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Enhanced Photocatalytic Activity of ZnO/CuO Nanocomposites Synthesized by Hydrothermal Method

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Abstract: In this paper, we have demonstrated a facile and low-cost synthesis of the ZnO/CuO nanocomposites by two-step hydrothermal methods. The photocatalytic properties of the as-synthesized ZnO/CuO nanocomposites have been evaluated by the photodegradation of methylene blue (MB) and methyleneorange (MO) under UV irradiation. Experimental results show that MB and MO can be degraded completely within 15 and 25 min by the ZnO/CuO nanocomposites and its photodegradation rate is 6 times faster than that of pure ZnO. This enhanced photocatalytic activity can be ascribed to the low recombination probability of photo-induced carriers due to the efficient charge transfer in the nanocomposites. The as-synthesized ZnO/CuO nanocomposite may be a promising candidate for dye photodegradation of wastewaters.
Keywords: Photocatalytic degradation; Nanocomposites; ZnO/CuO; Hydrothermal

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Introduction

In the past years, the photocatalytic degradation of environmental organic pollutants using nanocatalysts has attracted extensive attention because of their high photocatalytic efficiency, low-cost and nontoxic end products [1]. As a well-known photocatalyst, zinc oxide (ZnO) possesses a wide band-gap of 3.37 eV and a large exciton binding energy (60 meV). Nanostructural ZnO has widely been used to degrade various organic dyes (methylene blue (MB), methylene orange (MO) and Rhodamine 6G) in wastewater due to its environmental stability, low-cost and strong oxidizing power [2-6]. Nevertheless, the low photocatalytic efficiency has been recognized as a major obstacle to the degradation of pollutant treatments in large-scale. To improve the photocatalytic efficiency of ZnO nanostructures, many efforts have been done by changing the morphologies of ZnO nanostructures [7,8], loading noble metal [9,10] and compositing with charge-accepting nanomaterials [11-13]. Previous researches have demonstrated that the recombination rate of the photo-induced electron–hole pairs in ZnO plays an important role in the photocatalytic degradation process [13], which is usually faster than surface redox reactions [14]. Therefore, the incorporation of charge-accepting nanomaterials is considered to be one of the most effective strategies to suppress the electron–hole recombination, leading to high photocatalytic efficiency.

Recently, the nanocomposites based on ZnO and other metal oxides have been studied and demonstrated that a higher photocatalytic activity can be obtained due to the effective transfer of charge carriers [15-17]. As an important *p*-type narrow bandgap semiconductor, CuO has been applied to improve the photocatalytic efficiency of some wide bandgap semiconductors [18-20]. Liu *et al.* [19] have investigated the photodegradation of MO using ZnO/CuO nanocom-

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posites, and found that ca. 90% MO can be decomposed under UV–vis illumination for 60 min. Li *et al.* [20] reported that the ZnO/CuO nanocomposites with an open and porous surface exhibit higher degradation efficiency than pure ZnO synthesized by the identical synthetic route. Wang *et al.* [21] synthesized ZnO/tetrapod-like ZnO whisker nanocomposites by photo-deposition method, and the photocatalytic degradation results suggest that ca. 80% MO in the MO solution (10 mg/l) can be degraded after under UV irradiation (254 nm) for 2 h. Therefore, the photocatalytic efficiency of ZnO/CuO nanocomposites needs to be further enhanced. In this paper, we demonstrated a one-step synthesis of ZnO/CuO nanocomposites by two-step hydrothermal method. The photocatalytic properties of the as-synthesized ZnO/CuO nanocomposites were investigated though the degradation of MB and MO under UV irradiations. Compared with pure ZnO nanostructures, the ZnO/CuO nanocomposites exhibit remarkably enhanced photocatalytic efficiency. This photocatalytic enhanced mechanism has been also proposed in detail.

Experimental

Preparation of pure ZnO nanostructures

Pure ZnO nanostructures were synthesized by hydrothermal method. In a typical experiment, 278 mg $ZnCl_2$ (2 mmol) was firstly dispersed into 15 ml deionized water and 15 ml isopropanol under stirring. The pH value of the solution was adjusted to be about 11 using KOH, followed by ultrasonication for 30 min. Then the solution was transferred to a 50-ml Teflon-lined autoclave and heated at 120℃ for 10 h. Finally, the pure ZnO nanostructures were collected after washing and centrifugation.

Preparation of the ZnO/CuO nanocomposites

After centrifugation, the as-synthesized ZnO nanostructures were redispersed into 40 ml deionized water, and then 80 mg (0.4 mmol) copper(II) acetate was added into the abovementioned solution under ultrasonication. After hydrothermal reaction at 120℃ for 8 h, the ZnO/CuO nanocomposites were synthesized and collected through washing, centrifugation and drying.

Characterizations

The microstructures morphologies and crystal structures of the as-synthesized pure ZnO and ZnO/CuO nanocomposites were characterized by scanning electron microscope (SEM, Quanta 250 FEG) and X-ray diffraction (XRD, D8 ADVANCE) with Cu-Kα radiation (λ=0.154178 nm). Energy dispersive spectrometer (EDS) mapping analysis was used to analyze the element distribution of the as-synthesized nanocomposites. The UV-vis absorption spectra were measured on a UV/Vis spectrophotometer (Hitachi, U-4100). The photocatalytic properties of ZnO/CuO nanocomposites were characterized by decomposing MB and MO solutions (50 ml, 10 mg/l) at ambient temperature under UV irradiation (365 nm, 200 W) after 10 min adsorption equilibrium.

Results and discussions

Figure 1 shows typical images of pure ZnO and the as-synthesized ZnO/CuO nanocomposites. The ZnO nanoplates with smooth surface and high crystallinity can be observed from Fig. 1(a). The sizes are typically in the range 100∼300 nm and the thicknesses are in the range 40∼50 nm. After incorporation of CuO by hydrothermal method, a typical SEM image is shown in Fig. 1(b). It is found that the CuO nanopariticles with 300∼500 nm are well-mixed with ZnO uniformly in the nanocomposites. The EDS mapping scanning was employed to evacuate the uniformity of element distribution in the nanocomposites. Figure 2 shows the distribution of the O, Zn, and Cu, respectively. One can see clearly that both Cu and Zn elements are distributed uniformly, confirming that CuO and ZnO are well-distributed in the nanocomposites, which will be beneficial for charged carrier transfer between ZnO and CuO.

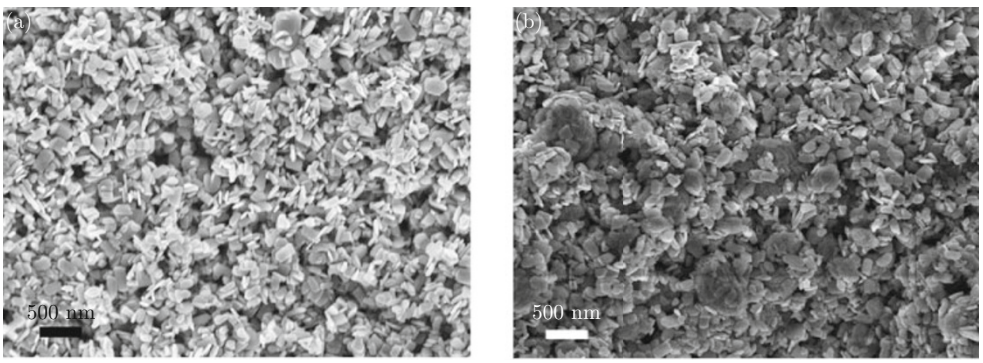

Fig. 1 SEM images of (a) pure ZnO and (b) ZnO/CuO nanocomposites.

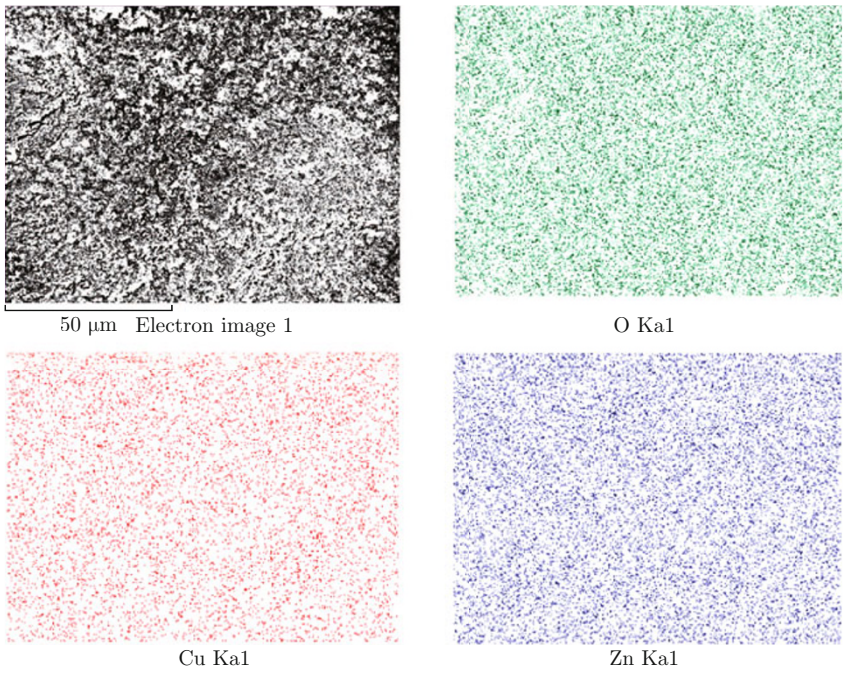

Fig. 2 EDS element mapping of the as-synthesized ZnO/CuO composites.

Figure 3 shows typical XRD patterns of pure ZnO and the as-synthesized ZnO/CuO nanocomposites. It is found that the XRD pattern of pure ZnO consists of five diffraction peaks at 32.6°, 35°, 36.8°, 47.8° and 56.5°, corresponding to the (100), (002), (101), (102) and (110) planes of the hexagonal wurtzite ZnO phase (JCPDS 65-3411), respectively. After the synthesis of the ZnO/CuO nanocomposites, four new diffraction peaks at 36.4°, 39.2°, 48.9° and 58.7° are observed, which can be attributed to ($\bar{1}11$), (111), ($\bar{2}02$) and (202) peaks of the monoclinic CuO (JCPDS 5-0661), respectively. The existence of diffraction peaks of CuO in the nanocomposites further confirms that the formation of the ZnO/CuO nanocomposites.

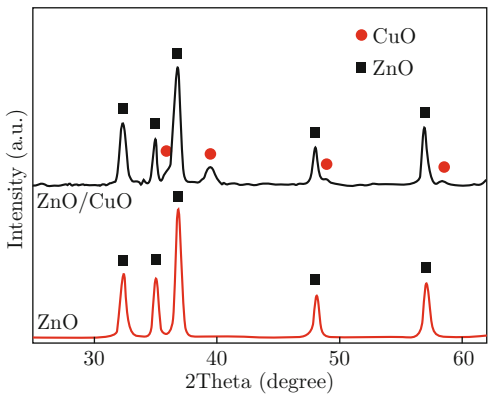

Fig. 3 XRD patterns of pure ZnO and ZnO/CuO composites.

To investigate the photocatalytic activities of the as-synthesized ZnO/CuO composites, the photocatalytic degradations of MB solution have been performed under UV irradiation using pure ZnO and ZnO/CuO nanocomposites as catalysts. Figure 4(a) shows typical absorption spectra of MB solution under exposure to UV light. It can be clearly that the absorption peaks of the MB solution diminish gradually as the exposure time increases. About 99% MB can be decomposed in 10 min, and the MB solution becomes gradually colorless, as illustrated by optical photograph in Fig. 4(b).

The relative intensity of the absorption peaks disappears completely after UV irradiation for 15 min, which is much better than previous reports [15,16,22]. Four cyclic photodegradation experiments were performed using the same ZnO/CuO nanocomposites under the same conditions. As shown in Fig. 4(c), the nanocomposite exhibits a stable photocatalytic activity with little loss after four cycles, which emphasizes the chemical stability of the as-synthesized ZnO/CuO nanocomposites. As we know, the CuO content has a significant influence on the photocatalytic activity [23]. The comparative experiments in photodegradation rates of MB solution have also been performed by using pure ZnO NWs, different ZnO/CuO nanocomposites and without catalysts, as shown in Fig. 4(d). One can be seen clearly that the degradation time using pure ZnO is six times longer than that of ZnO/CuO nanocomposites, revealing that the ZnO/CuO nanocomposites exhibit remarkably enhanced photocatalytic efficiency. Meanwhile, the photodegradation rates increase from 35 min to 15 min when the ratio of CuO/ZnO increases from 5% to 20%.

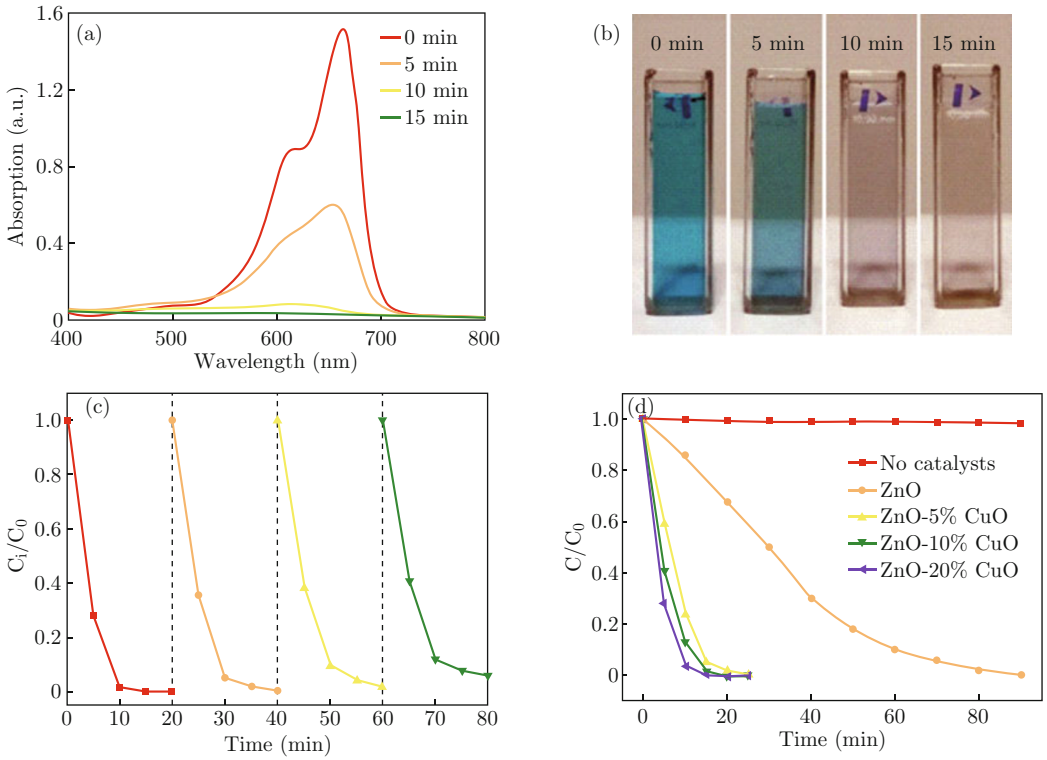

Fig. 4 (a) UV-vis absorption spectra of MB solution under exposure to UV light. (b) Digital photographs after the photodegradation with different times. (c) Cyclic photodegradation of MB under UV irradiation for four cycles. (d) Decomposition rate of MO solution with pure ZnO and ZnO/CuO composites and without catalysts.

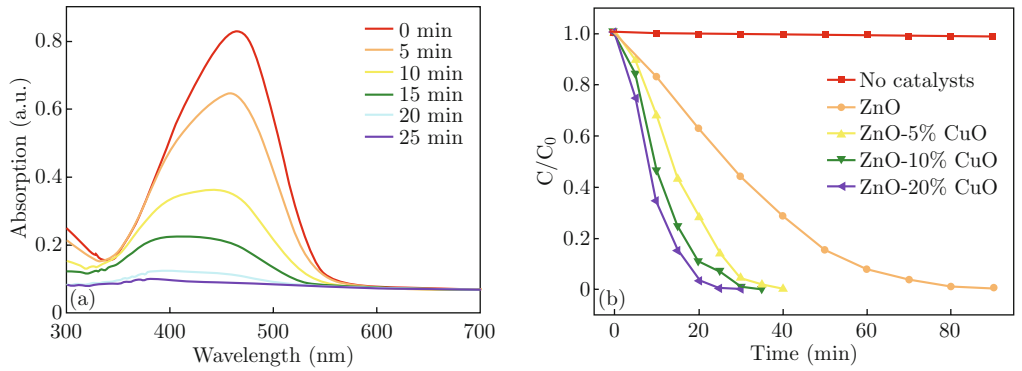

Fig. 5 (a) UV-vis absorption spectra of MO solution during the photodegradation. (b) Decomposition rates of the MO solution with pure ZnO and different ZnO/CuO composites and without catalysts.

To further investigate the photodegradation efficiency of other dyes using the as-synthesized ZnO/CuO nanocomposites, the MO solution (10 mg/l) has also been decomposed under UV irradiation. As shown in Fig. 5, it is found that the absorption peaks of MO disappear completely after UV irradiation for 25 min, giving a high photodegradation efficiency which is higher than previous report [21]. The photodegradation rates of MO solution without catalysts and with pure ZnO NWs and ZnO/CuO nanocomposites have also been analyzed in Fig. 5(b). It is observed obviously that the ZnO/CuO nanocomposites also exhibit much faster photodegradation rate than pure ZnO, which further confirms the enhanced photocatalytic efficiency of the ZnO/CuO nanocomposites. Increasing the CuO content can improve the photocatalytic efficiency of the ZnO/CuO nanocomposites.

The aforementioned results suggest that the ZnO/CuO nanocomposites exhibit much higher photocatalytic activities than pure ZnO. One can conclude that the enhancement in photocatalytic efficiency of the nanocomposites is closely related to the incorporation of CuO. The schematic band structure and charge-transfer process of the ZnO/CuO nanocomposites are illustrated in Fig. 6. The photo-induced electron–hole pairs are separated from each other in ZnO under UV

irradiation. The electrons transit from the valence band (VB) to the conduction band (CB) and leave positive holes (h^+) in VB. After separation of electrons and holes, the dissolved oxygen (O_2) adsorbed on ZnO surface will react with photo-induced electrons to form superoxide radical ($\cdot O_2^-$). Considering the band structures of ZnO and CuO, direct transfer of photo-induced holes from ZnO to CuO thermodynamically occurs in the ZnO/CuO nanocomposites [21,24,25], leading to low recombination rate of the photo-induced electron-hole pairs. The hydroxyl ions (OH^-) will be oxidized into hydroxyl radicals (-OH) by photo-induced holes [26]. Finally, the dye molecules are decomposed into simple organics by the continuous generated reactive oxidation species and further converted into CO_2 and H_2O. Therefore, the enhanced photocatalytic degradation of the ZnO/CuO nanocomposites should be attributed to the effective charge-transfer between ZnO and CuO.

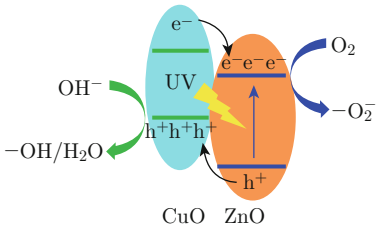

Fig. 6 Schematic diagram of the band structure and charge-transfer process in the ZnO/CuO composites.

Conclusions

We have reported a facile and low-cost approach to synthesize ZnO/CuO nanocomposites by two-step hydrothermal methods. The photocatalytic properties of the as-synthesized ZnO/CuO nanocomposites have been investigated under UV irradiation. Experiment results show that MB can be degraded completely within 15 min and its photodegradation rate is six times faster than that of pure ZnO, exhibiting an enhanced photocatalytic activity. This enhanced photocatalytic activity of ZnO/CuO nanocomposites is ascribed to the low recombination probability of photogenerated carriers due to the efficient charge transfer between ZnO and CuO.

Acknowledgements

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