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Research Article

Preparation, Characterization, and Photocatalytic Property of Cu_2O-TiO_2 Nanocomposites

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The Cu_2O-TiO_2 nanocomposites were successfully synthesized by the homogeneous hydrolysation, followed by the solvothermal crystallization and ethylene glycol-thermal reduction process, respectively. The obtained products were characterized by means of X-ray diffraction(XRD), Uv-vis diffuse reflectance spectroscopy, laser particle size analysis, and scanning electron microscopy (SEM), respectively. The photocatalytic performance of Cu_2O-TiO_2 nanocomposites was evaluated by the degradation of methyl orange (MO) as a model compound. The experimental results showed that the prepared Cu_2O-TiO_2 nanocomposite exhibited higher photocatalytic activity for the decomposition of MO than the pure Cu_2O and the commercial Degussa P25 TiO_2 under visible light irradiation.

1. Introduction

The semiconductor photocatalysis has been used to mineralize the organics via a series of intermediates into inorganic substances such as H_2O and CO_2 in the presence of light. To date, many semiconductors have been found to be good photocatalysts to decompose various organics. Among various semiconducting materials, much attention has been given to TiO_2 [1–4] because of its high photocatalytic activity, resistance to photocorrosion, chemical and biological inertness, commercial availability, and inexpensiveness. However, the photoinduced charge carrier in single bare semiconductor particles like TiO_2 has a very short lifetime owing to the high-recombination rate of the photogenerated electron/hole pairs, which reduces photocatalytic efficiency. On the other hand, Titania has a large band gap (about 3.2 eV for anatase phase) and only a small fraction of solar light can be absorbed. These hinder the wide-scale engineering applications of pure titanium dioxide. Therefore, in order to improve the photocatalytic activity of TiO_2, it is important to prevent the photoelectron/hole recombination until a designated chemical reaction takes place on the surface of semiconductor particles as well as to extend the light absorbing property of TiO_2. Some previous researches have found that the coupling of two semiconductors can improve the photoexcited charge separation and enhance the photocatalytic activity [5–11]. On the other hand, Cu_2O is a p-type semiconductor with direct band gap of 2.0 eV and has a noticeable light absorption capability in the visible-light region [12–14]. Accordingly, it is expected to prepare Cu_2O-TiO_2 nanocomposite with the highly efficient photoexcited charge separation, the enhanced photocatalytic efficiency and the remarkable visible-light photoresponse by coupling TiO_2 with Cu_2O, which has been reported in the few previous studies [15–18].

In this study, using the ethylene glycol as the solvent and the reducing agent, and titanium tetrabutoxide and Cu (II) acetate as precursors, the Cu_2O-TiO_2 nanocomposite was successfully synthesized by the homogeneous hydrolysation, followed by the solvothermal crystallization treatment and the ethylene glycol-thermal reduction reaction, respectively. The process would develop a new method for preparing Cu_2O-TiO_2 nanocomposite with the visible-light photocatalytic activity under mild conditions.

2. Experimental

2.1. Materials and Apparatus. The reagents (titanium tetrabutoxide, copper (II) acetate monohydrate, glacial acetic acid,

ethylene glycol, and methyl orange) are all analytic reagent grade. A Bruker D8 Advance X-ray diffractometer with Cu Kα radiation ($\lambda = 0.15418$ nm), the accelerating voltage of 40 kV, emission current of 40 mA, and the scanning speed of 8°/min was used to determine the crystal phase composition and the crystallite size of the coupled oxides prepared. And a scanning electron microscope (LEO1530VP) was used to observe the shape and size of the prepared products. The UV-Vis diffuse reflectance spectroscopy was obtained using a UV-visible spectrophotometer (TU-1901, Beijing Purkinje General Instrumental Co., China), and the particle size analysis was performed on a Zetasizer Nano ZS90.

2.2. Synthesis Procedure. All of the chemical reagents used in the experiments were analytical grade without further purification and treatment. The synthesis procedures of Cu_2O-TiO_2 were as follows: 0.01 mol of titanium tetrabutoxide and 0.04 mol of glacial acetic acid were dissolved in 50 mL of ethylene glycol. The solution is taken in Teflon-lined stainless-steel autoclave, heated to 120°C at a rate of 5°C/min, and kept under the temperature for 2 hr. Uniform hydrolysis of $Ti(OBu)_4$ was accomplished via in situ homogeneous generation of water, which is formed by the esterification reaction of ethylene glycol with acetic acid. As Result, the amorphous hydrous titanium oxide precursor $TiO_2 \cdot nH_2O$ was obtained, and then the autoclave was heated up to 200°C and held at this temperature for 10 hr, and the amorphous precursor was transformed into the nanosized TiO_2 with stable crystal structure. After the autoclave was allowed cooling to room temperature, the solution of copper (II) acetate in ethylene glycol was added into the autoclave in certain mole ratio of Ti/Cu under stirring condition. The reaction mixture was heated in the temperature range of 150–190°C for 6 hr in order to load Cu_2O onto the surface of TiO_2 by ethylene glycol-thermal reduction process. Subsequently, the product Cu_2O-TiO_2 was separated from the solid-liquid mixture by low pressure distillation at 150°C and grinned in agate mortar to obtain the powder samples.

2.3. Photocatalytic Activity Measurement. The photocatalytic activity tests of the obtained Cu_2O-TiO_2, the pure Cu_2O, and the commercial Degussa P25 TiO_2 were performed at ca. 30°C in a 250 mL glass reactor, respectively. A 36-W fluorescent lamp used as a visible light source was placed above the reaction mixture approximately 10 cm away from solution surface. The initial concentrations of MO and photocatalyst powders were 0.02 and 3 g·L^{-1}, respectively. Prior to irradiation, the suspension was stirred in a dark to establish adsorption-desorption equilibrium. Once the concentration of MO 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.

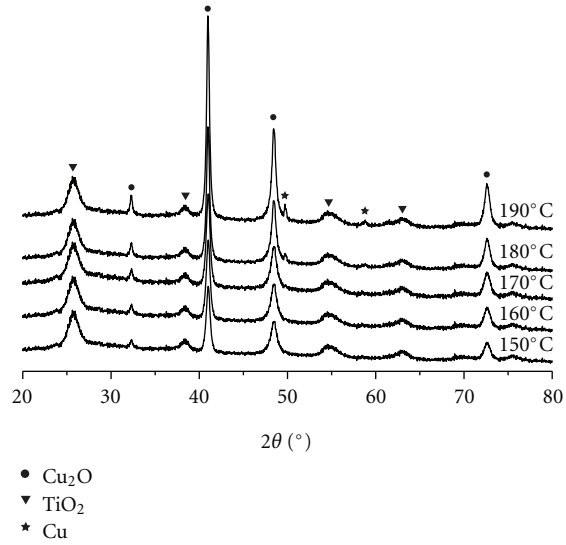

Figure 1: XRD patterns of the Cu_2O-TiO_2 samples.

3. Results and Discussion

3.1. Influence of Thermal Reduction Temperature on Phase Composition and Crystal Size. To determine the crystal phase composition and crystal size of the prepared photocatalyst, X-ray diffraction(XRD) measurements were carried out at room temperature over the diffraction angle (2θ) 20°–80°. Figure 1 showed the XRD patterns of Cu_2O-TiO_2 powders prepared by ethylene glycol-thermal reduction at 150, 160, 170, 180, and 190°C for 6 hr, respectively. From Figure 1, we can observe that there is a continuous sharpening and intensifying of the diffraction peaks for Cu_2O in Cu_2O-TiO_2 with increasing thermal reduction temperature, indicating that the crystal size of Cu_2O increased as the thermal reduction temperature went up. The crystal size of Cu_2O in different reduction temperature can be calculated according to the Scherrer equation. The results showed that the mean sizes of Cu_2O in Cu_2O-TiO_2 were 12.7, 23.9, 35.1, 50.1, and 79.7 nm at 150, 160, 170, 180, and 190°C, respectively. On the other hand, we can see the diffraction peaks of Cu in the Cu_2O-TiO_2 samples as the thermal reduction temperature rising to 180°C and above indicated that part Cu_2O was reduced further to metallic copper.

3.2. Morphology and Size Distribution of Couple Oxides. In order to study the morphology of the prepared Cu_2O-TiO_2, scanning electron microscopy (SEM) was used. Figure 2 showed the TEM image of the Cu_2O-TiO_2 sample prepared at the thermal reduction temperatures of 160°C. SEM micrograph indicated that the obtained Cu_2O-TiO_2 sample was homogeneously distributed nanocomposite particles, and the particle size of them was in the range of 40−60 nm.

In the present study, the particle size and size distribution of the Cu_2O-TiO_2 sample prepared at the thermal reduction temperatures of 160°C also was measured on a Zetasizer Nano ZS90 (Malvern Instrument, Worcestershire, UK). As shown in Figure 3, the Cu_2O-TiO_2 particles size was found

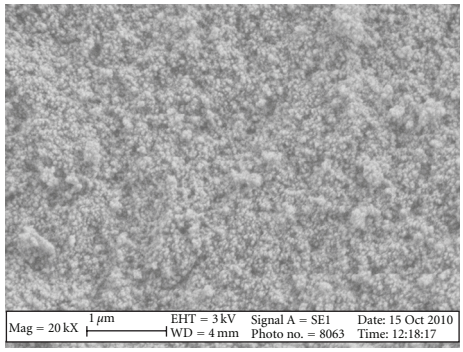

Figure 2: SEM pattern of Cu_2O-TiO_2.

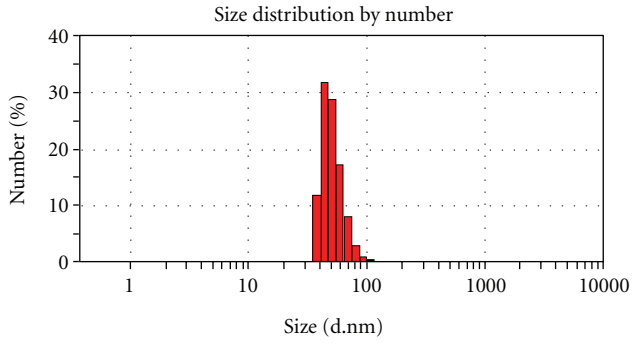

Figure 3: Particle size distribution of Cu_2O-TiO_2.

in the range of 35–105 nm, and the average particle size was about 64 nm. The particle size measured by the zetasizer was larger than that observed in XRD and SEM. Because Malvern Instruments' Zetasizer used light scattering techniques to measure hydrodynamic size of nanoparticles, a increase in particle size can be the result of particle agglomeration.

3.3. UV-Vis Diffuse Reflectance Spectra. The absorption spectra of Cu_2O, P25 TiO_2, and Cu_2O-TiO_2 prepared at the thermal reduction temperatures of 160°C were given in Figure 4. Figure 4 showed that all the samples had a strong absorption at the wavelength range from 230 to 380 nm. In addition, it can be also observed from Figure 4 that the absorption spectroscopy of the Cu_2O-TiO_2 sample was red-shifted compared to that of TiO_2, and the Cu_2O-TiO_2 sample had obvious absorption in the visible region (>400 nm). The absorption wavelength of the Cu_2O-TiO_2 nanocomposites was extended to a visible region due to absorption of visible light by Cu_2O.

3.4. Photocatalytic Activities of Samples. The photocatalytic activities of the Cu_2O-TiO_2 samples through the photodegradation of MO under the visible light irradiation for 3 hours were evaluated and were also compared with that of the commercial Degussa P25 TiO_2 powder and the pure Cu_2O powder. The experimental results were

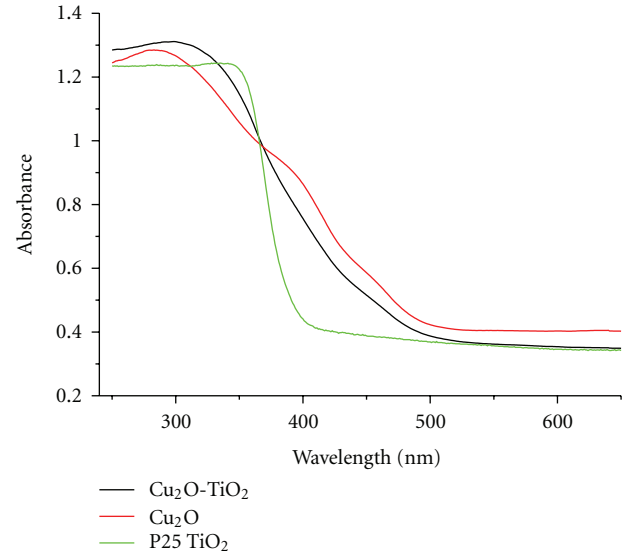

Figure 4: UV-Vis diffuse reflection spectra.

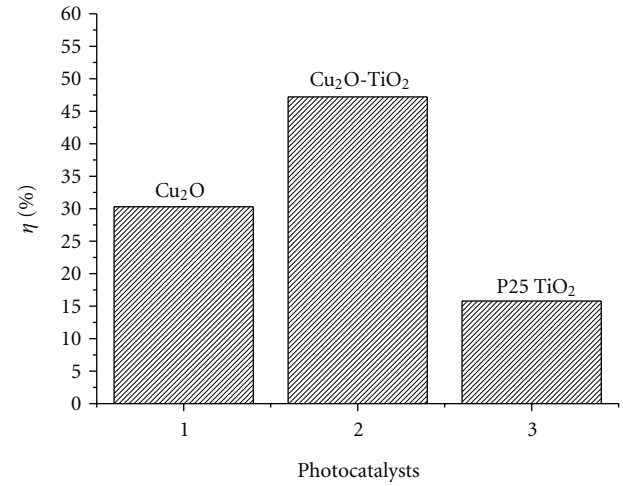

Figure 5: Photocatalytic activities of different photocatalysts under visible-light irradiation (the Cu_2O-TiO_2 sample was prepared at a thermal reduction temperature of 160°C).

illustrated in Figure 5. Obviously, the synthesized Cu_2O-TiO_2 showed higher photocatalytic activity than the pure TiO_2 and Cu_2O under UV-vis light irradiation. The high photocatalytic activity of Cu_2O-TiO_2 can be attributed to the more efficient separation of photoinduced hole-electron (h-e) pairs in the Cu_2O-TiO_2 composite, that is, to say that the photogenerated holes migrate towards the interface while the electrons migrate towards the bulk due to Cu_2O-TiO_2 p-n heterojunction. Meanwhile, the excited electrons on Cu_2O can also transfer to TiO_2 because the conduction band of TiO_2 lies more positive than that of the Cu_2O. Therefore, the Cu_2O-TiO_2 composite exhibited much higher photocatalytic activity than the pure TiO_2 and Cu_2O.

4. Conclusions

The nanoscale Cu_2O-TiO_2 couple oxide photocatalyst was successfully prepared and was characterized by X-ray diffraction, laser particle size analysis, and scanning electron microscopy, respectively. The characterization results indicated that the couple oxide samples consisted of the nanosized Cu_2O and TiO_2 phases when the thermal reduction temperature was not more than 180°C. The results also showed that the crystal size of Cu_2O was obviously affected by the thermal reduction temperatures, that is, the Cu_2O particle size increased with increasing thermal reduction temperature. Besides, there was a phase change from Cu_2O to Cu in the obtained samples when the thermal reduction temperatures were over 180°C. In addition, the photocatalytic activity experiment results showed that the couple oxide Cu_2O-TiO_2 exhibited much higher photocatalytic activity than the pure TiO_2 and Cu_2O.

Acknowledgments

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