Microstructure and photocatalytic activity of TiO$_2$-SiO$_2$ composite materials

Jun Wang$^{1\ast}$, Wenjuan Zhang$^{1\ast\ast}$, Binghua Zhu$^1\ast\ast\ast$, and Yueyuan Xiao$^{1\ast\ast\ast\ast}$

$^1$Jiangxi Key Laboratory of Surface Engineering, Jiangxi Science and Technology Normal University, Nanchang, Jiangxi, 330013, China

$\ast$email: wangjun460@jxstnu.edu.cn, $\ast\ast$email: 143654103@qq.com, $\ast\ast\ast$email: 1815430914@qq.com, $\ast\ast\ast\ast$email: 1942832506@qq.com

Abstract TiO$_2$-SiO$_2$ composite materials with different composition (from 0 to 50 mol % SiO$_2$) were prepared by sol-gel method. Microstructure, optical property and photocatalytic activity of TiO$_2$-SiO$_2$ composite materials were characterized by Raman scattering, ultraviolet-visible (UV-vis) spectrometer and photocatalytic degradation of methylene blue. The Raman spectra results showed that TiO$_2$-SiO$_2$ composite materials contained only a single crystalline phase of anatase TiO$_2$. It also indicated the inclusion of SiO$_2$ suppressed the growth of anatase TiO$_2$. The UV-vis absorption spectra showed that the absorption edge of TiO$_2$-SiO$_2$ composite materials has a blue shift as the SiO$_2$ increased. The optical band gap of TiO$_2$-SiO$_2$ increased from 3.06 eV to 3.32 eV for TiO$_2$ and 0.5TiO$_2$-0.5SiO$_2$. The adsorption performance and photocatalytic activity of TiO$_2$-SiO$_2$ was enhanced with the increase of SiO$_2$ content. 0.5TiO$_2$-0.5SiO$_2$ has the best absorption performance and photocatalytic activity in our experiment. And it has potential application value in the field of photocatalytic materials.

1. Introduction

In recent years, composite materials have attracted a great deal of attention for their special structure and novel properties. Various composite materials were investigated by using inorganic oxides such as TiO$_2$, SiO$_2$, WO$_3$, ZnO, Fe$_2$O$_3$, and so on [1-7].

Among them, TiO$_2$ and SiO$_2$ are safe and low cost materials. They have stable chemical, thermal and mechanical properties. TiO$_2$ and SiO$_2$ are widely used as for optical application because of the high transparency and low absorption in visible and near infrared region. Moreover, many studies have investigated TiO$_2$-SiO$_2$ to achieve novel properties [3, 8, 9]. TiO$_2$ is one of the most promising photocatalysis materials. However, the effect of composition on microstructure, optical property and photocatalytic activity of TiO$_2$-SiO$_2$ composite materials need to be further investigated.

We have studied the optical properties and wettability of TiO$_2$-SiO$_2$ thin films[10, 11]. The aim of this work was to investigate the relationship between composition and photocatalytic activity for TiO$_2$-SiO$_2$. For this purpose, TiO$_2$-SiO$_2$ composite materials with different composition were prepared by sol-gel method. Microstructure and optical property were carried by Raman and spectroscopy ellipsometry. The photocatalytic activity was judged by degradation of methylene blue.

2. Experimental

To prepare TiO$_2$-SiO$_2$ sol, ethyl orthosilicate and tetrabutyl titanate were used as silicon source and titanium source. Ethanol was used as solvent. Concentrated nitric acid (65%) and water were used for acid catalyst and hydrolysis agent. The mole ratio of ethyl orthosilicate and tetrabutyl titanate: ethanol: nitric acid: water is 1: 1: 1: 1.
The amount of ethyl orthosilicate and tetrabutyl titanate was determined by the composition of TiO2-SiO2 composite. In our experiment, TiO2 sol, 0.9TiO2-0.1SiO2 sol, 0.7TiO2-0.3SiO2 sol and 0.5TiO2-0.5SiO2 sol were prepared. The detail process of sol preparation can be found in elsewhere [11].

All TiO2-SiO2 sols were aged for 24 hours. Afterwards, all sols were dried and ground. Finally, dry gel powders were heat treated at 500°C for 1 h. Figure 1 showed the flow chart of TiO2-SiO2 composite materials prepared by sol-gel.

![Flow chart of TiO2-SiO2 composite materials prepared by sol-gel](image)

The phase structure was investigated by Raman spectrometer working in back-scattering configuration. Ultraviolet-visible (UV-vis-) diffuse reflectance absorption spectrum of TiO2-SiO2 composite materials were measured on UV-vis spectrometer with an integral sphere.

The photocatalytic performance of the TiO2-SiO2 composite materials were determined from the photobleaching of methylene blue (MB) solution (4 mg/L) under high-voltage halogen tungsten lamp. 0.1 g TiO2-SiO2 powders were added to MB solutions (4 mg/L) and mixed for 30 minutes to achieve absorption equilibrium. The distance between MB solution and lamp was about 8 cm. The photocatalytic experimental setup was shown in Figure 2. The absorbance of MB solution was tested at different irradiation time by UV-vis spectrometer. And the effect of composite composition on photocatalytic was discussed.
3. Results and discussion

To evaluate the microstructure of composite materials, Figure 3 gives the Raman spectrum of TiO2-SiO2. The band at 399 cm\(^{-1}\), 514 cm\(^{-1}\) and 640 cm\(^{-1}\) are assigned to anatase TiO2. The intensity of the peaks decreased with the increase of SiO2 content. It means that the addition of SiO2 inhibit the growth of TiO2 anatase phase in the TiO2-SiO2 composite materials. This is in agreement with other works\[12\]. The peak position did not change with the composite composition. No Raman shift of SiO2 was found may be due to the Raman signal of the amorphous SiO2 was very weak\[13\].

Absorbance spectrum of TiO2-SiO2 composite materials from 300 nm to 420 nm was shown in Figure 4. The absorbance increase rapidly at wavelength below 405 nm was attributed to the absorption of light caused by excitation of electrons from the valence band to the conduction band\[14\]. When the photo energy exceeds the band gap energy, electron in the valence band will absorb photos. It can be seen that the absorption edge of TiO2-SiO2 composite materials gradually blue shift with the increase of SiO2 concentration. The band gap was an important parameter for optical materials. It can be calculated by the follow equation\[15\]:

\[
E_{\text{gap}} = \frac{h \nu}{2} - C
\]
Eg=1240/\lambda

where \( \lambda \) is absorption edge, the calculated band gap was 3.06 eV, 3.22 eV, 3.25 eV and 3.32 eV for TiO2, 0.9TiO2-0.1SiO2, 0.7TiO2-0.3SiO2 and 0.5TiO2-0.5SiO2, respectively. Addition SiO2 caused the TiO2-SiO2 optical band gap shift toward higher energies. The band gap of powders was smaller than that of thin films [10]. However, the addition of SiO2 can increase the band gap for TiO2-SiO2 powders and films.

![Absorbance spectra of TiO2-SiO2 composite materials](image)

Fig. 4 Absorbance spectra of TiO2-SiO2 composite materials

The absorption spectra of MB solution with different TiO2-SiO2 composite materials after irradiation 20 minutes were shown in Figure 5(a). Figure 5(b) was the corresponding experimental photography. The absorption band of MB solution decreased significantly with the increased of SiO2 content. Meanwhile, the color of MB solution became lighter. The composition of TiO2-SiO2 was obvious influence on photocatalytic properties.

![Absorption spectra and experimental photography](image)

Fig. 5 Absorption spectra (a) and experimental photography (b) of MB solution with different TiO2-SiO2 composite materials after irradiation 20 minutes

To further evaluate photocatalytic activity, the absorbance of MB solutions at 664 nm for different irradiation times was tested, as shown in Figure 6. The absorbance of MB solution decreased as the content of SiO2 in TiO2-SiO2 composite materials increased before irradiation. It indicated that the absorption performance of TiO2-SiO2 composite materials increased with the increase of SiO2 in our
This may be due to the changes in microstructure of composite materials. The absorption performance of the materials was closely related to the photocatalytic degradation properties.

The absorbance of MB solution decreased with the irradiation time. Compared to pure TiO$_2$, the absorbance of MB solution sharply decreased with TiO$_2$-SiO$_2$ composite material. It showed that the photocatalytic property of TiO$_2$-SiO$_2$ composite material was better than pure TiO$_2$. And the higher content of SiO$_2$ in TiO$_2$-SiO$_2$ composite materials, the faster the degradation rate of MB solution. The MB solution with TiO$_2$-SiO$_2$ composite materials degradation was completed after irradiation for 40 minutes.

![Absorbance at 664 nm for different irradiation times](image)

**Fig. 6 Absorbance at 664 nm for different irradiation times**

### 4. Summary

In this study, TiO$_2$-SiO$_2$ composite materials with different SiO$_2$ content (from 0 to 50 mol %) were prepared by sol-gel method. The influence of composition on microstructure, optical band gap and photocatalytic properties were studied. The composite materials contained anatase TiO$_2$ phase and amorphous SiO$_2$ phase. SiO$_2$ inhibited the growth of anatase TiO$_2$ phase. The optical band gap of TiO$_2$-SiO$_2$ composite materials increased with the increase of SiO$_2$ content. Meanwhile, the higher SiO$_2$ content, the stronger adsorption performance of TiO$_2$-SiO$_2$ were found. The photocatalytic active of TiO$_2$-SiO$_2$ was better than pure TiO$_2$.

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