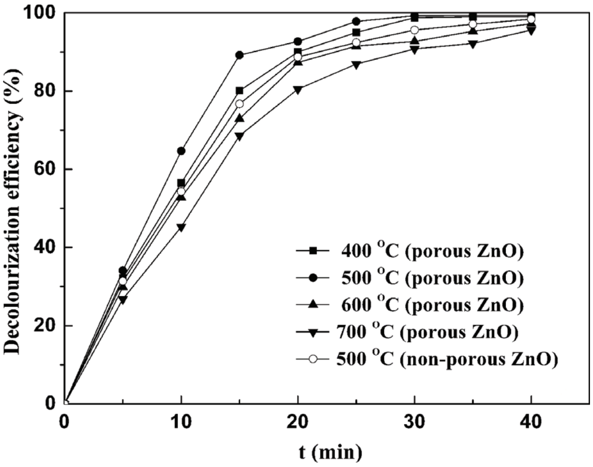

Fig. 5. Effect of calcination temperature on the decolorization efficiencies of MB Experimental conditions: [ZnO] = 0.5 g/l, pH = 6.0, and [MB] = 15 mg/l.

of the as-prepared ZnO, which is favorable for improving the photocatalytic activities. However, when the calcination temperature is beyond 500°C, it can be seen from Figs. 2 and 4 that the average crystal size and aggregation of the synthesized ZnO increase rapidly with the increasing of the temperature. The relatively large crystal size, severe aggregation and small specific surface area consequently lead to the low photocatalytic activities.

To investigate the effect of porous structures on the photocatalytic activities, the non-porous ZnO is synthesized using the same preparing procedure as that of the porous ZnO except the addition of ammonium persulfate (initiator). It can be seen from Fig. 5 that the porous ZnO exhibits higher photocatalytic activity than that of non-porous ZnO when the two samples are calcined at the same temperature. The possible explanation is that the mesoporous structures can enhance the adsorption efficiency of light and the diffusion rates of reactants, which consequently results in high photocatalytic activity.

4. Conclusions

Mesoporous ZnO Nanoparticle with relatively uniform pore size distribution (centered at about 40.2 nm) was prepared by polystyrene microemulsion method and the probable mechanism of pore formation was proposed. The experimental results indicated that the numbers of pore and the specific surface area of the synthesized ZnO decreased with the increasing of the calcination temperature. Moreover, all of the synthesized ZnO exhibited high photocatalytic activities because of its mesoporous structures enhancing the adsorption efficiency of light and the diffusion rates of reactants. It is believed that the present study provides a new way to synthesize mesoporous ZnO and further studies are needed to thoroughly understand the mechanism of pore formation.

Acknowledgement

This work was supported by The Natural Science Research Project of Henan Province Office of Education (Grant No. 2010B150014).

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