Preparation and characterization of Cu$_2$O–ZnO immobilized on diatomite for photocatalytic treatment of red water produced from manufacturing of TNT

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ABSTRACT

Cuprous oxide and zinc oxide composites have been successfully immobilized on natural diatomite by two-step deposition. X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), ultraviolet–visible diffuse reflection absorptive spectroscopy (UV–vis/DRS), and Raman spectroscopy were used to characterize the materials. Gas Chromatography/Mass Spectroscopy (GC/MS) was employed to analyze the organic compositions of red water from TNT manufacturing. The zinc oxide content and the carrier affect the optical properties of the composites and the photocatalytic activity of the composites determined by visible-light-induced degradation of red water. The results show that when the molar ratio of ZnO versus Cu$_2$O is 4:2.5, the Cu$_2$O–ZnO/diatomite composite exhibits optimal optical properties and photocatalytic activity and can degrade 72.8% of red water under the irradiation of the visible light for 4 h, while Cu$_2$O/diatomite and the non-immobilized Cu$_2$O–ZnO can only degrade 33.3% and 39.5% of red water, respectively. Most of the organics except 1,3,5-trinitrobenzene can be effectively photocatalytically degraded.

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1. Introduction

Visible-light-sensitive semiconductor photocatalysts have been attracting increasing attention because of applications to advanced oxidation processes (AOP) with regard to the treatment of organic pollutants. Titanium dioxide, which is one of the common photocatalysts, has relatively low photocatalytic activity because the photo-induced holes recombine easily with the photo-induced electrons [1]. In addition, on account of the wide band gap, the application of titanium dioxide is typically limited to the ultraviolet light range [2]. Zinc oxide is also a semiconductor with potential applications in photocatalysis. It has a wide band gap of 3.37 eV and large exciton binding energy (60 meV) at room temperature [3]. Furthermore, cuprous oxide, a p-type semiconductor with a direct band gap of about 2.2 eV, is a very promising photocatalyst because it can be activated by visible light, but it can also be deactivated easily due to photo-induced corrosion [4]. To circumvent the problems, two or more semiconductors are often combined or a semiconductor is coalesced with other material, for instance, TiO$_2$–Cu$_2$O, WO$_3$–TiO$_2$, TiO$_2$–ZrO$_2$, CeO$_2$–ZnO, CdSe–TiO$_2$, TiO$_2$–ZnO, CaFe$_2$O$_4$/ZnO, ZnO–Cu$_2$O, and so on [1,2,5–12]. And some researchers have also loaded some semiconductors on minerals or other matrix to improve the photocatalytic or other characteristics [13–18].

Diatomite, a siliceous biological sedimentary rock with a porous structure, is an important carrier for catalysts because of its high surface area and retention capacity [19]. TiO$_2$ loaded onto diatomite has been used to enhance the photocatalytic degradation of organic contaminants [15,17]. However, the combination of cuprous oxide and zinc oxide immobilized on diatomite has been scarcely reported, although they are promising photocatalysts for the degradation of refractory organic pollutants. Red water generated from the manufacturing of explosives, especially during the purification of crude TNT is traditionally disposed of by evaporation from the materials followed by incineration. The process is quite polluting and much work is being conducted to develop better disposal processes. Photocatalysis, a high efficiency and environmentally friendly technology, has hitherto been seldom applied to the treatment of industrial red water.

Here, we report our detailed studies on the preparation and characterization of Cu$_2$O–ZnO composites immobilized on diatomite and the resulting photocatalytic activity for the treat-
ment of red water produced from the manufacturing of TNT. The previous scanty reports on Cu$_2$O–ZnO mainly focus on the solar cell and ZnO was selected as a candidate n-type semiconductor because of its stability in the presence of Cu$_2$O [11]. In this study, Cu$_2$O–ZnO was immobilized on the natural diatomite and used firstly as efficient photocatalyst for visible light induced degradation of refractory red water from TNT manufacturing. Zinc oxide plays an important role of tuning the photocatalytic activity of the composites besides its stability when combined with cuprous oxide. Moreover, diatomite also improves the photocatalytic performance of Cu$_2$O–ZnO composite. Our results show that the red water degradation rate on the Cu$_2$O–ZnO immobilized on diatomite is 72.8%, which is 1.84 and 2.19 times of that on the non-immobilized Cu$_2$O–ZnO and the Cu$_2$O loaded on diatomite, respectively. The Cu$_2$O–ZnO/diatomite composite is a potential photocatalyst in the treatment of red water from TNT manufacturing.

2. Experimental

2.1. Materials

All the chemical reagents were purchased from Beijing Chemical Reagent Factory. They were analytical reagents and used without further purification. Natural diatomite employed in this study was provided by Beijing Chuangqingyuan Co. Ltd., China. The red water supplied by Dongfang Chemical Corporation, Hubei Province, China, had a red color with a density of 1.101 g/mL and had complex organic components listed in Table 1.

2.2. Preparation of the samples

Before preparing the ZnO–Cu$_2$O/diatomite composites, the natural diatomite was treated by the following procedures. 100 g of the natural diatomite were dispersed in 500 mL of deionized water while magnetically stirred. Then 100 mL of 95% sulfuric acid was added, and the mixture was heated at 110 °C for 2 h under constant magnetic stirring. The precipitate was separated by filtration and washed with deionized water to a pH value of about 7. Finally, the products were heated at 500 °C for 2 h in a muffle stove.

To prepare the different ZnO–Cu$_2$O/diatomite composites, 5.0 g of diatomite treated by sulfuric acid was added to a 500 mL conical flask containing a mixture of 100 mL of zinc chloride solution with different concentrations (0.05 M, 0.1 M, 0.2 M, and 0.3 M, respectively), 100 mL of 1.0 M sodium potassium tartrate and 3.0 mL of 5% (w/v) polyvinyl pyrrolidone (average molecular weight = 27,000–33,000, PVP-K30) under magnetic stirring. Sodium potassium tartrate used here acts as surface-modification agent to promote zinc oxide and cuprous oxide immobilized on the surface of diatomite. After the pH was adjusted to 8 using sodium hydroxide, the solution was heated to 95 °C for 10 min to obtain zinc oxide on the diatomite. Then 50 mL of 0.5 M copper sulfate solution and 50 mL of 1.0 M reductant glucose were added sequentially and the pH value was adjusted to 11 using sodium hydroxide. Excessive glucose was used to prevent cuprous oxide from being oxidized in the solution at high temperature. After stirring and heating for 5 min at 95 °C, the precipitates were filtered and washed several times with distilled water and absolute ethanol. Finally, the precipitates were dried in vacuum at 80 °C for 2 h and designated DZC-1, DZC-2, DZC-4, and DZC-6, in which the molar ratios of ZnO versus Cu$_2$O are, respectively, 1:2.5, 2:2.5, 4:2.5 and 6:2.5.

To compare the results, only zinc oxide or cuprous oxide immobilized on diatomite and unsupported ZnO/Cu$_2$O composites (labeled DZ, DZC-0 and ZC, respectively) were also prepared. To obtain DZ by the process mentioned above, instead of a zinc chloride solution, 50 mL of 0.5 M copper sulfate solution was added directly and then 50 mL of 1.0 M glucose was added. The pH was adjusted to 11 using sodium hydroxide and heated to 95 °C for 5 min. After loading the zinc oxide onto the diatomite, copper sulfate, glucose, and sodium hydroxide were no longer added in the following process with other conditions being the same. Sample ZC on which cuprous oxide and zinc oxide were not loaded on the diatomite was prepared using the similar method as sample DZC-4 but without adding the diatomite. More details can be found in Table 2.

2.3. Characterization

The phases and composition of the samples were determined on a D/Max-RC X-ray diffractometer (XRD, Rigaku, Japan) with Cu-K$_\alpha$ radiation (2 kV rotating anode, $\lambda = 1.54056\AA$), which was operated at 40 kV and 80 mA at a scanning rate of 0.06/°s. The SEM images were obtained on a JSM-6700F field emission scanning electron microscope (FESEM) (JEOL, Japan) and S4800 FE-SEM (Hitachi, Japan) operated at an accelerating voltage of 15 kV. The ultraviolet–visible diffuse reflection absorbive spectra (UV–vis/DRS) were acquired on a Lambda-900 UV/vis/NIR spectrophotometer (PerkinElmer, USA) equipped with an integration sphere at room temperature. The scanning range was 200–800 nm and the scanning rate was 0.2 nm/s. The Raman spectra were recorded in the range of 300–1600 cm$^{-1}$ by a Renishaw RM2000 Raman spectrometer coupled to a Leica optical microscope and a charge-coupled device (CCD) camera. The excitation wavelength here was at 514.5 nm (Ar$^+$ laser line). The specific surface area on the particles was determined by an Automated Surface Area and Pore Size Analyzer (Quadrasorb SI-MP, Quantachrome, USA) using Brunauer–Emmett–Teller (BET) nitrogen sorption (outgassing temperature and time were 100 °C and 3 h, respectively). The optical absorption spectra were acquired on a Hitachi-UV3010 UV–vis spectrophotometer. A Gas Chromatography/Mass Spectroscopy (GC/MS) (GC6890N/MSD5973, Agilent Technologies, USA) was employed to analyze the organic compositions of red water before and after treated by photocatalysts. A DB-35 MS capillary column with inner diameter of 0.25 mm and length of 60 m was adopted in the separation system. Pure helium gas was employed as carrier gas at a flow rate of 1.0 mL/min. 1.0 µL of sample was injected into the GC/MS operated from 40 to 280 °C at a programming rate of 2.0 °C/min.

2.4. Photocatalytic treatment of red water

In the typical photocatalytic experiment, 1.0 g of the photocatalyst was added to 200 mL of red water diluted 200 times using deionized water. The photocatalysts were dispersed under ultrasonic vibration for 10 min. Prior to light irradiation, the reactor was left in the dark for 1 h until an adsorption–desorption equilibrium was established. A 500 W mercury–tungsten lamp located at a distance of 150 mm above the surface of the solution was used as the visible light source. During irradiation, about 25 mL of the suspension was sampled at regular intervals of 1 h and separated by filtration. The absorbance of the remaining red water was measured by a UV–vis spectrophotometer in order to monitor the photocatalytic degradation rate of red water.

3. Results and discussion

3.1. XRD image of samples

The XRD patterns of diatomite stabilized Cu$_2$O–ZnO nanoparticle with various copper and zinc contents are shown in Fig. 1.
Table 1
GC/MS results of the initial and the photocatalytic treated red water.

<table>
<thead>
<tr>
<th>Retention time (min)</th>
<th>The initial red water</th>
<th>The photocatalytic treated red water</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.0</td>
<td>2-Nitrotoluene</td>
<td>63.5</td>
</tr>
<tr>
<td>33.8</td>
<td>4-Nitrotoluene</td>
<td>1,3,5-trinitrobenzene</td>
</tr>
<tr>
<td>34.6</td>
<td>3-Methyl-2-nitrophenol</td>
<td></td>
</tr>
<tr>
<td>36.7</td>
<td>5-Methyl-2-nitrophenol</td>
<td></td>
</tr>
<tr>
<td>50.8</td>
<td>2,6-Dinitrotoluene</td>
<td></td>
</tr>
<tr>
<td>53.5</td>
<td>2,4-dinitrotoluene</td>
<td></td>
</tr>
<tr>
<td>55.0</td>
<td>2,5-Dinitrotoluene</td>
<td></td>
</tr>
<tr>
<td>60.1</td>
<td>3-Methyl-6-nitrobenzoic</td>
<td></td>
</tr>
<tr>
<td>60.6</td>
<td>2-Methyl-3,5-dinitrophenol</td>
<td></td>
</tr>
<tr>
<td>67.1</td>
<td>1,3,5-Trinitrobenzene</td>
<td></td>
</tr>
<tr>
<td>67.8</td>
<td>2,4,6-Trinitrotoluene</td>
<td></td>
</tr>
<tr>
<td>79.7</td>
<td>3,5-Dinitro-p-toluidine</td>
<td></td>
</tr>
</tbody>
</table>

Table 2
Main physical properties of the samples and the degradation rates of red water by various samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diatomite</th>
<th>DZC-0</th>
<th>DZC-1</th>
<th>DZC-2</th>
<th>DZC-4</th>
<th>DZC-6</th>
<th>DZ</th>
<th>ZC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu2O:ZnO (molar ratio)</td>
<td>–</td>
<td>5:0</td>
<td>5:2</td>
<td>5:4</td>
<td>5:8</td>
<td>5:12</td>
<td>0:8</td>
<td>5:8</td>
</tr>
<tr>
<td>Band gaps (eV)</td>
<td>–</td>
<td>2.02</td>
<td>2.27</td>
<td>2.40</td>
<td>2.44</td>
<td>2.48</td>
<td>3.31</td>
<td>2.32</td>
</tr>
<tr>
<td>S_{BET} (m2/g)</td>
<td>2.08</td>
<td>5.771</td>
<td>2.446</td>
<td>2.286</td>
<td>10.267</td>
<td>14.634</td>
<td>6.180</td>
<td>5.771</td>
</tr>
<tr>
<td>Degradation rate (%)</td>
<td>–</td>
<td>33.3</td>
<td>36.8</td>
<td>43.9</td>
<td>72.8</td>
<td>62.1</td>
<td>10.5</td>
<td>39.5</td>
</tr>
</tbody>
</table>

According to the JCPDS card No. 05-0667 and 36-1451, characteristic peaks can be observed at 2θ values of 36.5°, 42.4°, 61.5°, 73.7° corresponding to the crystal planes of (1 1 1), (2 0 0), (3 1 1) of Cu2O as well as 31.7°, 34.4°, 36.2°, 56.6°, 62.9°, 67.9°, 69.0° corresponding to (1 0 0), (0 0 2), (1 0 1), (1 0 3), (1 1 2), (2 0 1) of zinc oxide, respectively. Three other peaks at 2θ = 21.8°, 31.2° and 48.4° are also found. According to JCPDS card No. 39-1425, they correspond to the planes of (1 0 1), (1 0 2) and (2 1 2) of crystalline SiO2 with the cristobalite structure, respectively. The peaks corresponding to the crystal planes of (1 1 0), (2 0 0), (2 2 0) and (3 1 1) of Cu2O weaken and even vanish gradually with the increasing zinc oxide concentration, whereas the peaks corresponding to the crystal planes of (1 0 0), (1 0 1), and (1 1 0) of zinc oxide are enhanced correspondingly. This phenomenon may be due to the increasing content of ZnO on silica, resulting in the change of alignment and combination of cuprous oxide and zinc oxide crystals. The results demonstrate that the concentration of the constituent affects significantly the structure of the composites and the structural change will lead to different chemical and physical properties.

3.2. Morphology analysis

The morphology of the composites is investigated by FE-SEM. Fig. 2 depicts the SEM images of the natural diatomite after acid treatment revealing the porous structure. The natural diatomite is purified and the impurities in the pores are disposed of by acidification with 95% sulfuric acid and subsequent calcination at 500°C. From the magnified SEM images, it can be seen that the pore structure is cleaned well and the mean aperture is round 300 nm (Fig. 2b). The specific surface area (S_{BET}) of the diatomite is 2.08 m2/g determined by the Quadrasorb Si-MP Automated Surface Area and Pore Size Analyzer. Removal of impurities decreases the specific surface area and increases the average pore diameter of the diatomite. This may be explained by that the impurities in the crude diatomite have more micro-pores and larger surface area compared to the diatom skeleton. When the impurities are removed from the diatomite by acidification, washing and calcination, the surface area and pore volume decrease while the average pore diameter increases [20]. It can also be seen from the scan-
ning micrograph that diatomite has a large void volume besides its highly porous structure. The high porosity bodes well for its potential applications as a sorbent for heavy metals and a carrier for catalysts.

The SEM images of the Cu$_2$O–ZnO composites with different contents of Cu$_2$O and ZnO immobilized on the natural diatomite are shown in Fig. 3. All the Cu$_2$O–ZnO composites are immobilized on the natural diatomite well and there are scarcely any discrete particles. Acidification and calcination thus improve the surface properties of the diatomite so that the Cu$_2$O–ZnO composite particles can recombine with diatomite firmly through the interaction force at the interface and the stabilized composites are obtained.

Likewise, zinc oxide and cuprous oxide particles are also loaded on the diatomite well, respectively. Fig. 4 depicts the SEM images of sample DZC-0 and DZ on which only cuprous oxide or zinc oxide is immobilized on the diatomite, respectively. A number of Cu$_2$O and ZnO particles with a size of approximately 20 nm adhere to the surface of the diatomite firmly.

3.3. Raman spectra

Typically a Raman spectrum is a distinct chemical fingerprint for a particular molecule or material, and can be used to very quickly identify the material, or distinguish it from others. In our work, Raman investigation was used as a technique for the identification of Cu$_2$O and ZnO and their distribution on the surface of diatomite. The Raman spectra of Cu$_2$O–ZnO immobilized on natural diatomite are shown in Fig. 5 together with those acquired from the host diatomite. The sharp bands at 980 cm$^{-1}$ and 1120 cm$^{-1}$ are, respectively, associated with the Si–O$^-$ bending mode and Si–O–Si stretching band[21,22]. The Raman spectra of the diatomite immobilized Cu$_2$O–ZnO composites with different contents of zinc oxide are very similar. The abroad peak centered at 600 cm$^{-1}$ due to the E$_{1T}$ mode of ZnO[23] as shown in Fig. 5b gets sharper. The results demonstrate the effect of zinc oxide on the optical property of the composite. On the other hand, 284, 345 and 620 cm$^{-1}$ attributed to the CuO cannot be found. It can be further ascertained that there are no CuO impurities derived from oxidation of Cu$_2$O.

3.4. UV–vis DRS and the calculated band gaps

The ultraviolet–visible diffuse reflectance absorptive spectra (UV–vis DRS) obtained from the samples with various cuprous oxide and zinc oxide loadings are displayed in Fig. 6a together with that of the host diatomite. All the Cu$_2$O–ZnO/diatomite composites exhibit a clear absorption edge beyond 600 nm whereas the unmixed diatomite shows an absorption edge at about 350 nm. All the absorption bands show higher intensity as the content of ZnO increases up to the molar ratio of ZnO to Cu$_2$O reaches 4:2.5. However, when the molar fraction of ZnO in Cu$_2$O is too large (the molar ratio of ZnO versus Cu$_2$O beyond 6:2.5), the intensity is attenuated. The addition of zinc oxide affects the crystal structure resulting in the improvement of the surface property of cuprous oxide. When the molar ratio of ZnO/Cu$_2$O exceeds 4:2.5, the zinc oxide particles are predominant in the composite and thus the composite displays mainly the performance of zinc oxide. Consequently, the intensity diminishes.

From Fig. 6b depicting the UV–vis spectra of DZC-0 and DZ, the absorption edge of cuprous oxide loaded on diatomite (DZC-0) is over 600 nm, but that of zinc oxide loaded on diatomite (DZ) is under 400 nm. When the wavelength is less than 400 nm, DZ shows stronger absorbance than DZC-0. It implies that the photocatalytic performance of DZC-0 is superior to that of DZ in visible light, whereas the photocatalytic activity of DZC-0 is inferior to that of DZ in ultraviolet light.

To further study the optical properties of the composites, we estimate the band gap energy. Both zinc oxide and cuprous oxide are of direct gap semiconductors. For semiconductor, a direct band gap means that the minimum energy of the conduction band lies directly above the maximum energy of the valence band in momentum space. The direct band gap is one of the desirable properties of photocatalyst because this kind of material can absorb more efficiently the light than the material with an indirect band gap[24,25]. The relationship between absorption coefficient ($\alpha$) and photon energy ($h\nu$) of the semiconductor with a direct band gap can be expressed as [26]:

$$ah\nu = C(h\nu - E_G)^{1/2}$$  \hspace{1cm} (1)

where $C$ is a constant which does not depend on the photon energy and $E_G$ is the band gap energy. The band gap is estimated from the intercepts of the tangents to the $(ah\nu)^2$ versus photon energy ($h\nu$) plots. Fig. 7 depicts the plots of $(ah\nu)^2$ versus $h\nu$ for different amounts of Cu$_2$O–ZnO loaded on natural diatomite. The direct band gaps of DZC-1, DZC-2, DZC-4 and DZC-6 are estimated to be 2.27, 2.40, 2.44 and 2.48 eV, respectively. The blue shift in the direct band gap occurs as the content of zinc oxide increases because incorporation of zinc oxide which has a wide intrinsic band gap of 3.37 eV [27] widens the band gap.

Similarly, sample DZC-0 and sample DZ have an estimated direct band gap of 2.02 eV and 3.31 eV, respectively. The band gaps of both samples show a red shift compared to the original materials. It may
be attributed to the effects of the carrier diatomite on the crystal structure. Owing to the influence of the interface of the diatomite on the growth direction of the crystals, development of the active dominant facets is promoted and thus the surface properties of the crystals are improved.

3.5. Photocatalytic performance

The photocatalytic activity of Cu$_2$O–ZnO composites stabilized on natural diatomite is evaluated by monitoring the decomposition of red water from TNT manufacturing in an aqueous solution under visible light irradiation. In order to assess the significance of the data, a control experiment without catalysts is conducted by photolysis of red water under visible light irradiation. As shown in Fig. 8, the photolysis rate of red water is 4.91% when irradiated for 6 h, suggesting that the photolysis is negligible here.

Fig. 9 depicts the UV–vis results obtained from remaining red water degraded by sample DZC-4. There is a more change in the absorbance at round 420 nm, and we chose the absorbance of red water in the wavelength of 420 nm as the research object and calculated the degradation rate by the following relationship:

$$D_i (\%) = \frac{C_0 - C_i}{C_0} \times 100 = \frac{A_0 - A_i}{A_0} \times 100$$

(2)

where $D_i$ (%) is the degradation rate of red water when treated for $i$ hours, $A_0$ is the initial absorbance, and $A_i$ is the absorbance in the wavelength of 420 nm when treated for $i$ hours. The absorbance values of the remaining red water decrease with irradiation time demonstrating that red water is degraded to some degree due to visible-light induced photocatalysis after illumination for 4 h. As a
result, 72.8% of the red water can be degraded (as shown in the insert). On the other hand, red water exhibits some degradation in the first hour without light irradiation and 14.6% of the red water is removed by adsorption. It may be attributed to the large specific surface area and surface structure of DZC-4.

In our work, GC/MS analysis was used to detect the organic molecule compositions of red water and its remains after degraded by photocatalysts. The mass spectra obtained were utilized to identify the components according to NIST05 mass spectral library database. The GC/MS results of the initial and the photocatalyti-
of visible light. When the molar ratio of ZnO versus Cu2O does not exceed 4:2.5, Cu2O is predominant and ZnO as a modifier promotes the utilization of photon by cuprous oxide. Consequently, the optimal optical performance which corresponds to the visible-light-induced photocatalytic activity in the degradation of red water. After illumination by visible light for 4 h, 72.8% of the red water can be degraded by photocatalysis of sample DZC-4. In comparison, in the first hour without light irradiation, 14.6% of the red water is removed by adsorption. None of the organics but 1,3,5-trinitrobenzene in the remaining red water treated by photocatalysts can be detected by GC/MS analysis, implying these components were mostly degraded. The Cu2O–ZnO immobilized on diatomite exhibits high photocatalytic activity and has potential in the treatment of red water from TNT manufacturing.

4. Conclusions

In summary, cuprous oxide and zinc oxide composites have been immobilized on natural diatomite by two-step deposition. The zinc oxide concentrations affect the photocatalytic activities of the Cu2O–ZnO/diatomite composites. According to the UV–vis DRS and Raman results, sample DZC-4 (ZnO:Cu2O = 4:2.5) exhibits the optimal optical performance which corresponds to the visible-light-induced photocatalytic activity in the degradation of red water.

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