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Synthesis of Cu²⁺ doped mesoporous titania and investigation of its photocatalytic ability under visible light

Le Yu, Shuai Yuan *, Liyi Shi **, Yin Zhao, Jianhui Fang

Research Center of Nanoscience and Nanotechnology, Shanghai University, 99 Shangda Road, Shanghai 200444, PR China

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ABSTRACT

A simple method to prepare Cu²⁺ doped mesoporous TiO₂ with improved visible sensitive photocatalytic activity is reported. The mesoporous samples were characterized by low angle and wide angle X-ray diffraction (XRD), transmission electron microscopy (TEM), N₂ adsorption–desorption, X-ray photoelectron spectra (XPS) and UV–visible absorbance spectroscopy. The degradation of methylene blue under visible light irradiation was investigated to evaluate the photocatalytic activity of these materials. Analytical results demonstrate that Cu²⁺ doping amount is crucial to affect the photocatalytic ability of the mesoporous titania. Among the samples, 0.05 at.% Cu²⁺ doped mesoporous TiO₂ exhibits the highest photocatalytic activity.

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1. Introduction

Environmental pollution has increased public concern nowadays and the photocatalytic degradation of organic pollutants in waste water has been the subject of numerous investigations in recent years. In this field, TiO₂ photocatalyst has led the relevant applications to the stage of commercialization due to its photochemical stability, low cost and non-toxicity [1–4].

Nevertheless, there are still three key issues to be resolved which limit the application of titania as a photocatalyst. One issue is to increase the specific surface area of TiO₂, which may enhance the light harvesting and the adsorption for reactant molecules [5]. As TiO₂ is activated only by irradiated under ultraviolet (UV) light, the other key issue is to make it visible light sensitive, which will increase the efficiency of solar energy utilization. Furthermore, TiO₂ presents a relatively high electron–hole recombination rate, which is restrictive to its photocatalytic activity [6].

Herein, mesoporous TiO₂ may show greater potentiality in photocatalytic application, as a result of its well-defined pore structure, high surface-to-volume ratio, enhanced accessibility and framework composition [7]. Many researches have been investigated to prepare highly ordered mesoporous TiO₂ since 1995. Among them, evaporation induced self-assembly (EISA) method is demonstrated to be a promising strategy to obtain mesoporous structures with highly crystalline frameworks [8–11].

In order to enhance its utilization ratio of solar energy and indoor light, doping with metal ions has been attempted. Generally,

the introduction of doped ions can result in the formation of a doping energy level between the conduction and valence bands of TiO₂, and thus shifts the absorption band to the visible region [6,12]. Besides, transition metal ions can increase the quantum efficiency of the photocatalytic property of titania by influencing generation and recombination of the charge carriers under light [13]. There are some examples in the literatures of the metal-doping systems to make TiO₂ visible light sensitive [14–16]. Especially, the activity of Cu²⁺ ion as a catalyst in many oxidation and reduction reactions makes it very attractive as a doping agent for titania [17–19].

Hence, it makes sense to introduce Cu²⁺ species into mesoporous TiO₂. But neither traditional impregnation nor ion exchange method is a good choice. The former will give rise to surface segregation of metal ions, and the latter will cause the drain of doping ions. Based on our previous works [10,20], a simple and effective route is reported in this contribution to obtain Cu²⁺ doped mesoporous TiO₂ with large specific surface by EISA strategy. Cu²⁺ species were introduced to the system along with Ti⁴⁺ precursor. During the whole process, there was no loss of dopant except volatile matters and organic template. The photocatalytic activities of these mesoporous materials were evaluated by degradation of methylene blue under the irradiation of fluorescent light.

2. Experimental section

2.1. Chemicals

Tetrabutyl titanate (Ti(OBu)₄) and methyl blue were CP grade. Butyl alcohol (BuOH), hydrochloric acid (36–38%) and cupric

* Corresponding author. Tel./fax: +86 21 66134852.

** Corresponding author. Tel./fax: +86 21 66134852.

E-mail addresses: s.yuan@shu.edu.cn (S. Yuan), shiliyi@shu.edu.cn (L. Shi).

nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) were all AR grade. $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ (P-123) was a commercial product from Aldrich.

2.2. Synthesis of Cu^{2+} doped mesoporous TiO_2

In the typical synthesis process, P-123 was dissolved in BuOH under vigorous stirring for 30 min. Then $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Ti}(\text{O}-\text{Bu})_4$ were added into the P-123 solution, followed by stirring for an additional 60 min. The solution consisting of hydrochloric acid and an amount of additional water was added dropwise to the above mixture under stirring. In all conditions the molar ratio of P-123:HCl:H₂O:BuOH:Ti was kept 0.025:1:6.5:6.5:1, while the molar ratio of Cu:Ti varied from 0 to 0.20 at.%. After 30 min, the transparent sol was transferred from reactor to an open flat glass (30 cm × 30 cm). The sol extended sufficiently and formed a uniform thin layer. In the aging stage, the environmental humidity was kept at 75% by saturated NaCl solution in the first day. After aging at 298 K for 4 day, at 413 K for 2 h and then at 473 K for 2 h, the crack-free thin layer was calcined at 673 K for 2 h in air-flow. The heating-up rate was 1 K min⁻¹. Then the samples were cooled to room temperature in the muffle.

The samples prepared with different doping content of cupric ions are noted as TiO_2 -*n*. For example, TiO_2 -0.05 means the molar ratio of Cu/Ti is 0.05 at.% (0.0005:1).

2.3. Characterization

Low angle X-ray diffraction (LAXRD) patterns of all samples were collected in θ - 2θ mode using Rigaku D/MAX-2550 diffractometer (Cu $K\alpha_1$ radiation, $\lambda = 1.5406 \text{ \AA}$), operated at 40 kV and 200 mA. Wide angle XRD (WAXRD) diagrams were collected in the same mode, but operated at 100 mA. The crystallite size was estimated by applying the Scherrer equation to the FWHM of the (1 0 1) peak of anatase, with α -silicon (99.9999%) as a standard for the instrumental line broadening.

The sample morphology was observed under transmission electron microscopy (TEM) on a JEOL 200CX microscope (200 kV) using copper grids. The porous texture of the powders was analyzed from nitrogen adsorption-desorption isotherms at 77 K. By using a Micromeritics ASAP 2000 system, the BET and BJH methods were applied for the determination of the specific surface area, and the mean mesopore equivalent diameter, respectively. These samples were degassed over 6 h at 473 K before N_2 adsorption-desorption analysis. X-ray photoelectron spectroscopy (XPS) measurements were carried out under ultra high vacuum ($<10^{-6}$ Pa) at a pass energy of 93.90 eV on a Perkin-Elmer PHI 5000C ESCA system equipped with a dual X-ray source by using Mg-K α (1253.6 eV) anode. All binding energies are calibrated by using contaminant carbon (C 1s = 284.6 eV) as a reference. UV-visible absorbance spectra were obtained for the dry-pressed disk samples using a Scan UV-visible spectrophotometer (Varian, Cary 500) equipped with an integrating sphere assembly, using BaSO_4 as reflectance sample. The spectra were recorded at room temperature in air, in the range 300–500 nm.

The visible light photocatalytic activity of the prepared Cu^{2+} doped mesoporous TiO_2 samples was evaluated from an analysis of the photodegradation of methylene blue (MB) solution under irradiation of fluorescent lamp (Philip, TCH-114, 28 W). The lamp possesses strong emission wavelength at visible region ($\lambda \geq 400 \text{ nm}$). Commercial TiO_2 (Degussa P-25) was used as a reference photocatalyst to compare the activity of the samples prepared. Titania powder (0.05 g) was dispersed in 50 ml methylene blue solution (6 mg L^{-1}) by 10 min ultrasonic treatment. After stirring for 30 min, the adsorption was balanced. The distance between the light source and the reaction tubes was 3 cm. The progress of reactions was monitored by later with a SPSIC

760CRT UV-visible spectrophotometer every 2 h. The photocatalytic degradation of MB was calculated from the following

$$\text{MB degradation (\%)} = (C_0 - C_r) / C_0 \times 100\% \quad (1)$$

Here C_0 stands for the original MB concentration after the adsorption/desorption reached equilibrium, C_r stands for the residual MB concentration after reaction.

3. Results and discussion

3.1. Structure analysis

The mesoporous structure of Cu^{2+} doped TiO_2 was characterized by low angle X-ray diffraction (LAXRD), TEM images and N_2 adsorption-desorption. Fig. 1 displays LAXRD patterns of TiO_2 samples calcined at 673 K. The well-resolved (1 0 0) diffraction peak suggests the existence of ordered mesoporous structure in the sample TiO_2 -0 to TiO_2 -0.10. However, for the sample TiO_2 -0.20, there is no such significant peak, indicating the loss of long-range order and the collapse of mesostructure.

Highly crystalline architectures provide a direct and rapid pathway for charge transport and decrease the carrier-path length, which in turn reduce recombination losses. As a result, crystallized mesoporous TiO_2 offers unique advantages for application in photocatalysis [21]. Wide angle powder XRD (WAXRD) patterns confirm that all the samples are well crystallized. Six distinctive peaks of TiO_2 are found at 25.26°, 38.16°, 48.17°, 54.03°, 55.12° and 64.69° in Fig. 2, corresponding to reflection planes of crystal of anatase (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 1 1), and (2 0 4), respectively (as per JCPDS 84 1285). The crystallite size of anatase was calculated by Scherrer equation to the FWHM of the (1 0 1) anatase peak. For the sample TiO_2 -0, its crystallites size is 11.5 nm. The dopant enhances the growth of the TiO_2 nanocrystals. The crystallites size of anatase increases from 11.5 to 12.1 nm with the increase of doping amount. As it can be seen in LAXRD for sample TiO_2 -0.20, the crystal growth is reported to be one of the reasons for the collapse of mesoporous structure [22].

Just as TEM images shown in Fig. 3, the long-range ordered mesoporous geometry is maintained when the doping amount is relatively low and the wall thickness is 5 nm. The average size of anatase nanocrystals obtained from the Scherrer equation is larger than the wall thickness. Ozin and his group proposed that when crystallites meet at this interface between the channel walls and

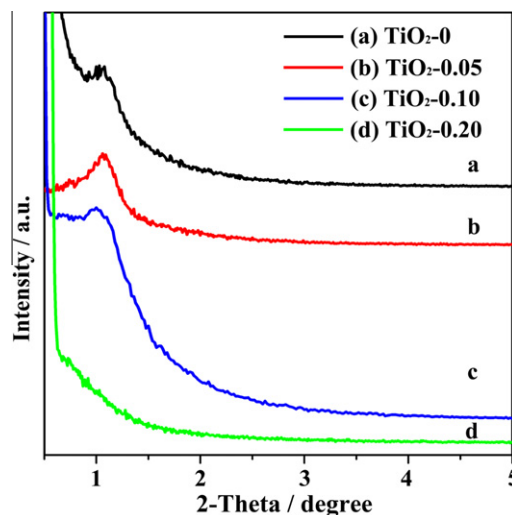


Fig. 1. Low angle XRD patterns of the samples: (a) TiO_2 -0, (b) TiO_2 -0.05, (c) TiO_2 -0.10, and (d) TiO_2 -0.20.

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