Preparation and Photocatalytic Properties of ZnO/CuO/ZnAl$_2$O$_4$ Composite Hollow Microspheres by One-Pot Method

Yan Jianhui$^{1, 2}$, Zhang Li$^{1, 2,*}$, Li Xiaoyan$^{1, 2}$, Zhang Xiumiu$^{1}$ and Dai Chaohua$^{1}$

$^1$School of Chemistry and Chemical Engineering, Hunan Institute of Science and Technology, Yueyang 414006, China
$^2$College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China

Abstract

ZnO/CuO/ZnAl$_2$O$_4$ composite hollow microspheres have been fabricated using glucose as template by a polyethylene glycol (PEG-4000)-assisted one-pot hydrothermal method. The as-prepared samples were characterized by XRD, SEM, HRTEM, BET, EDS, UV-Vis DRS and TG-DTA. The photocatalytic activity of the as-prepared samples was evaluated by photocatalytic decolorization of methyl orange (MO) aqueous solution under the irradiation of the simulated sunlight (100 mW/cm$^2$). The effects of the calcination temperature, amount of PEG and the molar ratio of metal ion on the structure, composition, and photocatalytic properties of the as-prepared samples were investigated in detail. The results indicated that the highest photocatalytic degradation efficiency was observed at n(Zn$^{2+}$):n(Cu$^{2+}$) ratio of 1:1, 10wt.%, mass ratio of PEG to ZnO/CuO/ZnAl$_2$O$_4$ and calcinations temperature of 600 ºC. The maximum photocatalytic decoloration rate of 92.4% within 60 min was obtained at 0.5 g·L$^{-1}$ concentration of ZnO/CuO/ZnAl$_2$O$_4$ photocatalysts.

Keywords: hydrothermal method; composite hollow; ZnO/CuO/ZnAl$_2$O$_4$; microspheres; photocatalytic decoloration; methyl orange

*Correspondence
Zhang Li,
Email: hgx.zl@163.com

Introduction

Spinel ZnAl$_2$O$_4$ has been attracting considerable attention since it can be used as catalyst$^{[1]}$, catalyst support$^{[2]}$, and even as optical material$^{[3]}$ due to its high thermal stability, low surface acidity, and high mechanical resistance$^{[4]}$. However, a broad bandgap of 3.8 eV is the major limitation in achieving high photocatalytic efficiency. To solve the above issue, different methods have been explored and designed in extending light response range and promoting the separation of photoinduced charge carriers, such as improving preparation method$^{[5]}$, doping of noble metal nanoparticles$^{[6]}$ and composite of different semiconductors$^{[7]}$. In particularly, the coupling of the bandgap structure of both ZnO and ZnAl$_2$O$_4$ phase in the ZnO/ZnAl$_2$O$_4$ nanocomposite ensured the efficient separation of photogenerated e- and h$^+$ pairs, which was prerequisite for the enhanced photocatalytic performance$^{[8, 9]}$. However, conventional powdered photocatalysts have a serious limitation to post-treatment separation in a slurry system after photocatalytic reaction. Furthermore, CuO with a band gap of 1.8 eV have been proven to be beneficial to the catalytic activity enhancement by selecting other semiconductor combined with it$^{[10]}$. In this study, novel ZnO/CuO/ZnAl$_2$O$_4$ composite hollow microspheres were fabricated by one-pot hydrothermal method.

The structure, composition, morphology, textural, UV–vis absorbing properties of the resulting composites were investigated by SEM, XRD, BET and UV-vis spectra. Subsequently, the photocatalytic activities of the ZnO/CuO/ZnAl$_2$O$_4$ composites were evaluated by the decolorization of MO.

Chem Sci Rev Lett 2014, 3(12), 1080-1090
Experimental

Sample preparation

ZnO/CuO/ZnAl$_2$O$_4$ sample was prepared by a polyethylene glycol (PEG)-assisted hydrothermal synthetic method using the glucose based carbonaceous materials as template. In a typical synthetic procedure, a mixture of glucose (15 g, as a template agent), Cu(NO$_3$)$_2$·3H$_2$O (1.208g), Al(NO$_3$)$_3$·9H$_2$O (3.75g) and a certain amount of Zn(NO$_3$)$_2$·6H$_2$O was dissolved in deionized water (120 mL), and polyethylene glycol (PEG, as a dispersion agent, ensuring that the content of PEG in catalysts was 5 wt.%, 10 wt.%, 15 wt.%, respectively) was subsequently added with constant stirring to the above solution until complete dissolution. Then ammonia solution (NH$_3$·H$_2$O) was added dropwise into the mixture solution under magnetic stirring until the pH reached 7.0. After mixing, the reaction solution was transferred into a 200 mL Teflon-lined autoclave. The autoclave was sealed and kept at 180 ◦C for 24 h, and then cooled to room temperature naturally. After filtration and washing with distilled water and ethanol for several times, the obtained sample was dried in oven at 80 ◦C overnight. Finally, the samples were obtained after annealing under certain temperatures. These samples were denoted as R$_1$, R$_2$, R$_3$, R$_4$, where R -- the ratio of Zn and Cu, and corresponding with Zn/Cu molar ratio of 0, 0.5, 1.0, 1.5, respectively.

Characterization

The crystalline phase and the crystal size of the samples were identified by X-Ray diffraction (XRD, Bruker D8) using Cu Kα radiation (=1.5418Å) at a scan speed of 0.05° s$^{-1}$, a voltage of 40 kV and a current of 300 mA. The surface morphologies of the samples were observed by scanning electron microscope (SEM, Nova Nano230) operated at 30 kV. The transmission electron microscopy (TEM) measurements were conducted on a Tecnai G2 F20 S-TWIN microscope working at 200 kV. UV–vis diffused reflectance spectra of the samples were obtained using a UV-vis spectrophotometer (UV-2550, Shimadzu, Japan). BaSO$_4$ was used as a reflectance standard in a UV-vis diffuse reflectance experiment. The chemical composition was analyzed by Energy-dispersive X-ray spectroscopy (EDS) during TEM experiments.

Measurement of photocatalytic activity

The photocatalytic reaction was carried out in homemade tubeshaped quartz reactor including three layers connected with gas collecting devices, and water was used as the external circulation cooling and wind as the internal cooling. The reaction temperature was kept at 25 ± 0.2 ◦C by controlling the external circulation water in the water jacket of the reactor during the entire experiment. The photocatalyst powder (0.3 g) was dispersed by a magnetic stirrer in a 600 mL MO solution with the concentration of 25 mg·L$^{-1}$. A 150-W xenon lamp with $\lambda$= 200-900 nm was used as the simulated sunlight source. The luminous intensity was measured at 100 mW/m$^2$ by the auto-range ST-85 optical radiometer (Photoelectric Instrument Factory of Beijing Normal University). Prior to light illumination, the suspension was strongly magnetically stirred for 30 min in the dark for adsorption/desorption equilibrium. During irradiation, the catalyst was kept in suspension state by a magnetic stirrer. Samples for analysis was extracted through pipette every 10 min and centrifuged immediately. Absorbance of the suspension and initial solution was determined, respectively. A 752 UV–vis spectrophotometer was used at the maximum absorption wavelength (max = 465 nm) of MO. Decoloration rate are presented as C/C$_0$, where C$_0$ and C are the initial concentration of MO under adsorption equilibrium and the concentration of MO at different irradiation time, respectively. Experiments for comparison were carried out under the same condition, but one was done without catalyst and another was in the dark. Each set of photocatalytic measurements was repeated three times, and the experimental error was found to be within ±5%.

Results and discussion

XRD study

Figure 1 shows XRD patterns of the samples with addition of 10 wt.% PEG and the starting Zn to Cu molar ratio of 1:1 (R$_3$) annealed at different temperatures. From Figure 1, the sharp diffraction peaks indicate the poor crystallinity.
of the synthesized sample at 500°C. While most diffraction peaks from this pattern can be indexed to reflections of CuO (JCPDS Card No. 45-0937) and ZnO (JCPDS Card, No. 36-1451) except for a minor peak ascribed to a amount of ZnAl₂O₄ at 600°C, indicating that the sample consists of CuO, ZnO and ZnAl₂O₄ ternary complexes. With further increasing the calcination temperature, the peaks of ZnO start to decrease in intensity and more ZnAl₂O₄ is formed. This indicates that a solid-state reaction of ZnO and Al₂O₃ starts after 600°C, resulting in the formation of spinel ZnAl₂O₄. While calcination temperature increases to 900°C, the diffraction peaks are mainly indexed to CuO and ZnAl₂O₄. It is obvious that five main diffraction peaks of the (200), (311), (422), (511) and (400) reflections are observed in Figure 1, which can be indexed to spinel ZnAl₂O₄ (JCPDS Card No. 05-0669). No peaks of ZnO are appeared in the patterns, suggesting that most of ZnO is transferred to ZnAl₂O₄.

![Figure 1 XRD patterns of R₃ samples annealed at different temperatures](image1)

Figure 2 shows XRD patterns of the samples with addition of 10 wt.% PEG and different molar ratio of Zn to Cu (R₁, R₂, R₃, R₄) annealed at 600°C. From Figure 2, the XRD patterns of sample with Zn²⁺/Cu²⁺ ratio of 0:1 (R₁) only display a feature of CuO reflections. The intensities of diffraction peaks of ZnO and ZnAl₂O₄ oxides gradually increase with the increasing Zn²⁺/Cu²⁺ ratio, the intensities of diffraction peaks of the sample with Zn²⁺/Cu²⁺ ratio of 1:1 (R₃) are stronger than that of the other samples. It can be speculated that the photocatalytic activity of the sample with Zn²⁺/Cu²⁺ ratio of 1:1 is the best among the four samples. At this time, the diffraction peaks of CuO exist, indicating that the sample consists of CuO, ZnO and ZnAl₂O₄ ternary complexes.

![Figure 2 XRD patterns of samples with different Zn/Cu molar ratio](image2)
Figure 3 shows XRD patterns of the R₃ samples with different content of PEG annealed at 600 °C. It is obvious that the main diffraction peaks (2θ = 35.6, 38.8) can be indexed to the hexagonal phase of CuO (JCPDS Card No. 45-0937), with the increase of PEG additives, the diffraction peak intensity of CuO increases gradually, while the other diffraction peak have no obvious changes, which indicates that adding PEG can slow the reaction process of CuO and Al₂O₃ form CuAl₂O₄, so as to to maintain high photocatalytic activity[13].

![XRD patterns of R₃ samples with different addition of PEG](image)

**Figure 3** XRD patterns of R₃ samples with different addition of PEG  
(a) 5%; (b) 10%; (c) 15%

**The morphology analyze**

The morphology of the samples with addition of 10 wt.% PEG and the starting Zn to Cu molar ratio of 1:1 (R₃) annealed at 600 °C was investigated by SEM in Figure 4. Figure 4a,b show that the samples are nearly in spherical shape with diameters of ca.2-3 μm in the present of glucose, and especially some microspheres are open and hollow due to the removal of carbon by calcinations[14]. This indicates that glucose plays a critical role for the formation of the hollow microspheres, some of which are not flat with rough superstructure[15].

![SEM images of R₃ sample](image)

**Figure 4** SEM images of R₃ sample

Figure 5 shows the TEM and HRTEM images of the samples with addition of 10 wt.% PEG and the starting Zn to Cu molar ratio of 1:1 (R₃) annealed at 600 °C. Fig 5(a) shows that the sample is irregularly spherical and its particle sizes
are relatively identical. The particle size of sample is 15-20 nm. More detailed morphology about the ZnO/CuO/ZnAl\textsubscript{2}O\textsubscript{4} nanocomposites was indicated by HRTEM (Figure 5(b)). HRTEM image reveals that both ZnO, CuO and ZnAl\textsubscript{2}O\textsubscript{4} form a heterojunction nanostructure proven by well-defined lattice fringes: the spacing of 2.64 Å represents the lattice-resolved (002) crystalline plane of ZnO phase, the spacing of 2.37 Å represents the lattice-resolved (200) crystalline plane of CuO phase, and the spacing values of 2.86 Å correspond to the (220) facets of ZnAl\textsubscript{2}O\textsubscript{4} phase, respectively, which are in good agreement with report in Ref.\textsuperscript{[16]}.

**Figure 5** HRTEM images of R\textsubscript{3} sample

The elemental composition of the ZnO/CuO/ZnAl\textsubscript{2}O\textsubscript{4} sample was further determined by EDS. The EDS survey spectrum (Figure 6a, b) indicates that the prepared sample consists of Zn, Cu, O, Al and C elements. Thus, both XRD and EDS analysis indicate that the as-prepared hollow microspheres are composed of ZnO, CuO and ZnAl\textsubscript{2}O\textsubscript{4}.

**Figure 6** EDS images of R\textsubscript{3} sample

**TG-DTA analyze**

Fig 7 shows the TG-DTA curves of R\textsubscript{3} sample with addition of 10 wt.% PEG. The first mass loss before 200 °C may be attributed to the evaporation of absorbed water, meanwhile the corresponding endothermic peak is observed from the thermogravimetric curve. The second mass loss occurs at 180-340 °C, and the corresponding exothermic peak at about 280 °C can be ascribed to the decomposition of the residual organic compounds. The third mass loss at 340-600 °C is due to the decomposition of the nitrate and synthesis of the ZnO, CuO and ZnAl\textsubscript{2}O\textsubscript{4} compounds, and then the mass loss becomes almost constant when the temperature is more than 600 °C. The corresponding endothermic peak at about 720 °C is perhaps owing to the forming of ZnAl\textsubscript{2}O\textsubscript{4}.

*Chem Sci Rev Lett* 2014, 3(12), 1080-1090
Table 1 shows the BET surface area, pore volume, and average pore size of samples prepared with addition of 10 wt.% PEG and different molar ratio of Zn to Cu (R₁, R₂, R₃, R₄) annealed at 600 °C. The pore volume of as-prepared samples increases gradually in corresponding with average pore size with increasing the molar ratio of Zn/Cu to 1:1, at this point, the pore volume and the average pore size reach the maximum. With increasing the molar ratio of Zn to Cu, the BET surface area increases and reaches its highest value of 229.3 m²·g⁻¹ with Zn to Cu molar ratio of 3:2. However, when the molar ratio of Zn to Cu is further decreased to 1:1, the surface area of sample decreases from 229.30 to 209.07 m²·g⁻¹. Consequently, specific surface area of the obtained ZnO/CuO/ZnAl₂O₄ has proved to be strongly dependent on the composition. Such phenomena are closely related with the structural feature of different ZnO/CuO/ZnAl₂O₄ composites. Moreover, the large porous structure is believed to facilitate the transportation of reactant molecules and products through the interior space due to the interconnected porous networks and to favor the harvesting of exciting light due to enlarged surface area and multiple scattering within the porous framework[17,18].

Table 1 The specific surface property of different n(Zn):n(Cu) ratio samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>S_BET/(m²·g⁻¹)</th>
<th>Adsorption average pore width/nm</th>
<th>Pore volume (cm³·g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R₁(0)</td>
<td>197.82</td>
<td>8.8</td>
<td>0.56</td>
</tr>
<tr>
<td>R₂(1:2)</td>
<td>229.30</td>
<td>10.0</td>
<td>0.72</td>
</tr>
<tr>
<td>R₃(1:1)</td>
<td>209.07</td>
<td>11.3</td>
<td>0.73</td>
</tr>
<tr>
<td>R₄(3:2)</td>
<td>138.73</td>
<td>10.4</td>
<td>0.45</td>
</tr>
</tbody>
</table>

Figure 8 shows the N₂ adsorption-desorption isotherm and the corresponding pore-size distribution curve for the samples prepared with addition of 10 wt.% PEG and different molar ratio of Zn to Cu (R₁, R₂, R₃, R₄) annealed at 600 °C. Figure 8a shows that all the samples have a type IV isotherm according to Brunauer-Deming-Deming-Teller (BDDT) classification with two capillary condensation steps, implying bimodal pore size distributions in the mesoporous (2-50 nm) and macroporous (>50 nm) regions[9,19]. With increasing the molar ratio of Zn to Cu, the
shapes of nitrogen adsorption and desorption isotherms underwent obvious changes, implying a significant variation of pore structures. Firstly, the isotherms corresponding to the $R_3$ samples show higher absorption at high relative pressures ($P/P_0$ approaching 1), indicating the formation of larger inter-aggregated pore between the secondary aggregated particles and/or an increasing pore volume of interaggregated pores, as further confirmed in Figure 8b. This may be related to the hollowing of the interior space of ZnO/CuO/ZnAl$_2$O$_4$ microspheres (as shown in Figure 4a and 4b). For the $R_3$ sample, the bimodal poresize distribution consisting of fine intra-aggregated pores and larger inter-aggregated pores. These mesopores and macropores presumably arise from the interstices among the different-sized nanoparticles within the shells of ZnO/ZnAl$_2$O$_4$ hollow microspheres. When the molar ratio of Zn to Cu was further increased to 3:2, the hysteresis loop shifted to relative lower pressure ($P/P_0$) region ($0.65 < P/P_0 < 0.9$), implying the formation of finer intra-aggregated pore within the primary agglomerated particles, as confirmed by a drastic decrease in the corresponding pore volume (Figure 8b).

Figure 8 (a) N$_2$ adsorption-desorption isotherms and (b) pore size distribution curves of different n(Zn):n(Cu) ratio samples (a) $R_1$ (0); (b) $R_2$ (1:2); (c) $R_3$ (1:1); (d) $R_4$ (3:2)

UV–vis diffuse reflectance spectra

Figure 9 UV–Vis DRS spectra of ZnO/ZnAl$_2$O$_4$ and $R_3$ samples (a) ZnO/ZnAl$_2$O$_4$; (b) $R_3$

The UV–vis diffuse reflectance spectra (Figure 9) of the samples with addition of 10 wt.% PEG and the starting Zn to Cu molar ratio of 1:1 ($R_3$) annealed at 600 °C. The $R_3$ sample displays a significant increase in the absorption at
wavelength ≥ 400 nm compared with ZnO/ZnAl₂O₄ (Figure 9b). Furthermore, it can be seen that R₃ sample shows a certain absorption in the visible light region (the wavelength ranging from 400 to 800 nm), while no absorption can be observed for ZnO/ZnAl₂O₄. This experimental result can be attributed to the coupling interaction between the ZnO, CuO and ZnAl₂O₄ phase, the optimizing molar ratio of Zn to Cu and the form of heterojunction structure, which leads to the enhancement of utilization of light and photocatalytic activity.[21].

**Photocatalytic activity**

**Effect of calcination temperature on photocatalytic degradation activity:**

Figure 10 reveals the photocatalytic activities of the ZnO/CuO/ZnAl₂O₄ nanocomposites with addition of 10 wt.% PEG and the starting Zn to Cu molar ratio of 1:1 annealed at different temperatures. From Figure 10, the photocatalytic activities vary greatly for the samples. The sample annealed at 600 °C shows the highest photocatalytic activity. The maximum photocatalytic degradation rate of 92.4% in 60 min is obtained. For the other samples annealed at 500, 700, 800, and 900 °C, the degradation rates of MO within 60 min are decreased. The difference in photocatalytic activity may be ascribed to the crystalline quality of the nanocomposition. The sample annealed at 500 °C shows the lower activity than that annealed at 600 °C, which may be ascribed to the relatively poor crystallinity (shown in Figure 1). The sample annealed at 600 °C shows a better crystalline quality. The photocatalyst with good crystallization can provide a shorter migration distance for electrons and holes and reduce the chances of their recombination. Therefore, the photocatalytic reaction efficiency is accelerated and the catalytic activity is improved.[22].

![Figure 10](image_url)

**Figure 10** Effects of calcination temperature on photocatalytic activity
(a) 500°C; (b) 600°C; (c) 700°C; (d) 800°C; (e) 900°C

**Effect of the molar ratio of Zn to Cu on photocatalytic degradation activity:**

Figure 11 reveals the photocatalytic activities of the ZnO/CuO/ZnAl₂O₄ nanocomposites with addition of 10 wt.% PEG and different molar ratio of Zn to Cu (R₁, R₂, R₃, R₄) annealed at 600 °C. It can be seen that the photocatalytic activities of ZnO/CuO/ZnAl₂O₄ samples first increase with the molar ratio of Zn to Cu up to 1:1, and then slightly decrease when the molar ratio exceeds 1:1. The sample with the starting Zn to Cu molar ratio of 1:1 shows the highest photocatalytic activity. The maximum photocatalytic degradation rate of 92.4% in 60 min is obtained. For the other samples with the starting Zn to Cu molar ratio of 1:2, 3:2, the degradation rates of MO within 60 min are all decreased. The difference in photocatalytic activity may be ascribed to the BET surface area and the nanocomposition.[23,24]. Although the sample with the starting Zn to Cu molar ratio of 1:2 possesses a larger specific surface area, the photocatalytic activity is lower. The reason is attributed to the existing of heterojunction and the content of ZnO, CuO in the ZnO/CuO/ZnAl₂O₄ nanocomposite. When they are coupled together to form a
heterostructure which is energetically favorable to separate photogenerated e− and h+ pairs. The efficient separation of the photogenerated e− and h+ pairs is regarded as the key factor for the high photocatalytic activities. On the other hand, the high photocatalytic activity of sample with the Zn to Cu molar ratio of 1:1 is also attributed to the higher specific surface area than the sample with the starting Zn to Cu molar ratio of 3:2 (shown in Table 1). A larger surface area provides more surface active sites for the adsorption of reactants molecules, making the photocatalytic process more efficient [25].

![Figure 1](image)

**Figure 1** Effects of different Zn/Cu molar ratio on photocatalytic activity
(a) Zn/Cu=1:2; (b) Zn/Cu=1:1; (c) Zn/Cu=3:2

Conclusions

1. The ZnO/CuO/ZnAl₂O₄ composite hollow microspheres have been fabricated using glucose as template by a polyethylene glycol (PEG)-assisted one-pot hydrothermal method and characterized in detail. The results showed that the coupling of the ZnO, CuO and ZnAl₂O₄ not only enhanced light absorption range compared with ZnO/ZnAl₂O₄ but increased BET.
2. The photocatalytic degradation activity of the ZnO/CuO/ZnAl₂O₄ nanocomposites can be improved by varying the molar ratio of Zn to Cu and calcination temperature.
3. The decoloration rate of 92.4% for MO in 60 min is obtained at the molar ratio of Zn to Cu of 1:1, PEG of 10 wt.% and annealing temperature of 600 °C, which may be attributed to the fact that ZnO, CuO and ZnAl₂O₄ can form heterojunction structure.

Acknowledgements

This project was financially supported by the National Nature Science Foundation of China (No. 21271071, 21306041), and Aid Program for Science and Technology Innovative Research Team in Higher Educational Institutions of Hunan Province (No.12K117).

References


© 2014, by the Authors. The articles published from this journal are distributed to the public under “Creative Commons Attribution License” (http://creativecommons.org/licenses/by/3.0/). Therefore, upon proper citation of the original work, all the articles can be used without any restriction or can be distributed in any medium in any form.

Publication History
Received 29$^{th}$ Oct 2014
Revised 15$^{th}$ Nov 2014
Accepted 22$^{nd}$ Nov 2014
Online 30$^{th}$ Nov 2014