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Effect of silica on the microstructure and photocatalytic properties of titania

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Abstract

A series of TiO_2/SiO_2 composite with different Ti/Si ratios were prepared by sol–gel technique. The samples were characterized by different analytical techniques such as XRD, FT-IR, BET and XPS. Grain size of anatase TiO_2 calculated using Scherrer's formula was found to be in the range of 2.1–8.7 nm, and the content of anatase phase in TiO_2 ranges from 45% to 40.1%. The photocatalytic properties on methyl orange (MO) solution were also studied. The degradation rate of the composite is much higher than that of the pure TiO_2 in the same conditions.

Keywords: TiO_2/SiO_2 composite; Photocatalytic property; Sol–gel technique

1. Introduction

Photocatalysis is known as a promising technique for water spitting to produce hydrogen as well as dealing with volatile organic compounds that are toxic to human life. Among the metal oxides semiconductors suitable for photocatalytic process, titanium dioxide is the most widely used due to its relatively favorable band-gap energy and its photocorrosion stability in the reaction conditions [1,2]. The photocatalytic properties of titania is affected by several factors, such as crystal structure, morphology, surface area and porosity [3]. It is well known that titania has three kinds crystal phases: anatase, rutile and brookite. The anatase titania has the highest photoactivity in the three phases. However, the photocatalytic property of the mixture of anatase and rutile titania with appropriate ratio is higher than that of the pure anatase titania. Much work has been conducted on the optimization of photoactivity of titania by doping metal ions, such as Fe^{3+}, Mo^{5+}, Re^{5+} and V^{4+} ions [4–7]. The mixed oxides as Al_2O_3/TiO_2, ZrO_2/TiO_2, SnO_2/TiO_2 and SiO_2/TiO_2 also have good photoactivitic properties [8–10]. Especially, the SiO_2/TiO_2 nanocomposites are more efficient photocatalysts than pure TiO_2 [11]. The addition of silica in titania enhances the thermal stability for the phase transformation of titania particles from anatase to rutile. Also, silica acts as the carrier of titania, which can help to obtain a large surface area.

In this work, we report the preparation of nanosized SiO_2/TiO_2 composites via sol–gel process. The phase structure and photocatalytic properties of SiO_2/TiO_2 composites have been measured.

2. Experimental

2.1. Synthesis

TiO_2/SiO_2 nanosized composites with different Ti/Si ratios were prepared by sol–gel process. Tetraethylorthosilicate (TEOS) and tetrabutylorthotitanate (TBOT) were used as sources of silicon and titanium, respectively. In view of the different hydrolysis rates of TEOS and TBOT, TEOS and TBOT were firstly introduced into a mixture solution of ethanol, distilled water, and nitric acid under stirring separately. Then the obtained silicon sol and titanium sol were mixed at 80 °C and stirred for another 1 h. Different sols of TiO_2/SiO_2 were obtained by varying the ratio of TBOT to TEOS. The gels was calcined at the temperatures ranging from 450 °C to 950 °C for 2 h, and then ground into fine powders.

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2.2. Photodegradation and characterization

The methyl orange (MO) solution (with a concentration of 30 mg/l) was chosen for photodegradation. A total of 0.5 g TiO_2/SiO_2 powders were added into 20 ml MO solution with agitation, and the muddy solution were dispersed with ultrasonic instrument for 0.5 h. The photoreactor is a DDG250/H dysprosium lamp with the power of 250 W (14,000 lm, 6000 k). The distance between the bottom of the lamp and the top of the solution is 20 cm. The irradiation time is about 2 h. The decomposition rate (η) was replaced by the decolor rate (D), and was calculated by the following formula:

$$\eta = D = \frac{(A_0 - A)}{A_0} \times 100\%$$

The "A" in the formula is the absorbency of the MO solution at 460 nm. A UV-240 ultaviolet–visible spectrometer was used to record the change of the absorbency of the MO solution after radiation for 2 h.

XRD patterns were made using a D/max-rB X-ray diffractometer with Cu Kα radiation over the scan range 20–80° for wide angle XRD. The crystallite size of the powders was determined by Scherrer equation, and the relative concentration of anatase titania was determined by the following equation:

$$X_\mathrm{A} = \frac{1}{(1 + 0.8 I_\mathrm{A}/I_\mathrm{R})}$$

FT-IR spectra were recorded in MAGNA-IR 750 FT-IR spectrometer. XPS spectrum was measured on ESCAAB MK II XPS spectrometer. All the measurements were done at room temperature.

3. Result and discussion

3.1. Characterization

Fig. 1 shows the XRD patterns of pure TiO_2 heat-treated at different temperatures. Both of the anatase ($2\theta = 25.2°$) and rutile ($2\theta = 27.5°$) phases exist in the samples at temperatures from 450 °C to 650 °C, and the anatase phase can transform to rutile phase completely when the temperature is higher than 650 °C. Also when the temperature is higher than 650 °C, the peaks at 27.5° become much sharper owing to the further crystallization of rutile phase. The crystallite size of the two phases and the concentration of anatase phase are shown in Table 1. The crystallite size of anatase TiO_2 is in the range of 20–43 nm, and the rutile TiO_2 range from 20 nm to 53 nm. The crystallite size increase with the temperatures from 450 °C to 950 °C. Also from Table 1 we can find that the concentration of anatase is about 37% when the temperature is 450 °C, and it decreases with the increase of temperatures. When the temperature reaches 750 °C, anatase phase disappears.

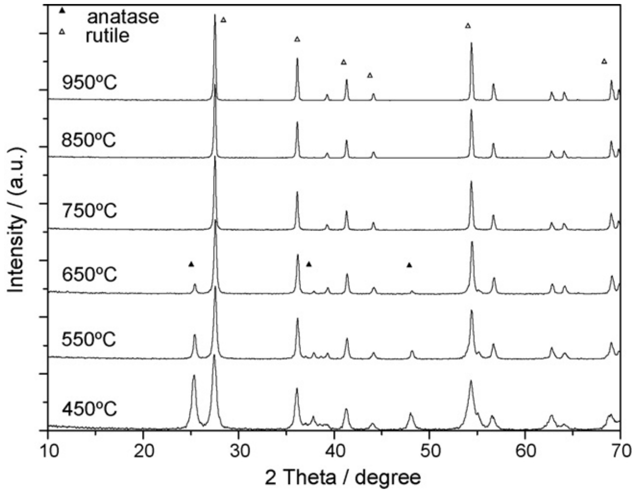

Fig. 1. XRD spectra of TiO_2 heat-treated at different temperatures.

Table 1
Effect of heat-treating temperature on the crystal of TiO_2

Temperature (°C)	Grain size (anatase) (nm)	Grain size (rutile) (nm)	Concentration of anatase (%)
450	21.1	21.9	37.0
550	32.2	35.3	21.0
650	43.3	39.8	10.0
750	–	48.7	–
850	–	49.9	–
950	–	53.2	–

Fig. 2 shows the XRD patterns of TiO_2/SiO_2 composite heat-treated at temperatures from 450 °C to 950 °C. The Ti/Si ratio of this composite is 1:1. At the temperatures from 450 °C to 950 °C, rutile and anatase TiO_2 exist in all samples, and the silica is amorphous phase. According to the Scherrer equation, the grain size of the rutile and anatase TiO_2 is much smaller than that of pure TiO_2 (see Table 2). Compared with pure TiO_2 calcined at 450 °C, the grain size of anatase TiO_2 in TiO_2/SiO_2 composite is only 2.11 nm and the rutile grain size is 8.1 nm. The grain size grows up with the increase of temperature. However, at 950 °C the grain size of anatase and rutile TiO_2 are only 8.7 nm and 15.6 nm separately. It is confirmed that silica can effectively prevent the growth of titania grains during the heat-treatment. The concentration of anatase TiO_2 in TiO_2/SiO_2

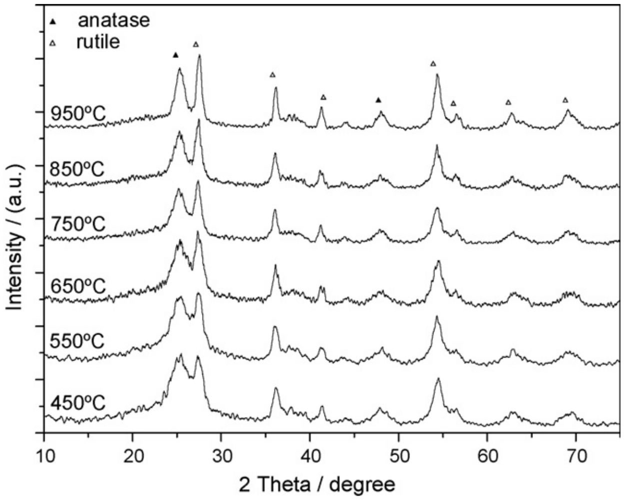

Fig. 2. XRD spectra of TiO_2/SiO_2 heat-treated at different temperatures (Ti/Si = 1:1).

Table 2
Effect of heat-treating temperature on the crystal of TiO_2/SiO_2

Temperature (°C)	Grain size (anatase) (nm)	Grain size (rutile) (nm)	Concentration of anatase (%)
450	2.1	8.1	45.0
550	4.5	9.2	43.3
650	5.0	9.9	41.4
750	6.8	13.3	41.4
850	8.5	15.3	40.1
950	8.7	15.6	40.1

is also shown in Table 2. Anatase TiO_2 in TiO_2/SiO_2 composite is quite steady, and its concentration is about 45% at 450 °C. Even heat-treated at 950 °C, 40% anatase phase still exist in the composite. It indicates that silica in TiO_2/SiO_2 composite can effectively prevent the transformation of anatase to rutile phase during the heat-treatment.

From the comparison of Tables 1 and 2, it can be clearly seen that the grain size of anatase and of rutile phase are nearly the same in pure TiO_2, but the grain size of rutile is larger than that of anatase phase in the TiO_2/SiO_2 composite. This difference may due to the formation of an anatase solid solution with silica, but such a solid solution of rutile and silica cannot be formed.

The XRD patterns of TiO_2/SiO_2 composite with different Ti/Si ratio heat-treated at 550 °C are shown in Fig. 3. In all samples silica is in amorphous. With the increase of the concentration of silica, peaks of the two phases of titania become wide and low, which means the growth of the grain is inhibited. For example, when the Ti/Si ratio is 3:1 the grain size of anatase and rutile phases are 7.9 nm and 10.5 nm, and the content of anatase in the composite is 45.13%. The prevention of silica on the nucleation of rutile by impeding the mutual contact of titania particles and the formation of anatase solid solution containing silica are the two explanations for the inhibiting effect by silica. This solid solution has been confirmed by Cheng et al. [12]. They found that compared with the pure anatase, $SiO_2/TiO_2(SiO_2\ 30\%)$ powder shows about 0.5% reduction in lattice parameter c when the calcinations temperature increased from 400 °C to 800 °C.

Table 3
Surface area of TiO_2/SiO_2 composite with different Ti/Si ratios (550 °C)

$n(Ti):n(Si)$	TiO_2	3:1	1:1	1:2
Surface area (m^2/g)	80.088	238.41	325.48	453.09

Table 3 shows the surface area of TiO_2/SiO_2 composite with different Ti/Si ratios. For comparison, the surface area of pure TiO_2 is also measured. All the composites are heat-treated at 550 °C for 1 h. From Table 3, it can be clearly seen that the surface area of TiO_2/SiO_2 composite is much larger than that of pure TiO_2, and the surface area of TiO_2/SiO_2 composite increase when the Ti/Si ratios change from 3:1 to 1:2. It is only 80.088 m^2/g for pure TiO_2, but it increases to 453.09 m^2/g for the composite with Ti/Si ratio of 1:2. The addition of silica in titania can evidently enhance the surface area of the particles, which is consistent with the reduction of grain size.

Fig. 4 shows the FT-IR spectra of the TiO_2/SiO_2 composites with the Ti/Si ratio of 3:1 heat-treated at 550 °C and 850 °C separately in the wave number range from 400 cm^{-1} to 2000 cm^{-1}. The absorption band at 1626.3 cm^{-1} is attributed to stretching mode of O–H bonds in absorption water. The peaks at 935.5 cm^{-1} and 1078.6 cm^{-1} correspond to the vibration of Si–O–Ti and the asymmetric stretching vibration of Si–O–Si. The band at 478.4 cm^{-1} can be assigned to the stretching vibration of Ti–O bonds in Ti–O–Ti. Silica and titania are connected by the Ti–O–Si bonds.

XPS spectra of TiO_2/SiO_2 composite with Ti/Si ratio of 3:1 heat-treated at 850 °C are presented in Fig. 5. The peaks at 459.4 eV and 465.1 eV represent $Ti2p_{1/2}$ and $Ti2p_{3/2}$ of Ti^{4+} ions, respectively, while the peak at 103.15 eV represents Si2p of Si^{4+} ions. Also, C1s photoelectron peak is shown at 285 eV, which may come from the carbon pollution in air or the remained organic components. The enlarged spectrum of O2p photoelectron peaks are shown in Fig. 5(b). There are two peaks at 530.67 eV and 532.85 eV, which represent O1s of Ti–O and

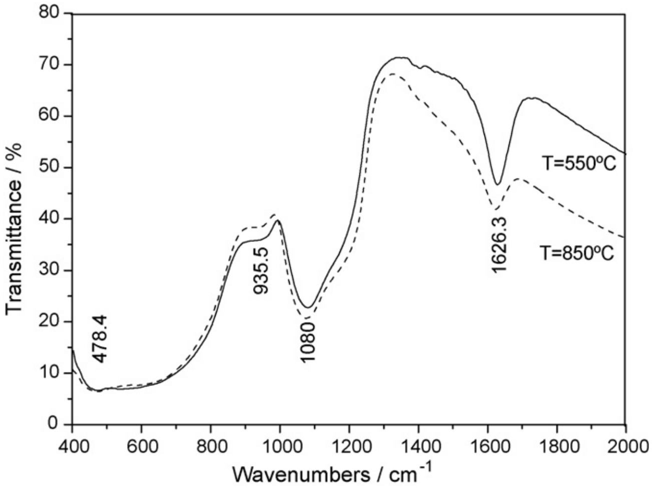

Fig. 4. IR spectra of TiO_2/SiO_2 heat-treated at 550 °C and 850 °C with the Ti/Si ratio of 3:1.

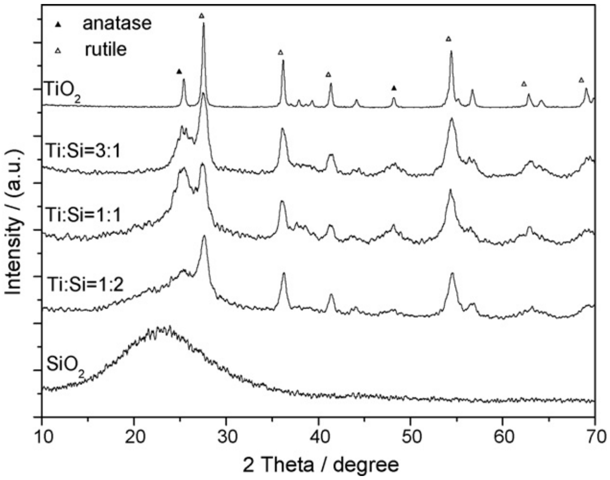

Fig. 3. XRD spectra of TiO_2/SiO_2 heat-treated at 550 °C with different Ti/Si ratio.

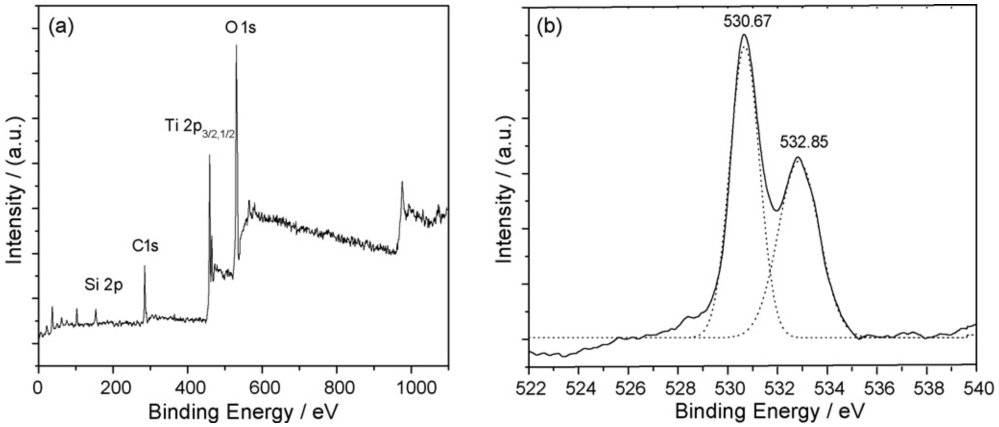

Fig. 5. XPS spectra of TiO_2/SiO_2 heat-treated at 850 °C with the Ti/Si ratio of 3:1 (a) survey spectrum; (b) O 1s spectrum.

Si–O separately. The binding energy of O1s electron of Ti–O in the composite is 1.37 eV larger than that in pure titania, and the binding energy of O1s electron of Si–O in the composite is 0.26 eV smaller than that in pure silica. The shifts of the binding energy of O1s electron can be ascribed to the interaction of Ti and Si ions in Ti–O–Si linkage.

3.2. Photocatalytic activity

Fig. 6 shows the variation of photocatalytic activity of TiO_2/SiO_2 composite heat-treated at different temperatures (Ti/Si = 3:1). It can be clearly seen that when the heat-treatment temperature is at 550 °C, the degradation rate of TiO_2/SiO_2 composite reaches the maximum of 64.85%. At higher temperatures, the degradation rate falls down. Especially when heat-treated at 850 °C, the degradation rate is only 28.67%.

Fig. 7 shows the photocatalytic properties of TiO_2/SiO_2 composite with different Ti/Si ratios. For comparison, the photocatalytic properties of pure TiO_2 and SiO_2 are also measured. All the samples are heat-treated at 550 °C for 1 h. It can be clearly seen that the degradation of pure TiO_2 at the same conditions is only 10.3%. With the increase of the content of SiO_2, the degradation of composite grows rapidly. And when the Ti/Si ratio is at 3:1, the degradation rate reaches the maximum of 64.85%, which means at this Ti/Si ratio the composite has the best photocatalytic properties. The farther increase of the heat-treating temperature makes the degradation rate fall down and the pure SiO_2 has no photocatalytic properties. The addition of SiO_2 can decrease the grain size of anatase phase, and prevent the transformation of anatase phase to rutile phase during heat-treating process. Moreover, addition of silica in titania can evidently enhance the surface area of the particles. For these reasons, the photocatalytic properties of the composite should be better than that of pure TiO_2. In view that more SiO_2 addition in TiO_2 will decrease the concentration of TiO_2, the degradation rate of the composite decrease.

The comparison of photocatalytic properties between pure TiO_2 and TiO_2/SiO_2 composite with the Ti/Si ratio of 3:1 is shown in Fig. 8. Both of the two samples have been heat-treated at 550 °C for 1 h. The degradation rates of the two samples are increased with the radiation time. But the degradation rate of the composite is much higher than that of the pure TiO_2. This can be explained by the grain size of anatase TiO_2 and the concentration of anatase phase in TiO_2. In pure TiO_2 the grain size of anatase phase is 32.2 nm but is only 7.9 nm in the composite, and the concentration of anatase phase in TiO_2 is

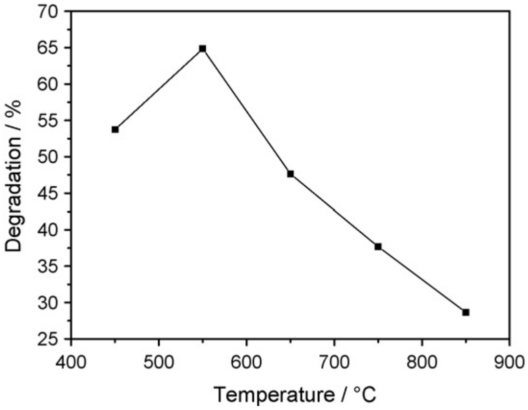

Fig. 6. Variation of photocatalytic activity of TiO_2/SiO_2 composite heat-treated at different temperatures (Ti/Si = 3:1).

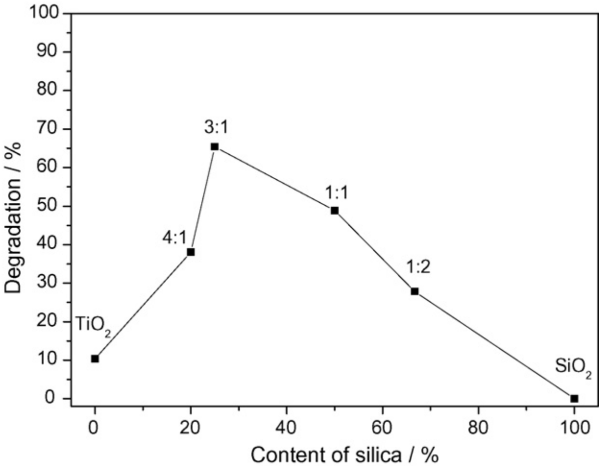

Fig. 7. Variation of photocatalytic properties of TiO_2/SiO_2 composite with different Ti/Si ratios (550 °C).

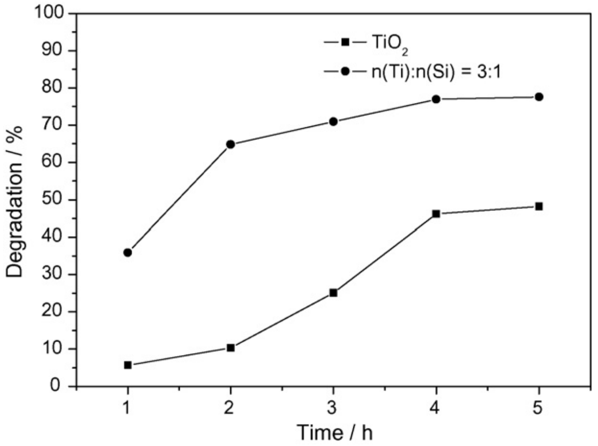

Fig. 8. Comparison of the optic-catalysis properties of the pure TiO_2 and TiO_2/SiO_2 composite with the Ti/Si ratio of 3:1 (550 °C).

21% in pure TiO_2 but is 45.13% in the composite. More anatase TiO_2 with small grain size makes the composite have better photocatalytic properties.

4. Conclusion

The TiO_2/SiO_2 composites with different Ti/Si ratios were prepared using TBOT and TEOS as precursors by sol–gel technique. The addition of silica into titania can effectively suppress the transformation of titania from anatase phase to rutile phase and prevent the growth of titania grains during the heat-treatment process. The addition of silica into titania can increase the surface area of titania particles and promote the formation of Ti–O–Si cross-linking bonds. All these effects contribute to the higher photocatalytic properties of The TiO_2/SiO_2 composite. However, excessive addition of silica can decrease the content of titania in the composite, which is bad to the photocatalytic properties. The optimum material for higher photocatalytic properties is TiO_2/SiO_2 composite with Ti/Si ratio of 3:1 heat-treated at 550 °C with the grain size of 7.9 nm and 45.13% anatase phase in TiO_2. Its degradation rate in MO solution can reach 64.85 at 2 h.

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