Synthesis of ZnO-CuO/MCM-48 photocatalyst for the degradation of organic pollutions
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ABSTRACT
The photocatalytic properties of ZnO-CuO catalysts supported on siliceous MCM-48 (Mobil Composition of Matter No. 48) for the degradation of organic pollutions such as methylene blue and salicylic acid under UV light irradiation were investigated. These catalysts were prepared by impregnation of MCM-48 with a mixed aqueous solution of copper acetate and zinc acetate. X-ray diffraction, N2-physisorption, high resolution transmission electron microscopy, scanning electron microscopy, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy and photoluminescence were used to characterize these samples. Results from characterizations showed that the addition of ZnO to CuO/MCM-48 could markedly improve the photocatalytic degradation properties. The enhanced photocatalytic behaviors of ZnO-CuO/MCM-48 may be due to the formation of p-n heterojunctions between ZnO and CuO, resulting in the effective separation of photogenerated electron–hole pairs. Moreover, the photocatalysts were easily recovered and reused for five cycles without considerable loss of activity.

Key words | catalytic properties, CuO, heterojunction, zinc

INTRODUCTION
In recent years, the treatment of toxic and refractory organic pollutants into the aquatic environment has gained much attention and is one of the most significant challenges faced by environmental scientists. Important organic compounds in industrial wastewater include dyes, phenols, aliphatic alcohols, aromatics, carboxylic acids, etc. (Nageswara Rao et al. 2009). At present, heterogeneous photocatalysis processes are one of the most available methods for degrading dyes and organic pollutants in aqueous media (Shargh & Behnajady 2016; Zheng & Jiao 2017), and semiconductors (e.g. TiO2, ZnO) are the most widely used photocatalysts (Chowdhury et al. 2012; Marien et al. 2016; Birben et al. 2017). However, the reaction performance was still far from satisfactory. Therefore, many efforts have been carried out to develop new photocatalysts with high catalytic properties.

In the last decade, the use of semiconductor copper oxide as a photocatalyst has been intensively studied (Moon et al. 2014; Nezamzadeh-Ejihieh & Karimi-Shamsabadi 2014; Wu et al. 2015). However, poor adsorption capacity and recycling difficulties restricted the utilization of CuO for various applications. To overcome these drawbacks, CuO photocatalysts supported on different adsorbents such as activated carbon, activated alumina or zeolite in waste water treatment were studied, and some good results were obtained (Jeong & Lee 2003; Nezamzadeh-Ejihieh & Karimi-Shamsabadi 2014). Recently, mesoporous silicates which offer super adsorption, unique uniform pores, and high surface area, have received much attention as new materials for catalyst supports (Duan et al. 2011; Zhao et al. 2015; Romero et al. 2016). The cubic form, MCM-48, provides favorable mass transfer to bulk molecules, which reduces diffusion limitations, and renders MCM-48 resistant to pore blockage and more appealing for catalytic reactions, compared with the one-dimensional pore system of MCM-41 (Fechete et al. 2011; Romero et al. 2016). On the other hand, coupling two semiconductors with different energy levels is an effective way to enhance the separation efficiency of photogenerated electrons and holes, thus achieving a higher photocatalytic activity (Bera et al. 2014; Yu et al. 2014). Coupled semiconductors formed by CuO and other metal oxides, such as TiO2, SnO2 and BiVO4, have been reported and high photocatalytic performances achieved (Xia et al. 2007; Li et al. 2008; Jiang et al. 2009). Although there is much reported about CuO-ZnO...
composites, most of them are used for hydrogen production and gas sensors (Fierro et al. 1996; Xu et al. 2014), and few have been used for the photodegradation of organic compounds (Sathishkumar et al. 2011).

In the present work, ZnO-CuO/MCM-48 samples with different content of zinc were synthesized and used for the photocatalytic degradation of methylene blue (MB) and salicylic acid in water. It was found that the so-prepared catalysts exhibited high photocatalytic activities, which may be ascribed to their large specific surface areas and formation of p-n heterojunctions between ZnO and CuO.

**EXPERIMENTAL**

Catalyst preparation

The mesoporous material MCM-48 was synthesized by a method described in detail elsewhere (Schumacher et al. 1999). The ZnO-CuO/MCM-48 samples with different content of ZnO (0, 3, 5, 7, 10 wt%) were obtained by co-impregnation of MCM-48 with a mixed aqueous solution of copper acetate and zinc acetate, using a volume of solution/weight of MCM-48 of 8.0 mL/g, and the loading of CuO was 10 wt%. Afterward, the prepared samples were dried by vacuum evaporation at 80 °C, then calcined at 550 °C for 4 h. Catalysts used during this investigation were abbreviated as ZnO(x)-CuO/MCM-48, where ‘x’ represents the amount of ZnO in the catalyst (wt%).

Catalyst characterization

The N2 adsorption-desorption isotherms of samples were measured at −196 °C on a Micromeritics ASAP 2000 apparatus. Before measurements, the samples were degassed under 300 °C and 1 × 10−3 Torr (Duan et al. 2011). The pore structural data were analyzed by the Barrett-Joyner-Halenda method of adsorption.

X-ray diffraction (XRD) patterns of samples were collected on a Philips PW 3830 diffractometer in 2θ ranges: 2θ = 5° and 15°–80° using Cu Ka radiation (λ = 1.5418 Å), a nickel filter, and an X-ray detector as a detector, using the real time multiple strip detection technique.

Infrared spectra were recorded on a Bruker Tensor 27 using DRIFT (diffuse reflectance infrared Fourier transform spectroscopy) techniques, scanning from 4,000 cm−1 to 400 cm−1. The sample was ground with KBr and pressed into a thin wafer.

Scanning electron microscopy (SEM) micrographs were obtained in a JEOL model JSM 6380 LV, working voltage: 20 kV. Energy-dispersive X-ray spectroscopy (EDX detector: Quantax 200, Bruker Resolution 126 eV) was employed for the elemental analysis or chemical characterization of catalysts.

High resolution transmission electron microscopy (TEM) images were taken using a JOEL JEM-2100 microscope equipped with energy-dispersive spectroscopy (EDS). Samples were prepared by grinding, suspending and sonicating them in ethanol and placing a drop of the suspension on a copper grid with a perforated carbon film.

X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo ESCALAB 250 instrument (USA) using nonmonochromatic AlKα (hv = 1,486.6 eV) radiation. The pressure of the analysis chamber was kept at 4 × 10−10 Torr. All samples were previously reduced in situ under hydrogen at 500 °C for 1 h. Binding energies were referred to the C 1 s peak at 284.8 eV.

The photoluminescence (PL) spectra were taken with a fluorescence spectrophotometer (FS2500, Japan) using a Xe lamp as excitation source with optical filter.

Photocatalysis tests

The photocatalytic properties of the as-prepared samples were evaluated using MB dye as a model compound. In the experiments, 50 mL MB aqueous solution with a concentration of 4 × 10−5 M was mixed with 5 mg catalyst, which was illuminated by a high pressure mercury lamp (100 W, Shanghai Mengya) through a 320 nm cutoff filter (Mihai et al. 2010). The distance between the reactor and the lamp was fixed at 10 cm. The light intensity reaching the external surface of the reactor was 0.47 mW/cm2, as measured by a UV-irradiance meter (UV-A, Instruments of Beijing Normal University, China). Prior to illumination, the suspension containing MB and photocatalyst was magnetically stirred for 1 h until an adsorption–desorption equilibrium between the catalyst surface and the dye was established. Samples were then taken out regularly from the reactor, and immediately centrifuged (4,000 rpm) to remove particles. The concentration of MB in each sample was determined by a UV-Vis spectrophotometer at a wavelength of 664 nm. The photocatalytic degradation efficiency X was calculated by the following equation:

\[
X(\%) = \left(\frac{C_0 - C_t}{C_0}\right) \times 100\%
\]

where t is the reaction time; \(C_0\) and \(C_t\) represent the concentration of MB initially and at irradiation time \(t\).
By the same method, the photocatalytic degradation of salicylic acid in the presence of ZnO-CuO/MCM-48 could be researched. The maximum adsorption of salicylic acid is 296 nm.

RESULTS AND DISCUSSION

Catalyst characterization

The nitrogen adsorption–desorption isotherms of MCM-48 and different catalysts are exhibited in Figure 1. A standard IV type classification typical of mesoporous materials is observed for MCM-48 (Sowri Babu et al. 2015). Generally, for the material containing ordered cubic-phased mesopores, monolayer coverage of N₂ molecules on the pore wall occurs at low relative pressure (P/P₀ < 0.2), and a steep inflection can be observed at P/P₀ between 0.2 and 0.4. Compared with MCM-48, the isotherms of these catalysts do not show steep inflection, indicating the copper and (or) zinc species are not present in the pores as an ideally homogeneous layer (Mihai et al. 2013). The physicochemical properties of MCM-48 and different catalysts are shown in Table 1. In comparing the parent MCM-48 with these catalysts, one can observe an appreciable decrease in the surface areas and pore volume, which implies the pore filling processing has happened (Sowri Babu et al. 2012). It is noteworthy that these catalysts still possess high BET (Brunauer–Emmett–Teller) surface areas and pore volumes, which are conducive to their catalytic application, although these properties are decreased after the modification of copper and zinc species.

The XRD patterns of MCM-48 and different catalysts are shown in Figure 2. It can be seen from Figure 2(a) that the MCM-48 sample exhibits a strong d 211 reflection peak sited at about 2.9°, which can be indexed to the Ia3d cubic structure (Peng et al. 2015). As for ZnO(0)-CuO/MCM-48, the intensity of the reflection peak is decreased markedly, which is because the quality of the cubic phase was partially compromised (Jiang et al. 2015). As the zinc content increased, a small shift in the position of the reflection peak to the higher angles is observed, implying partial distortion of the mesoporous structure has taken place (Sorolla et al. 2015). Figure 2(b) presents the wide-angle XRD patterns of MCM-48 and different catalysts. It can be observed that all of these materials exhibit a broad peak sited at around 23°. This peak can be attributed to silica, and the broadness of this peak implies its amorphous nature (Maneesuwan et al. 2014). Apart from this peak, all the diffraction peaks of these catalysts are indexed to the monoclinic structure of CuO (JCPDC no: 801,916). Moreover, no characteristic peaks from ZnO are observed, from which it can be concluded that zinc species are highly dispersed. A similar phenomenon has been reported for TiO₂ particles loaded on MCM-48 (Liou & Lai 2015).

Table 1 | Physicochemical properties, and amount adsorbed by MCM-48 and different catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sₐec (m²/g)</th>
<th>Pore diameter (nm)</th>
<th>Pore volume (cm³/g)</th>
<th>Amount of MB adsorbed (mol/g)</th>
<th>Amount of salicylic acid adsorbed (mol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCM-48</td>
<td>1,350</td>
<td>2.62</td>
<td>0.70</td>
<td>4.3 × 10⁻⁴</td>
<td>2.4 × 10⁻⁴</td>
</tr>
<tr>
<td>ZnO(0)-CuO/MCM-48</td>
<td>823</td>
<td>2.79</td>
<td>0.48</td>
<td>2.2 × 10⁻⁴</td>
<td>1.1 × 10⁻⁴</td>
</tr>
<tr>
<td>ZnO(2)-CuO/MCM-48</td>
<td>784</td>
<td>2.83</td>
<td>0.44</td>
<td>2.0 × 10⁻⁴</td>
<td>9.6 × 10⁻⁵</td>
</tr>
<tr>
<td>ZnO(5)-CuO/MCM-48</td>
<td>759</td>
<td>2.88</td>
<td>0.43</td>
<td>1.7 × 10⁻⁴</td>
<td>9.2 × 10⁻⁵</td>
</tr>
<tr>
<td>ZnO(7)-CuO/MCM-48</td>
<td>665</td>
<td>2.96</td>
<td>0.41</td>
<td>1.5 × 10⁻⁴</td>
<td>9.0 × 10⁻⁵</td>
</tr>
<tr>
<td>ZnO(10)-CuO/MCM-48</td>
<td>621</td>
<td>3.17</td>
<td>0.38</td>
<td>1.4 × 10⁻⁴</td>
<td>8.7 × 10⁻⁵</td>
</tr>
</tbody>
</table>

Figure 1 | Nitrogen physisorption isotherms for (a) MCM-48, (b) ZnO(0)-CuO/MCM-48, (c) ZnO(2)-CuO/MCM-48, (d) ZnO(5)-CuO/MCM-48, (e) ZnO(7)-CuO/MCM-48, and (f) ZnO(10)-CuO/MCM-48.
The Fourier transform infrared (FT-IR) spectra for MCM-48 and different catalysts in the region of 400–1,400 cm\(^{-1}\) are shown in Figure 3. Bands at 463, 802, 1,095 and 1,232 cm\(^{-1}\) are ascribed to the asymmetric and symmetric stretching vibration of Si-O-Si bridges, and the band at 963 cm\(^{-1}\) for MCM-48 is characteristic of the stretching vibration of Si-OH (Huang et al. 2018). The FT-IR spectrum of each catalyst is similar to that of MCM-48, and no obvious band between 400 cm\(^{-1}\) and 600 cm\(^{-1}\) which is assigned to the metal-oxygen stretching vibration can be observed (Srivastava et al. 2013). All these indicate that the copper and zinc species are well dispersed on the surface, which is beneficial to the catalytic reaction.

The SEM micrographs of MCM-48, ZnO(0)-CuO/MCM-48 and ZnO(7)-CuO/MCM-48 are exhibited in Figure 4. It can be observed that these two catalysts possessed small spherical-like or worm-like particles with an average of 3–6 \(\mu\)m, which were similar to MCM-48. In other words, the morphology of MCM-48 was not affected significantly upon the modification of copper and zinc species. Figure 4(d) and 4(e) show the EDS spectra of ZnO(0)-CuO/MCM-48 catalyst (which contained only the elements Si, O and Cu) and ZnO(7)-CuO/MCM-48 which confirmed the presence of the elements Si, O, Cu and Zn, respectively. The absence of extra peaks, apart from the expectable ones in the EDS spectra, shows that the obtained catalysts have no impurities.

A deep insight into the fine structure of ZnO(7)-CuO/MCM-48 was obtained using TEM. Figure 5(a) shows clearly that copper and zinc species are well dispersed on the support. Moreover, from the high resolution TEM image (Figure 5(b)), the lattice fringes of 0.28–0.25 nm are assignable to the (100) plane of wurtzite ZnO and the (002) plane of monoclinic CuO (JCPDS card No. 801916), respectively (Singh et al. 2012).

XPS measurement was used to determine the chemical composition and surface properties of ZnO(7)-CuO/MCM-48 catalyst. The Si 2p XPS spectrum is shown in Figure 6(a), and the peak centered at about 102.9 eV is attributed to silica in MCM-48 (Dai et al. 2014). The O1s peak is broad and asymmetric as shown in Figure 6(b), implying the presence of more than one chemical environment for oxygen species, and can be divided into two peaks. The first peak located at 530.9 eV is assigned to the O1s binding energy in the CuO and ZnO, while the second located at 552.2 eV is attributed to the adsorbed oxygen in noncrystalline MCM-48 (Dai et al. 2014). In
Figure 6(c), the peaks centered at 1,021.6 eV and 1,044.9 eV are indexed to Zn_{3/2} and Zn_{1/2}, respectively, which indicates that the oxidation state of Zn is +2 in this catalyst (Bai et al. 2011). The characteristic peaks of Cu 2p sited at 932.7 eV (Cu 2p_{3/2}) and 952.7 eV (Cu 2p_{1/2}) and their corresponding satellite peaks around 944.6 eV and 960.6 eV can be observed in Figure 6(d), all of which indicate that the oxidation state of Cu is +2 in this catalyst (Dai et al. 2014).

In order to better understand the trends in the photocatalytic activities and obtain a structure–activity relationship, PL was carried out at ambient conditions. The PL spectra of different catalysts are shown in Figure 7. As the PL is the result of recombination of excited holes and electrons, the lower PL intensity implies the decrease in recombination rate, thus higher photocatalytic activity (Fu et al. 2011). It can be observed that the PL intensity is decreased with increase in the zinc content. The
lowest intensity is obtained at a zinc content of 7 wt%, which indicates that the lowest recombination of excited holes and electrons is in the ZnO(7)-CuO/MCM-48 catalyst. Therefore, among these catalysts studied, the ZnO(7)-CuO/MCM-48 catalyst is expected to exhibit the best photocatalytic activity.

The performance of photocatalysts

The photocatalytic performance of the as-prepared catalysts has been investigated by the degradation of MB aqueous solution under UV light irradiation. Before being irradiated, the suspension was magnetically stirred for 1 h to reach the
adsorption–desorption equilibrium between the catalyst surface and the dye, and the obtained adsorption data are listed in Table 1. The as-prepared catalysts have high adsorption capabilities for MB, owing to their much higher specific surface area and pore volumes. Among these catalysts, ZnO(0)-CuO/MCM-48 has the highest specific surface area of 823 m²/g (seen in Table 1), and the highest adsorption capacity of 2.2 × 10⁻⁴ mol/g is attained.

Although good adsorption capabilities have been attained for the as-prepared catalysts, adsorption only transfers the organic pollutants from one phase to another. Thus, to mineralize the dye molecules, photocatalytic degradation should be carried out.

Figure 8(a) displays the degradation of MB for all the prepared catalysts under UV light irradiation. In the absence of photocatalyst, MB self-photodegradation is almost unobserved within 75 min, indicating that MB is stable toward incident light. ZnO(0)-CuO/MCM-48 catalyst has a photocatalytic degradation efficiency of 31.0% after UV light irradiation for 75 min, which is due to the fact that CuO particles supported on the SiO₂ surface can effectively decrease the recombination of the conduction band (CB) electrons and valence band (VB) holes, thus achieving the MB photocatalytic degradation properties (Batista et al. 2010). When CuO supported on MCM-48 is combined with ZnO to form hybrid catalysts, their photocatalytic activities can be obviously improved. Especially, the ZnO(7)-CuO/MCM-48 catalyst has excellent catalytic degradation efficiency of 96.6%, which is almost two times higher than that of ZnO(0)-CuO/MCM-48, under the same experimental condition. The BET surface of the prepared ZnO(2)-CuO/MCM-48 and ZnO(7)-CuO/MCM-48 catalysts are 784 and 665 m²/g, respectively. This result shows that the surface area is not a major element that contributes to the ZnO(7)-CuO/MCM-48 catalyst’s enhanced photocatalytic performance. It can be found that the amount of ZnO in the ZnO-CuO/MCM-48 catalyst has an important influence on its photocatalytic performance. When the amount of ZnO in the hybrid catalysts is increased from 2.0 to 10.0 wt%, the ZnO(7)-CuO/MCM-48 exhibits the best catalytic activity. At a low content of ZnO (2.0 wt%, 5.0 wt%), the utilization of ZnO particles for photocatalytic performance is lower, and thus, a lower degradation efficiency was observed, whereas a higher content of ZnO (10 wt %) may lead to agglomeration of ZnO clusters, resulting in lower activity towards the degradation of MB.

To verify the stability of catalyst, repetitive use of ZnO(7)-CuO/MCM-48 for MB photocatalytic degradation has been carried out. In each experiment, the catalyst was reused after washing by simple filtration followed by ultrasonic cleaning with a mixture of 30% ethanol in water,
then drying at 140 °C for 5 h, while other factors were kept identical. According to Figure 8(b), a small and gradual decrease in the photocatalytic degradation is observed, and the degradation efficiency of 91.7% is obtained after five degradation cycles of MB. This indicates that the ZnO(7)-CuO/MCM-48 catalyst possesses excellent long-lived stability and is not photocorroded during the photocatalytic degradation of MB under UV light irradiation.

To further investigate the catalytic applications of the so-prepared catalysts, the photocatalytic performance towards the degradation of salicylic acid was investigated and the results are shown in Figure 9. With this different organic pollutant, the results are similar to those for MB. In other words, the ZnO(7)-CuO/MCM-48 exhibits the best photocatalytic performance for salicylic acid among all these catalysts.

Based on the remarkably enhanced photocatalytic activity and excellent stability of ZnO-CuO/MCM-48 heterojunction catalyst, a possible mechanism for the photocatalytic degradation of organic pollutions is proposed (Figure 10). Under UV light irradiation, the electrons in the VB of CuO and ZnO are excited to the CB; the photogenerated electron in the CB of CuO would transfer to the CB of ZnO as the photogenerated hole in the VB of ZnO would be transferred to the VB of CuO. The electric field at the interface enables the migration of electrons from the VB of CuO to that of ZnO, which would lead to the aggregation of photogenerated electrons on the surface of ZnO and photogenerated holes on the surface of CuO. These electrons, upon interacting with oxygen molecules dissolved in the solution, produce super-oxide anion (O$_2^-$), which further indirectly generates highly reactive hydroxyl radical (OH$^-$). In addition, holes, by reacting with OH$^-$, form highly reactive hydroxyl radicals. All these reactive hydroxyl radicals can oxidize organic molecules. Generally, the internal field created by the heterojunction between ZnO and CuO suppresses the photogenerated electron–hole recombination and thus improves the photocatalytic degradation efficiency for organic pollutions.

**CONCLUSION**

An obvious improvement in photodegradation efficiency was achieved over ZnO-CuO/MCM-48. However, the performance of ZnO-CuO/MCM-48 was strongly dependent on the ZnO content. The maximum degradation efficiency was obtained over ZnO(7%)-CuO/MCM-48.

Moreover, the ZnO-CuO/MCM-48 catalyst showed excellent photocatalytic stability in the recycling
experiment, which was vital for practical applications. The improved photocatalytic performance could be ascribed to its large specific surface areas of support and the p-n heterojunctions between ZnO and CuO, which suppressed the photogenerated electron–hole recombination.

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REFERENCES


assisted degradation of a textile dye in aqueous solution. 

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