The Correlation Between Structure and Photocatalytic Activity of ZnO Particles Prepared by Mild Wet Chemical Method

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Abstract: Flower-like and roughly spherical ZnO nanocrystalline have been successfully synthesized through mild wet chemical method. The photocatalytic activities of the prepared photocatalysts were evaluated by degradation of rhodamine B (RhB) and phenol under UV light irradiation. Remarkably, the roughly spherical ZnO powder via homogeneous precipitation method exhibited superior photocatalytic performance and better photo-stability than that of flower-like ZnO substrate by hydrothermal synthesis way. The enhanced photocatalytic properties could be attributed to more active catalytic sites and superior charges separation efficiency.

1. Introduction
Zinc oxide nanoparticles possess several interesting properties such as high photosensitivity, non-toxicity, low cost and long time stability [1-3]. Additionally, the use of ZnO nanosized semiconductor particles is advantageous in this regard the large surface and abundant catalytically active sites [4]. Hence, nano-sized range ZnO particles are superior to their bulk counterpart [5]. However, nanosized ZnO materials are normally unstable, easy to be agglomerated result in poor resistance to photo-corrosion and rapid performance decay. The ability to control narrow size distributions and particle morphology are important objective in nanocrystal synthesis, as size and shape can significantly influence properties [6, 7].

Zinc oxide nanoparticles (ZnO-NPs) can be prepared by a variety of synthetic strategies include sol-gel [8], hydrothermal [9], solvothermal[10], thermal decomposition [11], high energy mechanical ball milling [12], vapor deposition [13], solid state [14] and so forth. However, most of these approaches generally required high-energy, tedious procedures, long reaction time, which might further hinder their application. Among all these methods, the homogeneous precipitation method offers well-established control of uniform particle size, environmental-friendly and preparing samples at low temperature in short time in large scale production, not using any special equipments and expensive raw materials. To improve the activity of ZnO-NPs photocatalysts, most research efforts have been devoted to homogeneous precipitation method synthesis of ZnO with desired morphology, size/dimension. Sharma et al. [3] have reported the successful synthesis of ZnO-NPs by a simple homogeneous precipitation method without using any surfactant, it was noticed that the ZnO-NPs...
obtained on calcinations at 400°C exhibited a fairly uniform distribution of hexagonal shape. Gancheva et al. [15] have used homogeneous precipitation, tribo-physical treatment and sonochemistry three different synthesis methods to fabricate ZnO-NPs with different particles size, morphology and structural defects. The ZnO-NPs obtained by homogeneous precipitation has better photocatalytic efficiency due to high specific surface area and the low level of band gap. To the best of our knowledge, although there are many studies of ZnO photocatalysts, it remains a big challenge to produce ZnO-NPs photocatalysts with both good photocatalytic performance and in large quantity via a cost-effective method. In addition, deep understanding of the relationship between the homogeneous precipitation method of synthesis, nanostructure, and optical properties of ZnO-NPs is lacking.

In this work, we have employed two facile wet chemical methods (i.e. homogeneous precipitation method and hydrothermal pathways) to prepare ZnO nanostructures with two kinds of morphologies including nearly spherical and flower-like. The ZnO-NPs with different size and shape could be obtained via simply altering synthesized condition. Moreover, we were able to clearly understand the dependence behavior of photocatalytic activity on the structural and morphological characteristics of the ZnO nanomaterials.

2. Experimental procedure

2.1. Raw materials

All chemicals were of analytic grade and used as received without further purification, unless otherwise stated. Zinc nitrate hexahydrate (Zn(NO$_3$)$_2$•6H$_2$O), phenol (C$_6$H$_5$OH, AR), sodium sulfate (Na$_2$SO$_4$, AR) and sodium hydroxide were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Urea and trisodium citrate dehydrate (C$_6$H$_5$Na$_3$O$_7$•2H$_2$O) were obtained from Xilong Chemical Co., Ltd (Shantou, China). All aqueous solutions were prepared with deionized water.

2.2. Fabrication of ZnO nanoparticles

The ZnO nanoparticles were synthesized via a homogeneous precipitation-assisted heat treatment method. In a typical synthesis, to 0.2M Zn(NO$_3$)$_2$ solution, the surfactant 1mmol C$_6$H$_5$Na$_3$O$_7$•2H$_2$O was added into zinc nitrate solution under constant stirring. Then, different concentrations of urea (urea/ zinc nitrate molar ratio= 2.5) were added slowly with constant stirring until a homogeneous solution was achieved. This solution was then heated ~90°C with continuous stirring for 2h. During the reaction, a milky white precipitate was obtained, which was found to be hygroscopic. The hygroscopic products were preserved in a desiccators, and then were annealed in air at 450°C at a heating rate 10°C /min for 2h inside a muffle furnace. For comparison, we also synthesized ZnO nanostructured powder via hydrothermal pathways. To 1.75mmol Zn(NO$_3$)$_2$ solution, 2M NaOH was added to make solution pH = 12 (sodium citrate as chelating agent), then, transferred into a Teflon liner stainless-steel autoclaves with effective volumes of 100ml. The autoclaves were filled with 70ml of above solution, seal and then kept in an oven at 120°C for 3h. After cooling to room temperature, the precipitate was washed repeatedly with deionized water and then dried at 60°C for 12h.

2.3. Characterization

The crystal phase was studied with powder X-ray diffraction analysis (XRD, D/Max-2550 V, Rigaku, Japan; CuK$_\alpha$, $\lambda$=0.15406 nm) in the wide angle region from 10° to 80° with a scanning speed of 2°/min. Scherrer equation (eq 1) [16] was employed for the precise calculation of the average crystallite size of ZnO samples after appropriate background correction from X-ray line broadening of the diffraction peaks of three largest characteristic (100), (002), and (101) planes.

$$\Phi = \frac{K\lambda}{\beta \cos \theta}$$ (1)
Where \( \Phi \) is the crystallite size, \( \lambda \) is the wavelength of X-ray used; \( K (K = 0.9 \text{ for spherical nanoparticles}) \) is the shape factor, \( \beta \) is the full line width at the half-maximum height of the main intensity peak, and \( \theta \) is the Bragg angle. Lattice parameters \( a \) and \( c \) of the ZnO samples were calculated from (100) and (002) oriented XRD peaks using eqs 2 and 3 [17]. For hexagonal system the volume \( V \) of the unit cell was determined by using eq 4 [18].

\[
a = \frac{\lambda}{\sqrt{3} \sin \theta} \tag{2}
\]

\[
c = \frac{\lambda}{\sin \theta} \tag{3}
\]

\[
V = 0.866 \times a^2 \times c \tag{4}
\]

The structure and morphology of products were examined with field emission scanning electron microscopy (FESEM, S-4800, Hitachi, Japan) equipped with an energy dispersive spectrometer (EDS, INCA Energy, Oxford, UK). Thermogravimetric-differential thermal analysis (TG-DTA) curves were recorded on a Hengjiu HCR-2 instrument at a heating rate of 10°C/min and using \( \alpha \)-Al2O3 as the standard material. UV-visible absorbance spectra were obtained for the dry-pressed disk samples with a UV-visible spectrophotometer (Lambda750, Perkin Elmer, USA). BaSO4 was used as a reflectance standard in a UV-visible diffuse reflectance experiment.

2.4. Photoelectrochemical measurement

Photocurrent measurement was performed in a three-electrode quartz cells with 0.5M \( \text{Na}_2\text{SO}_4 \) electrolyte solution. Saturated calomel electrode (SCE) used as reference electrodes, and platinum wire was used as counter electrode respectively. ZnO films electrodes (1cm × 1 cm) on ITO glass served as the working electrode. Photocurrent responses of photocatalysts under UV irradiation by two germicidal lamp (\( \lambda = 254 \text{ nm, 16W} \)) at room temperature. The photoelectrochemical experiment results were recorded with an electrochemical system (CHI-660E Instruments). The \( I-t \) curve was measured at 0.0 V with light on-off switches of 30s. The distance between the surface of working electrode and the light source was set to about 10cm.

2.5. Evaluation of photocatalytic performance

A 300W UV lamp with maximum emission at 365nm was used as UV light source. The distance between the liquid surface of the suspension and the light source was set to about 11cm. The photodegradation experiments were performed with the sample powder (30mg) suspended in solutions of the pollutants (60ml; phenol 20mg/L, and RhB 15) with constant stirring. Prior to irradiation, the suspensions were stirred in dark for 30min to ensure adsorption/desorption equilbrium. At certain time intervals, 3ml solution was drawn out each time and centrifuged at 5000rpm for 5min to get clear liquid. The quantitative determination of RhB and phenol were performed by measuring its intensity of the absorption peak (RhB at 553 nm; phenol at 270nm) with a UV-vis spectrophotometer (Lambda35, Perkin Elmer, USA).

3. Results and discussion

3.1. Structure and morphology

An X-ray diffraction pattern of the as-prepared ZnO products is shown in Fig. 1. It also can be found that the diffraction peaks of hydrothermal synthesized (HT) and homogenous precipitation (HP) prepared ZnO consisted of the characteristic peaks of the hexagonal wurtzite structure of ZnO (JCPDF No 36-1451). All of the ZnO samples and their lattice parameters (Table 1) matched well with the bulk ZnO, which could be indexed as no crystalline hydroxide phase can be observed, confirming the purity of the synthesized powders.
Table 1. Lattice parameters of ZnO (c and a), cell volume, and c/a ration.

| Samples      | a (Å) | c (Å) | c/a | Unit cell volume (Å³) |
|--------------|-------|-------|-----|-----------------------|
| HP ZnO       | 3.247 | 5.203 | 1.602 | 47.51                 |
| HT ZnO       | 3.245 | 5.198 | 1.602 | 47.41                 |
| JCPDS 36-1451| 3.249 | 5.206 | 1.602 | 47.63                 |

Figure 1. XRD of ZnO samples: (a) hydrothermal synthesized, (b) homogenous precipitation prepared.

Figure 2. FESEM images of ZnO samples: (a) hydrothermal synthesized, (b) homogenous precipitation prepared.

The differences in morphologies of the obtained ZnO nanoparticles via a hydrothermal pathways and homogenous precipitation prepared were characterized by FESEM (see in Figure 2). Figure 2a exhibited the obtained HT ZnO is flower architectures self-assembled by nanorods. The mean size of the flowers were approximately 1.5 ~ 2.5 μm. While the morphologies of HP ZnO nanoparticles, at urea/Zn²⁺ molar of 2.5, were roughly spherical shape (see in Figure 2b). Figure 2b reveals grains with a mean diameter of ~24 nm for the HP ZnO, also the individual particles appear to agglomerated. In addition, the BET results in Figure 3 confirmed that the HP ZnO was larger than HT ZnO sample may be due to the smaller grain size. The specific surf ace area for HP ZnO and HT ZnO particles are, 6.15 and 16.84 m²/g, respectively. A single-modal size pore size distribution was formed in HP ZnO nanoparticles, and strong pore peak at about 22nm. While the broad pore size distribution and weak pore peaks was exhibited for HT ZnO.
Figure 3 N\textsubscript{2} adsorption-desorption isotherms of ZnO samples and their corresponding pore size distribution (inset): (a) hydrothermal synthesis, (b) homogenous precipitation prepared.

Figure 4. TEM images of ZnO samples: (a) hydrothermal synthesis, (b) homogenous precipitation prepared.

As shown in Figure 4a, HT ZnO displays flower architectures self-assembled by sub-microrods, which consisted with SEM image (seen in Figure 2a). The TEM images of HT ZnO appear dark gray due to its large diameter. Obviously, from Figure 4b under high magnifications, the HP ZnO with spherical shape and well dispersed, which guaranteed the more active reaction surface in the photocatalysis process. Moreover, the TEM image clearly shows the individual HP ZnO particles possessed the size of 20 ~ 25 nm, which good agree with BET and SEM result.

3.2. Growth process of ZnO crystallites
Based on the results and some previous works, we proposed a growth process and mechanism of the flower-like ZnO nanostructures. In our experiments, the growth process of HT ZnO crystallites can be described as the following mechanism:

$$\text{Zn}^{2+} + \text{H}_2\text{O} \rightarrow \text{Zn(OH)}_2 \rightarrow \text{ZnO}$$  (5)
Zn\(^{2+}\) + OH\(^-\) \rightarrow [\text{Zn(OH)}\(_4\)]^{2-} \quad (6)

[\text{Zn(OH)}\(_4\)]^{2-} \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{OH}^- \quad (7)

Under this special hydrothermal condition, the precipitates would transform into ZnO nuclei (Eq. (5)). Then, Zn\(^{2+}\) from Zn(NO\(_3\))\(_2\)-6H\(_2\)O would react with OH\(^-\) to generate the growth unit of [Zn(OH)\(_4\)]\(^{2-}\) (Eq. (2)). Afterward, [Zn(OH)\(_4\)]\(^{2-}\) ions would diffuse and adsorb on the surface on the ZnO seeds. To the best of our knowledge, the fastest growth direction of the wurtzite ZnO is along the direction of the c-axis [0001], resulting in rod-based flower-like ZnO microstructure.

Simultaneous TG-DTA curves for the dried powder prepared by the homogeneous precipitation method are shown in Figure 5. The TG curve shows a marked weight loss with increasing temperature. The weight loss is due to the elimination of adsorbed water, chemically bonded water, and ammonia [19]. However, little weight loss in the TG curve is observed at temperatures above 450\(^\circ\)C. In the DTA curve a weakly broad endothermic peak are observed at about 90\(^\circ\)C and 130\(^\circ\)C which correspond to the evaporation of physically adsorbed water and bonded water respectively [20]. A strong exothermic peak around 385\(^\circ\)C may be related to the decomposition of carbonates and NH\(_4^+\) in the powders.

![Typical TG-DTA curves for the dried precipitate prepared by the homogeneous precipitation method.](image)

In our experiments, the growth process of HP ZnO crystallities can be described as the following equations:

\[ \text{CO(NH}_2\text{)}_2 + 3\text{H}_2\text{O} \rightarrow 2\text{NH}_3\cdot\text{H}_2\text{O} + \text{CO}_2 \] (8)

\[ \text{NH}_3\cdot\text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^- \] (9)

\[ \text{CO}_2 + 2\text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \] (10)

\[ 4\text{Zn}^{2+} + \text{CO}_3^{2-} + 6\text{OH}^- + \text{H}_2\text{O} \rightarrow \text{Zn}_4(\text{CO}_3)(\text{OH})_6\cdot\text{H}_2\text{O} \] (11)

\[ \text{Zn}_4(\text{CO}_3)(\text{OH})_6\cdot\text{H}_2\text{O} \rightarrow 4\text{ZnO} + \text{CO}_2 + 4\text{H}_2\text{O} \] (12)

During the reaction process, sodium citrate acted as a capping agent adsorbed on the surface of ZnO nuclei to minimize their surface area and decrease their energy. In addition, the super-saturation of configuration ion in solution was uniform result in ZnO precursor particle size small.
3.3. Optical properties
The optical absorption plays an important role in the photocatalysis, especially in the ultraviolet light photodegradation of contaminants. Actually, the absorption is calculated using the Kubelka-Munk function [19]:

\[
F(R) = \frac{\alpha}{S} = \frac{(1-R)^2}{2R}
\]  

(13)

Where \(R\), \(\alpha\) and \(S\) are the reflectance, the absorption coefficient and the scattering coefficient, respectively. As expected, ZnO has a fundamental absorption edge at \(\sim 387\) nm. Then, the optical band gap energy of ZnO samples can be obtained by assuming a direct transition between valence and conduction bands using the following equation [20]:

\[
(\alpha h\nu)^2 = A(h\nu - E_g)
\]  

(14)

Where \(\alpha\) is the absorption coefficient, \(A\) is a constant; \(h\nu\) is photon energy and \(E_g\) is the band gap energy of the semiconductor. \(E_g\) was determined through the extrapolation of linear region to \((\alpha h\nu)^2 = 0\) [21]. The estimated band gap values of the samples are about 3.18 and 3.20 eV, approximately, corresponding to HP ZnO and HT ZnO (see inset in Figure 6). The band gap values for the synthesized ZnO nanoparticles were lower than the standard value obtained for the bulk ZnO materials (3.37 eV).

![Figure 6. UV-vis DRS for (a) hydrothermally synthesized ZnO and (b) homogeneous precipitation prepared ZnO. The inset displays Kubelka-Munk plots of ZnO samples for band-gap estimation.](image)

3.4. Photocatalytic activity
The photocatalytic performance of the prepared photocatalysts were evaluated by degradation of rhodamine B (RhB) and phenol as model contaminants. From the Figure 7a, all ZnO samples presented the low adsorption capacity for the RhB, indicating that the fading mainly resulted from photocatalytic of the RhB. The degradation efficiency of RhB solution over HT ZnO was about 84\% in 2.0 h. However, the HP ZnO at urea/Zn\(^{2+}\) molar of 2.5 displayed higher photocatalytic efficiency (2.0 h, 90\%) than that of HT ZnO. Figure 7b also shows the photodegradation of phenol over HT ZnO and HP ZnO. When no photocatalyst was added, the self-decomposition of phenol almost was...
negligible. The photocatalytic degradation of phenol follows the order: HP ZnO (3.0 h, 81%) > HT ZnO (3.0 h, 29%). This observation implied that HP ZnO manifested the higher degradation efficiency.

**Figure 7.** Photocatalytic activity of the hydrothermally synthesized (HT) ZnO and homogeneous precipitation prepared (HP) ZnO for degradation of (a) RhB and (b) phenol.

Photocurrent response is an effective method to understand the generation, separation, and migration of photo-generated carriers in the photocatalytic process. Figure 8 shows the photocurrent responses of HT ZnO and HP ZnO samples in the light and dark. It can be clearly seen that the photocurrent density of HP ZnO is about 10 μA/cm², while the photocurrent density of HT ZnO is only about 4 μA/cm². In general, the enhanced photocurrent response indicated a more effective separation of photo-induced electron-hole pairs and a faster interfacial charge carriers transportation in the HP ZnO samples. Thus, the photocurrent increases in the order HT ZnO and HP ZnO, which exactly corresponded with their photocatalytic activity.

Compared with HT ZnO, HP ZnO particles with much higher specific surface area, determined by N₂ adsorption-desorption isotherms, not only facilitate the surface absorption of the UV light but also...
provide more active catalytic sites, resulting in the high ROS production. Additionally, the superior crystalline quality of HP ZnO may improve its charges separation efficiency and prolong the lifetime of charge carriers, which supported by photocurrent results. As a result, HP ZnO exhibited enhanced photo-catalytic activity.

4. Conclusions
In summary, we have successfully synthesized the flower-like and spherical ZnO nanoparticles through mild wet method at a relative low temperature. The SEM and TEM analysis indicated that the HP ZnO with spherical shape and well dispersed and HT ZnO displays flower architectures self-assembled by submicrorods. The result of DRS revealed that all ZnO samples exhibited similar light adsorption range. The HP ZnO showed higher photocatalytic activity than that of HT ZnO due to higher specific surface area and superior charges separation efficiency.

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