

Photocatalytic activities of sulfur doped SrTiO₃ under simulated solar irradiation

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ABSTRACT

S-doped SrTiO₃ was synthesized by the solid state reaction method between S and SrTiO₃ powder under the N₂ flow. The effect of temperature, calcination time and S-content on the formation and photocatalytic activity of SrTiO₃ were investigated. The morphology and properties of obtained powders were characterized by XRD, UV-DRS, UV-VIS, SEM,

BET. The photocatalytic activities of S-doped SrTiO₃ was also investigated through the decomposition of methylene blue. As a result, the 10 %S-doped SrTiO₃ contributed to the decrease of band gap energy to 2.73 eV and enhanced the photocatalytic activity for methylene blue degradation of 74.5 % after 180 min irradiation.

Keywords: *S-doped SrTiO₃, photocatalytic activity, methylene blue.*

1. INTRODUCTION

Strontium titanate (SrTiO₃) is one of important materials which has applications in photocatalysis and electronics industry and has attracted much attention from both fundamental and practical viewpoints [1]. As an efficient photocatalyst, strontium titanate (SrTiO₃) has been widely researched for the degradation of various organic contaminants, such as dyes and other organic compounds, contributing to solve the environmental problems or for water splitting to produce clean energy [2]. However, there has been the drawback of pure SrTiO₃ which just could respond to UV light due to its

large energy gap (3.0–3.2eV), and thus, more than 95% solar light would be wasted [3].

In recent years, some groups have carried out the studies on the doping sulfur into TiO₂ lattice to red shift the absorption edge. It was found that sulfur is more efficient for improving the photocatalytic activity under visible light region [4]. For example, Zhou Zhiqiang et al [5] prepared S-doped nanosized TiO₂. The as-prepared S-doped TiO₂ nanosized possessed strong absorption for visible light of 400–650 nm, and showed high photocatalytic activity for decomposition of methylene blue under irradiation of visible light. Besides, Mohamad et

al. [6] demonstrated that the visible light responsible sulfur-doped TiO_2 samples (STN) was successfully synthesized. The results indicated that the amount of sulfur doping could enhance the photocurrent. These STN samples are interesting candidates to drive photochemical reactions, such as water reduction (H_2 production) and oxidation of pollutants. Furthermore, Teruhisa Ohno et al. [7] succeeded in preparing S-doped TiO_2 photocatalysts which shows relatively high photocatalytic activity under visible light at wavelengths longer than 500 nm, may have a wide range of applications.

Regarding to efficiency of doping of sulfur, Teruhisa Ohno et al [8] modified SrTiO_3 by doping S and C that improved the photocatalytic activity of the doped SrTiO_3 for oxidation of 2-propanol. Under a wide range of light irradiation (at wavelengths longer than 350 nm) the photocatalytic activity levels of C, S cation-codoped SrTiO_3 were about two times higher than those of pure SrTiO_3 .

In this research, the modified SrTiO_3 by sulfur photocatalytic material were synthesized and characterized using analytical techniques such as XRD, SEM, UV-vis (DRS). Finally, their photocatalytic activities were evaluated by studying the degradation of methylene blue under visible light irradiation.

2. EXPERIMENT

2.1. Materials

S-doped SrTiO_3 (STO) powders were synthesized using strontium nitrate $\text{Sr}(\text{NO}_3)_2$ (>99.5%), tetra-n-butyl orthotitanate $\text{Ti}(\text{OC}_4\text{H}_9)_4$ (99%-Merck), hydrogen peroxide H_2O_2 (30%), ammonia solution NH_3 (25%), citric acid (CA) $\text{C}_6\text{H}_8\text{O}_7$ (99.5%) ethylene glycol $\text{C}_2\text{H}_6\text{O}_2$

(>98%) and S as reagents without any further purification.

2.2. Synthesis of SrTiO_3

The SrTiO_3 powder was prepared by sol-gel method. The process was as follows: 0.015 mol of $\text{Ti}(\text{OC}_4\text{H}_9)_4$ was dissolved in 120 mL H_2O_2 and 60 mL NH_3 , the mixture was stirred at room temperature until the solution became clear. Then, the solution was added into 100 mL citric acid solution, following by 0.015 mole $\text{Sr}(\text{NO}_3)_2$ (the mole ratio of Sr^{2+} : CA is 1:3). Next, 0.9311 g ethylene glycol was added into the solution for esterification. The resulting solution was heated at 80 - 90 °C for 5-6 hours to form a gelation. The gel was dried at 150 °C in 2 hours and then ground, named as raw sample, calcined at different temperatures and duration.

2.3. Synthesis of S-doped SrTiO_3

The modification of SrTiO_3 by sulfur was carried out by grinding mixture of 800 °C calcined STO and S power for 2h with various weight percentage of 5, 10, 20. The obtained mixture was calcined under the N_2 flow at 400-600 °C for 2h. This process synthesized the S doped STO at various S contents namely 5%, 10% and 20%.

2.4. The characterization of products

X-ray diffraction (XRD) patterns of S-doped SrTiO_3 and undoped powders were using monochromatic high intensity CuK_α radiations ($\lambda = 0.15418$ nm) at the scanning rate of 0.03 °/s and in the scanning range from 20 ° to 75 °. Specific surface area using Brunauer–Emmett–Teller (BET) analysis was obtained by nitrogen adsorption–desorption isotherms at 77 °K after degassing the sample at 300 °C for 2 hours

under nitrogen gas, using Quantachrome NOVA 1000e. The band gap energy of samples was determined by diffuse reflectance spectra (DRS) from 300 to 800 nm, scanning step was 2 nm, at 400 nm/min speed, using Solid UV-vis JASCO Corp equipment.

2.5. The decomposition of Methylene Blue

Photocatalytic activity of the material was evaluated by determining the decomposition efficiency of MB in isothermal condition room temperature. Each experiment consisted of 0.1 g catalyst, which was dispersed into 200 mL solution of 10 ppm methylene blue, the solution was kept in darkness for 1 hours in order to reach absorption/desorption equilibrium. Then, the mixture was lightened by 195W Compact light (simulated solar), the wavelength (λ) of which was from 390 to 750 nm. During the process, the solution was stirred constantly and cooled to room temperature by water-jacket system. Every period of time, approximately 3-5 mL solution was taken out and filtered using GC (PTFE 0.45 μ m). The filtered solutions were then determined concentration of excess of methylene blue by Spectro 2000-RS, respectively, with maximum absorption wavelength of 664 nm. Then those excess solutions were brought back to reactor to maintain the volume. Blank sample, which had

no catalyst in it, was also carried out in this experiment for comparison purpose. The photocatalytic degradation efficiency is C/C_0 (C , C_0 are of certain and initial concentration solution, respectively).

A total organic carbon (TOC) was used for the determination of MB as TOC content.

3. RESULTS AND DISCUSSION

The XRD patterns of different calcined temperature STO are shown in Figure 1(a). As can be seen, at the 600 °C there is the formation of the dominant peaks at $2\theta = 32.5, 39.9, 46.6, 57.9, 77.08^\circ$ correlated to the indexed peaks in SrTiO₃ JCPDS card number of 35-0734. Moreover, the intensity of peaks increases with the increase of calcination temperature resulting in the rise of crystallinity.

The influence of calcination times (0.5, 1, 3, 6 h) on the purity phase and crystallinity of STO was also investigated through the X-Ray diffraction represented in Figure 1(b). It is clearly that the structure of STO was formed after 30 min of calcination due to the appearance of peaks at $2\theta = 32.5, 39.9, 46.6, 57.9, 77.08^\circ$. However, there is the peak of impurity attributed to the presence of TiO₂ as shown in the Figure. When increasing the calcination time, the intensity of impurity peak decreases gradually and disappears after 3 h soaking.

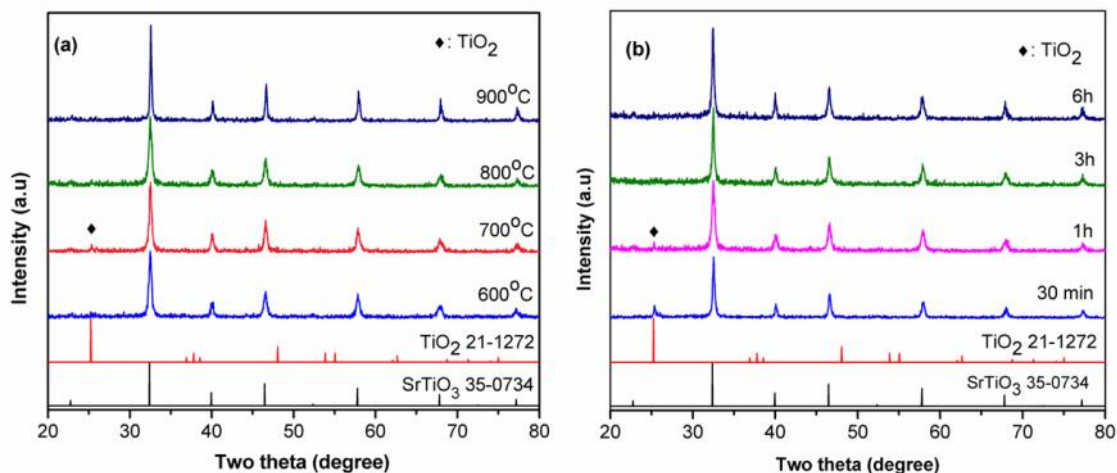


Figure 1. The XRD patterns of SrTiO₃ at different temperatures (a) and times (b).

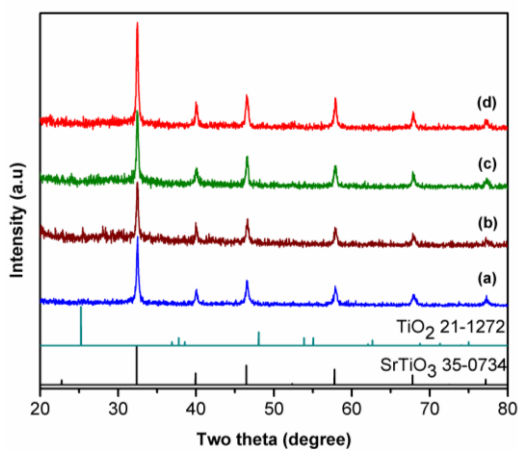


Figure 2. The XRD patterns of 800 °C calcined samples: (a) SrTiO₃, (b) 5%, (c) 10% and (d) 20% S-doped SrTiO₃

Figure 2 describe the XRD patterns recorded from S-doped SrTiO₃ (S-STO) with the various S contents. The higher S contents lead to

the increase of intensity of peaks and there is no impurity phase of sulfur compound detected. Therefore, it can be concluded that the solid solution of S-doped SrTiO₃ was successfully prepared.

From the table 1, there is the presence of a small amount of S in all doped samples and this amount increased with the increase of initial ratio between S : SrTiO₃. According to the calculation from the SEM-EDX results, the ratio of the total amount of (%O + %S) to the Sr is approximately equal 3:1 indicating that S was dispersed and just partially substituted for oxygen in the STO structure. As the results, the formulars for the doped SrTiO₃ with 5%, 10% 20% of S is SrTiO_{2.99}S_{0.01} (A1), SrTiO_{2.97}S_{0.03} (A2), SrTiO_{2.71}S_{0.29} (A3), respectively

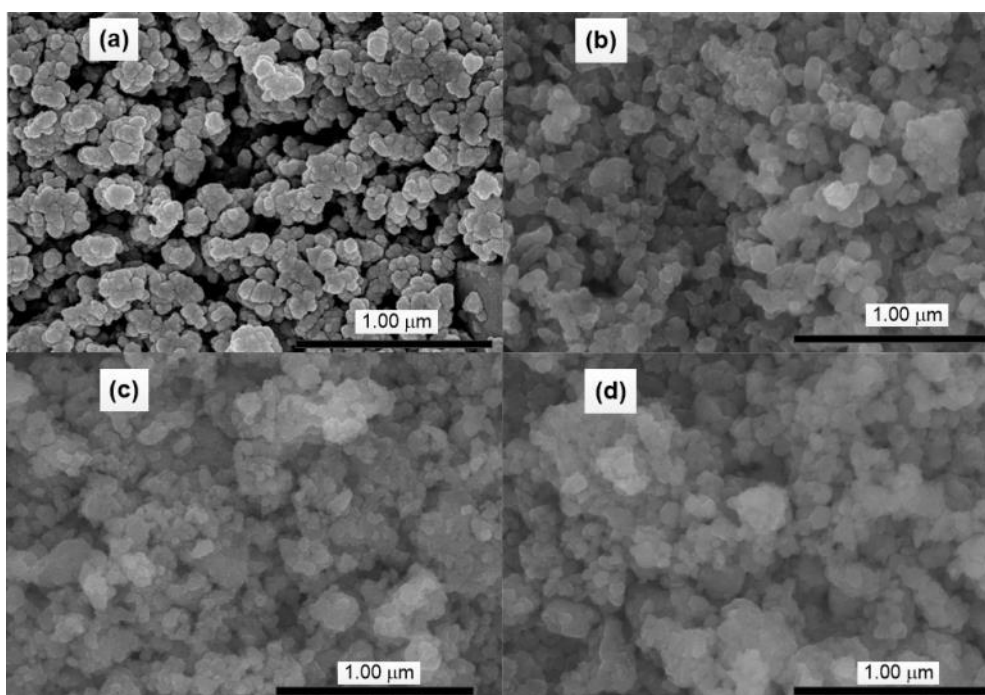


Figure 3. Morphologies of the 800 °C calcined powder samples: (a) SrTiO₃, (b) 5%, (c) 10% and (d) 20 % S-doped SrTiO₃

Table 1. The EDX results of S–doped SrTiO₃ with the various S contents.

Element	STO	5%S-STO	10%S-STO	20%S-STO
O	59.25	61.15	60.63	54.31
S	–	0.23	0.62	5.87
Ti	19.48	20.21	20.23	19.78
Sr	21.27	19.41	18.52	20.04
Total	100	100	100	100

The morphologies of the S-doped SrTiO₃ powder are represented in Figure 3. In general, the particles sizes are in range of 80-150 nm and there is the agglomeration among particles.

Besides, the particle size of S-doped STO are smaller (around 80-100 nm) and less agglomeration than that of undoped sample. Moreover, it seems that the degree of agglomeration increase with increasing the S content. Therefore, the specific surface area of samples was increases with the increasing of sulfur contents, as shown in Table 2.

Table 2. Specific surface area of S-doped SrTiO₃ samples

Sample	STO	5%S-STO	10%S-STO	20%S-STO
BET (m ² /g)	12.11	17.964	18.153	22.345

Table 3. The band gap energy of S-SrTiO₃ (0%, 5%, 10% and 20%).

S-SrTiO ₃	0%	5%	10%	20%
E _g (eV)	3.20	2.87	2.73	3.00

UV-vis diffuse reflectance spectra of S-doped STO with the different sulfur contents is shown at Fig. 4 and the band gap energy is also calculated using the formular of $E_g = 1240/\lambda$ (eV) [9]. As can be seen, the photo-absorption of S-STO in the visible region increases with the increase of dopant content. Besides, the results from the Table.3 indicated that the band gap energy decrease gradually from 3.2 eV (SrTiO₃) to 3.04 eV (A1) and 2.75 eV (A2).

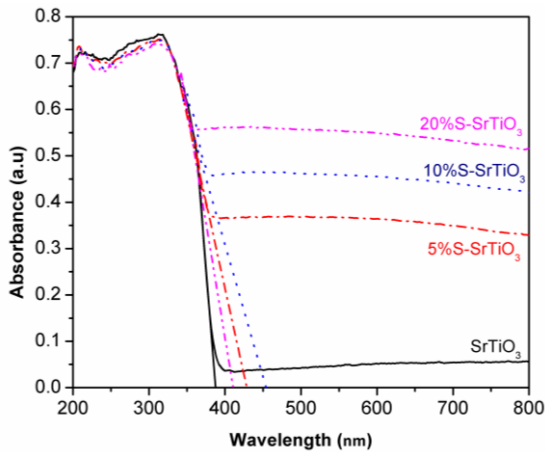


Figure 4. UV-vis diffuses reflectance spectra of (a) SrTiO₃, (A1), (A2) (A3) samples.

The photocatalytic activity of STO at various calcined temperatures is represented in Figure 5(a). The yield of decomposition of MB increase with the calcined temperature, from 25% (at 600°C) to 45% (at 800°C) after 180 min irradiation. However, the activity of 900°C calcined samples is lower than that of 800°C calcined STO. It can be explained that the

higher calcination temperature leads to the rise of crystallinity and simultaneously decrease the specific surface area due to the agglomeration of particles. As a result, the STO calcined at 800°C could get the highest decomposition yield of MB. In addition, the calcination time also affect the crystallinity and particle sizes. The yields of decomposition are described at Fig.5b. The sample calcined at 800°C for 3h give the highest rate of decomposition of MB after 3h exposing, being 45%.

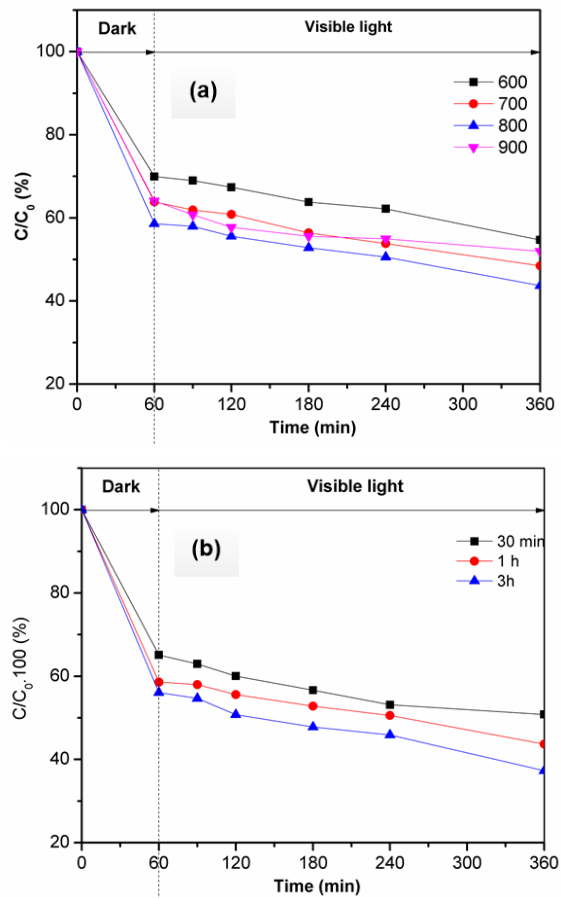


Figure 5. The MB decomposition of STO with (a) various calcined temperature and (b) calcined duration

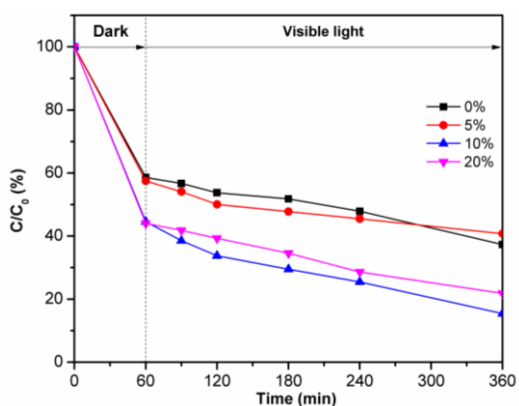


Figure 6. MB decomposition of various samples

Figure 6 provide the photocatalytic activity for the MB decomposition of S doped SrTiO_3 (SrTiO_3 , A1, A2, A3). The proportion of degradation raised from 52.1% (SrTiO_3) to 54.5 % (A1) to 74.5 % (A2) and decrease to 71.4 % (A3). The increase and decrease in MB degradation due to the band gap energy decrease from 3.20 eV (SrTiO_3) to 2.73 eV (A2) and increase to 3.0 eV (A3) Moreover, the specific surface area also increases with the higher S contents which contributed to enhancing the yield of decomposition. The depression of MB degradation in the 20% S-doped sample can be explained of the bandgap larger.

The photocatalytic activities of SrTiO_3 and 10 % S-doped SrTiO_3 were examined by studying the TOC degradation of MB at an initial concentration of 10 mg/L MB, pH 6.7 and a catalyst dose of 0.5 g/L after 180 min solar simulated irradiation. The results show a higher

TOC removal for 10 %S doped sample of 52.2 % compared with the undoped sample of 35.4 %. This can be attributed to a lower band gap energy of 10 %S-doped SrTiO_3 (2.73 eV) compared with band gap energy of SrTiO_3 (3.2 eV). Narrower band gap of 10 %S-doped SrTiO_3 lead to enhance the photocatalytic activities for MB degradation. Moreover, lower TOC of 52.2 % than MB degradation yield of 74.5% revealed that MB could not fully mineralize to CO_2 .

4. CONCLUSION

This study prepared the S-doped SrTiO_3 applying for the decomposition of Methylene Blue. The XRD, BET, SEM, UV-Vis results indicated the obtained S-doped SrTiO_3 was single phase and had the spherical shape, the specific surface area also increased with the increase of S content. Regarding to the photocatalytic activity, The $\text{SrTiO}_{2.97}\text{S}_{0.03}$ (A2) could get the highest rate of decomposition in the comparison with the remaining samples. In conclusion, the presence of small amount of S content could decrease the band gap energy and enhance the photocatalytic activity of SrTiO_3 through the decomposition of MB.

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Hoạt tính quang xúc tác của SrTiO₃ biến tính với lưu huỳnh trong vùng ánh sáng khả kiến.

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TÓM TẮT

S biến tính SrTiO₃ đã được tổng hợp bằng phương pháp phản ứng pha rắn của lưu huỳnh và bột SrTiO₃ trong dòng khí N₂. Những ảnh hưởng của nhiệt độ, thời gian nung kết và hàm lượng lưu huỳnh lên sự hình thành và hoạt tính quang xúc tác của SrTiO₃ được khảo sát. Hình thái và các thuộc tính của vật liệu được chỉ ra thông qua XRD, UV-DRS, UV-VIS, SEM, BET.

Từ khoá: S-doped SrTiO₃, hoạt tính xúc tác quang, methylene blue.

Hoạt tính quang xúc tác của S-doped SrTiO₃ được khảo sát thông qua thí nghiệm phân huỷ methylene blue. Dựa trên các kết quả thu được có thể kết luận rằng, sự có mặt của lưu huỳnh đã góp phần giảm năng lượng vùng cấm và đồng thời nâng lên hiệu quả xúc tác quang học của SrTiO₃.

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