Research Article

The Effects of Doping Copper and Mesoporous Structure on Photocatalytic Properties of TiO_2

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This paper describes a system for the synthesis of Cu-doped mesoporous TiO_2 nanoparticles by a hydrothermal method at relatively low temperatures. The technique used is to dope the as-prepared mesoporous TiO_2 system with copper. In this method, the copper species with the form of Cu^{1+} , which was attributed to the reduction effect of dehydroxylation and evidenced by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD), was well dispersed in the optimal concentration 1 wt.% Cu-doped mesoporous TiO_2 . In this as-prepared mesoporous TiO_2 system, original particles with a size of approximately 20 nm are aggregated together to shapes of approximately 1100 nm, which resulted in the porous aggregate structure. More importantly, the enhancement of the photocatalytic activity was discussed as effects due to the formation of stable Cu(I) and the mesoporous structure in the Cu-doped mesoporous TiO_2 . Among them, Cu-doped mesoporous TiO_2 shows the highest degradation rate of methyl orange (MO). In addition, the effects of initial solution pH on degradation of MO had also been investigated. As a result, the optimum values of initial solution pH were found to be 3.

1. Introduction

Titanium dioxide (TiO_2) is the most widely used semiconductor as a stable photocatalyst, and its photocatalytic activity is mainly limited by the number of photogenerated electron-hole pairs and their life. Although a lot of effort is being spent on improving these weaknesses, the efficient and effective method has yet to be developed.

The study found: doping metal ions not only can effectively reduce the band gap of TiO_2 to increase the number of photogenerated electron-hole pairs; the doping metal ions can form the corresponding oxide space-charge layer to promote the photogenerated electron-hole pairs effective separation [1, 2]. Sangpour et al. [3] modified TiO_2 by Au, Ag, and Cu incorporation and showed that doping increases the probability of radical formation. The photoenhancement of the studied elements was determined in the following order: $\text{Cu}:\text{TiO}_2 > \text{Au}:\text{TiO}_2 > \text{Ag}:\text{TiO}_2 > \text{TiO}_2$. Park et al. [4] fabricated metal (Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+}) doped TiO_2 ,

Zn-doped TiO_2 , and Cu-doped TiO_2 which were found to be promising materials for the photocatalytic decomposition of methylene blue. Among various metallic doping elements, the copper doping has been proved to be a simple and effective way to increase the visible light absorption.

The construction of TiO_2 nano- or microstructures with interesting morphologies and properties has recently attracted considerable attention. It is well known that ordered mesoporous materials with larger specific surface area, pore size, and the relatively regular channel structure are ideal materials for catalyst. Ordered mesoporous materials researched as photocatalysts for the treatment of environmental pollutants are one of the research hot spots in recent years [5]. Zhu et al. [6] prepared hierarchical mesoporous TiO_2 microspheres with high crystallinity and high BET specific surface area. Comparing to P25, the degradation percentages by the mesoporous TiO_2 microspheres are more than twice of those by P25. In the work of Xiong et al. [7], results showed that the polymeric template as well as

calcination played an important role in tuning morphology, mesoporosity, and specific surface area of the synthesized mesoporous TiO_2 .

Considering the two aspects above and utilizing the existing knowledge in the area of nanometer metal oxides preparation, the Cu-doped mesoporous TiO_2 was prepared by a hydrothermal method at relatively low temperatures without calcination in this study. The chemical status of the main element was investigated with X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Particle size and pore structure were analyzed with electron microscopy photographs, laser particle size analyzer, and N_2 adsorption and desorption isotherms. The light absorption band edge was characterized by means of UV-Vis diffuse reflectance spectroscopy. The photocatalytic activities of the as-prepared Cu-doped mesoporous TiO_2 were evaluated by photo degradation of methyl orange (MO).

2. Experimental

2.1. Preparation of Catalysts. Herein, all chemicals were used as received without further purification.

The triblock copolymer, Pluronic P123 ($M = 5800$, Sinopharm Chemical Reagent Co., Ltd.), was used as the template. Tetrabutyl titanate (TBT, Sinopharm Chemical Reagent Co., Ltd., 97%) was used as the titanium source and calculated amounts of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ($M = 241.60$, Sinopharm Chemical Reagent Co., Ltd.) were chosen as the precursor of the dopant.

The synthesis of Cu-doped mesoporous TiO_2 was carried out with the following procedure according to the report [8].

7.5 mL tetrabutyl titanate and 3 g triblock copolymer pluronic P123 were ultrasonically dispersed in 10 mL ethanol, labeled as solution A. And then 10 mL ethanol, 5 mL deionized water, 15 mL acetic acid, and 0.2 g $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were mixed to form a homogeneous solution, labeled as solution B. The mixed solution, which was obtained by dropping solution A into solution B, should be stirred at room temperature for 1 h after mixing. Then the mixture was transferred to a 50 mL Teflon-lined stainless steel autoclave, followed by a hydrothermal treatment at 130°C for 24 h. After the reaction, the powder sample was centrifuged, rinsed with ethanol and deionized water, and dried in vacuum at 80°C for 12 h. After grinding, the product (1 wt.% Cu-doped mesoporous TiO_2) just desired was obtained without calcination.

For comparison, unsupported catalyst pure TiO_2 was also prepared using the same procedure without the addition of P123 or $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$.

2.2. Characterization of Catalysts. The crystallite structures of the materials were investigated by analyzing the X-ray diffraction (XRD) patterns obtained with a RIGAKU Ru-200B diffract meter equipped with Cu K α irradiation with a fixed power source (40 kV, 40 mA). Chemical compositions of the composites were analyzed using X-ray photoelectron spectroscopy (Thermo Scientific, ESCALAB 250Xi). The internal structures of the particles were studied with Transmission Electron Microscopy (TEM, JEOLJEM-2000

FX II). All the powders were ultrasonically dispersed in ethanol for 30 min prior to the measurement. And the surface features and morphologies of the synthesized materials were investigated with Scanning Electron Microscopy (SEM, JEOL JSM-6330F). The particle size distribution of the catalyst was examined using laser particle size analyzer (Malvern mastersizer2000). The specific surface area and pore size distribution were characterized by analyzing the N_2 adsorption and desorption isotherms obtained at -196°C using Quantachrome Quadrasorb SI automated surface area and pore size analyzer. All the materials were degassed at 150°C and 1.33×10^{-4} Pa for 6 h prior to the measurement. UV-Vis diffuse reflectance spectroscopy (Hitachi U3900) with a wavelength scan range of 250–800 nm was used to determine the light absorption of the catalysts.

Throughout the subsequent discussion on catalyst characterization, Cu-doped mesoporous TiO_2 refers to 1 wt. % Cu-doped mesoporous TiO_2 .

2.3. Photocatalytic Activity Test. The photocatalytic activities of the catalysts on the degradation of methyl orange under visible light in aqueous solution were determined with the following procedure [9].

We used a beaker as the degradation pool, in which 50 mL methyl orange aqueous solution (50 ppm) and 125 mg as-prepared sample were mixed. Prior to irradiation, the mixture solution was shocked in the dark for 30 min until adsorption/desorption equilibrium was reached. The solution was then irradiated under visible light. A certain mixture solution was removed at regular intervals and filtered through a syringe filter ($0.45 \mu\text{m}$). Finally, the degradation of methyl orange was analyzed by detecting the absorption at 462 nm using a UV-7504PC (CANY Shanghai). The xenon lamp (50 W, CEL-HXF300) was used to simulate the solar spectrum. The photocatalytic experiments were performed at pH 7 unless stated otherwise. When required, the initial pH values were adjusted to the desired values using HCl or NaOH solutions.

The photocatalytic activities of the pure TiO_2 and mesoporous TiO_2 were tested under the same experimental conditions.

3. Results and Discussion

3.1. XRD Characterization. The wide angle X-ray diffraction (XRD) patterns of Cu-doped mesoporous TiO_2 with different copper concentration were obtained and compared with pure TiO_2 diffraction pattern in Figure 1. All of as-prepared TiO_2 had (101), (004), (200), and (211) peaks at 2θ values of ca. 25.38° , 37.82° , 48.18° and 54.4° , indicating that all of the as-prepared TiO_2 had an anatase crystal structure according to JCPDS-21-1272.

It must be noted that no copper species (Cu, CuO, Cu_2O) were detected in the sample 1 wt.% Cu-doped mesoporous TiO_2 . The above observations may suggest that Cu was well dispersed in the TiO_2 . The similarity in the Cu and Ti ionic radii (0.072 nm for Cu and 0.068 nm for Ti) allows

FIGURE 1: X-ray diffraction patterns of Cu-doped TiO_2 with different copper concentration and pure TiO_2 .

the interstitial incorporation of the dopant into the titania network.

In this section, we also provide a simple method for understanding of the copper species in the Cu-doped mesoporous TiO_2 . The 3 wt.% Cu-doped mesoporous TiO_2 with larger copper concentration was investigated, in which Cu_2O crystal peaks were detected along with the anatase peaks of anatase TiO_2 , indicating that Cu phase dispersed in the form of micro- TiO_2 crystal with Cu_2O small clusters. It leads to the conclusion that the excess copper cannot replace Ti^{4+} entering into the TiO_2 to form stable solid solution. Without special instruction, the optimal concentration of 1 wt.% Cu-doped mesoporous TiO_2 was used as the experimental sample in the following results and discussion.

Reading Huang et al.'s work [10] for reference, the formation of Cu_2O may be due to acetic acid and ethanol, reducing Cu^{2+} to Cu^{1+} . This reduction effect was attributed to the dehydroxylation step, where OH radicals with strong reducing properties were produced [11]. The presence of Cu^{1+} also corroborated with the following XPS results.

3.2. XPS Characterization. X-ray photoelectron spectroscopy (XPS) analysis can provide information about the oxidation states and compositions of the superficial metals, and to identify the chemical status of the main element in the samples.

Figure 2 shows the X-ray photoelectron survey spectra of Cu-doped mesoporous TiO_2 composite. As can be seen, the XPS spectra pointed out that the copper has been successfully doped into the titanium dioxide structure.

Figure 3 shows the high resolution XPS spectra of $\text{Ti}2p$ region and $\text{Cu}2p$ region for the Cu-doped mesoporous TiO_2 . The peaks for $\text{Ti } 2p_{3/2}$ and $\text{Ti } 2p_{1/2}$, respectively, located at 458.58 eV and 464.38 eV are lower than those reported in the literature for the pure TiO_2 at 458.9 eV and 464.6 eV [12]. Thus it means that there are more lattice defects that existed in the Cu-doped mesoporous TiO_2 lattice. Lattice defect

FIGURE 2: XPS survey spectra of Cu-doped mesoporous TiO_2 .

is active to capture photogenerated electrons and improve catalytic activity.

It is necessary to note that the $\text{Cu}2p_{3/2}$ level binding energy of about 932.2 eV and 933.5 eV is related to Cu_2O and CuO , respectively. And $\text{Cu}2p_{1/2}$ of 952.9 eV and 953.6 eV are related to Cu_2O and CuO , which are too close to distinguish.

The next steps are useful and innovative to make a distinction between Cu_2O and CuO . The high resolution XPS spectra of $\text{Cu}2p$ region for uncalcined (blue) and calcined (red) Cu-doped mesoporous TiO_2 were analyzed in Figure 4. After calcination in air at 450°C, the $\text{Cu}2p$ peak broadened with the emergence of CuO characteristic peak in the red curve, indicating that the original Cu_2O was oxidized. It can be concluded that loaded copper existed as oxidation state Cu_2O in the Cu-doped mesoporous TiO_2 composite.

3.3. Particle Size and Pore Structure. As can be seen in Figure 5(a), the transmission electron microscopy image offers the information that the original particles are quite uniform and their size is about 20 nm but it is difficult to identify the channel structure, which can be attributed to that only a small portion of the sample was observed in the transmission electron microscopy analysis; moreover the sample was ultrasonically dispersed prior to observation. And in the scanning electron microscopy image of Figure 5(b), the aggregation of the original particles was observed and the size of aggregates is about 1000 nm. In addition to electron microscopy analysis, the particle size distribution with statistical significance was analyzed as shown in Figure 6, and the average size of aggregates is about 1100 nm, consistent with the SEM result.

With integrated analysis on results of the electron microscopy image and the particle size distribution, it can be concluded that the spherical nanocrystalline particles with a size of approximately 20 nm are aggregated together to shapes of approximately 1100 nm, which resulted in the porous aggregate structure. More details on pore structure are discussed later in this chapter.

As can be seen in Figure 7, the N_2 adsorption-desorption isotherms of pure TiO_2 , mesoporous TiO_2 and Cu-doped mesoporous TiO_2 were investigated to evaluate the pore structure and pore size. The isotherms of the samples mesoporous TiO_2 and Cu-doped mesoporous TiO_2 have classical

FIGURE 3: High resolution XPS spectra of Ti2p (a) region and Cu2p (b) region for Cu-doped mesoporous TiO₂.

FIGURE 4: High resolution XPS spectra of Cu2p region for uncalcined (blue) and calcined (red) Cu-doped mesoporous TiO₂.

hysteresis between the adsorption and desorption curves compared with pure TiO₂, indicating the presence of pore structures. And the Brunauer Emmet Teller surface area (S_{BET}) could be ranked as follows: S_{BET} (mesoporous TiO₂): 146 m²/g > S_{BET} (Cu-doped mesoporous TiO₂): 128 m²/g > S_{BET} (pure TiO₂): 57 m²/g. As can be seen, a narrow decrease has been identified for the copper-doped photocatalysts. That means copper doping will lead to the decrease of surface area due to the blockage of the pores by the copper oxide clusters [13].

3.4. Optical Properties. Cu-doped mesoporous TiO₂ and pure TiO₂ nanocomposites have been characterized by means of UV-Vis diffuse reflectance spectroscopy as shown in Figure 8. Compared with pure TiO₂, absorption band edge of Cu-doped mesoporous TiO₂ was noticeably shifted toward the visible light region. According to the work developed by Li and Zhang [14], the expanded absorption band might be assigned to presence of Cu¹⁺ clusters as well as the bulk Cu₂O.

Thus, it can be inferred that doping with a transition metal ion such as copper is effective for visible-light response and will play a significant role for enhancing the photocatalytic activity of the catalysts. However, excessive absorption of visible light and even infrared region will lead to a decline in photocatalytic oxidation ability. So it is important to tune the optical and electronic properties of semiconductor nanocrystals by controlling the type and concentration of dopant.

3.5. Photocatalytic Activity. The photocatalytic activities of the as-prepared TiO₂ were evaluated by photo degradation of methyl orange. Figure 9 shows enhanced photocatalytic activity of Cu-doped mesoporous TiO₂ as well as that of pure TiO₂ and mesoporous TiO₂ under visible light irradiation.

The relationship of photocatalytic abilities among the catalysts was as follows: Cu-doped mesoporous TiO₂ > Mesoporous TiO₂ > pure TiO₂. A discussion of possible reasons for the enhanced photocatalytic activity of composite catalyst under visible light irradiation is summarized as follows. Firstly, the light absorption extended into visible light region due to copper doping. Secondly, Cu¹⁺ acted as electron and hole trappers which could effectively reduce the photogenerated hole-electron recombination rate [15]. Finally, the higher adsorption of methyl orange onto the catalyst surface due to the mesoporous structures also played a role in enhancing the photocatalytic activity of composite catalyst.

Since pH play a vital role in the degradation of dyes and the pH values of the dyestuff waste could be different in practical application, additional experiments were carried out to examine the effects of initial pH values of methyl orange solution on the photocatalytic reaction. The catalyst used was the Cu-doped mesoporous TiO₂. The initial pH values of the test solution were in amplitude pH of 3–10 adjusted with HCl or NaOH without any modification during UV irradiation. All the other experimental conditions were identical [16].

Figure 10 demonstrated the degradation efficiency of methyl orange under different initial pH values of solution,

FIGURE 5: (a) TEM image of Cu-doped mesoporous TiO_2 ; (b) SEM image of Cu-doped mesoporous TiO_2 .

FIGURE 6: Particle size distribution of Cu-doped mesoporous TiO_2 .

FIGURE 8: UV-Vis DRS of selected catalysts.

FIGURE 7: Nitrogen adsorption and desorption isotherms of pure TiO_2 , Mesoporous TiO_2 , and Cu-doped mesoporous TiO_2 .

FIGURE 9: Photocatalytic degradation curves of photocatalysts.

FIGURE 10: Effects of initial pH on the degradation of methyl orange by Cu-doped mesoporous TiO₂.

and a higher methyl orange degradation efficiency at acidic pH can be noticed. The reason that the photodegradation efficiency of MO depended on solution pH was due to the absorption/desorption of MO on TiO₂ surface. In acidic solution, TiO₂ was positively charged and absorbed MO molecules by electrostatic attraction; in alkaline solution, TiO₂ was negatively charged and the absorption of MO molecules became weaker due to repulsive forces [17].

4. Conclusions

Cu-doped mesoporous TiO₂ was prepared by a hydrothermal method. The results confirmed that the high photocatalytic activity of as-prepared sample strongly depended on the stabilization of Cu (I) well dispersed in TiO₂. Copper doping greatly enhanced the absorption in visible-light region and played a significant role for enhancing the photocatalytic activity of the catalysts. Moreover, mesoporous structures with larger specific surface area, pore size, and the relatively regular channel structure had better adsorption capacity.

Conflict of Interests

The authors declare that they have no financial and personal relationships with other people or organizations that can inappropriately influence their work, and there is no professional or other personal interest of any nature or kind in any product, service, and/or company that could be construed as influencing the position presented in, or the review of, this paper.

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