Mechanochemical Synthesis of Fluorine-Doped SrTiO$_3$ and Its Photo-oxidation Properties

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Fluorine-doped SrTiO$_3$ powder was prepared by mechanochemical reaction and its photocatalysis has been studied in this paper. The photocatalytic experimental results show that the photocatalytic activity for nitrogen monoxide oxidation of SrTiO$_3$ can be improved by fluorine doping in both visible light and near ultraviolet light range. The photocatalytic activities of SrTiO$_3$ are ca. two and three times larger than those of pure SrTiO$_3$ under the irradiation of wavelength longer than 510 nm and 400 nm.

Environmentally harmonious photocatalysts can use solar energy to purify water, decompose NO$_x$, split water and so on. Using TiO$_2$ as the photocatalyst, NO can be oxidized into NO$_2$ and further transformed into HNO$_3$ in the presence of water.[1] SrTiO$_3$, as one of important photocatalysts, has been used for water splitting and mineralization of organic pollutants under UV radiation.[2,3] Recently, visible light active photocatalysts have aroused great attention in catalyst research area. Asahi et al. have succeeded in getting visible-light photocatalyst by doping nitrogen into TiO$_2$ lattice and they presented that visible light photocatalysis can be achieved by using other anionic substitutional species for doping.[4] Up to now, report on fluorine-doped SrTiO$_3$ has not been found yet, although many researchers have found that the electrical properties of SrTiO$_3$ and BaTiO$_3$ can be improved by doping fluorine.[5] So, we chose fluorine as the substitutional species for doping in this paper. In the past, the doping of fluorine into SrTiO$_3$ and BaTiO$_3$ required serious conditions, such as fluorine-containing atmosphere or dried air and high temperature.[6,7] In this paper, we used a novel and efficient way for the synthesis of material without heating, mechanochemical reaction. Compared with solid reaction method for the synthesis of fluorine-doped SrTiO$_3$, this is an environmentally friendly method which can avoid the pollution of fluoride-related gas at high temperature.

Analytical grade SrCO$_3$ and TiO$_2$ (anatase) were used as starting materials. SrTiO$_3$ was prepared by solid-state reaction of two substances above at 1100 °C for 2 h in air. SrF$_2$ was chosen as one fluoride source. Lee et al. have synthesized LaOF by using polytetrafluoroethylene (PTFE, [–CF$_2$CF$_2$–]$_n$,) as fluoride source.[8] So, we also selected PTFE for the doping of fluorine. A planetary mill was used for grinding the mixture. SrTiO$_3$ powder was mixed with 5 mol% SrF$_2$ or 5 mol% PTFE. Four grams of the mixture was put in the zirconia pot with seven zirconia balls of 15 mm diameter. The milling was performed at the rotation rate of 700 rpm for 1 h. The phase composition was identified by X-ray diffraction analysis. The absorption edge of the sample was determined from the onset of reflectance spectra measured by a UV-vis spectrophotometer. The photocatalytic activity for the oxidative decomposition 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 min^{-1}). A 450 W high pressure mercury arc was used as the light source. The concentration

of NO was determined by a NO$_x$ analyzer. Chemical composition analysis was carried out by a X-ray spectromer.

According to the X-ray powder diffraction data, these two samples, one mechanochemical reaction product made by SrF$_2$ and SrTiO$_3$ and the other product using PTFE as doping source followed by calcinations at 550 °C, were single phase SrTiO$_3$. The X-ray photoelectron spectra analysis was carried out to verify if fluorine has been doped successfully in SrTiO$_3$ lattice. Figure 1 shows F 1s XPS spectra of fluorine-doped SrTiO$_3$ sample and commercially available SrF$_2$ powder. The peak at 684.1 eV in SrF$_2$-doped SrTiO$_3$ might be assigned to the doping state of fluorine by comparison with that obtained for starting material SrF$_2$ since the binding energy of F 1s of SrF$_2$ shifted to 0.8 eV low energy side from 684.9 eV to 684.1 eV after doping. In other words, the XPS spectra illustrated that fluorine had been doped in SrTiO$_3$ lattice.
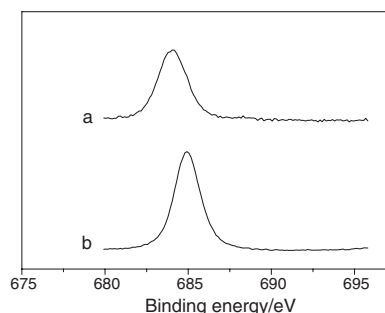

Figure 1. XPS spectra of F1s of SrF$_2$-doped SrTiO$_3$ sample and commercially available SrF$_2$ powder: (a) SrF$_2$-doped SrTiO$_3$, (b) pure SrF$_2$.

Figure 2 shows the diffuse reflection spectra of starting material SrTiO$_3$, the other two fluorine-doped samples and the commercial titania (Degussa P-25). SrTiO$_3$ had absorption edge at approximately 390 nm corresponding to the band gap of 3.18 eV, see Figure 2c. P-25 had the band gap of 2.98 eV (418 nm), shown in Figure 2d. Fluorine-doped SrTiO$_3$ sample prepared using PTFE as the doping source showed reflection spectrum similar to SrTiO$_3$ (Figure 2b). Taking SrF$_2$ as the starting material, SrTiO$_{3-x}$F$_x$ showed higher visible light absorption ability than other samples although the absorption edge of the sample had not changed a lot
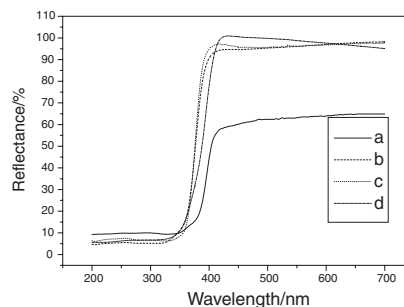

Figure 2. Diffuse reflection spectra of various samples: (○a) 5 mol% SrF$_2$-SrTiO$_3$ mixture milled 1 h, (b) 5 mol% PTFE-SrTiO$_3$ mixture milled for 1 h and calcined at 550 °C, (c) SrTiO$_3$, (d) P-25.

compared with pure $SrTiO_3$, see Figure 2a. After the grinding, the powder made by $SrTiO_3$ and SrF_2 turned its color from white to pale gray, which shows the doping of fluorine in $SrTiO_3$ lattice since pure $SrTiO_3$ still remained white after grinding.

Figure 3 shows the time change of the elimination of NO in the presence of SrF_2-doped $SrTiO_3$ under irradiating by a high pressure mercury arc using various cut filters. It showed that the degree of NO elimination increased with increasing photon number, i.e., decreasing the light filtered off. When the light was turned off, NO concentration returned to its initial level of 1 ppm within 10 min. These results suggested that light energy is necessary for the oxidation of NO, i.e., NO was photocatalytically eliminated.
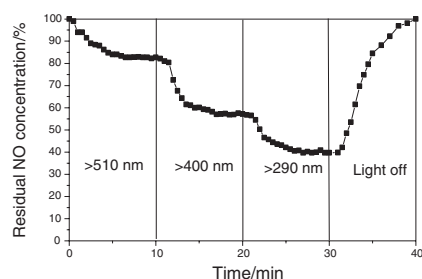

Figure 3. Time change of the NO elimination in the presence of SrF_2-doped $SrTiO_3$ under irradiating by a high pressure mercury arc with various cut filters.

Figure 4 shows the photocatalytic oxidation of nitrogen monoxide with various samples conducted under irradiation of lights $\lambda > 290$ nm, 400 nm, and 510 nm. In the visible light range, $SrTiO_{3-x}F_x$ prepared by using SrF_2 as the doping source showed the best photocatalytic ability. When the light wavelength was longer than 510 nm, NO elimination degree increased twice compared with $SrTiO_3$ and P-25 and 17.3% nitrogen monoxide could be eliminated as shown in Figures 4a, 4e, and 4f. Under the irradiation of light wavelength longer than 400 nm, the oxidation ratio of nitrogen oxide increased to 43.2% and ca. three times larger than that by pure $SrTiO_3$. However, the powder prepared by $SrTiO_3$ and PTFE had much lower photocatalytic activity than the fluorine-doped $SrTiO_3$ sample using SrF_2 mentioned above, see Figure 4b and 4a. This phenomenon might result from the bad effect of carbon produced during ball milling on the photocatalysis. Lee. et al. reported that polymerization degree of PTFE decreased owing to the cutting of chain as the grinding proceeded and carbon was formed in the sample.[8] We also found that the powder prepared by PTFE and $SrTiO_3$ had black color because of the coexistence of carbon and fluorine in the sample. TG-DTA curve of this sample showed that the carbon might be removed from the sample at temperature higher than 550 °C together with the loss of fluorine which could lead to the decrease in the oxidation ratio of nitrogen monoxide. The loss of fluorine could also be confirmed by the powder color change from black to white after calcinations. However, if the calcination temperature was as low as 400 °C, the carbon could not totally be oxidized into CO_2. Figure 4c and 4d illustrate that the sample calcined at 550 °C has higher capability for the oxidation of NO compared with that calcined at 400 °C, which confirmed the bad influence of carbon on the photocatalytic activity. All of these fluorine-doped $SrTiO_3$ samples had excellent photocatalytic activity in near ultraviolet light range. $SrTiO_{3-x}F_x$ made by 5 mol% SrF_2 and $SrTiO_3$ could enhance $SrTiO_3$ UV light activity by 54.6% and NO oxidation degree increased to more than 60%. On the other hand, ground $SrTiO_3$ without doping showed the lowest photocatalytic performance in the elimination of NO (see Figure
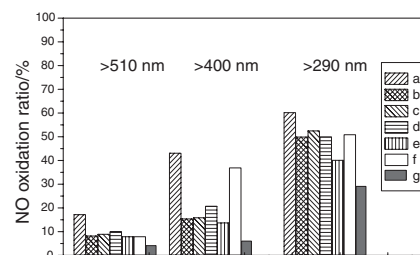

Figure 4. Photocatalytic activity of various samples under irradiation light with different wavelength: (a) 5 mol% SrF_2-$SrTiO_3$ mixture milled for 1 h, (b) 5 mol% PTFE-$SrTiO_3$ mixture milled for 1 h, (c) sample (b) calcined at 400 °C, (d) sample b) calcined at 550 °C, (e) $SrTiO_3$, (f) P-25, (g) $SrTiO_3$ milled for 1 h.

4g) since the lattice defects made by grinding could become the recombination centers of photogenerated holes and electrons.

The fluorescence X-ray results showed that no new element was found in fluorine-doped $SrTiO_3$ sample compared with the original elements of the mixture of $SrTiO_3$ and 5 mol% SrF_2 except that content of Zr increased from 0.259 wt% (which is the impurity of the raw material) to 0.310 wt% after grinding, indicating that the impurity has scarcely been introduced into the sample during the sample preparation process. The reflection spectrum of pure $SrTiO_3$ remained nearly the same after grinding. Although the high energy grinding might result in lowering the photocatalytic activity because of the lattice defects, the doping of fluorine into $SrTiO_3$ lattice improved the oxidation capability of NO. The possible reasons for enhancement of photocatalytic activity by fluorine-doping were as follows. Firstly, Ti^{3+} ions and/or cation vacancy produced by fluorine doping led to higher visible light absorption capability of the sample as shown in Figure 2 since the substitution of F^- to O^{2-} must be compensated by changing equivalent number of Ti^{4+} to Ti^{3+} or forming cation vacancy to maintain the electroneutrality. Secondly, the doping of fluorine increased the effective electron mobility. It is well known that the photogenerated electrons and holes must diffuse to the grain surface to take the function of redox. T. Endo et al.[9] claimed that the effective electron mobilities in the conduction band would increase with increasing the F^- by applying the hopping mechanism proposed by Hurd in $BaTiO_{3-x}F_x$ system. So the photogenerated electrons in $SrTiO_{3-x}F_x$ were easy to diffuse from the inner to the surface of the grains. Thirdly, fluorine-doped $SrTiO_3$ had relatively larger specific surface area (22.0 m²/g) and smaller particle size (20 nm evaluated by TEM observation) compared with the raw material $SrTiO_3$ with the specific surface area 4.1 m²/g and grain size 0.2–0.5 μm. The larger specific surface area had higher adsorption ability of NO. In addition, it needed less time for photogenerated carriers to diffuse from the inner of photocatalyst to its surface. As a result, the tendency for the recombination of photogenerated electrons and photogenerated holes could be decreased. However, since the data have not been clarified yet, further study is necessary.

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