Photocatalytic degradation of methyl orange with W-doped TiO₂ synthesized by a hydrothermal method

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ABSTRACT

Nanosized W-doped TiO₂ photocatalysts were synthesized by a simple hydrothermal method, and characterized by energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), transmission electron microscopy (TEM) and BET surface area analyzer. The photocatalytic activity of undoped TiO₂ and W-doped TiO₂ photocatalysts was evaluated by the photocatalytic oxidation degradation of methyl orange in aqueous solution. The results show that the photocatalytic activity of the W-doped TiO₂ photocatalyst is much higher than that of undoped TiO₂, and the optimum percentage of W doped is 2.0 mol%. The enhanced photocatalytic activity of the doped photocatalyst may be attributed to the increase in the charge separation efficiency and the presence of surface acidity.

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1. Introduction

Semiconductor photocatalysts have been gathering much attention due to their various applications to the environmental purification and dye sensitized photovoltaic solar cell [1]. Among various oxide semiconductor photocatalysts, titanium oxide (TiO₂) has been proven so far to be the most promising material used for both fundamental research and practical applications because of its high photoreactivity, biological and chemical inertness, cost effectiveness, non-toxicity, and long-term stability against photocorrosion and chemical corrosion. Anatase TiO₂ has been identified as the most effective and useful photocatalyst under near UV illumination [2]. Absorption of UV light excites electrons from the valence to the conduction band, creating electron–hole pairs with a high oxidative potential associated to the photo-generated holes and leading to highly oxidizing OH• hydroxyl radicals, which both initiate redox reactions with adsorbed surface species [3].

However, it has been also known that this type of photocatalyst has two typical defects. Firstly, TiO₂ is a high-energy band material that can only be excited by high energy UV irradiation. This

practically rules out the use of sunlight as an energy source for the photoreaction. Secondly, a low rate of electron transfer to oxygen and a high rate of recombination between excited electron/hole pairs result in a low quantum yield rate and also a limited photooxidation rate [4].

To improve photocatalytic activity of TiO₂ for wide range applications, several approaches [5–7] have been developed, including doping techniques, and nanosized process of enhancing the specific surface area of catalysts. Coupling of different kinds of semiconductor photocatalysts is a promising way and can enhance photocatalytic response to visible light by increasing the charge separation and extending wavelength for photoexcitation, so that the photocatalytic efficiency for liquid and gas phase reactions was increased [8,9]. Recently, most studies have been focused on the photocatalytic properties of metal ion-doped TiO₂, such as Fe [10], Cr [11], Co [12], Mn [13], Ag [14] and V [15] ions. The doping of metal ions, especially transition metal ions, makes it possible for TiO₂ to absorb visible light. Iwasaki et al. [12] reported that TiO₂ doped with Co²⁺ ions has highly photocatalytic activities under visible light irradiation as well as under UV–vis light irradiation. Sakata et al. [16] demonstrated that the photocatalytic activity of Cu⁺ doped TiO₂ particles is available under the irradiation $\lambda < 600$ nm. The band gap energy of WO₃ is 2.5 eV [17], which falls within the solar spectrum. Introducing WO₃ into TiO₂ was proved to be attractive for photocatalysis research [18,19]. The results showed that coupling TiO₂ with WO₃ presented improved photocatalytic performances compared with the corresponding bare oxides, and the

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Fig. 1. EDXA spectrum of the as-prepared 2.0 mol% W-doped TiO_2 photocatalyst.

mixed-oxide could be excited using visible light, i.e. with $E < 3.2$ eV [4].

Hydrothermal method is known as one of the excellent processes for nanocrystalline state synthesis [20], where low reaction temperature is available, and uniformity of product composition, phase and microstructure can be obtained. However, there have been few reports on the hydrothermal method applied to synthesize W-doped TiO_2 nanoparticles. In this study, nanosized W-doped TiO_2 photocatalysts were successfully synthesized by a simple hydrothermal method at a low synthetic temperature. By the photocatalytic degradation of methyl orange, the effect of W contents and the synthetic temperature on the photocatalytic activity of products were investigated.

2. Experimental

2.1. Catalysts preparation

$\text{Ti}(\text{SO}_4)_2$ and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ were used as starting materials, both of them are analytic grade without further purification. In a typical synthesis, 10 g $\text{Ti}(\text{SO}_4)_2$ and 0.28 g $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ were mixed in 70 ml of distilled water to form an aqueous solution. After stirring for 0.5 h, the solution was poured into a Teflon-lined stainless autoclave with 100 ml capacity. The autoclave was sealed and heated, and then

kept at a certain temperature in a range from 120 to 210 °C for 3 h. The resulting product was separated by centrifugation, and washed with distilled water and alcohol for several times, respectively, and finally, dried at 70 °C for 3 h. The sample was labeled as 2.0 mol% W-doped TiO_2 . Similarly, 0.5, 1.0, 3.0, 4.0 mol% W-doped TiO_2 and undoped TiO_2 samples were also prepared by repeating the above procedure, where undoped TiO_2 sample was prepared without adding $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$.

2.2. Characterization

To determine the crystal phase composition of the prepared photocatalysts, X-ray diffraction (XRD) patterns were obtained at room temperature using an X-ray diffractometer (D/max-rB, Rigaku, Japan). The X-ray source was $\text{Cu K}\alpha$ radiation. Energy dispersive X-ray spectroscopy (EDX) was taken on SEM (XL30, Philips) with US Phoenix EDX. Transmission electron microscopy (TEM) images were obtained by using a transmission electron microscope (JEM-1200 EX, Japan) to observe the particle size and morphology of the as-prepared photocatalysts. BET surface areas of the products were measured with a surface area and pore size analyzer (NOVA 1000e, Quantachrome Instruments Co., America). Samples were also studied by UV–vis absorption spectra using a U-3010 spectrophotometer (Japan).

2.3. Photocatalytic degradation experiments

The photocatalytic activity of the as-prepared powders was evaluated by comparing the degradation rates of methyl orange in aqueous solution. The photocatalyst (500 mg) was mixed in a Pyrex glass beaker with an aqueous solution of methyl orange (20 mg l^{-1} , 500 ml). Prior to UV light irradiation, the suspension was stirred for 30 min under oxygen atmosphere in dark conditions. It was then irradiated

Fig. 2. XRD patterns of 2.0 mol% W-doped TiO_2 photocatalyst obtained by the hydrothermal method at: (a) 120 °C, (b) 150 °C, (c) 180 °C and (d) 210 °C for 3 h.

Fig. 3. XRD patterns of W-doped TiO_2 photocatalysts obtained by the hydrothermal method at 150 °C for 3 h: (a) TiO_2 , (b) 0.5 mol% W- TiO_2 , (c) 1.0 mol% W- TiO_2 and (d) 4.0 mol% W- TiO_2 . Inset: the expanded view in the range of 22–28°.

at 25 °C using UV light from a 400-W high-pressure Hg lamp (with a maximum emission at about 365 nm) with continuous stirring under oxygen atmosphere. At periodic intervals, 5 ml suspension were taken from the system, centrifuged, and filtered through a 0.2- μ m millipore filter to remove the photocatalyst particles. The filtrates were then analyzed by using a spectrophotometer (723, Shanghai spectrum Instruments Co., Ltd.) at its maximum absorption wavelength of 464 nm [21].

3. Results and discussion

3.1. Characterization studies of the photocatalysts

In order to confirm whether W element existed in the as-prepared photocatalysts, a qualitative analysis of elemental compositions was performed on the samples by EDX. Fig. 1 shows a typical EDX spectrum of 2.0 mol% W-doped TiO₂ sample, whose

peaks can be only assigned to Ti, W and O (C peak arises from the electric pastern used). It is clear that W has been doped in TiO₂.

Fig. 2 shows XRD patterns of the as-prepared W-doped TiO₂ powders, obtained by the hydrothermal process at various synthetic temperatures from 120 to 210 °C for 3 h. Obviously, with the increase of the synthetic temperature, XRD peaks in intensity increase and become sharper, which imply that the crystallization of W-doped TiO₂ powders becomes more perfect on increasing the synthetic temperature. All the peaks can be indexed to anatase structure and the diffraction peaks characteristic of WO₃ cannot be found in XRD patterns. The similar results have been observed by other authors: Ma et al. [22] proposed that amorphous tungsten oxide phase covered the TiO₂ surface, while Shifu et al. [19] reported that WO₃ was highly dispersed in the bulk phase of the

Fig. 4. TEM images of the as-prepared photocatalysts obtained by the hydrothermal method at different synthetic temperatures for 3 h: (a) TiO₂ (150 °C), (b) 2.0 mol% W-TiO₂, (150 °C) and (c) 2.0 mol% W-TiO₂ (210 °C).

catalyst. However, our XRD patterns for the as-prepared samples with different amounts of doped W in Fig. 3 illustrate that doped WO_3 forms a solid solution with TiO_2 . As revealed in Fig. 3, when the W-doped amount is increased, the diffraction peaks shift a little toward higher angles. It is well known that the diffraction angles are related to the lattice parameters based on the Bragg equation:

$$d_{(hkl)} = \frac{\lambda}{2 \sin \theta}$$

$$d_{(hkl)}^{-2} = h^2 a^{-2} + k^2 b^{-2} + l^2 c^{-2}$$

where $d_{(hkl)}$ is the distance between the crystal planes of (hkl) ; λ is the wavelength of X-ray used in the experiment; θ is the diffraction angle corresponding to the crystal plane (hkl) , and a , b , and c are lattice parameters. Because the ionic radius of W^{6+} is a little smaller than that of Ti^{4+} (the coordination number of them is all 6) [23], and the cell volume after W ion substituted for Ti ion will become smaller to result in an increase in the diffraction angle. Furthermore, the diffraction angle will gradually increase with doped W amount, as shown in Fig. 3. So it suggests that WO_3 has formed a solid solution with TiO_2 phase with absence of secondary phase. However, the products prepared by physical [19] or chemical [24] method were reported to be just the mixture of two phases of TiO_2 and WO_3 , rather than a solid solution. It means that the phase/chemical compositions of the W-doped TiO_2 catalysts can be changed by different synthetic processes.

Surface areas of undoped and doped TiO_2 powders are given in Table 1. The results show an increase in surface area of the doped materials compared with the undoped counterpart synthesized at the same synthetic temperature of 150°C . The undoped TiO_2 has a specific surface area of $110.24 \text{ m}^2 \text{ g}^{-1}$ while that of the 0.5 mol% W-doped sample increases to $166.68 \text{ m}^2 \text{ g}^{-1}$. Then, the surface area decreases a little with further increasing the W-doped amount. Even so, the surface area of 3.0 mol% W-doped TiO_2 sample ($131.29 \text{ m}^2 \text{ g}^{-1}$) is still notably larger than that of undoped TiO_2 . It implies that introducing W into TiO_2 would curb the growth of the catalyst crystallites. On the other hand, Table 1 also indicates that the synthetic temperature is a significant factor that affects the surface area. On increasing the temperature from 120 to 150°C , the surface area increases considerably from 55.59 to $152.34 \text{ m}^2 \text{ g}^{-1}$. Nevertheless, further elevating the temperature would lead to obvious decrease in surface area possibly due to particle aggregations.

Fig. 4 presents the typical TEM images of undoped TiO_2 and 2.0 mol% W-doped TiO_2 photocatalysts synthesized by the hydrothermal method. Obviously, the crystallites obtained at the same synthetic temperature of 150°C are spherical particles. The average particle size of W-doped TiO_2 crystallites, compared with that of undoped TiO_2 decreases markedly from ca. 75 nm to ca. 6.5 nm . Meanwhile, the comparison of Fig. 4b with c proves that a soft aggregation appears at 210°C due to the increase of the synthetic temperature. This is in agreement with the XRD and BET surface area results.

Table 1

BET surface areas of undoped TiO_2 and W-doped TiO_2 photocatalysts obtained by the hydrothermal method

Sample	W content (mol%)	Synthetic temperature ($^\circ\text{C}$)	BET surface area ($\text{m}^2 \text{ g}^{-1}$)
TiO_2	0	150	110.24
0.5% W- TiO_2	0.5	150	166.68
3.0% W- TiO_2	3.0	150	131.29
2.0% W- TiO_2	2.0	120	55.59
2.0% W- TiO_2	2.0	150	152.34
2.0% W- TiO_2	2.0	180	124.18
2.0% W- TiO_2	2.0	210	76.61

Fig. 5 shows a typical absorption spectrum of W-doped TiO_2 , the onset of the absorption appears at about 410 nm . Obviously, it has red-shifted, compared with the onset of bulk anatase TiO_2 ($\lambda_E = 387 \text{ nm}$). It implies that the W-doped TiO_2 particles prepared in the present study should have a good photocatalytic potential not only in the ultraviolet light but also in the visible light region.

3.2. Photocatalytic activity of the as-prepared powders on the degradation of methyl orange

The effect of the synthetic temperature in the hydrothermal process on the photocatalytic activity of W-doped TiO_2 photocatalysts (2.0 mol% W-doped TiO_2) is shown in Fig. 6. It can be seen that the photocatalytic activity of W-doped TiO_2 increases when the synthetic temperature is increased from 120 to 180°C , but decreases significantly when further increased to 210°C . The main reason may be attributed to the influences of the surface area, the crystallization and aggregations of the photocatalyst crystallites. From Table 1, it can be known that the largest surface area of the 2.0 mol% W-doped TiO_2 photocatalyst appears when the synthetic temperature is 150°C . As the temperature increases to 180°C , without an obvious change in the surface area, but the W-doped TiO_2 photocatalyst has a better crystallization with accompanying the growing up of the crystallites, as shown in Fig. 2. The more perfect crystallization would lead to a better photocatalytic activity. The lower photocatalytic activity of photocatalysts obtained at higher or lower synthetic temperatures than 180°C should be assigned to a smaller surface area due to particle aggregations and/or bad crystallization, which is supported by TEM micrographs (Fig. 4) and XRD patterns (Fig. 2).

To evaluate the photocatalytic activity of the W-doped TiO_2 and find out the optimum amount of W doping, a series of degradation experiments on methyl orange were carried out by using different W-doped amounts of TiO_2 photocatalysts ranging from 0.0 to 4.0 mol%, and the results are given in Fig. 7. It demonstrates that all the W-doped TiO_2 photocatalysts, in general, are better in photodegradation efficiency than the undoped TiO_2 , and that 2.0 mol% W-doped TiO_2 photocatalyst achieves the highest efficiency. It is noteworthy that too high W amount seems to be detrimental to the photodegradation of methyl orange. W doping can promote the charge pair separation efficiency for TiO_2 photocatalysts in a certain range of W amount. Since W(VI) can be easily reduced to W(V) [25], the photoexcited electrons in the conduction band of TiO_2 can be accepted by W^{6+} in the solid solution [8], following the scheme

Fig. 5. UV-vis absorption spectrum of 0.5 mol% W- TiO_2 synthesized at 150°C for 3 h.

Fig. 6. The effect of different synthetic temperatures in the hydrothermal process on the photocatalytic activity of obtained 2.0 mol% W-doped TiO_2 photocatalysts (initial concentration of the methyl orange = 20 mg l^{-1} and photocatalyst = 1 g l^{-1}).

Fig. 7. The effect of W-doped amount on methyl orange degradation reaction (initial concentration of the methyl orange = 20 mg l^{-1} and photocatalyst = 1 g l^{-1}).

$\text{W}^{6+} + e_{(\text{TiO}_2)\text{cb}}^- \rightarrow \text{W}^{5+}$. In this case, the doped W helps in trapping of photogenerated electrons so as to limit the charge recombination, which is one of the limiting factors in photocatalytic reactions of TiO_2 . However, too high-loaded W would act as recombination centers for electron– h^+ pairs, according to the following schemes:

Therefore, as observed and confirmed in this paper, an optimum W-doped content is required to optimize its role of photogenerated electron trapping. As shown in Fig. 7, the optimum amount is about 2.0 mol%.

In addition, the enhanced photocatalytic efficiency of the W-doped TiO_2 is also attributed to the presence of a surface acidity. Keller et al. [26] reported that WO_3/TiO_2 catalysts would exhibit

surface acidity issued from the presence of Lewis and Bronsted acidic sites related to W^{6+} species. The acidic surface has a higher affinity for species with unpaired electrons, so it may adsorb a greater amount of OH^- or H_2O , which is considered to be necessary for the generation of OH radicals, and increase the hydrophilic properties of the surface. At the same time, the catalyst is able to more easily adsorb organic pollutants with polarized functional groups, which have high affinities with acidic surfaces.

4. Conclusions

W-doped TiO_2 photocatalysts were successfully synthesized at a low temperature of 120°C by a hydrothermal process. The photocatalytic activity of the prepared materials was investigated by the photocatalytic oxidation of methyl orange in aqueous solution. The sample prepared at 150°C with 2.0 mol% W-doped amount has the highest photocatalytic activity. The enhanced photocatalytic efficiency could be attributed to the presence of electron-trapping centers (W^{6+}) in the W-doped TiO_2 solid solutions and surface acidity.

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