Microwave synthesis of the flower-like ZnO microstructures and their photocatalytic property

HUAWA YU[a,b], HUIQING FAN[a,*], JING WANG[a], PENGFEI CHENG[b], LIANBI LI[b], XIAOJUN ZHANG[b]
[a] *State Key Laboratory of Solidification Processing, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an 710072, China*
[b] *School of Science, Xi'an Polytechnic University, Xi'an 710048, China*

A quick and facile microwave-assisted reaction is used to synthesize flower-like ZnO microstructures in the existence of hexadecyl trimethyl ammonium bromide (CTAB). X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques reveal the samples are composed of many rods with a hexagonal wurtzite structure. The optical properties of as-prepared ZnO microstructures were investigated by ultraviolet–visible spectroscopy, Raman spectroscopy and photoluminescence spectroscopy. The photocatalytic activity was evaluated by using the photodegradation of methylene orange (MO) dye under UV irradiation. Furthermore, the photodegradation mechanism of the as-prepared sample is also briefly discussed.

(Received December 16, 2014; accepted May 7, 2015)

Keywords: X-ray diffraction (XRD), Microwave, ZnO

1. Introduction

During the past decade, Human being enjoy the comfort and convenience which is brought by the rapid development of science and technology, also tasting the living environment worsening caused by the blind and shortsighted. Serious pollution incident brings not only health problems, but also causes social problems. To solve the problems, photocatalysis is a research topic of great importance in view of environmental treatment. it is normally based on the light absorption of semiconductor oxide photocatalyst, typically TiO_2 [1] or ZnO [2], although TiO_2 is worldwide accepted active photocatalyst for the degradation of wide range of organic matter, ZnO has recently receiving much attention because it exhibits more efficiency than TiO_2 in photocatalytic degradation of 2-phenylphenol [3], Reactive Blue 19 [4], Rhodamine 6G [5], and Acid Red 18 [6], even in aqueous solutions. As a potential semiconductor, ZnO is used in areas such as solar cells [7], pigments [8], gas sensors [9], electronics [10] and photocatalysts [2]. However, researches on the photodecompositions of many different kinds of dyes performanced only by ZnO are still a promising field [11].

Different methods have been used to synthesize variety of ZnO nano- and micro-architectures like hydrothermal route, sol–gel process, chemical vapour deposition(CVD), electrodeposition (ED), vapour–liquid–solid process, pulsed layer deposition and thermal decomposition [12–19]. However, most of these methodologies are limited due to use of high temperature, high pressure, toxic reagents, and long reaction time. Nowadays, microwave technique is extensively used for the synthesis of materials. Compared to the conventional heating process, microwave heating is promising due to its unique effects, such as rapid volumetric heating, higher reaction rates, higher reaction selectivity, higher yields of products, and energy saving. Herein, we report the synthesis of ZnO nanostructures with flower-like morphologies by a simple, fast and low cost microwave irradiation method. Subsequently, as-synthesized ZnO product were characterized in details in terms of their morphological, structural and optical properties by X-ray diffraction (XRD) and transmission electron microscopy (TEM), ultraviolet–visible spectroscopy, Raman and photoluminescence measurements. Finally, the photocatalytic properties of as-prepared product are evaluated by degradation of methyl orange under ultraviolet (UV) irradiation.

2. Experimental procedure

2.1 Synthesis of ZnO microstructures

All chemicals used in this work were analytical-grade and used reagents without any further purification. In a typical experiment, first, 1.3 mmol $Zn(CH3COO)_2 \cdot 2H_2O$ and 0.04 mmol NaOH were dissolved in 40ml deionized water with constant stirring, respectively. Secondly, a certain amount of CTAB was slowly added into the solution, followed by vigorous stirring for 15 min at ambient temperature. Then, the resulting whitish aqueous solution were irradiated by using the microwave oven at

130℃ for 60 min. The resulting precipitates were isolated by centrifugation, followed by washing with distilled water and ethanol for several times to remove the possible residues, then dried in air at 60℃ for 24 h to obtain final products.

2.2 Characterization of ZnO microstructures

The phase structure of the as-synthesized samples was examined by X-ray diffraction (XRD; D/Max2550VB+/PC, Philips, Eindhoven, The Netherlands) with Cu-Kα radiation (λ = 1.5406 Å). High resolution transmission electron microscopy (TEM/HRTEM; JEM-3010, Questar, New Hope, USA) was performed with an acceleration voltage of 300 kV. The Raman spectra (inVia, Renishaw, Gloucestershire, UK) were excited by a 532 cm Nd: YAG laser at room temperature. UV–Vis absorption spectra were recorded on a spertrophotometer (UV-3010, Hitachi, Tokyo, Japan). Photoluminescence property was studied by He-Cd laser with excitation wavelength of 325 nm.

2.3 Evaluation of the photocatalytic properties

The photocatalytic performance of the as-prepared samples was monitored using UV–vis spectrophotomer by photocatalytic degradation of MO .The samples (1.5 g/l) were dispersed in the 100 ml MO aqueous solution (10 mg/l). The mixed suspensions were magnetically stirred for 30 min in the dark to attain an adsorption–desorption equilibrium and irradiated by 365 nm UV light. At certain time intervals (20 min), 2 ml of the mixed suspensions were extracted and centrifugated to remove the photocatalyst. The degradation of MO was observed by recording the decrease in optical absorption peak at 463 nm with increasing time of light irradiation.

3. Results and discussion

3.1 Morphology and structure

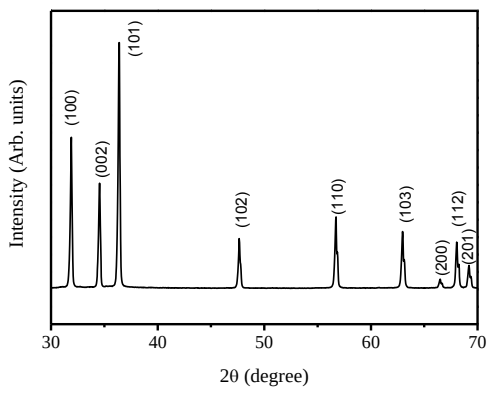

Fig. 1. XRD pattern of the as-synthesized ZnO microstructures.

Fig. 1 shows the XRD patterns of the ZnO sample prepared by microwave-assisted reaction. All of the diffraction peaks are well matched with the standard hexagonal structure of ZnO. No peaks other than ZnO were detected. Obviously, the XRD results showed that the as-prepared sample is pure ZnO. The sharp diffraction peaks of the as-synthesized product implied that the flower-like ZnO microstructures prepared in this work is highly crystalline.

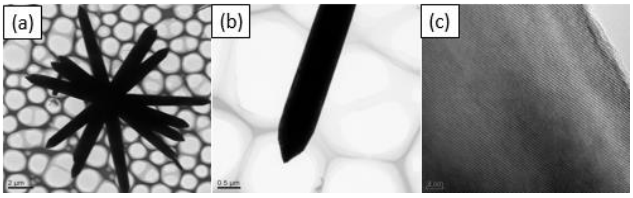

Fig. 2. (a)TEM image of the as-synthesized ZnO microstructures, (b) TEM image of individual ZnO nanorod and (c) HRTEM image of the individual ZnO nanorod.

The morphology and microstructure of the as-prepared sample were investigated by TEM as shown in Fig. 2a-c. It can be seen from Fig. 2a that the as-obtained sample present nearly the flower-like microstructures, which composed of nanorods, and each rod has a width of 300-400nm and a length of 3-4μm. The TEM image of an individual ZnO nanorod of the flower-like ZnO microstructures is shown in Fig. 2b, the image shows that the nanorod has a sword-like end. In Fig. 2c, the HRTEM results revealed that the lattice spacing is about 0.26 nm, corresponding to the (002) plane of ZnO, implying the growth direction of nanorod is [0001].

3.2 Optical properties

Fig. 3a displays the absorption spectrum of the as-synthesized sample at room temperature, which exhibits the absorption maxima at 374 nm which is well matched to the wurtzite hexagonal phase ZnO. Additionally, no peak related with impurities and structural defects was observed in the spectrum which confirmed that the synthesized samples were pure ZnO. The band gap energy can be determined by substituting the value of the absorption peak at given wavelength in the following equation [20]

$$E_g = h\nu_g = \frac{hc}{\lambda_g} \quad (1)$$

where h is plank's constant, c is the speed of light, and λ_g is cut-off wavelength [21,22]. Applying above equation, the band gap energy (Eg) for the flower-like ZnO microstructures synthesized via microwave method were calculated to be 3.31eV.

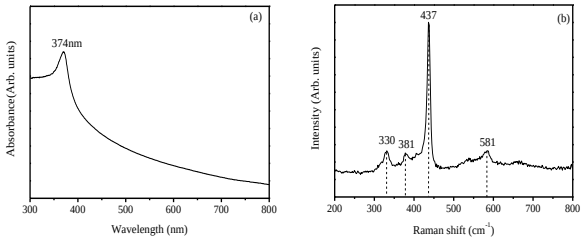

Fig. 3. (a)UV–Visible absorption spectra and (b) Raman spectra of the as-synthesized ZnO microstructures.

The Raman spectra of the ZnO samples synthesized are shown in Fig.3b. A narrow strong peak at 437 cm^{-1} assigned to the vibration mode $E_2(H)$ confirms that the products formed are the ZnO with hexagonal(wurtzite) structure. Two very small peaks at 330 and 381 cm^{-1} are attributed to the vibration mode $2E_2$ and $A_1(TO)$ respectively. In addition the peak located at 581cm^{-1} is assigned to $E_1(LO)$ modes.

The PL spectra of the as-synthesized ZnO sample were examined at room temperature under an excitation wavelength of 325 nm. Fig. 4 shows two peaks at 378, and 485 nm. Generally, the PL signal at 378 nm is a typical ZnO near-band-edge ultraviolet emission, attributed to the recombination of free excitons, while the blue–green emission at 485 nm may result from the electron transition from the level of the ionized oxygen vacancies to the valence band. The blue–green emission in our sample can be weak compared with the intensive sharp UV emission, which indicate the as-synthesized ZnO product are with a low concentration of oxygen vacancies and high optical quality.

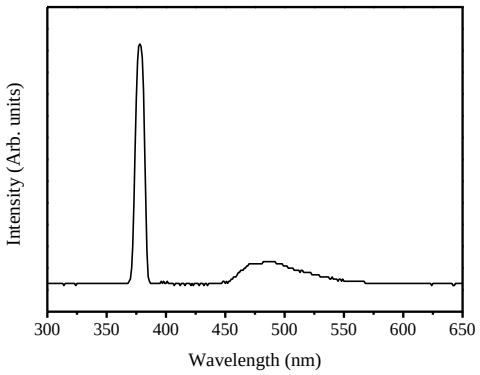

Fig. 4. Room temperature PL spectrum of the as-synthesized ZnO microstructures.

3.3 Photocatalytic properties

The photocatalytic degradation of MO under various UV irradiation durations was used to evaluate the photocatalytic performance of the as-synthesized ZnO microstructures as shown in Fig. 5a. It can be seen that the characteristic absorption of MO at 463 nm diminishes rapidly with increasing the exposure time and nearly disappears after 120 min. No new absorption bands appear in the whole spectrum, which indicate the total decomposition of MO aqueous solution during the reaction.

Fig. 5b shows the degradation rate of MO without catalysts, using the commercial ZnO powder and as-synthesized flower-like ZnO microstructures under UV light illumination. After irradiation for120min, the degradation efficiency of MO is found to be about 9.5% (self-degradation), 29.0% (with commercial ZnO powder) and 92.1% (with the as-synthesized ZnO microstructures), respectively. Obviously, the degradation efficiencies of MO clearly increased when the flower-like ZnO microstructures synthesized were added as catalyst. In order to further confirm this results, the ZnO product after degradation of MO was centrifuged, washed and then dried. It's morphology and microstructure were investigated by TEM as shown in Fig. 5(c). It can be seen from Fig. 5(c) that the as-obtained product presents still the flower-like microstructures rather than nanorods. Therefore, the significant improvement of photocatalytic activity of the as-synthesized ZnO samples can be attributed to its unique structure to absorb a large fraction of UV light. It is concluded that prepared flower-like ZnO microstructures is a better photocatalyst for the degradation of Methylene Orange. The whole mechanism of photocatalytic degradation has been depicted in Fig. 6.

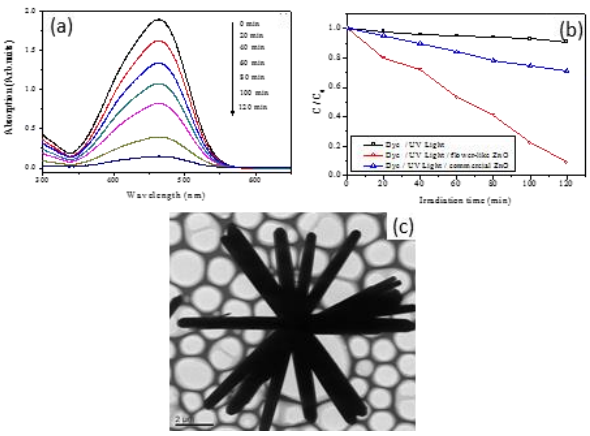

Fig. 5. (a) UV–visible absorption of MO in the solutions containing the as-synthesized ZnO samples (b) extent of decomposition(C/C_0) of MO dye with respect to time intervals(c) TEM image of the ZnO microstructures after degradation of MO.

In general, when semiconductor nanocrystals are irradiated by the light with energy higher or equal to the band gap energy, the electron-hole pairs can be generated, that is an electron in the valence band can be excited to the conduction band with the simultaneous generation of leaving a hole behind. The holes at the ZnO valence band

with strong oxidation can react with the matter adsorbed to the semiconductor surface, then to produce harmless products (Eq.(6)). Excited state electron and hole can also

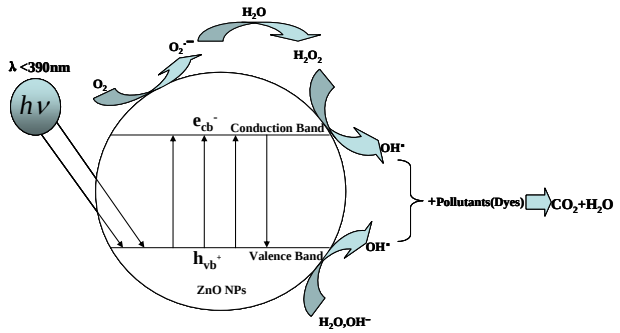

Fig. 6. Mechanism of photocatalytic degradation of Methylene Orange.

spread of movement by an electric field force, the hole migrated to the semiconductor surface can be easily trapped by water or hydroxide ions to produce $OH^{\bullet}$ which is a strong free radical oxidation to further oxidize organic pollutants. At the same time, the electron migrated to the semiconductor surface can be easily trapped by electron acceptors like adsorbed O_2 to produce $O_2^{\bullet -}$, $HOO^{\bullet}$ and other radical which can participate in various redox process to further oxidize organic pollutants into harmless products (Eq.(7)).

$$ZnO + h\nu(UV) \rightarrow e_{cb}^{-} + h_{vb}^{+} \quad (2)$$

$$h_{vb}^{+} + H_2O \rightarrow H^{+} + OH^{\bullet} \quad (3)$$

$$h_{vb}^{+} + OH^{-} \rightarrow OH^{\bullet} \quad (4)$$

$$e_{cb}^{-} + O_2 \rightarrow O_2^{\bullet -} \rightarrow\rightarrow HOO^{\bullet} \rightarrow\rightarrow H_2O_2 \rightarrow\rightarrow OH^{\bullet} \quad (5)$$

$$h_{vb}^{+} + dye \rightarrow \text{degraded product} \quad (6)$$

$$OH^{\bullet} + dye \rightarrow \text{degraded product} \quad (7)$$

4. Conclusions

In summary, the flower-like ZnO microstructures have been successfully synthesized via a simple microwave-assisted hydrothermal method. The detailed morphology of the synthesized samples was characterized by XRD, TEM, HR-TEM, which reveal that the as-synthesized product is well-crystalline ZnO with wurtzite hexagonal phase. UV–Visible absorption spectra depicts a strong narrow absorption peak at ~374 nm, and the band gap energy was calculated to 3.31eV. The photoluminescence spectrum of the synthesized ZnO microstructure exhibited a strong ultraviolet emission at 378 nm and a weak blue–green emission at 485 nm at room temperature. The photocatalytic activities of the synthesized ZnO microstructure were evaluated by the degradation of MO, and the results show that the synthesized products presents superior decolorization efficiency which might be due to its unique structure.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (51172187, 51277138, 51402230), the SPDRF (20116102130002), 111 Program of MOE (B08040), the National Natural Science Key Foundation of China (No. 61405151), the Natural Science Foundation of Shaanxi Province (No. 2014JQ8337, 2013KW12-02), the Scientific Research Program of Shaanxi Education Department (No. 2014JK1301), the SKLP Foundation (KP201421), and the Fundamental Research Funds for the Central Universities (3102014JGY01004) of China.

References

[1] Y. Liao, W. Que, Z. Tang, W. Wang, W. Zhao, J. Alloys Compd., **509**, 1054 (2011).
[2] O. Akhavan, M. Mehrabian, K. Mirabbaszadeh, R. Azimirad, J. Phys. D: Appl. Phys., **42**, 225 (2009).
[3] A. A. Khodja, T. Sehili, J. F. Pilichowski, P. Boule, J. Photochem. Photobiol, A , **141**, 231 (2001).
[4] C. Lizama, J. Freer, J. Baeza, H. D. Mansilla, Catal. Today, **76**, 235 (2002).
[5] S. K. Kansal, M. Singh, D. Sud, J. Hazard. Mater., **141**, 581 (2007).
[6] N. Sobana, M. Swaminathan, Sep. Purif. Technol. **56**, 101 (2007).
[7] K. Keis, L. Vayssieres, S. Lindquist, A. Hagfeldt, Nanostruct. Mater., **12**(1-4), 487 (1999).
[8] C. Li, Z. Liang, H. Xiao, Y. Wu, Y. Liu, Mater. Lett., **64**, 1972 (2010).
[9] J. Huang, Y. Wu, C. Gu, M. Zhai, Y. Sun, J. Liu, Sens. Actuators B,**155**, 126 (2011).
[10] S. M. Peng, Y. K. Su, L. W. Ji, S. J. Young, C. N. Tsai, W. C. Chao, Z. S. Chen, C. Z. Wu, IEEE Electron Device Letters, **32**, 533 (2011).
[11] Z. F. Zhu, D. Yang, H. Liu, Advanced Powder Technology, **22**, 493 (2011).
[12] W. Jin, I. Lee, A. Kompch, U. Dorfler, M. Wintere, J. Eur. Ceram. Soc., **27**, 4333 (2007).
[13] P. Mohanty, B. Kim, J. Park, Mater. Sci. Eng. B, **138**, 224 (2007).

[14] A. Eftekhari, F. Molaei, H. Armani, Mater. Sci. Eng. A, **437**, 446 (2006).
[15] B. Liu, H. C. Zeng, J. Am. Chem. Soc., **125**, 4430 (2003).
[16] K. D. Kim, D. W. Choi, Y. H. Choa, H. T. Kim, Colloids Surf. A., **311**, 170 (2007).
[17] T. Okada, B. H. Agung, Y. Nakata, Appl. Phys. A, **79**, 1417 (2004).
[18] S. Cho, S. H. Jung, K. H. Lee, J. Phys. Chem. C **112**, 12769 (2008).
[19] H. Cheng, J. Cheng, Y. Zhang, Q. M. Wang, J. Cryst. Growth, **299**, 34 (2007).
[20] D. Segets, J. Gradl, R. K. Taylor, V. Vassilev, Nano, **3**, 1703 (2009).
[21] P. S. Hale, L. M. Maddox, J. G. Shapter, N. H. Voelcker, M. J. Ford, E. R. Waclawik, J.Chem.Edu., **82**, 775 (2005).
[22] L. Kumari, W. Z. Li, Cryst. Res. Tech. **45**, 311 (2010).

*Corresponding author: hqfan3@163.com