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Synthesis and photocatalytic activity of fluorine doped $SrTiO_3$

JINSHU WANG*, SHU YIN, QIWU ZHANG, F. SAITO, T. SATO
Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan
E-mail: wangjsh@mail.tagen.tohoku.ac.jp

Fluorine doped $SrTiO_3$ powder prepared by mechanochemical reaction and its photocatalysis have been studied in this paper. It shows that mechanochemical reaction is an efficient way for the doping with fluorine. The photocatalytic experimental results show that the photocatalytic activity in the nitrogen monoxide destruction by $SrTiO_3$ can be improved by fluorine doping in the visible light and near ultraviolet light range. The photocatalytic activity of $SrTiO_3$ can be enhanced by 44% under irradiation of wavelength larger than 410 nm.

Energy and environment have become two important problems with the rapid development of industry. Photocatalytic reactions of semiconductor, such as splitting water and degradation of organic and inorganic pollutants have received great attention around the world [1, 2]. $SrTiO_3$, as one of important photocatalysts, has been used for water splitting and mineralization of organic pollutants under ultraviolet (UV) radiation [3–5]. It is well known that only 5% of solar spectrum is ultraviolet and large parts of the rest are visible light. So, to extend the high reactivity of the photocatalysts towards irradiation in the visible range is the main goal for researchers. In 2001, Asahi *et al.* succeeded in getting visible-light photocatalyst by doping nitrogen in TiO_2 lattice and they proposed that visible light photocatalysis can be achieved using other anionic substitutional species for doping [6]. Up to now, a report on fluorine doped semiconductor photocatalyst has not been found, although many researchers have reported that the electrical properties of $SrTiO_3$ and $BaTiO_3$ ceramics can be improved by doping fluorine [7–9]. So, we selected fluorine as the substitutional specie for doping in this paper. The doping of fluorine in $SrTiO_3$ and $BaTiO_3$ ceramics has been achieved by solid reaction in the past. However, the solid reaction method for fluorine doping requires difficult conditions, such as fluorine-containing atmosphere or dried air and high temperature [7–9]. In this paper, we used a novel and efficient way for the synthesis of the material without heating, namely mechanochemical reaction. Compared with solid reaction method for the synthesis of fluorine doped $SrTiO_3$, this is an environmental friendly method which can avoid the pollution of fluoride-related gas at high temperature.

Commercial $SrTiO_3$ powder (Nippon Aerosol Co., Japan) was used as the starting material. Strontium fluoride (Kanto Chem. Co., Japan) was chosen as one fluoride source. Lee *et al.* have synthesized LaOF by using polytetrafluoroethylene (PTFE, $[-CF_2CF_2-]_n$) as fluoride source [10]. So, we also selected PTFE for the doping of fluorine. A planetary mill (Pulverisette-7, Fritsch, Germany) was used for grinding the mixture. The mill was composed of a pair of pots made of zirconia installed on a rotating disc being driven by an electric motor. Commercial $SrTiO_3$ powder was mixed with 5 mol% SrF_2 and 5 mol% PTFE respectively. Four grams of the mixture were put in the zirconia pot (45 cm^3 inner volume) 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 (Shimadzu XD D1) system. The integrated intensity and the position of reflections were measured at the scanning rate of $0.5\,^\circ\cdot min^{-1}$. Silicon powders were used as an internal standard. The photocatalytic activity for nitrogen monoxide destruction was determined by measuring the concentration of nitrogen oxide at the outlet of the reactor under the irradiation of 450 W high pressure mercury lamp during the flow of 1 ppm mixed gas of NO and 50 vol% air (balance N_2). The absorption edge of the photocatalyst was determined from the onset of reflectance spectra measured by UV-VIS spectrophotometer.

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, are single phase, $SrTiO_3$ which was identified as a perovskite-type structure having cubic symmetry. Table I shows the lattice parameters and specific surface area of these samples. Compared with the parameter of raw material $SrTiO_3$, the cell constants of these two products are smaller. The structure can be regarded as a cubic close-packed lattice in which the Ti atoms are located at the corners, the O atoms at the centers of the twelve cube edges and Sr atoms at the centers of the cubic. Since the change in lattice parameter is directly reflected to that of the bonding distance between Ti and anion, the observed shrinkage would be due to the difference in ionic radii between O^{2-}(0.14 nm) and F^-(0.133 nm), which means the substitution of O^{2-} by F^- in $SrTiO_3$ lattice.

Fig. 1 shows the diffuse reflection spectra of starting material $SrTiO_3$ and the other two samples. $SrTiO_3$ has absorption edges at approximately 390 nm corresponding to the band gap of 3.18 eV, see curve c Fig. 1, which is consistent with the band gap of 3.20 eV for $SrTiO_3$

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[*] Author to whom all correspondence should be addressed.

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TABLE I Lattice parameters of different samples

Sample	$a = b = c$	Difference in parameter (nm)	BET (m^2/g)
$SrTiO_3$	3.9053		4.1
5 mol% PTFE after calcination	3.9041	−0.0012	18.9
5 mol% SrF_2	3.8998	−0.0055	22.0

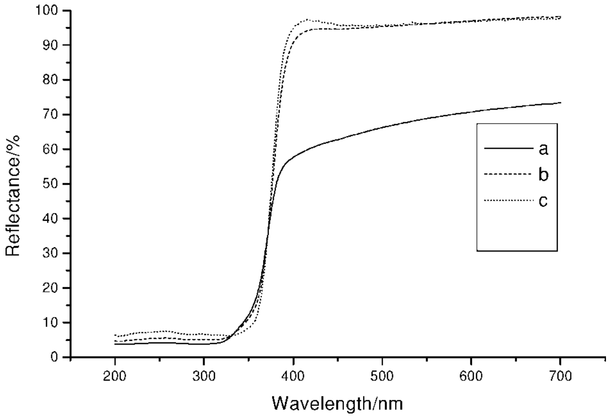

Figure 1 The diffuse reflection spectra of various samples. (a) 5 mol%SrF_2-$SrTiO_3$ mixture milled at 700 rpm for 1 h; (b) 5 mol%PTFE-$SrTiO_3$ mixture ground at 700 rpm for 1 h and calcinated at 550 °C; (c) $SrTiO_3$.

reported by Cardona [11]. Fluorine doped $SrTiO_3$ samples, (curve a and b in Fig. 1) have nearly the same band gap with $SrTiO_3$. After the grinding, the powder made by $SrTiO_3$ and SrF_2 turns from white to gray, which shows the doping of fluorine in $SrTiO_3$ lattice. At the same time, this kind of powder shows higher visible light absorption ability than pure $SrTiO_3$ and $SrTiO_{3-x}F_x$ prepared by PTFE and $SrTiO_3$.

Fig. 2 shows the photocatalytic oxidation of nitrogen monoxide with various samples conducted under irradiation of light of $\lambda > 290$, 410 and 510 nm. In the visible light range, $SrTiO_{3-x}F_x$ prepared by using SrF_2 as the doping source, showed good photocatalytic ability. When the light wavelength is larger than 410 nm, 43.2% nitrogen monoxide can be decomposed and NO decomposition ratio increased 44% percent compared with $SrTiO_3$ as shown by a and e. However, the powder prepared by $SrTiO_3$ and PTFE has a worse photocatalytic activity than raw material $SrTiO_3$ (compare b and e). This phenomenon may result from the detrimental effect of carbon produced during ball milling on the photocatalysis. Lee *et al.* reports that polymerization degree of PTFE decreases due to the cutting of chain as the grinding proceeds and carbon is formed in the sample [10]. We also find that the powder prepared by PTFE and $SrTiO_3$ has a black color because of the coexistence of carbon and fluorine in the sample. In order to remove the carbon from the sample, we calcined this sample at different temperatures. TG-DTA curve of this sample shows that the carbon may be removed from the sample at temperature higher than 550 °C together with the loss of fluorine which can lead to the decrease in the decomposition ratio of nitrogen monoxide. The loss of fluorine can also be confirmed by the powder color change from black to white after calcinations and the lattice parameter. Using PTFE as the doping source, the lattice parameter is only 0.0012 nm smaller than $SrTiO_3$, nearly one fifth of the lattice difference between $SrTiO_3$ and the sample made by SrF_2 and $SrTiO_3$ although these two samples have the same doping ratio of fluorine (5 mol%). However, if the calcinations temperature is low such as 400 °C, the carbon cannot totally be oxidized into CO_2 which escapes from the sample. c and d in Fig. 2 illustrate that the sample calcinated at 550 °C has higher capability for the decomposition of nitrogen monoxide compared with that calcined at 400 °C, which confirms the bad influence of carbon on the photocatalytic activity. But all of these fluorine doped $SrTiO_3$ samples have excellent photocatalytic activity in near ultraviolet light range. $SrTiO_{3-x}F_x$ made by 5 mol% SrF_2 and $SrTiO_3$ can enhance $SrTiO_3$ UV light activity 54.6% and NO decomposition ratio can be high to more than 60%.

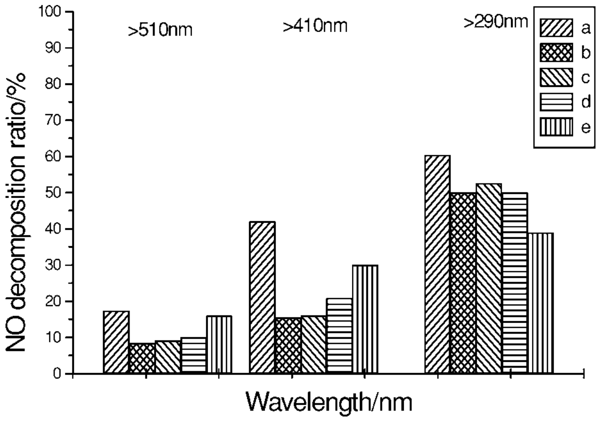

Figure 2 The photocatalytic activity of various samples under irradiation light with different wavelengths. (a) 5 mol%SrF_2-$SrTiO_3$ mixture milled at 700 rpm for 1 h; (b) 5 mol%PTFE-$SrTiO_3$ mixture ground at 700 rpm for 1 h; (c) sample b calcined at 400 °C; (d) sample b calcined at 550 °C; (e) $SrTiO_3$.

It is well known that $SrTiO_3$ particles must absorb light energy high enough to form electron-holes pairs because of its large band gap. So, under irradiation of light of $\lambda > 510$ nm, the photocatalytic activity is small. With the irradiation light energy increasing, the number of electron-hole pairs in the $SrTiO_3$ band gap increases and the related photocatalytic activity improves. As for $SrTiO_{3-x}F_x$, the substitution of O^{2-} by F^- must be compensated by an equivalent number of Ti^{4+} to Ti^{3+} to maintain the electroneutrality, so the general formula of $SrTiO_{3-x}F_x$ may be written as $SrTi^{4+}_{1-x}Ti^{3+}_{x}O^{2-}_{3-x}F^{-}_{x}$. Ti^{3+} ions lead to higher visible light absorption capability of the sample shown in Fig. 1, thus the number of electron-hole pairs in $SrTiO_3$ band gap increase with the result of improvement in the photocatalytic activity of $SrTiO_3$.

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