Fabrication of Cu$_2$O-TiO$_2$ Nano-composite with High Photocatalytic Performance under Simulated Solar Light

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Abstract: Cu$_2$O-P25 (TiO$_2$) nano-heterostructures with different mass ratios were synthesized via a wet chemical precipitation and hydrothermal method, and were characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), UV-vis diffuse reflectance spectra (DRS), and X-ray photoelectron spectroscopy (XPS). DRS results showed that the light absorption of P25 extended to the visible light region with the loading of Cu$_2$O. XPS results showed that Cu existed in the state of Cu$^+$ in the presence of hydroxylamine hydrochloride, confirming the formation of Cu$_2$O. The obtained products exhibited efficient photocatalytic performance in degradation of methyl orange (MO) and methylene blue (MB) under simulated solar light. The sample of 5% Cu$_2$O-P25 exhibited the highest photocatalytic activity among all as-prepared samples. And the photocatalysts can be recycled without obvious loss of photocatalytic activity.

Keywords: Fabrication; Cu$_2$O-TiO$_2$ composite; photocatalytic degradation; simulated solar light

1 Introduction

With the development of modern industrialization and urbanlization, serious environment pollution is becoming an intractable problem facing the world. Among all the treatment methods, photocatalysis is a promising technique for degradation of inorganic and organic pollutants in air and water [1]. And it is crucial to develop efficient and stable visible-light sensitive photocatalysts in photocatalytic degradation of industrial pollutant.

Up to now, TiO$_2$ is the traditional and most commonly used photocatalyst since 1972. However, a large band gap of TiO$_2$ (3.2 eV for anatase) restricts its use only to the narrow light-response range of ultraviolet. And the low quantum efficiency is another problem for TiO$_2$, which is due to the recombination of electrons and holes in the photocatalytic process.

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In order to utilize the solar energy efficiently, several approaches for TiO_2 modification have been proposed in the past decade, such as noble metal deposition, metal ions doping, non-metal ions doping, semiconductor coupling, dye sensitization, etc. Among which, semiconductor coupling is an important strategy to realize the visible light photocatalytic activity of TiO_2. In the heterostructures formed between two semiconductors, the photo-induced electrons and holes can be separated more easily and effectively due to the difference of energy levels of the two semiconductors, thus promote the quantum efficiency of TiO_2. In recent years, the p-type Cu_2O with a band gap of 2.0 eV has been reported as a good candidate for visible light photocatalysis and exhibits huge potential for solar light utilization [2,3]. The coupling of Cu_2O with TiO_2 has attracted great attention in recent years [4-7]. Zou et al reported the architecture of Cu_2O-TiO_2 core-shell heterojunction prepared by a facile soft chemical method using CuCl and tetrabutyl titanate ($Ti(OBu)_4$) as the raw materials, which exhibited high photocatalytic activity and stability for 4-nitrophenol degradation under simulated sunlight [8]. Peng et al synthesized the Cu_2O/TiO_2 hetero-structures by an alcohol-aqueous based chemical precipitation method, and found the dramatically improved photocatalytic activity of the heterostructure [9]. Lu et al prepared the Cu_2O-decorated mesoporous TiO_2 beads by a simple metal-salt-based hydrothermal and chemical bath deposition process as a highly efficient photocatalyst for hydrogen production [10]. However, to the best of our knowledge, the preparation of Cu_2O/TiO_2 heterostructure by hydrothermal method has never been reported. In this paper, the hydroxylamine hydrochloride was used as the reductant to prepare Cu_2O via a wet chemical precipitation firstly, and then the Cu_2O/TiO_2 mixture was further treated by the hydrothermal method. The obtained products exhibited efficient photocatalytic performance in degradation of methyl orange (MO) and methylene blue (MB).

2 Experimental

2.1 Material and methods

All reagents used in this work were of analytical grade and were used as it without further purification. Cu_2O-P25 composites were prepared via a wet chemical precipitation method and further treated by hydrothermal method. In a typical procedure, $Cu(NO_3)_2 \cdot 2.5\ H_2O$ was first dissolved into 25mL distilled water. Then, a certain amount of P25 and NaOH were dispersed in above solution under magnetic stirring for 30 min to obtain a uniform suspension. Subsequently, the hydroxylamine hydrochloride was added as the reductant during stirring. After stirring for 2h, the suspension was transformed into a 50 mL Teflon-lined autoclave. The autoclave was sealed and mainted at 150 °C for 12 h, and then the autoclave was cooled down to room temperature. The pricipitate was collected and washed with distilled water and ethanol respectively for 3 times by centrifugation at 8000 rpm. The solid composites were then dried at 85 °C in vacuum. The sample without addition of hydroxylamine hydrochloride was also prepared for comparison. Samples were denoted as x-Cu_2O-P25, where x corresponds to the mass percentage of Cu_2O in the composites (2%, 5%, and 10%).

2.2 Sample characterization

The XRD patterns were recorded on a a 6100 X-ray diffractometer using Cu Kα radiation as the X-ray source (30KV, 20mA). The morphology of nanoparticles was characterized using a JSM-7800F model scanning electron microscope (SEM). The diffused reflectance UV-visible spectra (DRS) of the samples were recorded by an SHIMADZU UV-2600 spectrometer with a diffuse reflectance accessory using $BaSO_4$ as the reference at room temperature. X-ray photoelectron spectroscopy (XPS) measurement was conducted by a

Quantera SXM spectrometer (Physical Electronics), and the radiation was provided by a monochromatized Al Kα X-ray source (1486.6eV) operated at a 50 W emission power and a 15 kV acceleration voltage. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon.

2.3 Photocatalytic activity evaluation of the samples

The photocatalytic activity was tested using MO and MB solutions in a slurry photocatalytic reactor. The photocatalytic degradation was carried out in 10 mg·L^{-1} aqueous MO or MB solution with catalyst concentration of 2 g·L^{-1} under magnetic stirring and air bubbling (0.5 L·min^{-1}). This mixture was stirred for 60 min to reach adsorption/desorption equilibrium in the dark. Then, the mixture was placed 10 cm away from the simulated solar light (HSX UV-300 Xe lamp). For comparison, a blank experiment for a system without catalyst was also done. The experiments were performed at room temperature, adequate aliquots of the mixture were taken at periodic intervals during the irradiation. And after filtration by a membrane filter (0.2μm), they were analyzed with an UV-visible spectrometer.

3 Results and Discussion

3.1 Characterization results

Fig.1 (a) shows the XRD patterns of Cu_2O-P25 composites with different mass ratios. The pure P25 and Cu_2O were also characterized as the contrast to Cu_2O-P25 composites. For pure Cu_2O, the diffraction peaks at 29.2°, 36.5°, 43.1°, 61.8°, 74.2°, 77.6° were assigned to (110), (111), (200), (220), (311), (222) planes of cubic Cu_2O (JPDS 34-1354) [11]. And the P25 consisting of anatase and rutile phases, matched well with the specification of the product provided by the Degussa Company. For Cu_2O-P25 composites, the diffraction peak positions referred to the peaks of P25 when the mass percentage of Cu_2O was below 5%, which is due to the low concentration and high dispersion of Cu_2O in the composite. Six characteristic peaks of Cu_2O at 29.3°, 36.7°, 43.3°, 62.0°, 74.4°, 77.8° are observed for 10% Cu_2O-P25 according to the cubic Cu_2O (JPDS 34-1354), and the peak appeared at 36.7°for 5% Cu_2O-P25. Thus, the heterostructures of Cu_2O-P25 formed for 5% Cu_2O-P25 and 10% Cu_2O-P25. Moreover, the peak positions of TiO_2 move to the low angle slightly with the increase of Cu_2O content as shown in the inset, indicating the change of the crystal lattice of P25. Thus, the structure of P25 changed slightly with the loading of Cu_2O.

Fig.1(b) shows the UV-vis diffuse reflectance spectra of P25, and Cu_2O-P25 composites. It is obvious that P25 can just absorb UV light with wavelength shorter than 400nm, which can be assigned to the intrinsic band-gap absorption of TiO_2. It is clear that all the Cu_2O-P25 composite samples showed an absorption in the visible light region, indicating the promoted light absorption ability of the products. It is obvious that both the UV-visible light absorption range and intensity raised with the increase of Cu_2O mass percentage. The enhancement of absorbance in the UV-vis region increases the number of photogenerated electrons and holes to participate in the photocatalytic reaction, which may be related with the enhancement of the photocatalytic activity of TiO_2. The "red shift" in the absorption onset value in Cu_2O-P25 composites indicates that the band gap of the composite catalyst decreases compared with the P25, resulting in the narrowing of the band gap, which is considered to be related with the photocatalytic activity of the photocatalysts.
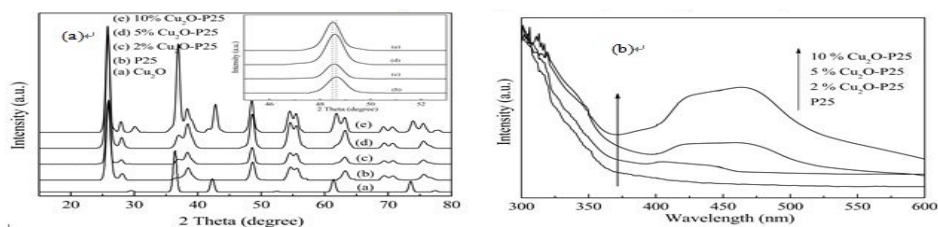
Fig.1 (a) XRD patterns of P25, Cu_2O and Cu_2O-P25 samples; (b) DRS spectra of P25 and Cu_2O-P25 samples

The morphology of 5% Cu_2O-P25 is characterized by SEM as shown in Fig.2(a). It is noticed that the particles are nearly homogeneously distributed, and no obvious Cu_2O particles are observed on P25 particles due to the low concentration and high dispersion, which indicated that P25 can be decorated by smaller Cu_2O particles to form nano-nano heterojunctions. The particle size was in the range of 50-80 nm, and there existed agglomeration in the samples.

To confirm the existence of Cu^+ to illustrate the photocatalytic mechanism of the composite, XPS is employed to obtain the surface existing state of Cu in the composite. The Cu doped sample of Cu-TiO_2 was also prepared with the same procedure as 5% Cu_2O-P25 just without addition of hydroxylamine hydrochloride in order to investigate the effect of Cu valence on the photocatalytic activity of the samples. The Cu2p XPS spectra of 5% Cu_2O-P25 prepared with and without hydroxylamine hydrochloride are shown in Fig.2(b). For the sample prepared with hydroxylamine hydrochloride as the reductant, the peaks at 931.8 eV (Cu $2p_{3/2}$) and 951.5eV (Cu$2p_{1/2}$) were assigned to the Cu^+ characteristic peak, which is the same as the standard binding energy of Cu2p in Cu_2O [12]. While, for the sample prepared without hydroxylamine hydrochloride, the binding energies located at 934.9 and 955.1 eV correspond to the Cu^{2+} characteristic peaks of CuO, indicating the Cu^{2+} can not be transformed to Cu^+ without the effective reduatant in the synthesis process.
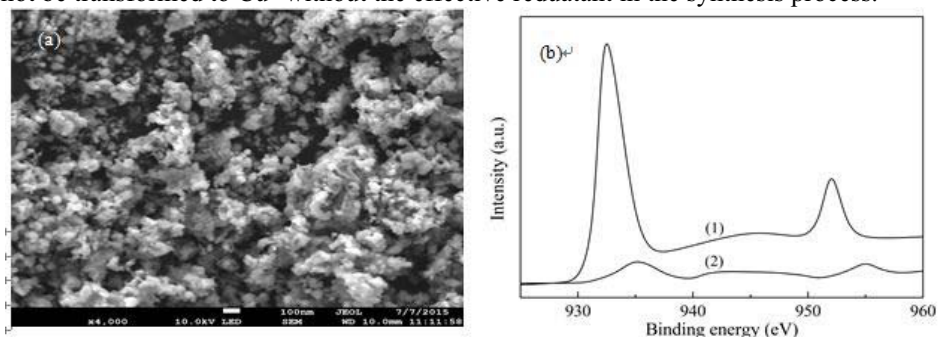

Fig.2 (a) The SEM image of 5% Cu_2O-P25; (b) Cu2p XPS spectra of 5% Cu_2O-P25 prepared (1) with and (2) without hydroxylamine hydrochloride

3.2 Photocatalytic activity evaluation

The photocatalytic performance of the samples was evaluated with the degradation of MO under simulated solar light. The typical evolution of the absorption spectra of MO during degradation process over 5% Cu_2O-P25 was shown in Fig. 3(a). With increasing illumination time, the characteristic absorption peak of MO gradually weakens, suggesting the excellent photocatalytic activity of 5% Cu_2O-P25. The photocatalytic degradation results of MO with different samples under simulated solar light are shown in Fig.3 (b). It is clear 5% Cu_2O-P25 displays higher activity than that of pure P25 and Cu_2O, and other composites, which may be attributed to the coupling effect of the composite, indicating the formation of

the heterojunction between Cu_2O and P25. Meanwhile, the blank experiment showed that the concentration of MO solution did not change without photocatalyst, illustrating that the MO could not be photo-decomposed.
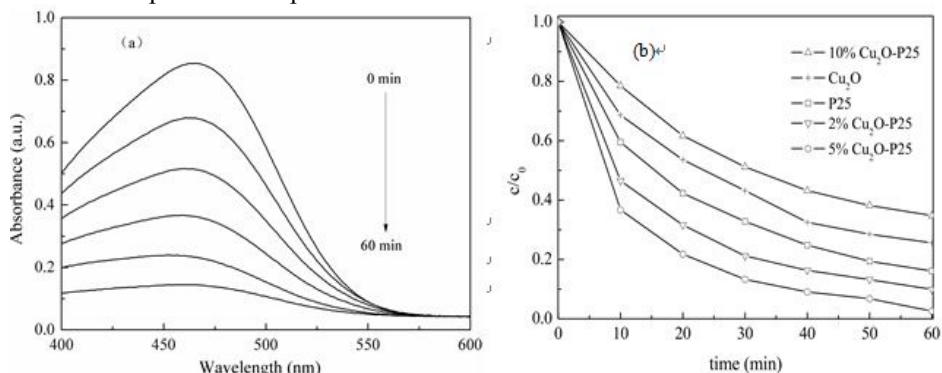

Fig.3 (a) Variation of the UV-vis spectra of MO by the 5% Cu_2O-P25 as a function of time; (b) Photocatalytic degradation curves of MO over different samples

For comparison, the degradation of MB solution with a concentration of 10 mg·L^{-1} by 5% Cu_2O-P25 as the photocatalyst was also done. The phnotocatalytic degradation rate of MB was shown in Fig.4(a), and the variation of the UV-vis spectra of MB by 5% Cu_2O-P25 as a function of time was shown in the inset. Clearly, after 60 min of illumination under simulated solar light, the degradation rate of MB reached 86.5%, indicating that the photocatalyst had good photocatalytic activity.

In order to evaluate the stability and reusability of 5% Cu_2O-P25, we also performed a recyclability test involving repeated photocatalytic degradation of MO for 4 cycles. As shown in Fig. 4 (b), after 4 cycles (30 min for one cycle) of photocatalytic degradation of MO, the catalyst did not exhibit significant loss of activity, suggesting its good stability for repeated use.
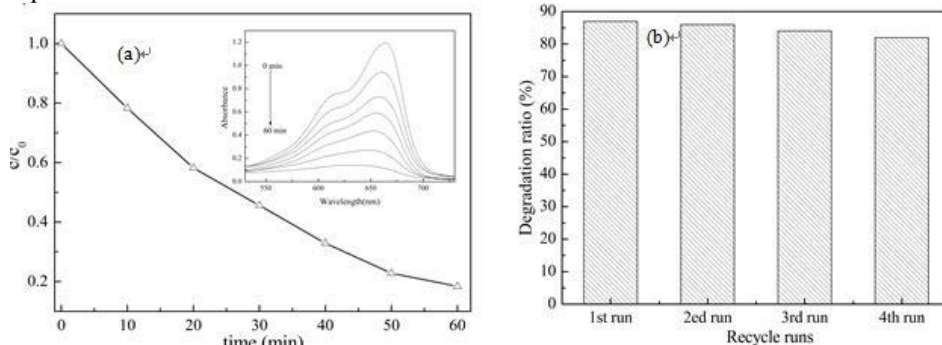

Fig.4 (a) Photocatalytic degradation curve of MB by 5% Cu_2O-P25; (b) Recycle test results of 5% Cu_2O-P25

4 **Summary**

Cu_2O-P25 nano-composites with different mass ratios were synthesized via a wet chemical precipitation and hydrothermal method. DRS spectra showed that light absorption extended to the visible light region and the band gap of the composites decreased with the loading of Cu_2O. Photocatalytic degradation of MO and MB were done to investigate the

activity of the samples under illumination of simulated solar light. The sample of 5% Cu_2O-P25 exhibited the highest photocatalytic activity and good reusability among all as-prepared samples. The efficient photocatalytic performance of the sample may be due to the formation of the heterojunction between the semiconductors.

Acknowledgments

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