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Visible-light photocatalytic decolorization of Orange II on Cu_2O/ZnO nanocomposites

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Abstract

Cu_2O/ZnO nanocomposites were synthesized by a coprecipitation method and were applied to degrade dye wastewater. The prepared nanocomposites were characterized by X-ray diffraction, scanning electron microscopy, high resolution transmission electron microscopy and UV–vis diffuse reflectance spectra. The effects of initial Orange II (OII) dye concentration, pH and dosage of catalyst amount were investigated in the decomposition of OII dye by the nanocomposites. The best conditions for the dye decomposition by Cu_2O/ZnO nanocomposites were found to be in the neutral solution when the dosage of catalyst was 200 mg/L with an OII concentration of 50 mg/L at room temperature. Under the above conditions, nearly 80% decolorization efficiency of OII was achieved by Cu_2O/ZnO nanocomposites within 2 h of reaction time and this efficiency was much higher than that of either pure Cu_2O or ZnO.

Keywords: Cu_2O/ZnO; Visible light degradation; Photocatalytic activity; Orange II

1. Introduction

In recent years, photocatalysis has attracted much attention due to its many advantages in remediation of pollution by organic compounds [1]. Zinc oxide, ZnO has been recognized as a preferred photocatalyst because of its low cost, high photocatalytic activity and non-toxic nature. However, ZnO can only work in the ultraviolet region of the electromagnetic spectrum because of its wide band gap of 3.2 eV. In order to make use of most of the visible light that accounts for a major component in solar energy spectrum, various methods have been adopted to extend the photoresponse of ZnO into visible light region. Systems consisting of coupled semiconductors have been shown to be very effective to satisfy the above criterion and achieve high photocatalytic activity in most of the visible light. So far, ZnO composited with other metal oxides such as TiO_2, CdS, SnO_2, $BiVO_4$, Ag_3PO_4 and others [2–5], have been investigated, in which some narrow band gap semiconductors served as visible-light sensitizers.

Cu_2O is a p-type semiconductor with a narrow band gap of 2.0 eV and therefore, has been considered to be a potential visible light photocatalyst [6]. The electrons of Cu_2O easily undergo excitation by visible light and thus get involved in the processes of degradation of dyes in wastewater. However, the easy recombination of photo-generated electrons and holes affect its photocatalytic activity. To date, graphene and some heavy and noble metals were composited with Cu_2O to remove generated electrons to prevent recombination with holes [7–9]. In addition, Cu_2O combined with other metal oxides have also become an effective means to overcome the above weakness of recombination of photo-generated electrons and holes [10–13]. It has been reported that the conduction band (CB) and valence band (VB) edge of Cu_2O lie above that of ZnO [14], so the electrons in the CB of Cu_2O generated by visual light can transfer to the CB of ZnO. In the ZnO–Cu_2O system, Cu_2O is a sensitizer absorbing visible light and ZnO is used as an acceptor to extract generated electrons. The fabrication and photocatalytic properties of ZnO–Cu_2O systems prepared by different methods

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such as soak [15], pulsed laser deposition [16] and magnetron sputtering [17] have been studied.

In this study, we prepared Cu_2O/ZnO nanocomposites through the coprecipitation method and tested them in the decomposition of Orange II (OII), which is considered as a model dye pollutant. The phase composition and microstructure of Cu_2O/ZnO composites were investigated by powder X-ray diffraction (XRD), Transmission electron microscopy (TEM) and scanning electron microscopy (SEM). In addition, UV–vis diffuse reflectance spectroscopy (DRS) was used to select absorption band. To optimize the photocatalytic conditions, the influences of various factors were studied and the photocatalytic mechanism was discussed.

2. Experimental

2.1. Materials

Orange II ($C_{16}H_{11}N_2NaO_4S$, OII) and ascorbic acid were supplied by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Other chemicals of analytical grade from different chemical suppliers were used.

2.2. Preparation of Cu_2O/ZnO nanocomposite

Three different Cu_2O/ZnO nanocomposites were synthesized by coprecipitation method with the ratios of 1:10, 1:2 and 1:1. Typically, the 1:1 Cu_2O/ZnO nanocomposite is synthesized as follows: 1.7048 g $CuCl_2 \cdot 2H_2O$ and 2.8756 g $ZnSO_4 \cdot 7H_2O$ were dissolved in 100 mL double distilled water. Then, 30 mL of sodium hydroxide (2 mol/L) was added drop-wise into the above solution. The composite precipitate formed rapidly and the color became deep blue. After stirring for 0.5 h, 2.2 g ascorbic acid was added into the above suspension to reduce Cu and stirred for 0.5 h. Finally, the yellow product was collected by filtration and washed several times with double distilled water followed by drying at 60 °C in a vacuum oven. For comparison, the pure Cu_2O and ZnO were also prepared by the same method as described above for Cu_2O/ZnO nanocomposite but without adding $ZnSO_4$ or $CuCl_2$ in solution, respectively.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns of samples were recorded by a D8 Advance X-ray diffractometer with Cu Kα radiation. Morphologies and particle sizes were investigated by an S-4800 scanning electron microscope. High-resolution transmission electron microscopy was done using a JEM-2100 F FEF electron microscope. Valence states of Cu and Zn were detected by X-ray Photoelectron Spectroscopy (Kratos Amicus). X-ray fluorescence (XRF, ARL ADVANT'X IntelliPowerTM 4200, ThermoFisher) was used to determine chemical composition. The ultraviolet-visible diffuse reflection spectra were determined by a UV–vis spectrometer (UV-2450).

2.4. Measurement of photocatalytic activity

The photocatalytic properties of the prepared powders were evaluated by the degradation of Orange II dye under visible-light at room temperature. A 500 W halogen lamp (λ: 350–2500 nm) equipped with UV cut-off filters ($\lambda > 420$ nm) was used as a visible light source. The photocatalysts were tested as follows: First, 100 mg of sample was dispersed in 500 mL of 50 mg/L OII solution. Then, the solution with sample was placed in dark with constant stirring for 1 h to achieve equilibrium of dye adsorption on the sample before exposing to visible light using the halogen lamp. Initial natural pH of OII solution was found to be 6.4. At certain intervals of time after exposure to visible light, 10 mL of the suspension was sampled and centrifuged. The supernatant was tested for dye content after reaction as measured by UV–vis spectrometer at 485 nm, and the removal efficiency was calculated by comparing to the initial dye concentration.

3. Result and discussion

3.1. Characterization of materials

3.1.1. XRD patterns of Cu_2O/ZnO nanocomposite

The XRD patterns of prepared photocatalysts are shown in Fig. 1. It can be seen that all the diffraction peaks match the standard data for Cu_2O (JCPDS no. 65-3288) and ZnO (JCPDS no.36-1451) and no additional phases were detected in the Cu_2O/ZnO sample. The crystallization of Cu_2O indicates that all the Cu^{2+} ions were reduced to Cu^{+} to form Cu_2O.

3.1.2. Particle size and morphology of 1:1 Cu_2O/ZnO nanocomposite and Cu_2O and ZnO

Particle size and morphology of the 1:1 Cu_2O/ZnO nanocomposite as determined by SEM and HETEM are shown in Fig. 2. From the SEM picture (Fig. 2a), it can be clearly seen that many small rounded particles with diameter of about 50 nm were deposited on the surfaces of flake-like particles. Fig. 2(b and c) shows SEM images of the pure ZnO and Cu_2O, respectively synthesized under the same conditions. They both showed

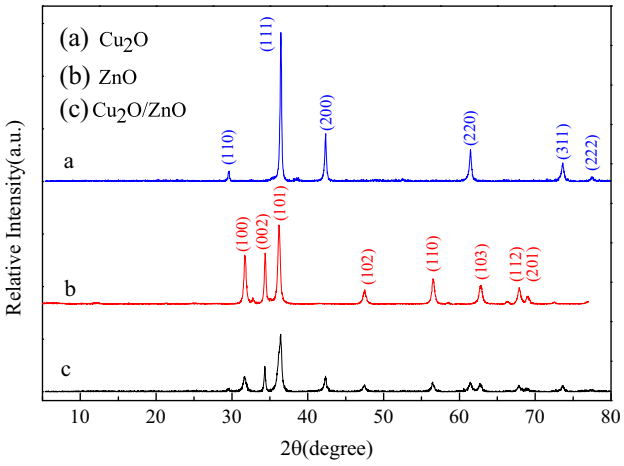

Fig. 1. XRD patterns of Cu_2O (a), ZnO (b) and 1:1 Cu_2O/ZnO nanocomposite (c).