Preparation and characterization of nitrogen doped SrTiO$_3$ photocatalyst

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Abstract

Nitrogen doped SrTiO$_3$ powders were prepared by the mechanochemical reaction of SrTiO$_3$ and 20 wt.% of three kinds of doping sources, hexamethylenetetramine, urea, and ammonium carbonate using a high energy planetary ball mill, followed by calcination at 400 °C for 1 h. The photocatalysis of nitrogen doped SrTiO$_3$ powders under the irradiation of wavelength $\lambda > 400$ nm and near ultraviolet light regions ($\lambda > 290$ nm) greatly changed depending on particle size, specific surface area and porosity. The absorption of visible light increased with increasing nitrogen content doped in SrTiO$_3$ lattice. Nitrogen monoxide elimination ability of SrTiO$_3$ could be greatly improved by nitrogen doping. The photocatalytic activity of nitrogen doped SrTiO$_3$ made by 20 wt.% hexamethylenetetramine-SrTiO$_3$ under light $\lambda > 400$ nm irradiation was about 3.5 and 1.4 times higher than those of pure SrTiO$_3$ and commercial titania powder (Degussa P-25).
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Keywords: Photocatalytic activity; NO elimination; SrTiO$_3$; Nitrogen doping; Mechanochemical reaction

1. Introduction

Strontium titanate has been known to possess photocatalytic activity [1–3]. Since SrTiO$_3$ is a wide-gap semiconductor (3.2 eV), UV light ($\lambda < 387$ nm) is necessary to generate electron/hole pairs by photo-excitation. However, UV light is expensive and its content in sunlight is less than 5%. In the past, transition metal ions and nonmetal elements have been doped into TiO$_2$ to red shift the absorption edge in order to use solar energy effectively [4–8]. It was reported that doping anion such as nitrogen is more efficient to improve its photocatalytic activity in visible region. However, substitution of oxygen by nitrogen is not easy because oxide is generally more stable than nitride. Asahi et al. [4] prepared TiO$_{2-x}$N$_x$ powder by calcining TiO$_2$ powder at high temperature in the atmosphere of NH$_3$. Mechanochemical method has been intensively reported as a unique method to synthesize a material by the solid state reaction without heating [9,10]. In this paper, we prepared nitrogen doped SrTiO$_3$ by mechanochemical reactions using commercially available chemical reagents such as hexamethylenetetramine, urea, and ammonium carbonate as the

nitrogen sources and grinding the mixture of SrTiO$_3$ and each nitrogen source at room temperature. Compared with the solid reaction method by calcining semiconductor such as TiO$_2$ powders in the atmosphere of NH$_3$ which is erosive and toxic gas, mechanochemical reaction method is an environmental friendly method, and simple and efficient for nonmetallic elements doping. To the best of our knowledge, we are first to report the synthesis of nitrogen doped SrTiO$_3$.

Photocatalytic elimination of NO is of great significance from the viewpoint of practical application because nitrogen monoxide is one of the typical pollutants in the gas exhausted from automobiles. So, we employed the elimination of NO as model reaction to investigate the photocatalytic activity of nitrogen doped SrTiO$_3$.

2. Experimental details

2.1. Catalyst preparation

All chemicals were reagent grade and used without further purification. Stoichiometric strontium titanate was synthesized by solid state reaction of SrCO$_3$ and TiO$_2$ at 1100 °C for 2 h as shown in Eq. (1)

$$SrCO_3 + TiO_2 \rightarrow SrTiO_3 + CO_2 \qquad (1)$$
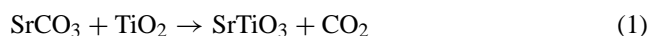
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SrTiO$_3$ powder was mixed with 20 wt.% of nitrogen source compound such as hexamethylenetetramine, urea, and ammonium carbonate (Kanto Chem, Japan). Four gram of the mixed powder was put in a zirconia pot (45 cm^3 inner volume) with seven zirconia balls of 15 mm in diameter and was ball milled using a high energy planetary mill (Pulverisette-7, Fritsch, Germany) at 700 rpm rotation speed for 2 h at room temperature. Then the ground powder was calcined at 400 °C to remove the organic compounds by-produced and remained nitrogen source compound.

2.2. Catalyst characterization

The phase composition was identified by X-ray diffraction system (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 77 K (Quantachrome NOVA 1000-TS). The binding energies of Sr, Ti, N, and O were measured at room temperature using an electron spectrometer (Perkin Elmer PHI 5600). The peak positions of each element were corrected by using that of C$1s$ (285.0 eV). The amount of nitrogen doped in the SrTiO$_3$ was determined by an oxygen–nitrogen analyzer (HORIBA, EMGA-2800) and the sensitivity of the nitrogen measurement was about 0.00001 wt.% (0.1 ppm). The amount of residual organic elements was identified by a CHN analyzer (Yanako,MT-6). The particle size and shape were evaluated by transmission electron microscope (JEM-2000EX). The particle size distribution was determined by a laser particle size analyzer (Shimadzu, SALD-2000).

2.3. Photocatalytic activity measurement

The photocatalyst sample was placed in a hollow place of 20 mm × 15 mm × 0.5 mm on a glass holder plate and set in the center of the reactor. After the NO concentration got to the equilibrium concentration 1 ppm, a 450 W high pressure mercury arc was turned on for the irradiation, where the light wavelength was controlled by selecting filters, i.e. Pyrex glass for cutting off the light of $\lambda < 290$ nm and Kenko L41 Super Pro (W) filter < 400 nm. 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 min^{-1}). The concentration of NO was determined by a NO$_x$ analyzer (Yanaco, ECL-88A).

3. Results and discussion

3.1. Characterization of the powder

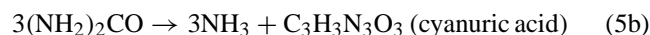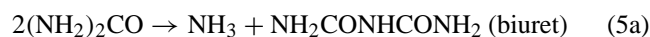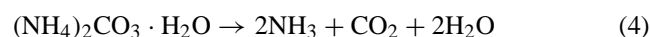According to the X-ray powder diffraction data, three samples prepared by the mechanochemical reaction of SrTiO$_3$ with urea, hexamethylenetetramine or ammonium carbonate followed by calcinations at 400 °C consisted of single phase SrTiO$_3$ with a perovskite-type structure of cubic symmetry. The compositions, specific surface areas of various samples are summarized in Table 1. The specific surface area of SrTiO$_3$ greatly increased by ball-mlling from 3.9 to 6.1–21.5 m^2 g^{-1}, and further increased by calcination to 14.0–37.2 m^2 g^{-1}, depending on the nitrogen source. This difference might result from the difference in the by-product by grinding of the nitrogen source. Since the powder produced using hexamethylenetetramine was black, carbon might be produced according to the following reaction.

$$C_6H_{12}N_4 \rightarrow 4NH_3 + 6C \tag{2}$$

Apart from the color change in the sample, a strong bad smell of HCHO was emitted when the pot lid was opened after grinding, which means that the following chemical reaction took place as a minor reaction in the mechanical attrition of this system:

$$C_6H_{12}N_4 + 6H_2O \xrightarrow{70\,°C} 6HCHO + 4NH_3 \tag{3}$$

It is known that the reaction (3) proceeds above 70 °C. During the high energy milling, the powders were plastically deformed with most of the mechanical energy expended in the deformation process being converted into heat, moreover, the heat converted from the friction energy produced between balls and pot was the other thermal source, as a consequence, the temperature rise during this process. Johnson claimed in his paper that the temperature was modest and was estimated to be $\leqq 100$–200 °C [11]. Water adsorbed on the surface of starting particle would serve as one reactant of Eq. (3). When ammonium carbonate and urea are used as the nitrogen sources, the following reactions might take place during the grinding:

$$(NH_4)_2CO_3 \cdot H_2O \rightarrow 2NH_3 + CO_2 + 2H_2O \tag{4}$$

$$2(NH_2)_2CO \rightarrow NH_3 + NH_2CONHCONH_2 \text{ (biuret)} \tag{5a}$$

$$3(NH_2)_2CO \rightarrow 3NH_3 + C_3H_3N_3O_3 \text{ (cyanuric acid)} \tag{5b}$$

All these by-products and remaining nitrogen source compounds were suspected to be homogeneously dispersed with the nitrogen-doped SrTiO$_3$ and to form pores when they were removed by calcination. This might be the reason why the specific surface area of the powder increased after calcination.

XPS is an efficient method for chemical state analysis and has been widely used for determining the doping of nitrogen in TiO$_2$ system [4,12,13]. The XPS analyses for these three samples have been carried out. Fig. 1 shows XPS spectra of N1s of pure urea and nitrogen doped SrTiO$_3$ using different nitrogen sources followed by heat treatment at 400 °C. All three kinds of nitrogen doped SrTiO$_3$ samples showed N1s peaks at about 398.45 eV assigned to the doping state of nitrogen by comparison with that obtained

Table 1
Initial compositions in weights, the amount of nitrogen, carbon and hydrogen and specific surface areas of the samples prepared

Sample	Nitrogen content (wt.%)	Residual element		Specific surface area ($m^2\,g^{-1}$) (before calcinations)	Specific surface area ($m^2\,g^{-1}$) (after calcinations)
		C (wt.%)	H (wt.%)		
$SrTiO_3$	0	0	0.18	3.9	
80 wt.% $SrTiO_3$ + 20 wt.% hexamethylenetetramine	0.12	0	0.16	16.2	37.2
80 wt.% $SrTiO_3$ + 20 wt.% urea	0.31	0	0.20	6.1	14.0
80 wt.% $SrTiO_3$ + 20 wt.% ammonium carbonate	0.07	0	0.25	32.2	27.1

for starting material urea since the binding energy of N1s of urea shifted to 1.25 eV low energy side from 399.70 eV (Fig. 1a) to 398.45 eV after doping. The irregularities of N1s spectra of the powders prepared using hexamethylenetetramine (Fig. 1c) and ammonium carbonate (Fig. 1d) resulted from the low content of nitrogen doped in $SrTiO_3$ lattice. The amount of nitrogen, carbon and hydrogen in various nitrogen-doped $SrTiO_3$ samples were also summarized in Table 1. It shows that none of the samples contained any detectable amounts of residual carbon. The small amount
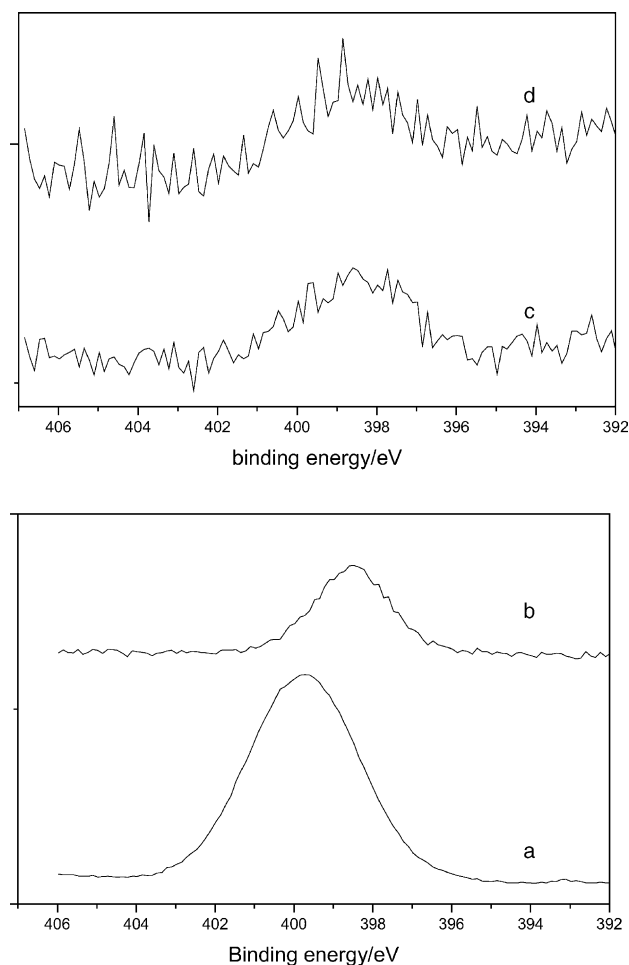

Fig. 1. XPS spectrum of N1s of (a) pure urea and nitrogen doped $SrTiO_3$ followed by heat treatment at 400 °C prepared using (b) urea, (c) hexamethylenetetramine, and (d) ammonium carbonate.

of hydrogen in the sample might be due to the absorbed water. The difference in the content of nitrogen doped in $SrTiO_3$ could also be explained from the states of products by grinding of different nitrogen sources. The solid-state interdiffusion reaction during reactive ball milling was triggered by fragmentation of $SrTiO_3$ powder thus creating new surfaces. These freshly created surfaces reacted with NH_3 to form a nitrogen doped $SrTiO_3$ surface layer over the unreacted core particles. With further milling this doping reaction continued and a homogenous $SrTi(O_{1-x}N_x)_3$ phase was formed and the undoped core of $SrTiO_3$ disappeared resulting in a nanostructured nitrogen doped $SrTiO_3$. The adsorption of by products such as CO_2, HCHO, carbon, biuret and cyanuric acid on the surface of $SrTiO_3$ powders seems to prevent the adsorption of NH_3, however, the adsorption degrees of solid phase biuret and cyanuric acid seemed to be far lower than those of gaseous compound CO_2 and HCHO. As a result, when urea was used as a nitrogen source, more NH_3 could be adsorbed on the surface of the unreacted $SrTiO_3$ core particles to proceed a nitrogen doping reaction. Since the amount of CO_2 formed from ammonium carbonate was much higher than HCHO formed from hexamethylenetetramine, the content of nitrogen doped in $SrTiO_3$ lattice changed depending on the nitrogen sources as urea > hexamethylenetetramine > ammonium carbonate.

The crystallite size of the powder was estimated from the line broadening of the corresponding X-ray diffraction peaks using Warren and Averbach equation [14]. Although the crystallite size of $SrTiO_3$ used as a starting material was quite large as 50.2 nm, the samples prepared by ball-milling using hexamethylenetetramine, urea and ammonium carbonate followed by calcination at 400 °C had crystallite sizes of 16.8, 29.9 and 22.6 nm, respectively. Direct observation of the particles by transmission electron microscopy is shown in Fig. 2. The starting material $SrTiO_3$ consisted of relatively large particles of about 0.2–0.5 μm in diameter (see Fig. 2a). It was noticeable that the particles after nitrogen doping were far smaller than that of starting material $SrTiO_3$. The nitrogen doped $SrTiO_3$ consisted of two kinds of particles in size, i.e. nanoscale particles and spherical sub-micrometer sized particles (Fig. 2b–d). The sizes of the nanoscale particles agreed with those determined by XRD. The surface of sub-micrometer sized particles was covered by tiny crystallites. During high energy milling, $SrTiO_3$ powders were subjected to severe mechanical deformation from the
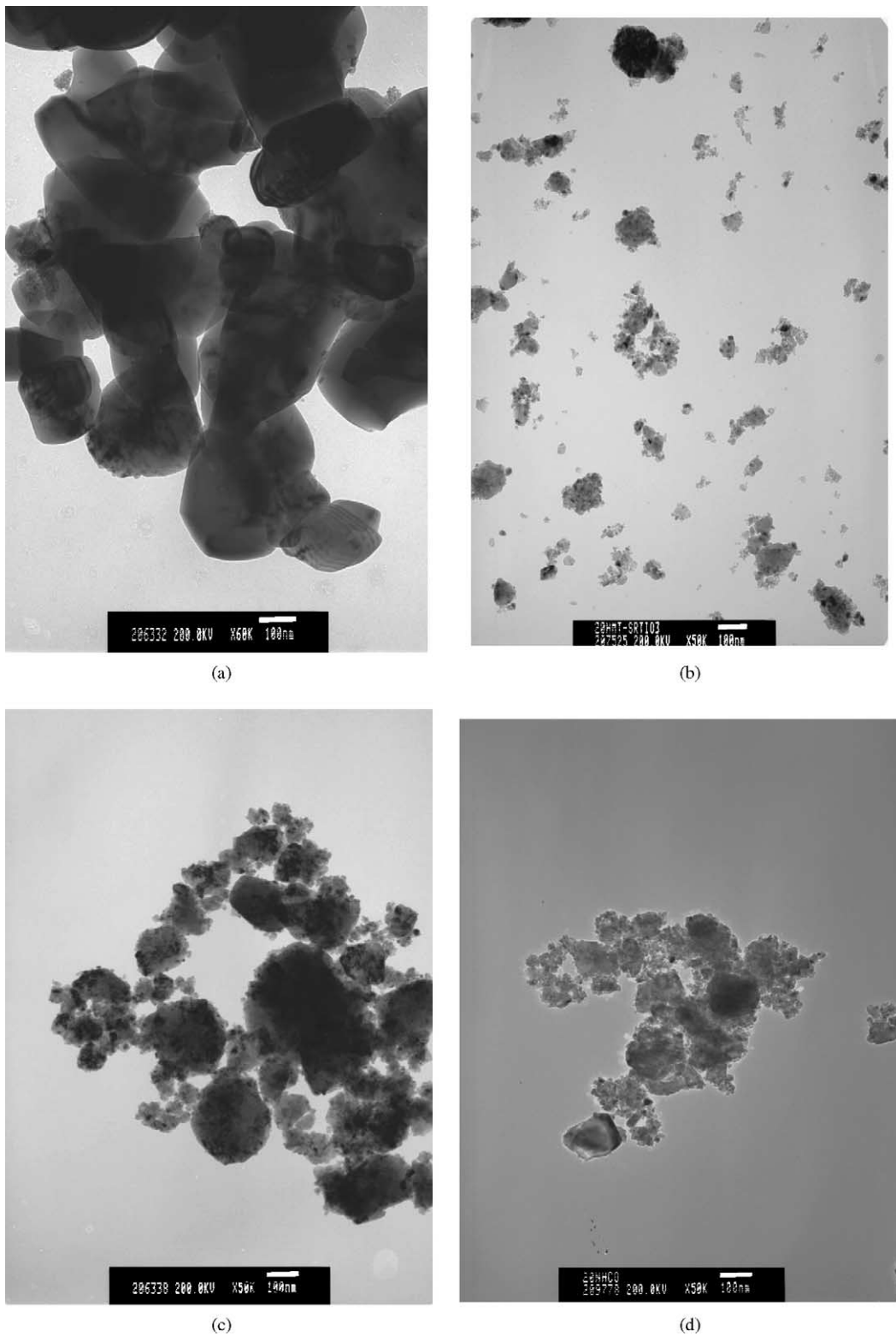
Fig. 2. Transmission electron micrographs of (a) pure $SrTiO_3$ and nitrogen doped $SrTiO_3$ prepared using (b) hexamethylenetetramine, (c) urea, and (d) ammonium carbonate.
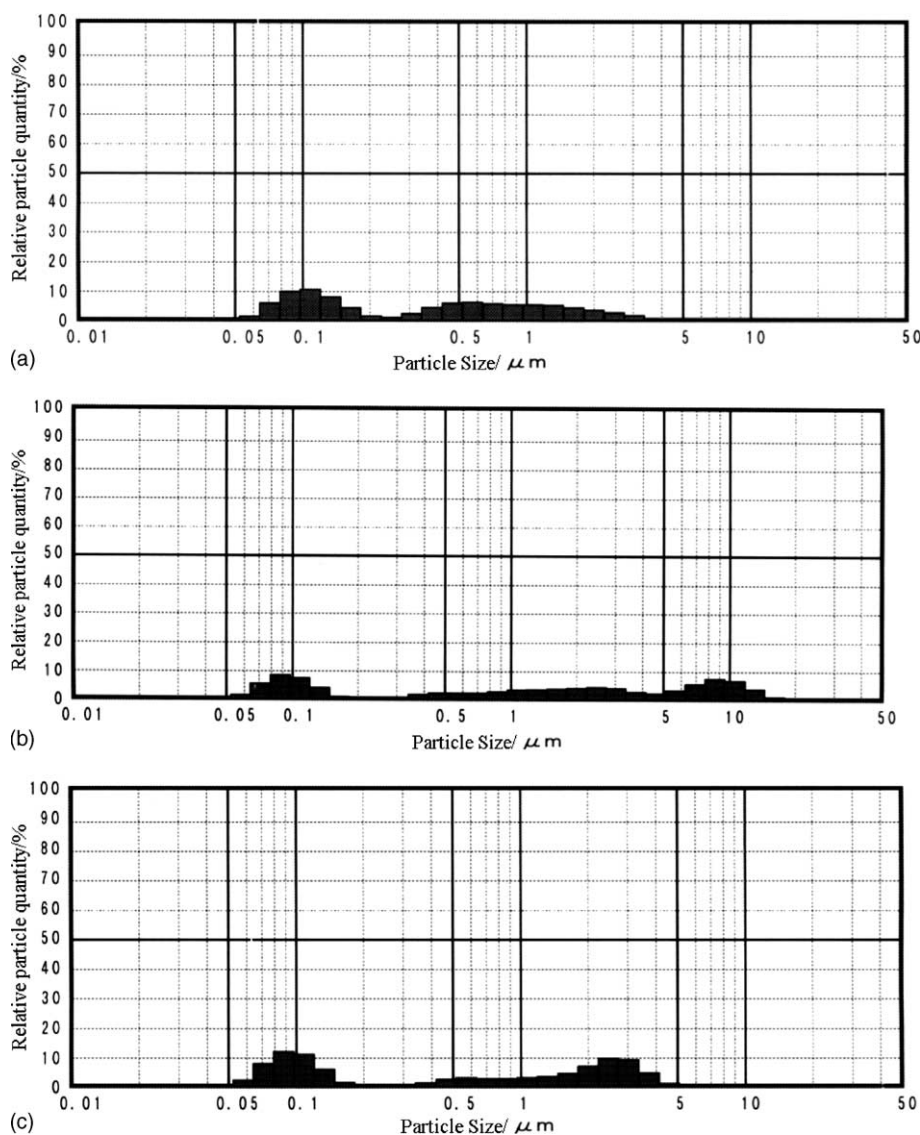
Fig. 3. Particle size distributions of nitrogen doped SrTiO$_3$ prepared with (a) hexamethylenetetramine, (b) urea, and (c) ammonium carbonate.

collisions with milling tools. Consequently, plastic deformation at high strain rates occurred within SrTiO$_3$ powders and the average grain size could be reduced to tens of nanometers.

The particle size distributions for three nitrogen doped samples are shown in Fig. 3. Since nanoscale particles of these three samples were easy to agglomerate to form secondary particles to minimize the total surface of the powders, the result shown in Fig. 3 illustrated the secondary particle size distributions. The powders prepared using hexamethylenetetramine and (NH$_4$)$_2$CO$_3$ as the nitrogen sources consisted of two kinds of particles in the size ranges of 0.05–0.2 and 0.3–5 μm (Fig. 3a and c), and that prepared with urea consisted of 0.05–0.2 and 0.3–22 μm (Fig. 3b). The average agglomerated particle sizes of these three samples prepared using hexamethylenetetramine, (NH$_4$)$_2$CO$_3$ and urea are 0.353, 0.505, and 1.117 μm, respectively.

Fig. 4 shows the pore size distribution of three samples. All samples exhibited two pore size families located around 2 and 4 nm although the total pore volume changed depending on the nitrogen source as hexamethylenetetramine > ammonium carbonate > urea.

Fig. 5 shows the diffuse reflection spectra of starting material SrTiO$_3$, three samples of nitrogen-doped SrTiO$_3$ prepared by ball milling and two kinds of mixtures of 20 wt.% urea-SrTiO$_3$ and 20 wt.% hexamethylenetetramine-SrTiO$_3$ followed by calcination at 400 °C. Although SrTiO$_3$ and two kinds of calcined mixtures were white, all nitrogen-doped SrTiO$_3$ obtained were yellow, indicating that high energy grinding is indispensable for the doping of nitrogen. SrTiO$_3$ had absorption edge at approximately 390 nm corresponding to the band gap of 3.18 eV (Fig. 5f), which agreed with the value of 3.20 eV in [15]. In addition, two mixtures had nearly the same diffusion reflectance spectra with pure
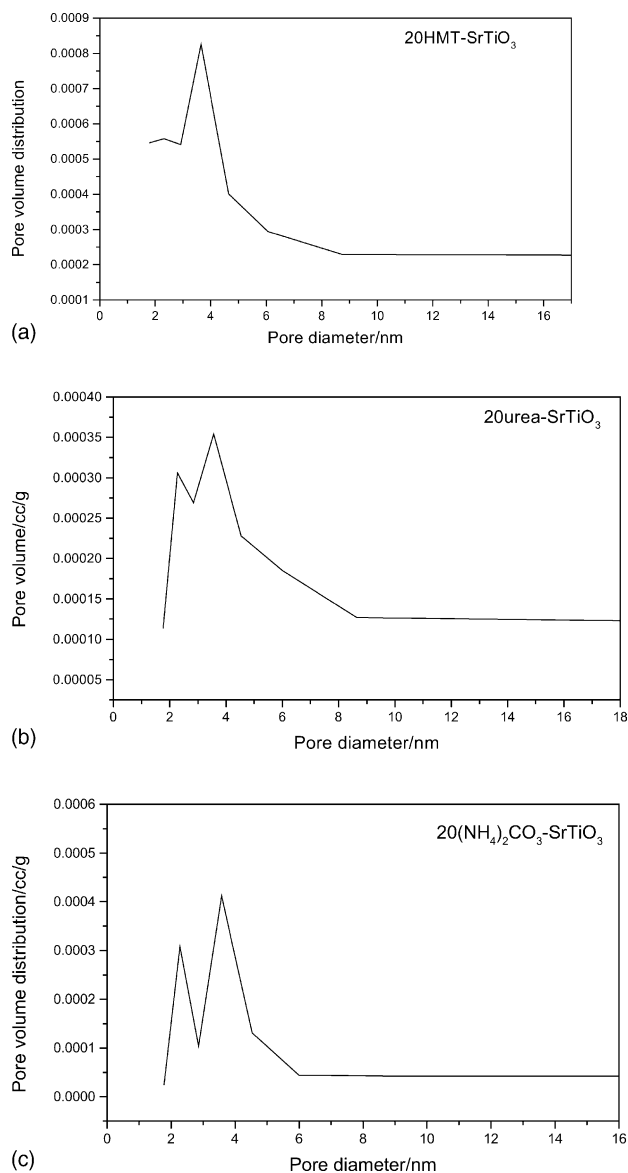
(a)

(b)

(c)

Fig. 4. Pore size distributions of nitrogen doped SrTiO$_3$ prepared with (a) hexamethylenetetramine, (b) urea, and (c) ammonium carbonate.

Fig. 5. The diffuse reflection spectra of various samples calcined at 400 °C (a) mixture of SrTiO$_3$–20 wt.% urea milled at 700 rpm for 2 h, (b) mixture of SrTiO$_3$–20 wt.% hexamethylenetetramine milled at 700 rpm for 2 h, (c) mixture of SrTiO$_3$–20 wt.% ammonium carbonate milled at 700 rpm for 2 h, and (d) mixture of SrTiO$_3$–20 wt.% hexamethylenetetramine, (e) mixture of SrTiO$_3$–20 wt.% urea, and (f) SrTiO$_3$.

3.2. Photocatalytic activity

The photocatalytic activities of the prepared samples were investigated under irradiating lights of various wavelengths. Fig. 6 shows the spectra of the light source filtered by different filters. It is seen that the light of the wavelength less than 290, 400 nm could be filtered out using a Pyrex glass jacket, 400 nm cut-off filter. Fig. 7 shows the time change of the elimination of NO in the presence of nitrogen doped

Fig. 6. Wavelength distribution of the light irradiated from a 450 W high-pressure mercury lamp (a) without filter, (b) light (a) filtered by Pyrex glass jacket, (c) light (b) filtered by a 400 nm cut-off filter.

SrTiO$_3$ (Fig. 5d and e). The powder prepared using urea and hexamethylenetetramine clearly showed two absorption edges at 390 and 470 nm (Fig. 5a and b). These peaks might be attributed to the absorption edge of SrTiO$_3$ and nitrogen doped SrTiO$_3$ lattice, respectively. On the other hand, taking ammonium carbonate as the starting material, the absorption edge around 470 nm was not clear probably due to the small amount of nitrogen doping (Fig. 5c). Comparing these three reflectance spectra, it might be concluded that the new absorption edge formation had been related to the nitrogen content doped in the sample. At the same time, the replacing O^{2-} with N^{3-} would result in the formation of anion defects for the charge compensation. The anion defects seemed to lead to high visible light absorption ability of the sample, according to Justicia et al's. [16] work.
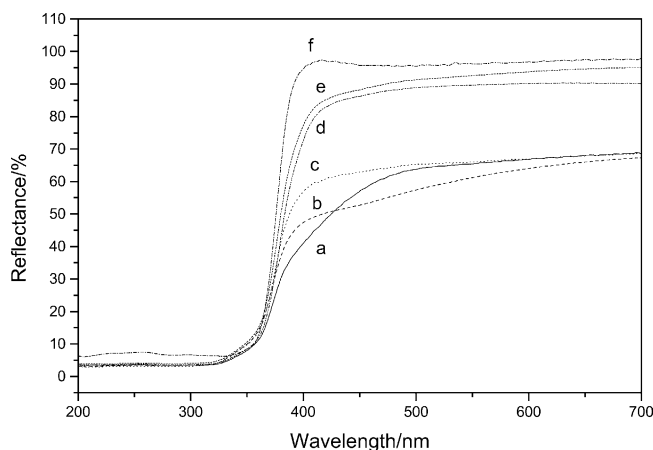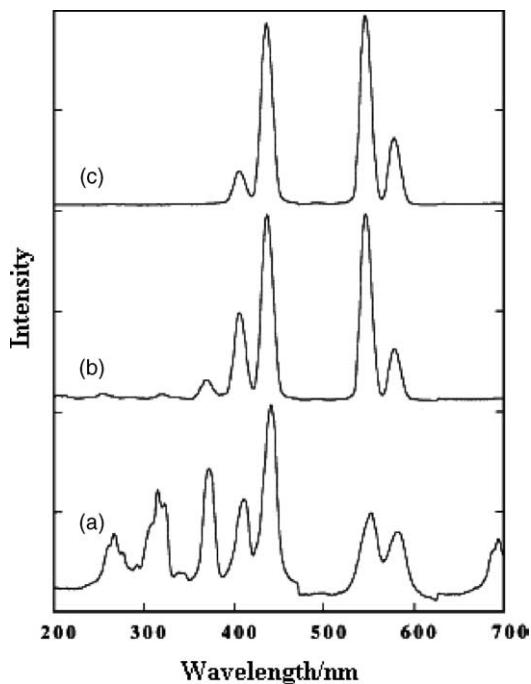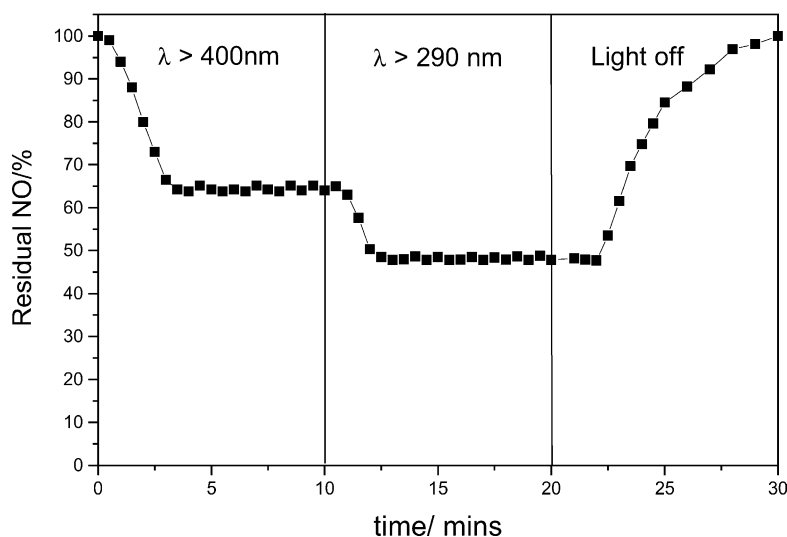
Fig. 7. Time change of the NO elimination in the presence of nitrogen doped SrTiO$_3$ prepared with urea under irradiating high pressure mercury arc filtered with cut filter.

SrTiO$_3$ under irradiating high pressure mercury arc filtered using cut filter. 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.

Fig. 8 illustrated the degree of elimination of nitrogen monoxide with various samples under irradiating high pressure mercury arc of $\lambda > 400$ nm and 290 nm, where the degrees of blank test without any photocatalyst were 9.6 and 20%, respectively (see Fig. 8i). It is clear that pure SrTiO$_3$ exhibited little photocatalytic activity under visible light irradiation ($\lambda > 400$ nm) because of its large band gap energy. The photocatalytic activity of SrTiO$_3$ in the visible light range was greatly increased by nitrogen doping. Among six

nitrogen doped SrTiO$_3$, the sample prepared with hexamethylenetetramine followed by calcination at 400 °C demonstrated the highest photocatalytic activity in the visible light range, i.e. 47.8% nitrogen monoxide could be removed. The value was about 3.5 and 1.4 times higher than those of pure SrTiO$_3$ and titania powder (Degussa P-25) (see Fig. 8b, g and h). The powder prepared with (NH$_4$)$_2$CO$_3$ and urea had lower NO elimination capability. According to the present carbon analysis result shown in Table 1, carbon did not exist in the sample, indicating that nitrogen doping resulted in the improvement of photocatalytic activity of SrTiO$_3$. However, the effect of carbon on the photocatalysis needs to be studied in the future work. Although the content of doped nitrogen in the powder prepared using urea as nitrogen source was higher than that using hexamethylenetetramine, the sample showed lower capability of NO elimination (35.9%),
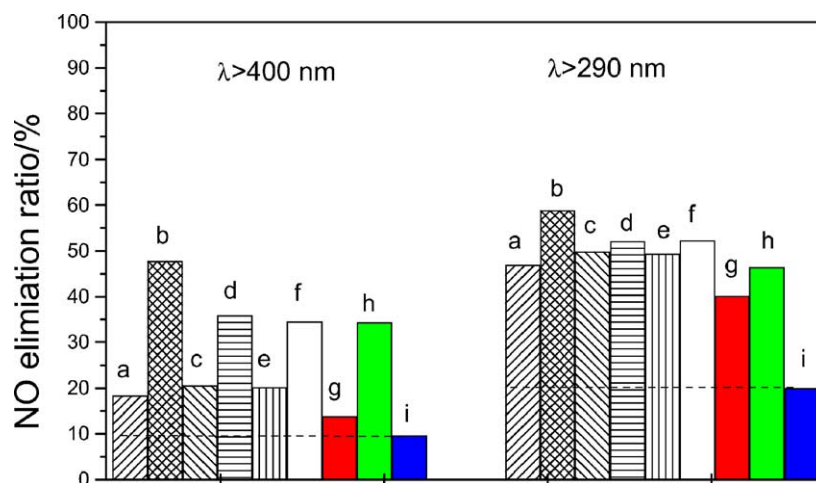

Fig. 8. The photocatalytic activity of various samples under irradiating light $\lambda > 400$ nm and ultraviolet light ($\lambda > 290$ nm). (a) As-ball milled with hexamethylenetetramine, (b) calcined (a) at 400 °C for 1 h, (c) as-ball milled with urea, (d) calcined (c) at 400 °C for 1 h, (e) as-ball milled with (NH$_4$)$_2$CO$_3$, (f) calcined (e) at 400 °C for 1 h, (g) SrTiO$_3$, (h) TiO$_2$(P-25), and (i) blank without sample.

indicating that higher content of nitrogen doped in $SrTiO_3$ lattice might not certainly lead to the higher photocatalytic activity. It is well known that the larger specific surface area results in higher adsorption ability of NO. In addition, it needs less time for photo-generated carriers to diffuse from the inside of a sample to the surface. As a result, the tendency for the recombination of photo-generated electrons and holes could be decreased with decreasing crystallite size. Furthermore, as shown in Fig. 4, the volume of mesopore, which were responsible for the effective adsorption of NO, in the powder prepared using hexamethylenetetramine was much larger than those of the other two nitrogen doped powders. Consequently, the powder prepared using hexamethylenetetramine which had higher specific surface area and mesopore volume had higher ability for the destruction of NO although the nitrogen content was lower. On the other hand, the nitrogen doped $SrTiO_3$ samples without calcination had lower capability for the elimination of NO. It might be due to the inhibition of NO adsorption by remaining nitrogen source compounds and by-products such as carbon, NH_3, CO_2, organic substance, etc. Heat treatment of these samples at appropriate temperature such as $400\,^\circ C$ 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. The elimination of lattice defects is favorable for the improvement of photocatalytic reactivity since the defects in the semiconductors might be the recombination center of photogenerated holes and electrons resulting in worse photocatalytic activity of the semiconductor.

In addition, it is also notable that these three samples exhibited higher NO elimination capability than P-25 and pure $SrTiO_3$ in near ultraviolet light range ($\lambda > 290\,nm$). Especially, for $SrTiO_{3-x}N_x$ made with hexamethylenetetramine followed by calcinations at $400\,^\circ C$ could destruct 58.9% NO which was 1.4 and 1.3 times higher than those of pure $SrTiO_3$ and TiO_2 (Degussa P-25) (see Fig. 8b, g and h).

4. Conclusions

(1) Mechanochemical treatment provides a simple and efficient method for doping nitrogen into $SrTiO_3$ lattices.

Single phase nitrogen doped $SrTiO_3$ could be produced by this method.

(2) New band gap in the visible light range could be formed by nitrogen doping and the absorption of visible light increased with increasing nitrogen content doped in $SrTiO_3$ lattice.

(3) The photocatalytic activity of $SrTiO_3$ both in visible light and near ultraviolet light range could be greatly improved by nitrogen doping. NO destruction capability of nitrogen doped $SrTiO_3$ made with 20 wt.% hexamethylenetetramine-$SrTiO_3$ was about 3.5 times and 1.4 times higher than those of pure $SrTiO_3$ under the irradiation of light wavelength larger than 400 nm and near ultraviolet light range.

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