XPS Study of Copper Doping TiO₂ Photocatalyst

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Abstract The copper doped titanium dioxide was prepared by immersion method. Photocatalytic activity was investigated with acetic acid as a model reactant, and the photocatalyst was analyzed by means of XPS. The enhanced degradation rate of acetic acid is attributed to increased charge separation and interfacial charge-transfer rate on the surface of the doped photocatalyst.

Keywords: Photocatalytic oxidation, Acetic acid, Copper ion doping, Titanium dioxide, XPS

1 Introduction

The photocatalytic destruction of organic pollutants on semiconductor surfaces is a promising and emerging process for water and air pollution control. Among all oxide semiconductors that have been studied, TiO₂ particles is the most effective for its high photoactivity and stability^[1]. It has been shown that the photocatalytic activity of TiO₂ depends, in part, upon the relative degree of branching of the reactive electron/hole pairs into interfacial charge-transfer reactions^[2]. In order to enhance interfacial charge-transfer reactions, it is essential to inhibit electron/hole pair recombination in TiO₂. A variety of methods^[3-5] such as modification of the TiO₂ surface by noble metals, coupling of two semiconductor particles with different energy levels and selective metal ion doped of TiO₂ matrix have been used for the purpose. Although several transition metal ion dopants in TiO₂ have been investigated previously^[2], there were very few reports about copper ion doping TiO₂. In this paper, copper ion doped TiO₂ was prepared by the immersion method. The photocatalytic activity as measured by the photocatalytic oxidation of acetic acid and the XPS study of copper ion doped TiO₂ are presented.

2 Experimental

The copper-doped TiO₂ was prepared by immersion method according to the following procedure: TiO₂ powders with anatase phase, which were prepared from the controlled hydrolysis of titanium tetrachloride^[6], were impregnated with Cu(NO₃)₂ aqueous solution under ultrasonic irradiation. The impregnated sample was dried at 373 K for 8 h and calcined at 723 K for 2 h in air. Based upon the assumption of quantitative incorporation of the dopant, the samples with a doping level from 0.08% to 10% (mass fraction *w*) were prepared according to the above procedure

by altering the amount of Cu²⁺ in Cu(NO₃)₂ aqueous solution.

The photocatalytic experiments were carried out in a glass photochemical reactor^[11] containing 0.6 g catalyst and 300 mL of 250 mg · L⁻¹ acetic acid. The immersion type UV-light source was a 125 W medium pressure, mercury vapor lamp with a maximum emission at approximately 365 nm. Photocatalytic activity was measured by the removal rate *D*(%) of acetic acid in 2.5 h, which was calculated by a standard analyzing method similar to that reported by Feng^[7] except that the contributions of photolysis and adsorption of reactant to removal rate has been subtracted.

3 Results and Discussion

Table 1 shows the comparison of photocatalytic activity between pure TiO₂ and copper-doped TiO₂.

It can be seen clearly that the removal rate varies with the dopant concentration, *i. e.* when the concentration ranges from 0.08% to 2%, the removal rate is always higher for the copper-doped TiO₂ than the pure TiO₂, and the highest one was found at the dopant concentration of 0.2%. It is, however, getting lower when the dopant concentration becomes higher than 2%.

The sample with the dopant concentration of 0.2% (*w*) was selected to study further in order to disclose the mechanism of the

Table 1 Comparison of photocatalytic activity before and after copper doping

Dopant concentration (%) , <i>w</i>	0	0.08	0.2	0.8	2	10	100
Removal rate <i>D</i> (%)	21.52	55.2	63.16	35.82	22.62	9.3	4.7

w: mass fraction

Fig. 1 The curve-fitting of the $\text{Cu}2p_{3/2}$ XPS of the copper-doped TiO_2

improved reactivity by doping. XRD analysis of copper-doped TiO_2 catalyst found no phase other than TiO_2 with anatase phase. Considering the low level dopant concentration (0.2%), copper species are either in the TiO_2 lattice or strongly bound and well dispersed on the surface of TiO_2 as indicated by Jian^[8].

Catalyst surface composition was studied by XPS, and surface copper content was found to be 0.8%, which is higher than the bulk one 0.2%. Fig. 1 shows the curve-fitting of the $\text{Cu}2p_{3/2}$ XPS of the copper doped TiO_2 .

From Fig. 1, it can be seen that two peaks exist, indicating that there are two kinds of copper species on the surface. Binding energy of 932.1 eV is characteristic for Cu_2O , while higher binding energy of 933.68 eV is characteristic for CuO ^[9]. It is supposed that coexistence of Cu^{2+} and Cu^+ can improve the photocatalytic efficiency through the following ways:

On the one hand, Cu^{2+} can trap the excited electron in conduction band, inhibiting the electron/hole pair recombination, on the other hand, Cu^+ can give electron to the oxygen adsorbed on the surface of catalyst, thus accelerating the interfacial electron transfer.

Table 2 shows the fitting results of $\text{O}1s$ XPS of the catalysts. From Table 2, it can be seen that there exist two kinds of oxygen species, i. e. the lattice oxygen and adsorbed oxygen^[10] on the surface of the sample before and after doping, but the content of adsorbed oxygen is raised on the sample after doping. It is well known that the adsorption oxygen is very important for trapping the excited electron to suppress the recombination with hole^[11]. Thus the doped catalyst has higher activity than the non-doped counterpart.

Table 3 gives the fitting results of $\text{O}1s$ and $\text{Cu}2p_{3/2}$ XPS of the catalysts with different dopant concentration. From Table 3, it

Table 2 Fitting results of $\text{O}1s$ XPS

	E_{BE}/eV	Oxygen species	Content(% , φ)
Before doping	529.60	Lattice oxygen	81.97
	530.65	Adsorption oxygen	10.03
After doping	529.45	Lattice oxygen	62.5
	530.59	Adsorption oxygen	37.5

φ : volume fraction

Table 3 Fitting results of $\text{O}1s$ and $\text{Cu}2p_{3/2}$ XPS of the catalysts

Dopant concentration(% , w)	0	0.08	0.2	2	10
Adsorption oxygen content(% , φ)	10.03	33.45	37.50	39.79	44.01
Cu^+ content(% , w)	0	27.25	36.31	25.52	0

w : mass fraction; φ : volume fraction

can be seen that the content of adsorbed oxygen rises with increasing of dopant concentration, in the mean time, Cu^+ content rises before the concentration reaches 0.2% (w), but then decreases and single Cu^{2+} species remains at the concentration of 10%. If the relation between photocatalytic activity and the content of Cu^+ and adsorbed oxygen is considered, it can be concluded that the coexistence of Cu^{2+} and Cu^+ is indispensable for the improving activity and the higher Cu^+ content, the higher photocatalytic activity. Although the higher adsorption oxygen at the dopant concentration of 10% does not result in the higher photocatalytic activity, the role of adsorbed oxygen in improving activity can not be ignored in the process of trapping of the excited electron. The disappearance of Cu^+ , the less amount of light absorbed by TiO_2 and the heterogeneity formation resulting from the surface enrichment of CuO at this dopant concentration may be responsible for the decreasing reactivity.

4 Conclusions

The photocatalytic activity of TiO_2 can be significantly improved by doping copper. The raised content of adsorbed oxygen and coexistence of Cu^{2+} and Cu^+ are believed to be responsible for the improved photocatalytic activity.

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掺铜二氧化钛光催化剂的 XPS 研究

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摘要 利用浸渍法制备了铜掺杂的二氧化钛, 以乙酸为模型物研究了催化剂的光催化活性, 利用 XPS 结果对改性后的催化剂进行了分析. 结果表明, 改性后的催化剂表面吸附氧的提高和 Cu⁺/Cu²⁺ 的共存有利于光生载流子的分离和界面电子转移, 因而改善了催化剂的光催化性能.

关键词: 光催化氧化, 乙酸, 铜掺杂, 二氧化钛, XPS

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