Journal of Ceramic Processing Research. Vol. 12, No. 4, pp. 420~425 (2011)

J O U R N A L O F
Ceramic
Processing Research

Investigation of nano-sized ZnO particles fabricated by various synthesis routes

Changchun Chen[a,*], Benhai Yu[a], Ping Liu[b], JiangFeng Liu[a] and Lin Wang[a]

[a]*College of Physics and Electronics Engineering, XinYang Normal University, XinYang 464000£¨Henan Province, China*
[b]*Nanjing University of technology, Nanjing 210009, Jiangsu Province, China*

Nano-sized ZnO particles were synthesized by a direct precipitation, a sol-gel, and a hydrothermal method. The structures, morphology, and optical properties of these ZnO nanoparticles fabricated by the above-mentioned methods were also characterized by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Ultraviolet-visible spectroscopy (UV-vis). In addition, the photocatalytic activities of the synthesized ZnO nanoparticles were evaluated via the degradation of methyl orange (MO) in an aqueous solution. These experimental results demonstrated that the photodegradation efficiency of MO solutions irradiated by UV for 120 minutes with ZnO nano-particles used as catalysts, which were fabricated by a direct precipitation method could reach 94.59% or so. The higher photocatalytic activity of methyl orange solutions by the ZnO nanoparticles synthesized by the direct precipitation method is probably ascribed to the spherical ZnO nanoparticles with a smaller crystalline size.

Key word: ZnO nanoparticles, Photocatalytic degradtion, Methyl orange.

Introduction

Semiconductor nanoparticles have attracted much attention in recent years due to novel optical, electrical and mechanical properties, which result from quantum confinement effects compared with their bulk counterparts. Among various semiconductor nanoparticles, nano-sized zinc oxide (ZnO) particles are the most frequently studied because of their interest as a fundamental study and also their applied aspects such as in solar energy conversion, varistors, luminescence, photocatalysis, as electrostatic dissipative coating, transparent UV protection films and chemical sensors [1-4]. Hitherto, searching new methodology to synthesize uniform nano-sized ZnO particles is of great importance for both a fundamental study and practical applications, and thus various methods such as a hydrothermal method [5], sol-gel [6], spray pyrolysis [7], and direct precipitation methods [8] have been adopted for the fabrication of nano-sized ZnO particles with a uniform morphology and size. Among these techniques, the hydrothermal route is known as one of the excellent processes for nanocrysyalline state synthesis because it is relatively easy to perform and allows us to tailor the morphology of the particles by controlling the rate of hydrolysis and condensation reactions [9]. Compared with other methods, a direct precipitation approach provides an easy way for low cost and large-scale production, which does not need expensive raw materials and complicated equipments. The sol-gel method is also popular because of its cheapness, reliability, repeatability, and simplicity, but we have to carefully control the sol-gel process and the growth of nuclei must be prevented. Therefore, in the present study, the nano-sized ZnO particles were synthesized by a direct precipitation method, a sol-gel method, and a hydrothermal method. A detailed comparison of the crystalline size, morphology, absorbency, and photocatalytic property of ZnO nanoparticles synthesized by the above mentioned methods was made.

*Corresponding author:
Tel :+86-0376-6391760
Fax: +86-0376-6391760
E-mail: ccc502@sina.com

Experimental

In this study, nano-sized ZnO particles were prepared by a direct precipitation method, a sol-gel method, and a hydrothermal method. $Zn(NO_3)_2$, $(NH4)_2CO_3$, ethanol, and de-ionized water (analytical grade) were used as the starting materials to prepare ZnO nanoparticles by a direct precipitation method, and the synthetic procedures were as follows. $Zn(NO_3)_2$ and $(NH_4)_2CO_3$ were firstly dissolved in high-purity water to form solutions with a 0.5 mol/*l* concentration. The $Zn(NO_3)_2$ solutions were slowly dropped into the $(NH_4)_2CO_3$ solutions with vigorous stirring at 40 °C and the mole ratio of CO_3^{2-} to Zn^{2+} kept to 1.5. The reaction between the $Zn(NO_3)_2$ solutions and the $(NH_4)_2CO_3$ solutions was kept for 60 minutes. And then, the precipitates derived from the reaction between the $Zn(NO_3)_2$ and the $(NH_4)_2CO_3$ solutions were collected by filtration and rinsed three times with high-purity water and ethanol. Subsequently, the washed precipitates were dried at 80 °C to form the precursors of ZnO. Finally, the precursors were calcined at 500 °C for 2 h in a muffle furnace to obtain white nano-sized ZnO particles.

Zinc acetate dehydrate ($Zn(COOCH_3)_2{\cdot}2H_2O$), oxalic

acid ($H_2C_2O_4{\cdot}2H_2O$) were used as the starting materials to prepare ZnO nanoparticles by a sol-gel method. The synthetic procedures for nano-sized ZnO particles by a sol-gel method were as follows. $Zn(COOCH_3)_2{\cdot}2H_2O$ and $H_2C_2O_4{\cdot}2H_2O$ were firstly dissolved in high-purity water to form solutions with 0.5, 0.15 mol/*l* concentrations. The 0.5 mol/*l* $Zn(COOCH_3)_2$ solutions were slowly dropped into the 0.15 mol/*l* $H_2C_2O_4$ solutions of identical volumes with vigorous stirring at 40 °C. The reaction between the $Zn(COOCH_3)_2$ solutions into the $H_2C_2O_4$ solutions was maintained for 90 minutes until a clear and homogeneous solution formed. Subsequently, the clear and homogeneous solutions were dried at 80 °C and calcined at 500 °C for 2 h in a muffle furnace to obtain white nano-sized ZnO particles.

$Zn(NO_3)_2$ solutions with 0.5 mol/*l* concentration, the NaOH solutions with 1.5 mol/*l* concentration were used to prepare ZnO nanoparticles by a hydrothermal method. The $Zn(NO_3)_2$ solutions were slowly dropped into the NaOH solutions with vigorous stirring at 80 °C and the mole ratio of OH^- to Zn^{2+} kept to 3. The reaction between the $Zn(NO_3)_2$ solutions and the NaOH solutions was maintained for 60 minutes. And then, the precipitates derived from the reaction between the $Zn(NO_3)_2$ and the NaOH solutions were collected by filtration and rinsed with high-purity water and ethano. Subsequently, the washed precipitates were dried at 80 °C and calcined at 500 °C for for 10 minutes in a microwave oven to obtain white nano-sized ZnO particles.

The structural properties of these nano-sized ZnO particles were investigated by the θ-2θ method of X-ray diffraction (XRD) with Cu $K_{\alpha 1}$(λ = 0.154 nm) radiation at 40 kV and 30 mA using a multipurpose XRD system (PANalytical). The morphology and particle size of these nano-sized ZnO particles were also analyzed by a scanning electron microscope (SEM, JXA840). SEM photographs for the nano-sized ZnO particles were recorded (LEO 435) at 30 kV from samples covered with a thin gold film. Room-temperature absorption properties of ZnO thin films were investigated using a conventional UV spectrometer. Low- temperature absorption was measured using a tungsten lamp and a spectrometer and recorded by a charge-coupled device (CCD) camera.

The MO solution with concentrations 10 mg/*l* was prepared by dissolving the MO powder in ultra pure water, and was immediately used. The reaction suspensions with a dosage of ZnO catalysts of 2.5 g/*l* were prepared by adding ZnO nanoparticles into the MO solutions. The suspensions were ultrasonically treated for 20 minutes and magnetically stirred in the dark for 45 minutes to ensure an adsorption/desorption equilibrium. The reaction suspensions containing MO and nano-sized ZnO photocatalysts were irradiated by a 300 W high-pressure mercury lamp with continuous stirring. Absorbance measurements were recorded in the range of 200-600 nm, using a UV-vis spectrophotometer (a Hewlett Packard 8453 spectrophotometer).

Results and Discussion

During the fabrication of ZnO nanoparticles by a direct precipitation via $(NH_4)_2CO_3$ as the precipitator, the main reaction processes including the generation of the ZnO precursor and thermal decomposition of the ZnO precursor are as following:

$$4Zn(NO_3)_2 + 4(NH_4)_2CO_3 + 3H_2O \rightarrow Zn_4(CO_3)(OH)_6\downarrow + 8NH_4NO_3 + 3CO_2\uparrow \quad (1)$$

$$Zn_4(CO_3)(OH)_6{\cdot}H_2O\downarrow \rightarrow 4ZnO + CO_2\uparrow + 4H_2O \quad (2)$$

Fig. 1 depicts the XRD pattern of the ZnO nanoparticles fabricated by the direct precipitation method. The XRD pattern of the ZnO precursor is also shown in the inset of Fig. 1. As is know, the general form of basic zinc carbonate can be written as $mZnCO_3{\cdot}nZn(OH)_2{\cdot}kH_2O$. As a matter of fact, $Zn_5(CO3)_2(OH)_6{\cdot}H_2O$ and $Zn_4(CO_3)(OH)_6{\cdot}H_2O$ of basic zinc carbonate were the well known forms in a previous study [10]. When verifying the structure and composition for the basic zinc carbonate, two typical XRD patterns in the database of XRD can be utilized. One is JCPDS 11-287, the other is JCPDS 19-1458. The former corresponds to the XRD pattern of $Zn_5(CO_3)_2(OH)_6{\cdot}H_2O$, and the latter corresponds to the XRD pattern of $Zn_4CO_3(OH)_6{\cdot}H_2O$. The XRD patterns shown in the inset of Fig. 1 were consistent with the values in the database of JCPDS 11-287. As a consequence, the composition of the basic zinc carbonate fabricated should be $Zn_4(CO_3)(OH)_6{\cdot}H_2O$. The nano-sized ZnO particles are of a wurtzite structure (hexagonal phase, space group *P*63*mc*). All the diffraction peaks can be well indexed to the hexagonal phase ZnO reported in JCPDS card (No. 36-1451, a = 0.3249 nm, c = 0.5206 nm). Diffraction peaks related to impurities were not observed in the XRD pattern, confirming the high purity of the product synthesized. Furthermore, it could

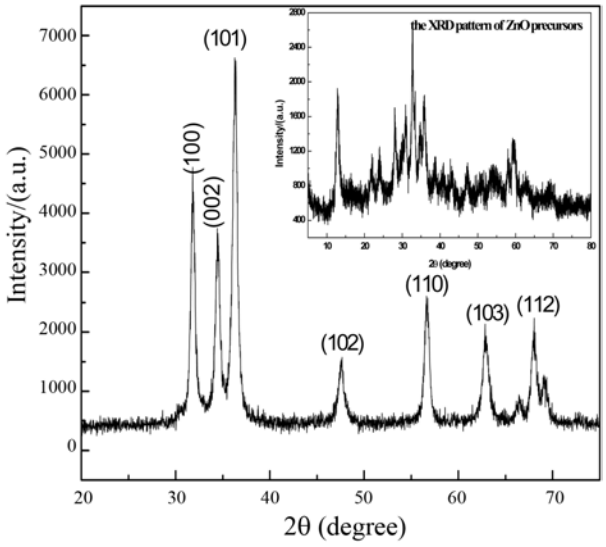

Fig. 1. XRD patterns of ZnO nanoparticles prepared by a precipitation method and the XRD pattern of ZnO precursors in the inset.

be seen that the diffraction peaks shown in Fig. 1 were more intensive and narrower, implying the good crystalline nature of the as-synthesized ZnO product. The average crystalline size (D) of the nano-sized ZnO particles can was estimated to be about 18.4 nm according to the Debye-Scherrer formula [11].

When the ZnO nanoparticles are synthesized by a sol-gel method, a $ZnC_2O_4{\cdot}2H_2O$ precursor is firstly obtained via the reaction between $Zn(CH_3COO)_2{\cdot}2H_2O$ and $H_2C_2O_4{\cdot}2H_2O$. The corresponding process is as following:

$$Zn(CH_3COO)_2{\cdot}2H_2O + H_2C_2O_4{\cdot}2H_2O \rightarrow ZnC_2O_4{\cdot}2H_2O + 2CH_3COOH + 2H_2O \quad (3)$$

After the $ZnC_2O_4{\cdot}2H_2O$ precursor is subjected to the following pyrolysis process, nano-sized ZnO can be obtained:

$$ZnC_2O_4{\cdot}2H_2O \rightarrow ZnC_2O_4 \rightarrow ZnO + H_2O + CO_2 \quad (4)$$

Fig. 2 shows XRD patterns of the ZnO nanoparticles fabricated by the sol-gel method. All the diffraction peaks can also be well indexed to the hexagonal phase ZnO reported in JCPDS card (No. 36-1451, $a = 0.3249$ nm, $c = 0.5206$ nm). The results indicate that the products consisted of a pure phase. The average crystalline size (D) of the nano-sized ZnO particles can was estimated to be about 21.7 nm.

When the ZnO nanoparticles are fabricated by a hydrothermal method, the reaction process is as follows. The XRD pattern of the ZnO nanoparticles fabricated by a hydrothermal method is shown in Fig. 3.

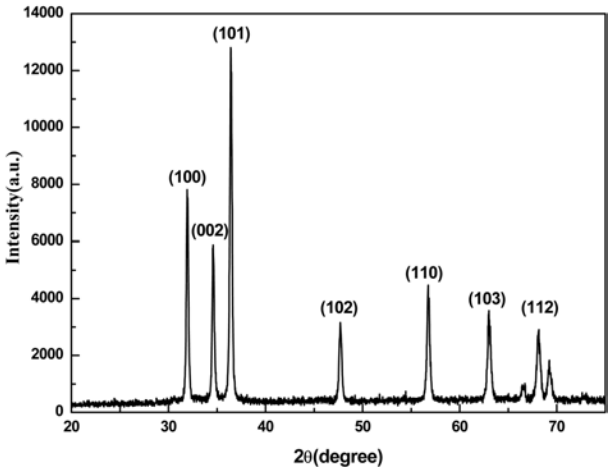

Fig. 2. XRD patterns of ZnO nanoparticles prepared by a sol-gel method.

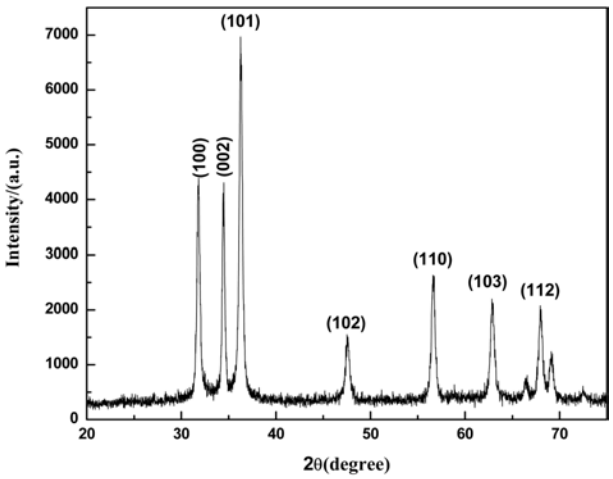

Fig. 3. XRD pattern of ZnO nanoparticles prepared by a hydrothermal method.

$$Zn(NO_3)_2 + 2NaOH = Zn(OH)_2 + 2NaNO_3 \quad (5)$$

$$Zn(OH)_2 = ZnO + H_2O \quad (6)$$

All the diffraction peaks can also be well indexed to the hexagonal phase ZnO reported in JCPDS card (No. 36-1451, $a = 0.3249$ nm, $c = 0.5206$ nm). Nine peaks appear at $2\theta = 31.7^o$, 34.4^o, 36.3^o, 47.5^o, 56.6^o, 62.3^o, 66.5^o, 67.9^o, and 69.1^o, which correspond to (100), (002), (101), (102), (110), (103), (200), (112) and (201), respectively. It seems that these ZnO particles possess a high crystallinity, since all the peaks are very sharp. The average crystalline size (D) of the nano-sized ZnO particles can was estimated to be about 27.1 nm. The average crystalline sizes (D) of the nano-sized ZnO particles fabricated by the different methods are listed in Table. 1.

Fig. 4 shows SEM micrographs of the ZnO nanoparticles synthesized by the different routes, respectively. It can be seen from Fig. 4(a) that the morphology of ZnO nano-sized particles fabricated by a direct precipitation method is spherical. Fig. 4(b) shows that the morphology of ZnO nanoparticles synthesized by a sol-gel method aggregated in a chainlike form [12]. In addition, rod-like ZnO nano-particles fabricated by a hydrothermal method could be found from Fig. 4(c). The formation of rod-like ZnO nanoparticles fabricated by a hydrothermal method maybe ascribed to the crystal habit and formation mechanism of polar crystals, which has been described in the literature [13]. The morphologies of ZnO nanoparticles analyzed from SEM images are tabulated in Table. 2.

Table 1. FWHM and crystalline size of ZnO prepared by different preparation methods

Fabrication methods		FWHM			crystalline size (nm)
		(100)	(002)	(101)	
Direct precipitation	$Zn(NO_3)_2/(NH_4)_2CO_3$	0.450	0.446	0.494	18.4
Sol-gel	$Zn(COOCH_3)_2{\cdot}2H_2O/(CH_3COOH)_2$	0.386	0.360	0.453	21.7
Hydrothermal	$Zn(NO_3)_2/NaOH$	0.335	0.282	0.366	27.1

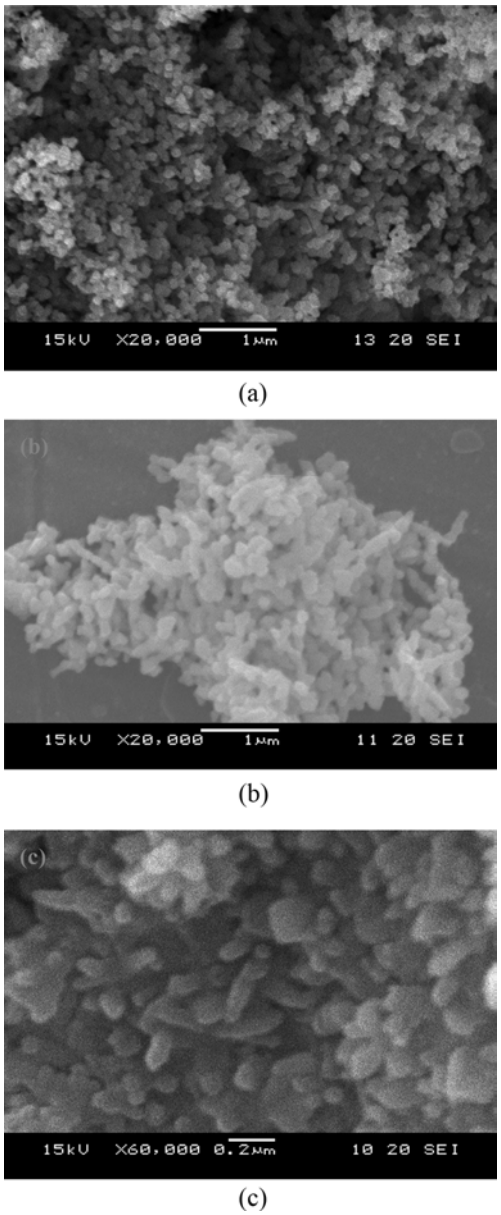

Fig. 4. SEM images of ZnO nanoparticles prepared by different methods: (a) direct precipitation using $Zn(NO_3)_2/(NH_4)_2CO_3$ as raw materials, (b) sol-gel using $Zn(COOCH_3)_2{\cdot}2H_2O/(CH_3COOH)_2$ as raw materials, (c) a hydrothermal method using $Zn(NO_3)_2$/NaOH as raw materials.

Table 2. The nano-sized ZnO particles prepared by different synthesis routes

Synthesis routes	Raw materials / precipitator	morphology
Direct precipitation	$Zn(NO_3)_2/(NH_4)_2CO_3$	spherical
Sol-gel method	$Zn(COOCH_3)_2.2H_2O/(CH_3COOH)_2$	chainlike
Hydrothermal method	$Zn(NO_3)_2$ /NaOH	rod-like

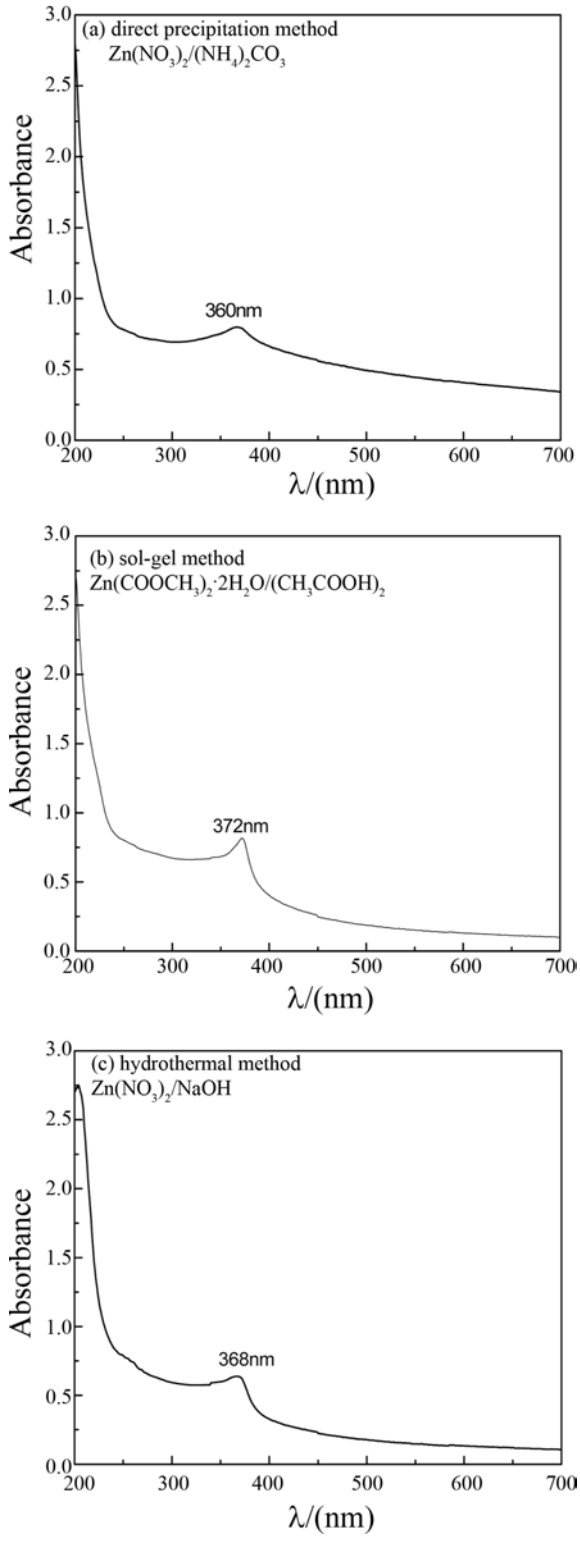

Fig. 5. The UV-Vis diffuse reflectance spectra of the ZnO nanoparticles prepared by different methods: (a) a direct precipitation method, (b) a sol-gel method, (c) a hydrothermal method.

Fig. 5 shows the absorption spectra of ZnO nanoparticles fabricated by different synthesis routes. All the absorption spectra show a typical absorption peak [14]. The band gap of nanosized ZnO particles was determined from the cut-off wavelength as $1240/l_g$, where the l_g is the wavelength value corresponding to the typical absorption peak. As shown in Fig. 5, the absorption onsets of ZnO nanoparticles fabricated by different methods are located at different wavelengths,

Table 3. The photodegradation efficiency of MO solutions catalyzed by ZnO obtained from the different routes irradiated by UV for 120 minutes

Synthesis routes	Raw materials/precipitator	morphology	Photodegradation efficiency
Direct precipitation	$Zn(NO_3)_2/(NH_4)_2CO_3$	spherical	94.59
Sol-gel method	$Zn(COOCH_3)_2.2H_2O/(CH_3COOH)_2$	chainlike	86.21
Hydrothermal method	$Zn(NO_3)_2$ /NaOH	rod-like	85.29

such as 368 nm for the ZnO nanoparticles fabricated by a direct precipitation method, 372 nm for the ZnO nanoparticles fabricated by a sol-gel method and 360 nm for the ZnO nanoparticles fabricated by a hydrothermal method. Consequently, the real band gap of ZnO nanoparticles synthesized by direct precipitation, sol-gel method, and hydrothermal method are 3.444, 3.333, and 3.369 eV, respectively. And then, the radii of ZnO nanoparticles (r) can be determined from the absorption onset of the UV spectra using the following expression [15]:

$$E^* = E_g^{bulk} + \frac{h^2\pi^2}{2er^2}\left(\frac{1}{m_e^* m_0} + \frac{1}{m_h^* m_0}\right) \quad (7)$$

where E^* is the real band gap of ZnO nanoparticles, E_g^{bulk} is the bulk band gap (eV), h is the reduced Planck constant; m_e, m_h are the effective mass of the ZnO semiconductor band electron and the valence band hole; m_0 is the electron rest mass ($m_e = 0.26$, $m_h = 0.59$). Combining Equation (7) with the real band gap of ZnO nanoparticles determined from Fig. 5, the crystalline size of nano-sized ZnO synthesized by a direct precipitation method could be worked out to be the smallest. These results were in good agreement with those determined from the XRD data.

In order to ascertain the influence of nano-sized ZnO synthesized by different methods on the photodegradation of methyl orange (MO) solutions, photocatalytic experiments were carried out by adding nano-sized ZnO with dosage of 2.5 g/*l* into the MO solution with an initial concentration of 10 mg/*l* and irradiated by a 300 W high-pressure mercury lamp. Fig. 6 shows the photodegradation efficiency of a 1*l* MO solution with a 10 mg/*l* concentration at different irradiation times. The photodegradation efficiency of MO solutions catalyzed by ZnO nano-particles fabricated by the different routes irradiated by UV for 120 minutes is tabulated in Table. 3. The photocatalytic activity of nano-sized ZnO synthesized by a direct precipitation method was superior to that of nano-sized ZnO synthesized by the other methods under identical conditions. The higher photocatalytic activity of nano-sized ZnO synthesized by a direct precipitation method is probably ascribed to its spherical morphology and small crystalline size.

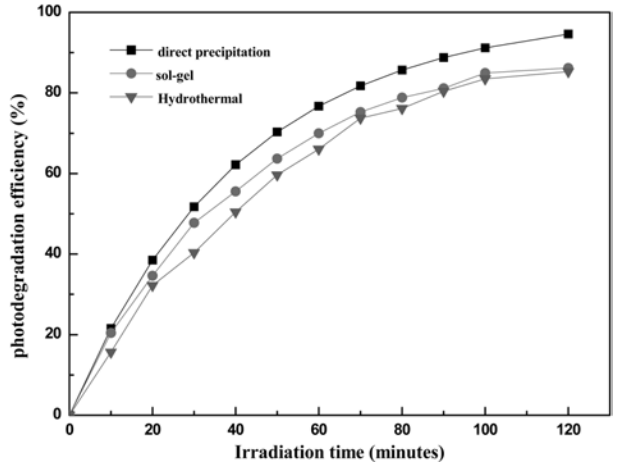

Fig. 6. Effect of ZnO nanoparticles prepared by different methods on the photodegradation of methyl orange.

Conclusions

Three types of ZnO nanoparticles were synthesized by a direct precipitation via $Zn(NO_3)_2/(NH_4)_2CO_3$ as starting materials, a sol-gel method via $Zn(COOCH_3)_2.2H_2O/(CH_3COOH)_2$ as starting materials, and a hydrothermal method via $Zn(NO_3)_2$/NaOH as starting materials. All the XRD patterns indicated that there was no obvious difference in crystal structure, but the crystalline size of synthesized ZnO nanoparticles was different. SEM images show that the shapes of ZnO nanoparticles synthesized by a direct precipitation, a sol-gel method, and a hydrothermal method are spherical, chainlike, and rod-like, respectively. Photocatalytic decomposition of MO shows that the ZnO nanoparticles synthesized by a direct precipitation method have a higher photocatalytic activity than those synthesized by the other methods.

Acknowledgements

This research was supported by the Planned Science and Technology Project of Henan Province, China, under Grant No. 082300410050.

References

1. Z.L.Wang, J. Song, Science 312 (2006) 242-246.
2. D.C. Look, Mater. Sci. Eng. B 80 (2001) 383-387.
3. M. Kitano and M. Shiojiri, Powder Technol. 93 (1997) 267-273.
4. I.O. Sosa, C. Noguez and R.G Barrera, J. Phys. Chem. B107 (2003) 6269-6275.
5. J. Zhang, L.D. Sun, J. Yin, H. Su, C.S. Liao and C. Yan, Chem. Mater. 14 (2002) 4172-4177.
6. J. Lee, A.J. Easteal b, U. Pal c and D. Bhattacharyya, Current Applied Physics 9 (2009) 792-796.
7. S.B. Park and Y.C. Kang, J. Aerosol Sci. 28 (Suppl.) (1997) S473-S474.

8. C.C. Chen, P. Liu and C.H. Lu, Chemical Engineering Journal 144 (2008) 509-513.
9. K. Byrappa and M. Yoshimura, Handbook of Hydrothermal Technology, William Andrew Publishing, (2001) p.875.
10. D. Klissurski, I. Uzunov and K. Kumbilieva, Thermochim. Acta 93 (1985) 485-488.
11. C. Chen, B. Yu, J. Liu, Q. Dai and Y. Zhu, Mater. Lett. 61 (2007) 2961-2964.
12. M. Kitano, J. Crystal Growth ,128 (1993) 1099-1103.
13. Zhong weizhuo, Xia changtai, Shi erwei, Wang buguo, Li wenjun and Hus sukun, Science in China, 40 (1997) 479-488.
14. A. Van Dijken, E.A. Meulenkamp, D. Vanmaekelbergh and A. Meijerink, J. Lumin. 87-89 (2000) 454-456.
15. Z. Hu, G. Oskam and P.C. Searson, J. Colloid Interf. Sci. 263 (2003) 454-460.