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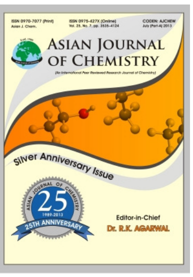

Effect of Sr-Ti Molar Ratio on Strontium Titanate Prepared by Sol-Gel Method

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Tetrabutyl titanate and strontium nitrate were used as initial materials in a sol-gel process to prepare strontium titanate. The effects of strontium-titanium molar ratio on phase composition, structure and photocatalytic activity of the prepared materials were studied. The produced material was mainly composed of $SrTiO_3$ and TiO_2 when $n(Sr)/n(Ti)$ ratio was less than 1:1, while the materials containing mainly Sr_2TiO_4 were prepared at $n(Sr)/n(Ti)$ higher than 1:1. The particles of all the samples presented irregular shape with rough surface, along with partly particles aggregation. Phase composition of the produced materials showed strong dependence on $n(Sr)/n(Ti)$ ratio. The sample prepared with $n(Sr)/n(Ti)$ of 1:1 possessed the optimal photocatalytic activity of 32.5 % after 0.5 h of irradiation.

Key Words: Strontium titanate, Photocatalytic, Methyl orange.

INTRODUCTION

Photocatalytic oxidation of organic pollutants has aroused much attention in consideration of dealing with severe environmental problems[1-3]. The aim of developing new kind of photocatalyst as well as promoting activity of currently well studied materials are the two major research focuses in this field. Perovskite structured composite metal oxides have different crystallite structure and electron configuration. It was well studied as a potential photocatalytic material due to high mobilization of charge carriers in it and its visible light responsible band structure[4,5]. Strontium titanate is a kind of perovskite structured material, which has been widely used as an electronic ceramic in various industrial applications[6]. As a functional material, strontium titanate has good photocatalytic activity and suitable band edge (3.2-3.8 eV) and has been used in photocatalytic field such as photochemical cell[7], photocatalytic water splitting[8] and degradation of organic pollutants[9].

In order to obtain strontium titanate with high purity and quality, many kinds of preparation methods have been investigated recently[10-16]. However, some key factors such as preparation conditions, crystallite control, cost and purity of the material are still far from accomplishment. Phase composition and structure of strontium titanate have close relationship with its photocatalytic activity and has become the research focus. In this paper, tetrabutyl titanate and strontium nitrate were used as initial materials in a sol-gel process to prepare strontium titanate. The main focus of this paper was to study effects of strontium-titanium molar ratio on phase composition, structure and photocatalytic activity of the prepared materials.

EXPERIMENTAL

In this paper, strontium titanate was prepared by a modified sol-gel method. 10 mL acetic acid was mixed with 10 mL deionized water and then different amount of strontium nitrate was dissolved in the former solution to obtain solution A, where molar ratios of $n(Sr)/n(Ti)$ were 0.3:1, 0.5:1, 0.8:1, 1:1, 1.2:1 and 1.4:1, respectively. 1.7 mL of tetrabutyl titanate was dissolved in absolute ethanol under magnetic stirring for 10 min to obtain solution B with volume ratio of $V[Ti(OC_4H_9)_4]$: $V(C_2H_5OH)$ = 1: 45. After that, solution B was dropped into warm solution A at a constant speed under continues vigorous magnetic stirring. A small amount of ethylene glycol was added into the mixture acting as stabilizer. The mixture was kept under stirring until a sticky sol formed. After 24 h of ageing at room temperature, the sol was dried at 110 ºC for 8 h to obtain a gel, followed by calcination of the gel at 800 ºC for 3 h. The calcination products were grinded to obtain strontium titanate with different $n(Sr)/n(Ti)$ ratios.

Scanning electron microscope images were taken on a HTACHI S-3400N scanning electron microanalyzer. The samples for SEM imaging were coated with a thin layer of gold film to avoid charging. The crystalline phases of the photocatalysts were measured by X-ray diffraction with D/max-rB diffractometer using a CuK_α radiation. FT-IR spectra of the samples were obtained using a Fourier transform infrared

(FT-IR) spectrometer (WQF-410) with KBr pellets. The samples were analyzed in the wavenumber range of 4000-400 cm^{-1}. The N_2-adsorption and desorption of the powder samples were measured by F-Sorb 3400 specific surface area and pore size distribution analytical instrument. Specific surface areas were calculated from N_2 desorption isotherms, according to BET equation.

Adsorption and photocatalytic activity: Prior to photocatalytic experiment, methyl orange adsorption on the photocatalyst in the dark was measured in the suspension of photocatalyst in methyl orange solution. 30 mL of 5 mg/L aqueous solution of methyl orange was mixed with 1000 mg/L photocatalyst in a 60 mL quartz reactor. The suspension was stirred magnetically for 25 min to reach adsorption equilibrium. After that, 5 mL of the suspension was taken out of the reactor and filtrated through a Millipore filter (pore size 0.45 mm) to remove the photocatalyst. Finally, absorbency of the solution was measured by a 721E spectrophotometer at the maximum absorption wavelength of methyl orange (468 nm).

Subsequently, photocatalytic activities of the prepared catalysts were evaluated in the above mentioned photocatalytic reactor. A 20 W UV lamp was located at the top of the reactor with the distance of 5 cm. The lamp can irradiate UV light at wavelength of 253.7 nm with the intensity of 2200 mW/cm^2. In prior to turn on the lamp, the solution was magnetically stirred for 25 min to ensure adsorption equilibrium. The suspensions were filtrated through the Millipore filter before measuring. If not indicated, the irradiation time in the subsequent experiments was set to 0.5 h.

The concentration of methyl orange was calculated by Lambert-Beer law. The adsorption and degradation rates of methyl orange were calculated by the following equation.

$$\omega(\text{Adsorption}) = (C_0 - C_1)/C_0 \times 100\ \%$$

$$\omega(\text{Degradation}) = (C_1 - C_2)/C_0 \times 100\ \%$$

where C_o is the initial dye concentration, C_1 is the concentration after adsorption-desorption equilibrium and C_2 is the concentration after certain time of irradiation. Total decolouration was composed of adsorption and photocatalytic degradation.

RESULTS AND DISCUSSION

Fig. 1 shows SEM images of strontium titanate prepared with different *n*(Sr)/*n*(Ti) molar ratio. The particles of all the samples presented irregular shape with rough surface, along with partly particles aggregation. Particle size increased gradually as *n*(Sr)/*n*(Ti) increased from 0.3:1 to 1.4:1. The increase of particle size at higher *n*(Sr)/*n*(Ti) ratio may come from different phases forming at using different initial precursors. The largest particles formed at the presented *n*(Sr)/*n*(Ti) ratios were not more than 5 μm and there were many small particles in the size around hundreds of nm dispersing among the large particles. Particle sizes of the prepared materials distributed in a suitable range, so that the particles could well suspend in solutions during photocatalytic process without fast deposition. The rough surface of the materials also provided a proper place for methyl orange adsorption and degradation.

XRD patterns of strontium titanate calcinated at 800 ºC for 3 h are shown in Fig. 2. The results reveal that production of strontium titanate was accompanied with the formation of anatase TiO_2 crystals and the phase state of strontium titanate also depended on the initial *n*(Sr)/*n*(Ti) molar ratio in the sol. Two phases of strontium titanate, $SrTiO_3$ and Sr_2TiO_4, were prepared with different *n*(Sr)/*n*(Ti) ratios.

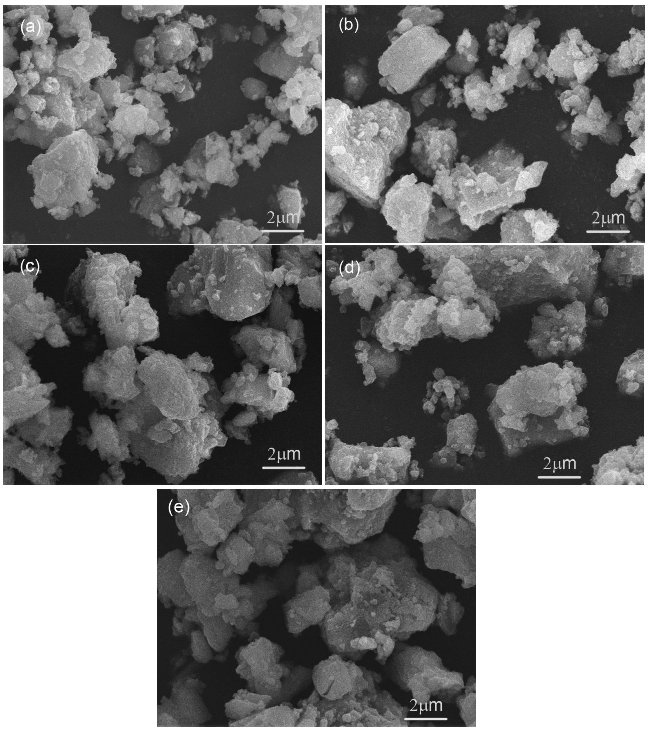

Fig. 1. SEM images of strontium titanate with respect to *n*(Sr)/*n*(Ti) molar ratio; (a) 0.3:1, (b) 0.5:1, (c) 0.8:1, (d) 1:1, (e) 1.2:1, (f) 1.4:1

The pattern of the sample prepared at *n*(Sr):*n*(Ti) = 0.5:1 showed relatively strong diffraction peaks of anatase TiO_2 when Sr content was low and the material was composed of $SrTiO_3$, TiO_2 and a small amount of Sr_2TiO_4. The main type of strontium titanate produced in this condition was $SrTiO_3$ because strontium atoms were not as many as titanium atoms. Meanwhile, a strong diffraction peak of anatase TiO_2 appeared at (120) plane, indicating that more TiO_2 crystals formed from the excessive titanium atoms at low *n*(Sr)/*n*(Ti) ratio.

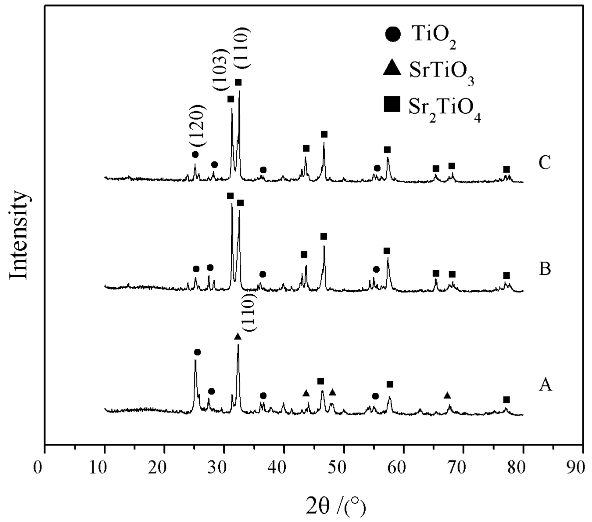

Fig. 2. XRD patterns of strontium titanate prepared with different *n*(Sr)/*n*(Ti) ratio; (A) 0.5:1, (B) 1:1, (C) 1.4:1

With increasing n(Sr)/n(Ti) molar ratio, diffraction peaks of Sr_2TiO_4 became stronger and diffraction peaks of $SrTiO_3$ disappeared at n(Sr)/n(Ti) = 1:1 and 1.4:1. The sample prepared with n(Sr)/n(Ti) = 1:1 showed strong and sharp characteristic diffraction peaks of Sr_2TiO_4, indicating that the main substance produced was Sr_2TiO_4 accompanied with a small amount of TiO_2. Sr_2TiO_4 phase was produced instead of $SrTiO_3$ in the products if there were sufficient strontium atoms provided at high n(Sr)/n(Ti) ratio. Anatase TiO_2 crystals were also produced in the two samples in spite of difference at relative ratios of strontium and titanium atoms involving in the reactions.

At the same time, Sr_2TiO_4 crystallite sizes of the two samples prepared with n(Sr)/n(Ti) = 1:1 and 1.4:1 were 23.6 nm and 25.5 nm, calculated through Sr_2TiO_4 (110) plane by Scherrer formula. As can be seen from the XRD results, the produced material was mainly composed of $SrTiO_3$ and TiO_2 when n(Sr)/n(Ti) was less than 1:1, while the materials mainly composed of Sr_2TiO_4 were prepared at n(Sr)/n(Ti) ratios higher than 1:1.

As indicated by SEM images, the strontium titanate materials showed fairly rough surface morphologies. Table-1 lists BET specific surface areas of strontium titanate prepared with different n(Sr)/n(Ti). Although specific surface areas of all the samples were not high, the sample prepared with n(Sr)/n(Ti) of 1:1 possessed the highest surface area of 9.02 m^2/g. The variation of surface area with the change of n(Sr)/n(Ti) ratio can also be attributed to phase composition of the produced materials. Not only different substances have unique surface areas, but also the same substance such as Sr_2TiO_4 may have different surface area in accordance to crystallite size and aggregation status related to different n(Sr)/n(Ti) ratios. Both particles aggregation of the same substance and phase boundaries of different substances may contribute to roughness of the produced materials and can result in holes on the external surface.

TABLE-1
BET SPECIFIC SURFACE AREAS OF STRONTIUM TITANATE PREPARED WITH DIFFERENT n(Sr)/n(Ti)

n(Sr)/n(Ti)	BET specific surface area ($m^2 g^{-1}$)
0.3	5.75
0.5	6.21
0.8	6.74
1.0	9.02
1.2	6.98
1.4	6.56

Photocatalytic degradation of methyl orange on the prepared materials as the factor of n(Sr)/n(Ti) ratio is shown in Fig. 3. Being prepared at the same temperature of 800 °C, degradation rates of the strontium titanates showed obvious dependence on the initial n(Sr)/n(Ti) ratio in the sol. The sample with n(Sr)/n(Ti) = 1:1 presented the optimal photocatalytic activity, where 32.5 % of the initial methyl orange was degraded after 30 min of irradiation.

Photocatalytic degradation rate on the sample with n(Sr)/n(Ti) = 0.3:1 was 21.3 %. Photocatalytic activities of the other samples increased with increasing n(Sr)/n(Ti) ratio up to 1:1. As indicated before, the main substance formed in the samples prepared with low n(Sr)/n(Ti) ratio was $SrTiO_3$, accompanied with small amounts of TiO_2 and Sr_2TiO_4. Photocatalytic activities of the samples mainly came from the contribution of $SrTiO_3$, since TiO_2 prepared at temperature as high as 800 ºC usually had very low activity.

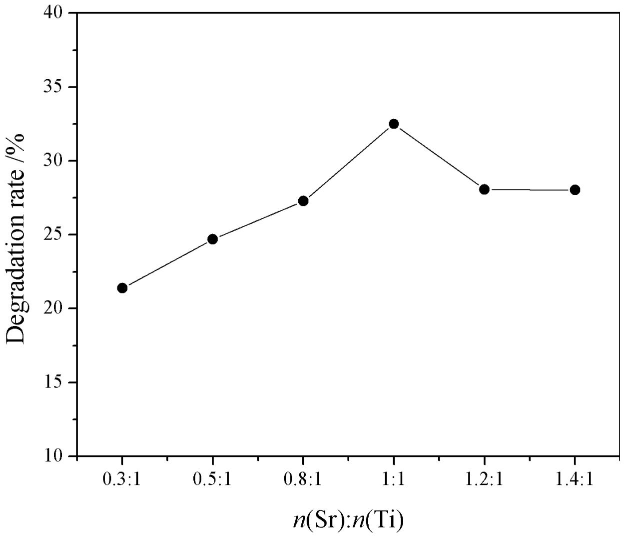

Fig. 3. Effect of n(Sr)/n(Ti) ratio on photocatalytic activity of strontium titanate

The samples prepared with high n(Sr)/n(Ti) ratio showed improved photocatalytic activity. Because the main substance produced in these samples was Sr_2TiO_4, it revealed that strontium titanate in the phase of Sr_2TiO_4 had better activity than that of $SrTiO_3$. The variation of photocatalytic activity with the change of n(Sr)/n(Ti) ratio was in close relationship with the composition of the samples. Since compositions of the samples obtained with n(Sr)/n(Ti) ratio higher than 1:1 were nearly the same, the slowly activity decrease at n(Sr)/n(Ti) ratios of 1.2:1 and 1.4:1 may come from increasing crystallite size and decreasing specific surface area.

Since the sample prepared with n(Sr)/n(Ti) = 1:1 had the optimal photocatalytic activity, further characterizations of the sample were investigated. As shown in Fig. 4, FT-IR spectrum of the strontium titanate [n(Sr)/n(Ti) = 1:1] indicates representative bond characteristics of the sample. There is no adsorption after 2000 cm^{-1}, indicating that organic substances decomposed totally during high temperature calcination. The adsorption peak at 1569 cm^{-1} represents bending vibration of -OH in H_2O, which was adsorbed on surface of the sample[17]. The adsorption peak situated at 837 cm^{-1} is assigned to vibration of $COOH^-$ contacted with Sr or Ti and the peak at 1046 cm^{-1} is assigned to vibration of Sr-O bond. The adsorption peak appeared at 489 cm^{-1} can be ascribed to be bending vibration of Ti-O-Ti[18]. The results are in accordance to composition revealed from XRD analysis[19,20]. As indicated before, the strontium titanate prepared with n(Sr)/n(Ti) = 1:1 was composed of mainly Sr_2TiO_4 and a small amount of TiO_2, the Sr-O bond and Ti-O-Ti bond were representatives of the produced substances.

When 1000 mg/L of strontium titanate [n(Sr)/n(Ti) = 1:1] was applied to the solution, 32.5 % of the initial methyl orange was degraded after 30 min of irradiation. Meanwhile, 37.8 % of the initial methyl orange was degraded when 3000 mg/L of strontium titanate was used during the same irradiation time period. Methyl orange decolouration on strontium titanate [n(Sr)/n(Ti) = 1:1] with respect to irradiation time is shown in Fig. 5. The results clearly revealed that degradation of methyl orange on the optimized strontium titanate photocatalyst increased constantly along with irradiation time. After 2 h of irradiation, 78 % of the initial methyl orange was degraded on the material. At the same time, methyl orange adsorption on the material was not more than 2.85 % during the same time period. Given enough time, all of the methyl orange can be expected to degrade on the material. The strontium titanate photocatalyst prepared in this study had fairly high activity on dye degradation.

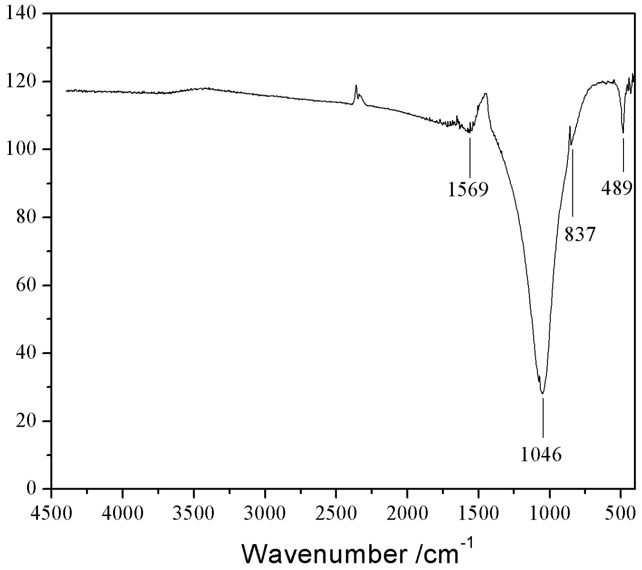

Fig. 4. FT-IR spectrum of strontium titanate [n(Sr)/n(Ti) = 1:1]

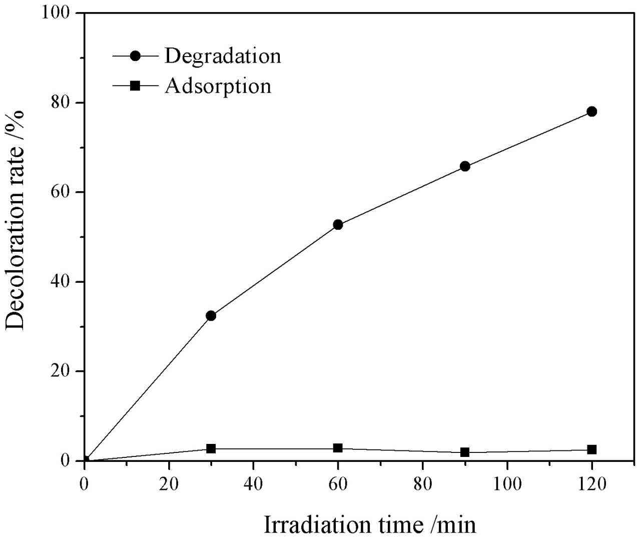

Fig. 5. Methyl orange decolouration on strontium titanate [n(Sr)/n(Ti) = 1:1] with prolonged irradiation time

Conclusion

The effects of strontium-titanium molar ratio on phase composition, structure and photocatalytic activity of the prepared strontium titanates were studied. Phase composition of the produced materials showed strong dependence on n(Sr)/n(Ti) ratios in the initial precursors. The sample prepared with n(Sr)/n(Ti) = 1:1 showed strong and sharp characteristic diffraction peaks of Sr_2TiO_4, indicating that the main substance produced was Sr_2TiO_4. The sample prepared with n(Sr)/n(Ti) = 1:1 had the optimal photocatalytic activity. After 2 h of irradiation, 78.0 % of the initial methyl orange degraded on the material.

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