Photo-oxidation Property of Nitrogen and Fluorine Co-doped SrTiO$_3$ Made by Mechanochemical Method

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Nitrogen and fluorine co-doped SrTiO$_3$ was prepared by high energy planetary grinding of the mixture of SrTiO$_3$, urea and SrF$_2$. The nitrogen doping content increased with fluorine doping fraction. The photocatalytic activity for nitrogen monoxide oxidation of SrTiO$_3$ in both visible light (λ>400nm) and near ultraviolet light (λ>290nm) regions could be improved greatly by co-doping of nitrogen and fluorine. Under the irradiation of light with wavelength larger than 400 nm, the photocatalytic activities of nitrogen and fluorine co-doped SrTiO$_3$ were 2.6 times greater than that of pure SrTiO$_3$. The high visible light photocatalytic activity of this substance may be due to the formation of a new band gap that enables to absorb visible light effectively.
Key words: nitrogen, fluorine, co-doping, SrTiO$_3$, visible light-driven

1. INTRODUCTION

The photocatalytic elimination of pollutants in water and air has attracted much interest around the world. Although strontium titanate (SrTiO$_3$) is one of important photocatalytic materials [1-3], it can utilize only ultraviolet (UV) light less than 390 nm of wavelength which is less than 5% of the solar beams on the earth because of relatively large band gap energy of 3.2 eV. In the past, many researchers have attempted to modify the electronic properties of semiconductors such as TiO$_2$ in order to extend its optical absorption edge to the visible light region and to improve the photocatalytic activity. Recently, some groups have carried out the doping nonmetal elements into TiO$_2$ lattice to red shift the absorption edge [4-8]. It was found that anion doping, especially nitrogen ion doping is more efficient for improving the photocatalytic activity. We found that nitrogen doping is also effective to improve visible light response photocatalytic activity of SrTiO$_3$. It is suspected, however, that replacing O^{2-} with N^{3-} would result in the formation of anion defects for the charge compensation and the anion defects would act as electron-hole recombination centers. It is expected that the charge compensation is satisfied if two O^{2-} are replaced with one N^{3-} and one F$^-$ simultaneously. Therefore, in this paper nitrogen and fluorine co-doped SrTiO$_3$ is reported as a novel stable photocatalyst for NO destruction under visible light irradiation. In the past, nonmetal atoms such as nitrogen and sulfur were doped into TiO$_2$ lattice by heat treatment of TiO$_2$ under NH$_3$ flow at 600 °C [4] and oxidative heating of TiS$_2$ powder at 500-600 °C[5]. In the present study we used a novel method, mechanochemical reaction, for the synthesis of nitrogen and fluorine co-doped SrTiO$_3$ without heating using commercially available chemical reagents such as urea and SrF$_2$ as the nitrogen and fluorine sources.

2. EXPERIMENTALS

2.1 Sample preparation

Stoichiometric strontium titanate was synthesized by solid state reaction of SrCO$_3$ and TiO$_2$ (Kanto Chem. Co. Inc. Japan) at 1100°C for 2 h as shown in Eq. (1)

$$SrCO_3 + TiO_2 \rightarrow SrTiO_3 + CO_2 \qquad (1)$$

SrTiO$_3$ powder was mixed with 22 mol% of urea or the mixture of 22 mol% urea and SrF$_2$ with different molar ratios (Kanto Chem. Co. Inc. Japan). A planetary ball mill (Pulverisette-7, Fritsch, Germany) was used to grind the mixture at 700 rpm rotation speed for 2 h at room temperature in air. Three grams of the mixed powder was charged in a zirconia pot of 45 cm^3 inner volume with seven zirconia balls of 15 mm in diameter. Then the ground powder was calcined at 400°C to remove the by-products.

2.2 Catalyst characterization

X-ray diffraction (XRD) patterns were obtained using Cu Kα radiation (Shimadzu XD-D1). Specific surface areas (BET), Barrett- Joyner- Halenda (BJH) pore distribution and pore parameters of the powder samples were determined by nitrogen adsorption-desorption isotherm measurements at 77K (Quantachrome NOVA 1000-TS). The binding energies of Sr, Ti, N, F and O were measured at room temperature using an electron spectrometer (Perkin

Elmer PHI 5600). The peak position of each element was corrected by using that of C1s (284.6 eV). The particle size and shape were evaluated by transmission electron microscope (JEM-2000EX).

2.3 Photocatalytic activity measurement

A 450 W high pressure mercury arc was used as the light source, where the light wavelength was controlled by selecting filters, i.e., Pyrex glass for cutting off the light of λ <290 nm, Kenko L41 Super Pro (W) filter < 400 nm. The photocatalyst sample was placed in a hollow place of 20 x 15 x 0.5 mm^3 on a glass holder plate and set in the center of the reactor. The elimination of nitrogen monoxide was determined by measuring the concentration of NO gas at the outlet of the reactor (373 cm^3) during the photoirradiation of constant flowed 1 ppm NO and 50 vol% air (balance N_2) mixed gas (200 $cm^3 \cdot min^{-1}$). The concentration of NO was determined by a NO_x analyzer (Yanaco, ECL-88A).
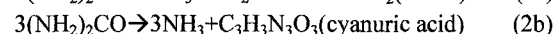
3. RESULTS AND DISCUSSIONS

3.1 Characterization

The powders made by grinding the mixtures of SrTiO₃ and urea, SrTiO₃, urea and SrF₂ consisted of single phase SrTiO₃ which is completely identified as a perovskite-type structure having cubic symmetry as revealed by X-ray pattern. In order to confirm the doping of nitrogen and fluorine in SrTiO₃ lattice, X-ray photoelectron spectra analysis was carried out in this experiment. Figure 1 shows (A) N/s and (B) F/s XPS spectra of different samples. Using urea and SrF₂ as the co-doping nitrogen and fluorine sources, all samples showed N1s peaks at about 398.45 eV. The peak was assigned to the doping state of nitrogen by comparison with that obtained for starting material urea since the binding energy of N/s of urea located at 1.25eV higher energy side, 399.70 eV (Fig.1(A)a). By comparison of F/s binding energies of pure SrF₂ and the sample, the peak positioned at 683.90 eV could be taken as the doping state of fluorine in SrTiO₃ lattice. The concentrations of the elements in various nitrogen and fluorine co-doped SrTiO₃ samples have been calculated from the XPS peak areas of individual elements through

sensitivity factors for these elements. Since no peak corresponding to urea and SrF₂ remained, the amount of nitrogen and fluorine calculated from XPS result could be taken as the doped content of these two elements. For the sample prepared with SrTiO₃ powder added 22mol% urea and 1mol% SrF₂, the atomic ratios of N/O and F/O were calculated as 0.0089 and 0.014, indicating that the anion defect could not be removed under present reaction conditions and the sample might be described as $SrTiO_{3-3x/2-y/2}N_xF_y\square_{(x-y)/2}$. The mole fraction of nitrogen and fluorine doped were calculated as 0.026 and 0.041, respectively, under the condition that both nitrogen and fluorine have a substitutional fraction of fs=1. The compositions, doping fractions of nitrogen and fluorine and the specific surface areas of the various samples are summarized in Table1. It should be noted that the content of nitrogen doped increased with fluorine doping fraction and the atomic ratio F/N was more than one.

The doping of nitrogen and fluorine seemed to proceed as follows. At first urea was decomposed during the grinding as

$$2(NH_2)_2CO \rightarrow NH_3 + NH_2CONHCONH_2(\text{biuret}) \quad (2a)$$
$$3(NH_2)_2CO \rightarrow 3NH_3 + C_3H_3N_3O_3(\text{cyanuric acid}) \quad (2b)$$

The solid-state interdiffusion reaction during reactive ball milling was triggered by fragmentation of SrTiO₃ powder thus creating new surfaces. These freshly created surface reacted with NH₃ and SrF₂ to form a nitrogen and fluorine co-doped SrTiO₃ surface layer over the unreacted core particles. With further milling this doping reaction continued to form $SrTiO_{3-3x/2-y/2}N_xF_y\square_{(x-y)/2}$ and the undoped core of SrTiO₃
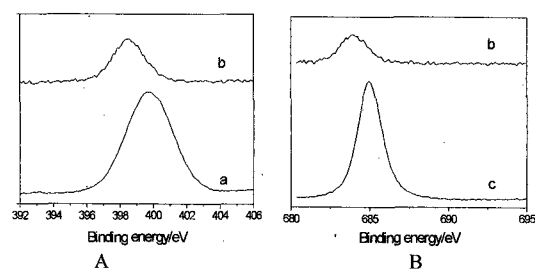

Fig.1 XPS spectra of (A) N/s and (B) F/s of (a) pure urea, (b) nitrogen and fluorine co-doped SrTiO₃ followed by heat treatment at 400°C and (c) pure SrF₂.

Table I Initial compositions in moles, doping fraction of nitrogen and fluorine and specific surface areas of the samples prepared

Samples	C_N/C_O (X 10⁻¹)	C_F/C_O	N doping fraction	F doping fraction	Specific surface area(m².g⁻¹)
SrTiO₃					3.9
Sample 1 (78% SrTiO₃ added 22% urea)	0.057	0	0.017		34.6
Sample 2 (77.5% SrTiO₃ added 22% urea and 0.5% SrF₂)	0.089	0.014	0.026	0.041	34.0
Sample 3 (76.5%SrTiO₃ added 22% urea and 1.5% SrF₂)	0.097	0.018	0.028	0.054	35.0
Sample 4 (75.5%SrTiO₃ added 22% urea and 2.5% SrF₂)	0.104	0.049	0.032	0.138	36.5

disappeared resulting in a nanostructured nitrogen and fluorine co-doped SrTiO₃.

The pore size distributions of these two samples are also depicted in Fig.2. Nitrogen and fluorine co-doped sample exhibits a rather narrow distribution with two pore size families (Fig.2b). The first one was located at
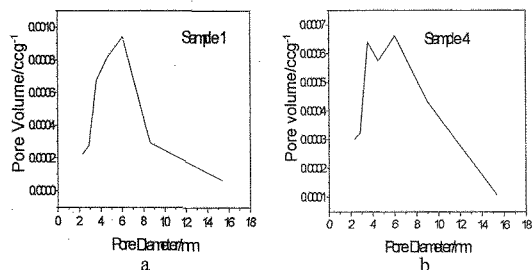

Fig.2 Pore size distribution for (a) Sample 1 and (b) Sample 4.

about 4 nm, and the second was at 6 nm. The sample prepared with urea and SrTiO₃ (Fig.2a) showed also pore size distribution in the diameter range 4-6 nm. The first peak at 4 nm has lower population, but the total pore volume (64.8 $cm^3 \cdot g^{-1}$) was higher than that of nitrogen and fluorine co-doped SrTiO₃ (54.6 $cm^3 \cdot g^{-1}$).

Crystallite size and particle size of starting material SrTiO₃ and nitrogen and fluorine co-doped SrTiO₃ were evaluated by broadening of XRD profile and TEM observation. The calculated results show that both nitrogen doped and nitrogen and fluorine co-doped SrTiO₃ have nearly the same grain size in the range 24.5-27.4 nm, whereas the starting material SrTiO₃ has larger grain size of 50.4 nm. Direct TEM observation shows that starting material SrTiO₃ consisted of relatively large particles of about 0.2-0.5 μm in diameter (see Fig. 3a), whereas the nitrogen and fluorine co-doped SrTiO₃ consisted of two kinds of particles in size (Fig. 3b). One is the spherical nano-sized particles about 20 nm in diameter which agreed with that calculated from XRD peaks. The other one was spherical aggregated particles in the size range 0.1-0.2 μm with the surface was covered by tiny crystallites. It is clear that the decrease in particle size was brought by high energy grinding. During high energy milling SrTiO₃ powders were subjected to severe mechanical deformation from the collisions with milling balls and pot. Consequently, plastic deformation at high strain rates occurred within SrTiO₃ powders and the average grain size could be reduced to about 20-30 nm.

The diffuse reflectance spectra of pure SrTiO₃, nitrogen doped SrTiO₃ (Sample 1) and the co-doped SrTiO₃ (sample 4) are depicted in Fig.4. Pure SrTiO₃ did not absorb visible light, but nitrogen and fluorine co-doped SrTiO₃ absorbed visible light over 500 nm. In other words, the absorption edge of SrTiO₃ shifted toward the visible light range after nitrogen and fluorine doping. The band gap of these samples could be

calculated by the following equation (3).

$$E = \frac{1239.8}{\lambda} \quad (eV) \quad (3)$$

λ, the absorption edge, was determined from absorption spectrum. SrTiO₃ had absorption edge at approximately 390 nm corresponding to the band gap of 3.18 eV (Fig. 4a), which agreed with the value of 3.20 eV in a literature [8]. After doping with nitrogen, the absorption edge of SrTiO₃ shifted to 19 nm longer wavelength, corresponding to 3.03eV. The nitrogen and fluorine co-doped SrTiO₃ showed two absorption edges at 390 (3.18 eV) and 500 nm (2.48eV), which may be attributed to those of SrTiO₃ and nitrogen and fluorine co-doped SrTiO₃ lattice, respectively.
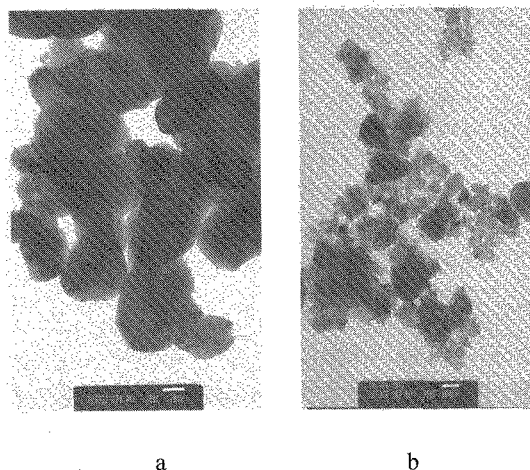

a   b

Fig. 3 Transmission electron micrographs of the samples: a, pure SrTiO₃; b, nitrogen and fluorine co-doped SrTiO₃ (Sample 4).
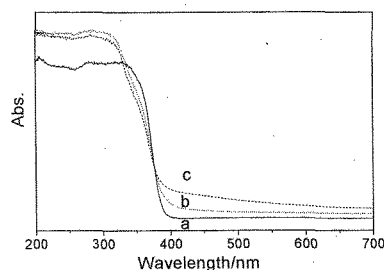

Fig.4 The diffuse reflection spectra of (a) pure SrTiO₃, (b) nitrogen doped SrTiO₃ (Sample 1), (c) nitrogen and fluorine co-doped SrTiO₃ (Sample 4).

3.2 Photocatalytic activity

The photocatalytic activities were evaluated by measuring the destruction degree of nitrogen monoxide by various samples by irradiating the visible light (λ > 400 nm) and ultraviolet light (λ >290 nm) as shown in Fig.5. The oxidation degrees of blank without sample were 9.6% and 20%, respectively (Fig.5f). As expected from its large band gap energy, the photocatalytic activity of pure SrTiO₃ under visible light irradiation was modest. On the other hand, the

nitrogen and fluorine co-doped $SrTiO_3$ followed by calcinations at 400 °C showed the highest NO elimination ratio under the visible light irradiation among the four nonmetallic elements doped samples. Namely, 36.2% NO could be destructed, and the value was about 2.6 times larger than that by pure $SrTiO_3$ (Fig.5d and 5e). Nitrogen doped $SrTiO_3$ calcined at 400 °C showed lower NO photo-oxidation capability (26.6%) than that of nitrogen and fluorine co-doped $SrTiO_3$, but the activity was still much higher than that of pure $SrTiO_3$ (Fig.5b and 5e). Both nitrogen doping and nitrogen and fluorine co-doping could shift the absorption edge of $SrTiO_3$ to the visible light range. It is clear from Fig.4 that the co-doped sample has higher visible light absorption capability than nitrogen doped sample whereas in the UV light range, nitrogen doped $SrTiO_3$ has relatively higher light absorption ability than the co-doped sample. This resulted in the co-doped $SrTiO_3$ had better performance in NO elimination than nitrogen doped sample under the irradiation of light with wavelength larger than 400nm, but it showed lower NO photo-oxidation capability than nitrogen doped sample in UV light range. Our previous work shows that fluorine doping could improve the visible light absorption ability of $SrTiO_3$[9]. We also found that both samples have a certain volume of mesopores, which were responsible for the effective adsorption of NO. According to the previous results in TiO_2 system [10], it is clear that in the presence of oxygen the electrons in the conduction band of $SrTiO_3$ generated by absorbing the light energy are trapped immediately by the molecular oxygen to form •O_2^-, which can then generate high active •OOH radicals. The NO reacts with these reactive oxygen radicals, hole, molecular oxygen and water to produce HNO_2 and HNO_3. The photocatalytic activity results indicate that nitrogen and fluorine co-doped $SrTiO_3$ could function as a stable visible light-driven photocatalyst with good NO elimination potential. On the other hand, the nitrogen and fluorine co-doped $SrTiO_3$ without calcination showed lower capability for the elimination of NO. It might be due to the inhibition of NO absorption by remaining by-products and unreacted nitrogen source compound. Heat treatment of these samples at appropriate temperature such as 400°C might remove these unfavorable contaminations and also decrease the number of defects in the lattice of $SrTiO_3$ produced during high energy grinding because of the high recovery rate of the lattice defect at elevated temperature. But all of these fluorine and nitrogen co-doped $SrTiO_3$ samples showed good photocatalytic activity in near ultraviolet light range. Namely, nitrogen and fluorine doped $SrTiO_3$ could decompose 54.2% of NO under UV light irradiation, which was 1.4 times higher than that of pure $SrTiO_3$. It is probably due to the increase in the
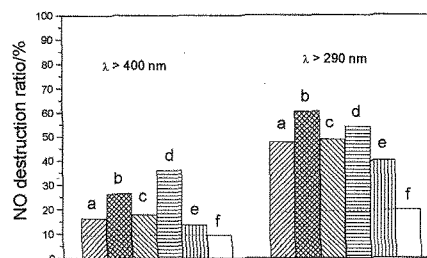
surface area by ball-milling.

Fig.5 The photocatalytic activity of various samples under irradiating visible light (λ>400 nm) and ultraviolet light(λ>290 nm). (a) As-ball milled with urea, (b) Calcined (a) at 400°C for 1 h, (c) As-ball milled with 22mol% urea and 2.5mol% SrF_2, (d) Calcined (c) at 400°C for 1 h, (e) $SrTiO_3$, (f) Blank without sample.

4. SUMMARY

Mechanochemical synthesis of nitrogen and fluorine co-doped $SrTiO_3$ by using urea and SrF_2 as the nitrogen and fluorine sources is a novel and suitable method for preparing nitrogen and fluorine doped $SrTiO_3$. This substance shows high absorption capability in visible light range and functions as a visible light responsible photocatalyst for the photo-oxidation of nitrogen monoxide. The photocatalytic activity of $SrTiO_3$ in NO elimination was improved by 2.6 and 1.4 times under visible light (>400 nm) and UV light (>290 nm) irradiation, respectively.

REFERENCES

1. K. Domen, A.Kudo, T. Onishi, J. Catal., **102**, 92-96(1986).
2. Q.S.Li,, K.Domen, S.Naito, T.Onishi and K.Tamaru, Chem. Lett., **3**,321-322(1983).
3. S. Ahuja, T.R.N. Kutty, J. Photochem. Photobio. A: Chemistry, **97**,99-107(1996).
4. R.Asahi, T.Morikawa, T.ohwaki, K.Aoki, and Y.Taga, Science, **293**,269-271(2001).
5. T. Umebayashi, T. Yamaki, S. Tanaka, and K. Asai, Chem. Lett. **4**, 330-331(2003).
6. S. U. M. Khan, M. Al-Shahry, and W. B. Ingler Jr., Science, **297**, 2243-2246(2002).
7. K. Nukumizu, J. Nunoshige, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi, and K. Domen, Chem. Lett. **2**, 196-197 (2003).
8. M.Cardona, Phys.Rev. **140**,A651-655(1965).
9. J. Wang, S. Yin, Q. Zhang, F. Saito, and T. Sato, J. Mat. Chem., **13**, 2348-2352 (2003).
10. S.Yin, and T.Sato, Ind.Eng.Chem.Res., **39**, 4526-4530 (2000)