Preparation of nano-Cu_2O/AC loaded photocatalyst and its visible-light photocatalytic activity

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A kind of Cu_2O/activated carbon (Cu_2O/AC) photocatalyst has been successfully synthesized by a convenient forced hydrolysis and solvent reduction method. The product was characterized by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). The photocatalytic efficiency of the Cu_2O//AC composite photocatalyst was evaluated by degradation of methyl orange (MO) as a target pollutant in water under visible light irradiation. It was found that the Cu_2O nanoparticles were uniformly loaded over the activated carbon, and the Cu_2O/AC photocatalyst exhibited the higher photocatalytic activity in comparison with commercial P25 TiO_2 powder under visible light irradiation.

(Received March 14, 2011; accepted June 9, 2011)

Keywords: Cu_2O/AC, photocatalyst, Forced hydrolysis, Solvothermal reduction

1. Introduction

Since 1977 the cyanide ion in aqueous solution had been oxidized successfully by a heterogeneous photocatalysis using TiO_2 as the photocatalyst under UV light irradiation [1], the semiconductor photocatalysis as an advanced oxidation process (AOP) has been used as an effective method for water or air purification [4-5]. However, most of the semiconductor photocatalysts such as TiO_2 and ZnO are only excited by UV light due to their wide band-gap, and promote photocatalysis upon illumination with UV radiation. Because of the low fraction of short wavelength solar spectrum, the photocatalysts with the wide band-gap show very low photocatalytic ability under solar illumination. Therefore, it is important to develop the photocatalysts with high photocatalytic activity under visible light irradiation. In 1998, Hara et al. [6] reported that Cu_2O, which can be activated by visible light due to its low band gap of ca. 2.0 ev, was used as photocatalyst for water splitting. From then on, Cu_2O had been extensively investigated as a high-efficiency visible-light responsive photocatalyst [7-9]. Considering the application of power catalysts in pollution treatment, a prominent problem is that it is difficult to be filtered or recycled after the photodecomposition of substrates. Given that powder photocatalyst can be anchored or embedded onto support materials with large surface areas, which could condense diluted polluted substances would be of great significance, not only to facilitate the filtration and recycle of photocatalyst particles, but also to improve the photocatalytic efficiency. Some previous researches [10-13] had found that the coupling of the TiO_2 and the activated carbon used as the supporting material could greatly improve the photocatalytic activity, which was attributed to the synergistic effect between the AC and the TiO_2. Accordingly, it was expected to prepare Cu_2O/AC loaded photocatalyst with the remarkable visible-light photoresponse and the enhanced photocatalytic efficiency by embedding Cu_2O nanoparticles onto AC.

In this work, a novel approach was proposed to prepare an adsorptive Cu_2O/AC composite photocatalyst with visible light response under mild conditions. Copper (II) acetate was used as copper source to synthesize Cu_2O nanoparticles deposited on activated carbon by means of forced hydrolysis and ethylene glycol-thermal reduction in a one-step process. The photocatalytic activity of the Cu_2O/AC was evaluated by degradation of methyl orange under visible light irradiation.

2. Experimental

2.1. Synthesis procedure and characterization

All chemical reagents were commercial available without further treatment. All chemical reagents except P25 TiO_2 were bought from Sinopharm Chemical Reagent Co., Ltd. and P25 TiO_2 powder was supplied by Degussa. The synthesis procedures of Cu_2O/AC were as follows: 0.01 mole copper (II) acetate monohydrate and 5.0 g activated carbon were added to 100 mL of a mixture of ethylene glycol and water (volume ratio of ethylene glycol to water is 4:1). Then the mixture was taken into a 250-mL flask, heated up to boiling under vigorous stirring, and kept boiling under reflux for 4 hrs. In this process, forced hydrolysis of copper (II) acetate was accomplished under the boiling reflux condition, copper (II) oxide or copper (II) dihydroxide were formed and deposited on the surface of activated carbon; in the same time, ethylene

glycol-thermal reduction took place at the boiling point temperature. As a result, the Cu_2O/AC loaded photocatalyst was obtained. The product Cu_2O/AC was separated from the solid-liquid mixture by centrifugation with several washings, and dried under the vacuum condition at 60℃.

The phase structure, the crystallite size and the shape of Cu_2O in Cu_2O/AC, and the distribution of Cu_2O particles on the surface of activated carbon were characterized by XRD (A Bruker D8 X-ray diffractometer with Cu Kα, λ= 0.15418 nm), SEM (LEO1530VP).

2.2. Photocatalytic activity measurement

The photocatalytic activity tests of the obtained Cu_2O/AC and the commercial Degussa P25 TiO_2 were performed at ca. 30℃ in a 250 ml glass reactor. A 500-W halogen lamp used as a visible light source was placed above the reaction mixture approximately 20 cm away from solution surface. The initial concentrations of MO and photocatalyst powders were 0.04 and 5.0 $g \cdot L^{-1}$, respectively. Prior to irradiation, the suspension was stirred in a dark to establish adsorption–desorption equilibrium. Once the concentration of methyl orange had stabilized, the reaction mixture was irradiated, signaling the start of photocatalysis. At given time intervals, sample was collected, centrifuged, and filtered through a 0.2 μm millipore filter. Then the filtrate was analyzed on a 722 visible spectrophotometer at 464 nm.

3. Results and discussion

3.1 Phase composition and microstructure

The crystal structure and composition of the synthesized products were characterized by XRD, SEM techniques. Fig. 1 showed the XRD pattern of the synthesized Cu_2O/AC. From Fig. 1, it was observed that the peak positions in X-ray diffraction profiles were in agreement with those of an octahedral Cu_2O. The mean crystallite size of Cu_2O in Cu_2O/AC could be calculated from diffraction peaks according to Scherrer equation, and the mean crystallite size of Cu_2O calculated from the most intense peaks is approximately 23.7 nm. The results showed that the nanostructured Cu_2O particle was synthesized from Cu^{2+} source under forced hydrolysis and ethylene glycol-thermal reduction conditions. Fig. 2 showed SEM image of the as-synthesized product. By observing SEM image, the Cu_2O in the composite were particles with a size smaller than 50 nm and were uniformly dispersed on the surface of activated carbon.

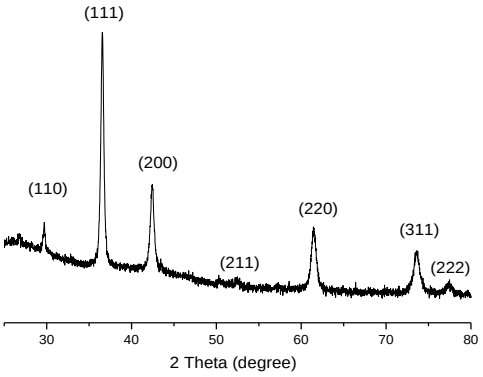

Fig. 1 XRD pattern of Cu_2O/ AC.

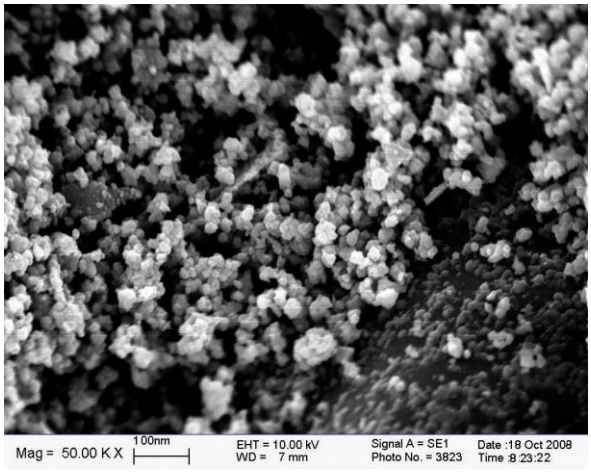

Fig. 2 SEM image of Cu_2O/AC

3.2 Photocatalytic activities

The photocatalytic activitie of the Cu_2O/AC was evaluated through the photodegradation of MO under the visible light irradiation and was compared with that of a commercial Degussa P25 TiO_2 powder. The experimental results were illustrated in Fig. 3. Obviously, the synthesized Cu_2O/AC showed higher photocatalytic activity than P25 TiO_2 powder under visible light irradiation. It can be explained as follows: Cu_2O is a visible-light activated photocatalyst due to its low band gap of ca. 2.0 ev, while TiO_2 is a wide band-gap semiconductor material, which is only excited by ultraviolet light, and hence the photocatalytic activity of Cu_2O/AC has the advantage over P25 TiO_2 under visible light irradiation. In addition, AC can adsorb MO molecules so that there is a partial high concentration of MO on surface of Cu_2O/AC composite photocatalyst. Those MO molecules adsorbed on surface of Cu_2O/AC photocatalyst are desorbed from AC, and move directly to the deposited Cu_2O, which is adhered on AC. The Cu_2O/AC composite photocatalyst shows the synergistic effect between the AC and the Cu_2O. In contrast, MO molecules move indirectly to the surface of TiO_2 via bulk

solution. Therefore, the Cu_2O/AC composite photocatalyst exhibited a much faster photocatalytic rate and better performance than a commercial Degussa P25 TiO_2 powder under visible light irradiation.

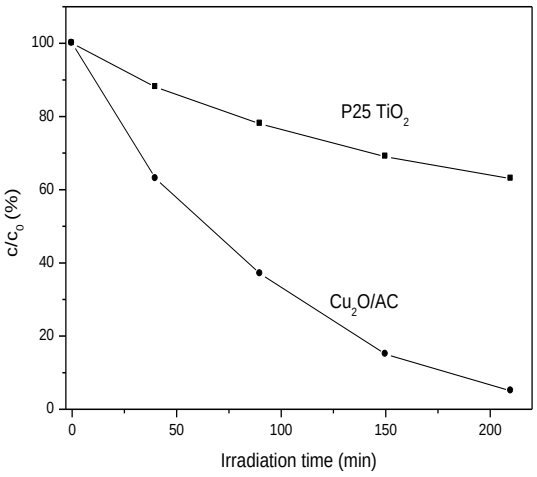

Fig.3 Photocatalytic activities of different photocatalysts under visible-light irradiation.

3. Conclusions

The Cu_2O/AC loaded photocatalyst was successfully prepared by a new method involving forced hydrolysis and ethylene glycol-thermal reduction. The synthesized product consisted of the nanometer-sized Cu_2O particles, which were uniformly adhered on AC. The photocatalytic activities of the Cu_2O/AC photocatalyst as well as P25 TiO_2 were estimated by degradation of MO under the visible light irradiation.The results showed that the Cu_2O/AC composite photocatalyst exhibited a much faster photocatalytic rate and better performance than a commercial Degussa P25 TiO_2 powder under visible light irradiation. The enhanced reactivity of Cu_2O/AC composite photocatalyst can be attributed to the visible-light photocatalytic activity of Cu_2O and the synergistic effect between the AC and the Cu_2O.

Acknowledgments

The authors thank anonymous reviewers very much. This work was supported by the Nature Science Foundation of Anhui Provincial Education Committee (Grant No. KJ2010A302).

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