Preparation and photocatalytic performance of Cu-doped TiO$_2$ nanoparticles

Xi-jia YANG, Shu WANG, Hai-ming SUN, Xiao-bing WANG, Jian-she LIAN

Key Laboratory of Automobile Materials of Ministry of Education, College of Materials Science and Engineering, Jilin University, Changchun 130025, China

Received 1 February 2014; accepted 16 May 2014

Abstract: Cu-doped TiO$_2$ nanoparticles with different doping contents from 0 to 2.0% (mole fraction) were synthesized through sol–gel method. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and field emission scanning electron microscope (FE-SEM) were used to characterize the crystalline structure, chemical valence states and morphology of TiO$_2$ nanoparticles. UV–Vis absorption spectrum was used to measure the optical absorption property of the samples. The photocatalytic performance of the samples was characterized by degrading 20 mg/L methyl orange under UV–Vis irradiation. The results show that the Cu-doped TiO$_2$ nanoparticles exhibit a significant increase in photocatalytic performance over the pure TiO$_2$ nanoparticles, and the TiO$_2$ nanoparticles doped with 1.0% Cu show the best photocatalytic performance. The improvement in photocatalytic performance is attributed to the enhanced light adsorption in UV–Vis range and the decrease of the recombination rate of photoinduced electron–hole pair of the Cu-doped TiO$_2$ nanoparticles.

Key words: TiO$_2$; Cu; nanoparticles; photocatalysis; doping; sol–gel method

1 Introduction

Industrial waste water and by-products produced by oxidation are clearly a threat to the ecological environment [1]. How to eliminate such contaminants in water arouses a hot spot in today's scientific research. Photocatalytic degradation of effluents is the simple and environment-friendship technology and has developed rapidly in recent years. TiO$_2$, as a promising semiconductor photocatalyst, has been widely used in wastewater treatment on account of its unique photo-electric properties, high chemical stability, low cost and safety toward both humans and the environment [2–5].

As a wide band semiconductor oxide, the largest wavelength of incident light for TiO$_2$ (anatase) is about 387 nm. Therefore, the photocatalytic efficiency is limited by the inadequate utilization of the sunlight. Meanwhile, the high recombination rate of photogenerated electron (d$^-$)-hole (h$^+$) pair also decreases the photocatalytic activity of TiO$_2$ [6]. In order to optimize the photocatalytic performance of TiO$_2$, different preparation methods [7–10] and a lot of modification methods have been tried [11–14]. The doping of transition metals into TiO$_2$ is an effective way to improve the photocatalytic performance [15–22]. In these studies, Cu, as a kind of transition metal, was found to be an effective dopant for TiO$_2$ to enhance the photocatalytic activity [23].

In the present study, the photocatalytic performance of pure TiO$_2$ and Cu-doped TiO$_2$ nanoparticles which were fabricated via sol–gel method was investigated, and the influence of Cu content on the photocatalytic performance tested by the photocatalytic degradation of methyl orange was discussed. The Cu-doped TiO$_2$ nanoparticles were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FE-SEM) and UV–Vis absorption spectrum. Meanwhile, the mechanism for the improvement of photocatalytic activity was discussed based on the characterization results.

2 Experimental

2.1 Preparation method

TiO$_2$ was synthesized through the sol–gel method.
by the hydrolysis of tetrabutyl titanate (Ti(OC\textsubscript{4}H\textsubscript{9})\textsubscript{4}, 10 mL). Tetrabutyl titanate was added dropwise into the mixture solution of 35 mL alcohol and 1 mL acetylacetone. Then, a mixed solution of 10 mL alcohol dissolved with Cu(NO\textsubscript{3})\textsubscript{2}·3H\textsubscript{2}O was added into the vessel dropwise according to the anticipated Cu content (0.5%–2.0%, mole fraction). Finally, the mixture of 2 mL glacial acetic acid, 2 mL deionized water and 20 mL alcohol was dropped in the solution. Stirring was held for the whole course and continued for 1 h. After stewing for 24 h, the sol was put in an oven to dry at 80 °C for 48 h to form the gel. The gels were then put in a muffle furnace and calcined at 450 °C for 2 h to acquire the Cu-doped TiO\textsubscript{2} powders with different Cu contents from 0.5% to 2.0%.

2.2 Characterization

The crystal structure of the powders was analyzed by XRD (Rigaku D/MAX 2500PC), and the XRD patterns were collected in 2θ range from 20° to 80° with a Cu target and a mono-chronometer at 40 kV and 250 mA. FE-SEM (JSM-6700F) was used to study the morphology of the nanoparticles. A tungsten lamp was employed and the acceleration voltage was 10 kV. Before the test, the samples were coated with gold to increase the conductivity. X-ray photoelectron spectrum (XPS) with an ESCALAB Mk II (Vacuum generators) spectrometer using unmonochromatized Al K\textsubscript{α} X-ray (240 W) was used to detect complementary information on the chemical combination state of dopant Cu in TiO\textsubscript{2}.

2.3 Measurement of photodecolorization activity

The photocatalytic performance of the Cu-doped TiO\textsubscript{2} nanoparticles was tested by degrading 20 mg/L methyl orange which was carried out in a home-built reactor. A 250 W high-pressure mercury lamp with light wavelength from 350 nm to 450 nm was used as a light source. In each run, after the mixture of 10 mg Cu/TiO\textsubscript{2} catalyst and 30 mL methyl orange solution of 20 mg/L was exposed for 10 min, the light was turned on to initiate the degradation process. A UV–6100(PC) spectrometer made by Meipuda Company was used to determine the concentration of methyl orange solution before and after the photocatalytic degradation every 20 min once. The UV–Vis spectrophotometer was also used to measure the absorbance spectrum of the TiO\textsubscript{2} nanoparticles.

3 Results and discussion

3.1 Structure analysis

The XRD patterns of Cu-doped TiO\textsubscript{2} and TiO\textsubscript{2} nanoparticles are shown in Fig. 1. The diffraction peaks were indexed to (101), (103), (004), (112), (200), (105), (211), (204), (116), (220) and (215) planes of anatase phase of TiO\textsubscript{2} (JCPDS No. 21–1272), and no other Cu or Cu relative peaks were observed, implying that Cu was doped into TiO\textsubscript{2} lattice. The crystallite size of the samples was calculated from full-width at half-maximum (FWHM) of the (101) peak of anatase TiO\textsubscript{2} by the Debye-Sherrer equation:

\[ d = \frac{k\lambda}{\beta \cos \theta} \]  

where \( d \) represents the crystallite size; \( \lambda \) represents the wavelength of incident X-ray; \( \beta \) is the FWHM of diffraction peak; \( \theta \) represents the scattering angle. All the XRD patterns show the increased FWHM values, indicating that the synthesized particles are in nanocrystalline range. For example, the calculated grain size of 1% Cu-doped TiO\textsubscript{2} particles is 24.73 nm. Real particle size can be directly revealed by FE-SEM observation. FE-SEM micrographs of pure TiO\textsubscript{2} and 1.0% Cu-doped TiO\textsubscript{2} are shown in Figs. 2(a) and (b), respectively. The particles are quite uniform and show round or polyhedron shape with particle size in the range of 40–70 nm for TiO\textsubscript{2} in Fig. 2(a) and 30–45 nm for 1.0% Cu-doped TiO\textsubscript{2} in Fig. 2(b). That is, a decrease in particle size due to Cu doping is observed. When Cu\textsuperscript{2+} ions doped into TiO\textsubscript{2} lattice, they like to dwell in grain boundary regions or on the surface of particles to inhibit the growth of TiO\textsubscript{2} crystals [24].

Quantitative XPS analysis of TiO\textsubscript{2} and 1.0% Cu-doped TiO\textsubscript{2} samples was performed. Figure 3(a) shows the Cu 2p spectrum of 1.0% Cu-doped TiO\textsubscript{2}. There are two characteristic peaks located at 932.9 and 953.2 eV, which are corresponding to the binding energies of Cu 2p\textsubscript{3/2} and Cu 2p\textsubscript{1/2} states, respectively. Cu exists as Cu\textsuperscript{2+} ions in TiO\textsubscript{2} [25]. Figure 3(b) illustrates the Ti 2p spectra of TiO\textsubscript{2} and 1.0% Cu-doped TiO\textsubscript{2}. For TiO\textsubscript{2}, the peaks located at 458.1 and 464.0 eV are Ti 2p\textsubscript{3/2} and Ti 2p\textsubscript{1/2} states, respectively, while for 1.0% Cu-doped TiO\textsubscript{2}, the binding energies of Ti 2p\textsubscript{3/2} and Ti 2p\textsubscript{1/2} states...
increase slightly to 458.4 and 464.4 eV, respectively, which may also reflect that Cu$^{2+}$ ions have been doped into TiO$_2$ lattice.

The XPS spectra of O 1s for TiO$_2$ and 1.0% Cu-doped TiO$_2$ are shown in Figs. 3(c) and (d), respectively. The spectra are fitted with the non-linear least square fit program using Gauss–Lorentzian peak shapes, and two O 1s peaks are observed, which are attributed to the lattice oxygen (529.9±0.1 eV) and the absorbed oxygen (531.8±0.1 eV) in TiO$_2$. The latter reflects not only the absorbed oxygen but also the adsorbed H$_2$O or hydroxyl oxygen (OH) groups on the surface [26]. There is more adsorbed oxygen (H$_2$O or OH groups) on the surfaces of 1.0% Cu-doped TiO$_2$ compared with the undoped TiO$_2$ nanoparticles. When introducing Cu into TiO$_2$, Cu$^{2+}$ ion should substitute Ti$^{4+}$ in TiO$_2$ lattice, which means that O—Ti—O turns to Cu—O, resulting in the increase of oxygen vacancies. The increased adsorbed oxygen (H$_2$O or OH groups) on the surface should balance the increased oxygen vacancies in TiO$_2$ lattices [27].
3.2 Optical performance Cu-doped TiO$_2$ nanoparticles

The UV-Vis absorbance spectra of TiO$_2$ nanoparticles with different Cu doping contents and undoped TiO$_2$ are illustrated in Fig. 4(a). Compared with the absorbance spectrum of undoped TiO$_2$ nanoparticles, Cu-doped TiO$_2$ nanoparticles have a higher light harvest performance reflected by not only the widening of its UV absorbance peak, but also the evident enhancement of light absorbance covering the whole visible range. The red shift of the band gap can be obtained by the plot of $(Ah\nu^2)$ vs $h\nu (E_g)$ in Fig. 4(b) ($A$ is the absorbance, $h$ is the Planck constant, $\nu$ is the frequency of incident light), which reveals that the band gap shifts from 3.28 eV for the undoped TiO$_2$ to 3.02–3.17 eV for the Cu-doped TiO$_2$.

3.3 Photocatalytic degradation of methyl orange

Figure 5 shows the photocatalytic activity of Cu-doped TiO$_2$ with different Cu contents and undoped TiO$_2$ on the degradation of 20 mg/L methyl orange. It is seen that the Cu-doped TiO$_2$ with Cu content of 0.5%–1.5% shows improved photocatalytic performance, and 1.0% Cu-doped TiO$_2$ shows the best photocatalytic performance among them. When the content of Cu doping reaches 2.0%, the photocatalytic performance decreases to the level similar to that of undoped TiO$_2$.

The increased photocatalytic performance of Cu-doped TiO$_2$ can be attributed to the following reasons. Firstly, as shown in Fig. 4(a), the absorbance spectra of Cu-doped TiO$_2$ exhibit the enhanced light harvest in both UV and visible light regions, which enable much more light energy to be utilized for photocatalysis. Secondly, Cu species (CuO/Cu$_2$O/metallic Cu) have smaller band gap and higher work function than bare TiO$_2$, so the electron can transfer from the conduction band of TiO$_2$ to metallic copper ion. This results in the formation of Schottky barrier in the metal-semiconductor contact region, which facilitates the charge separation, and hence enhances the photocatalytic performance of TiO$_2$. The induced impurity energy level by doping Cu also plays an important role in the effective separation of photoinduced electron-hole pair. Since the valence of Cu$^{2+}$ ion is less than that of Ti$^{4+}$, doping of Cu will induce oxygen vacancies, which act as the active sites for water dissociation on the surface of TiO$_2$, and can also capture the holes to restrain the recombination of hole-electron pairs. Thus, the photocatalytic performance of TiO$_2$ is enhanced [28].

However, when much more Cu$^{2+}$ ions are doped, they can trap the photoinduced electrons to form Cu$^{3+}$ ions. Since $\phi_{Cu^{2+}/Cu^+}(0.16\ V\ (vs\ NHE))$, while $\phi_{Cu^{3+}/Cu^+}(0.25\ V\ (vs\ NHE))$ [29], the formed Cu$^{3+}$ ions can capture the photoinduced holes and generate Cu$^{2+}$. Thus, a short-circuiting forms and both photoinduced electron and hole are consumed. Consequently, the photocatalytic activity is reduced. Therefore, there is an optimum Cu content (1.0% in this study) at which the Cu-doped TiO$_2$ can effectively separate the photoinduced electron-hole pair and perform the best photocatalytic performance.
4 Conclusions

1) Cu exists in the form of Cu$^{2+}$ ions in TiO$_2$ lattice, which induce more oxygen vacancies and trap much more absorbed oxygen (or H$_2$O or OH groups) on the surface of TiO$_2$ nanoparticles, as testified by the XPS spectrum of O 1s peaks.

2) Cu-doped TiO$_2$ shows an enhanced light harvest in both UV and visible light regions, which is beneficial to its photocatalytic performance.

3) With an appropriate content of Cu (0.5%-1.5%), the Cu-doped TiO$_2$ nanoparticles exhibit the improved photocatalytic performance in photo degradation of methyl orange, and the best performance is achieved at Cu doping content of 1.0%.

References


掺铜二氧化钛纳米颗粒的制备及其催化性能

杨希佳，王姝，孙海明，王晓兵，连建设

吉林大学 材料科学与工程学院 汽车材料教育部重点实验室，长春 130025

摘 要：采用溶胶−凝胶法制备掺铜量为0~2.0%(摩尔分数)的二氧化钛纳米颗粒。应用X射线衍射(XRD)、X射线光电子能谱(XPS)和场发射电子显微镜(FE-SEM)技术对二氧化钛纳米颗粒的晶体结构、化学价态和形貌进行表征。样品的光学吸收性能用紫外−可见吸收光谱进行表征；其光催化性能通过在紫外−可见光照射下分解20 mg/L甲基橙溶液进行表征。结果表明，掺铜二氧化钛纳米颗粒具有比纯二氧化钛更优的光催化性能，尤其是铜掺杂量为1.0%的二氧化钛TiO₂纳米颗粒具有最好的光催化性能，铜掺杂能提高二氧化钛在紫外−可见光区对光的吸收，减小电子−空穴对的复合，因此，铜掺杂使二氧化钛的光催化性能得到提高。

关键词：二氧化钛；铜；纳米颗粒；光催化；掺杂；溶胶−凝胶