
Keita Ikeue *, Yuta Yamamoto and Masashige Suzuki

Department of Applied Chemistry, Faculty of Engineering, Sanyo-Onoda City University, 1-1-1 Daigakudori, Sanyo-Onoda 756-0884, Yamaguchi, Japan; F118612@ed.socu.ac.jp (Y.Y.); F117604@ed.socu.ac.jp (M.S.)

* Correspondence: ikeue@rs.socu.ac.jp; Tel.: +81-836-88-4559

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Abstract: We developed a novel method to synthesize a visible-light-responsible photocatalyst from a composite of SrTiO₃ and a graphitic carbon nitride (g-C₃N₄) nanosheet. Heteroatoms were successfully doped into a lattice of SrTiO₃ by mild calcination of a composite that the g-C₃N₄ nanosheet adsorbed on to the SrTiO₃ surface. The absorption edge in the UV-Vis absorption spectrum of the doped sample was shifted to a longer wavelength region. The photocatalytic activity of the doped sample under UV light irradiation was higher than those of both pristine SrTiO₃ and the g-C₃N₄ nanosheet, suggesting that the photocatalytic property of SrTiO₃ was enhanced by doping. The doped sample showed photocatalytic activity under visible light irradiation (>420 nm), which was enhanced by Pt loading.

Keywords: photocatalyst; hydrogen evolution; visible light; SrTiO₃; g-carbon nitride nanosheet

1. Introduction

Hydrogen production by photocatalytic solar water splitting has received much attention as the next generation clean energy source because CO₂ emissions are minimal during electric power generation. Over the past few decades, a number of photocatalysts have been reported to achieve one-step overall water-splitting UV irradiation under visible light irradiation [1–10]. SrTiO₃ and TiO₂ have been widely used for water splitting photocatalysis under UV irradiation because of their non-toxicity and low cost [11–15]. However, these photocatalysts cannot operate under visible light irradiation because of their wide band gap. Many researchers have therefore developed visible-light-driven photocatalysts by band modification [16–20].

Doping, which includes replacing the host material with a foreign element at a crystal lattice point, is widely used to prepare visible-light-driven photocatalysts. Kudo et al. reported that co-doping of Cr³⁺-Ta⁵⁺ and Cr³⁺-Sb⁵⁺, and doping of Rh cations were effective, with doped SrTiO₃ showing high photocatalytic activity for H₂ evolution under visible light irradiation in the presence of a sacrificial agent [16,17]. The donor level was formed between the conduction band and the valence band. The transition from the donor level to the conduction bands of SrTiO₃ and TiO₂ responds to visible light absorption. For other band-modification methods in the oxide-based photocatalyst, sulfurization and nitridation have also been suggested. These processes were carried out by high-temperature calcination of an oxide-based photocatalyst in the flowing of H₂S and NH₃. The new bands based on S3p and/or N2p orbitals formed above O2p valence bands and led to a decrease in the band gap. Ohno et al. reported TiO₁₋ₓSₓ prepared by calcination of TiO₂ in the flowing of H₂S showed photocatalytic activity under visible light irradiation [18]. Domen et al., have reported on oxynitride- and oxysulfide-based photocatalysts for water splitting such as TaON, ATaO₂N (A = Ca, Sr, Ba),
(Ga$_{1-x}$Zn$_x$)(N$_{1-x}$O$_x$) solid solution and Ln$_2$Ti$_2$S$_2$O$_5$ (Ln = Pr, Nd, Sm, Gd, Tb, Dy, Ho and Er) [21–23]. In particular, an Rh$_{2-y}$Cr$_y$O$_3$-loaded (Ga$_{1-x}$Zn$_x$)(N$_{1-x}$O$_x$) solid solution synthesized by nitriding a mixture Ga$_2$O$_3$ and ZnO has been shown to achieve overall water splitting under visible light irradiation without noticeable degradation. The quantum efficiency of this photocatalyst for overall water splitting reached ca. 2.5% at 420–440 nm. However, doping and sulfurization/nitridation require high-temperature calcination and the use of toxic reactants, respectively. From the perspectives of energy consumption suppression and reducing environmental load, the development of a more environmentally friendly process is required.

In the present study, we investigated facile doping under mild conditions in order to obtain a visible-light-driven photocatalyst. Graphitic C$_3$N$_4$ (g-C$_3$N$_4$) nanosheets were used as a doping agent. The bulk g-C$_3$N$_4$, an organic, metal-free polymeric, layered semiconductor has recently attracted attention as a visible-light-responsible photocatalyst [9,24–28], and its photocatalytic property was first reported by Wang et al. [29]. Moreover, the composite photocatalysts using g-C$_3$N$_4$ were reported and show high photocatalytic activity [30–33]. The layered g-C$_3$N$_4$ can be exfoliated into 2D thinner nanosheets. Although many investigations on the photocatalysis using bulk g-C$_3$N$_4$ have been carried out, there are few studies using g-C$_3$N$_4$ nanosheets. Therefore, we focused on the synthesis of a photocatalyst using g-C$_3$N$_4$ nanosheets. The 2D g-C$_3$N$_4$ nanosheet will strongly interact with other oxide-based semiconductor surfaces due to its high surface energy. By using a strong interaction of 2D g-C$_3$N$_4$, doping was carried out by the calcination of g-C$_3$N$_4$ nanosheet-adsorbed SrTiO$_3$ nanoparticles in a nitrogen atmosphere. We optimized the amount of dopant by changing the volume of g-C$_3$N$_4$ nanosheet dispersion in the adsorption process. The photocatalytic hydrogen evolution in the presence of a sacrificial agent under UV and visible-light irradiation was studied. Moreover, we investigated the effect of co-catalyst loading on the photocatalytic activity under visible light irradiation.

2. Materials and Methods

2.1. Chemicals and Materials

Urea (99%), HNO$_3$ (70%), and HCl (37%) were purchased from FUJIFILM Wako Pure Chemical Co. Ltd. (Osaka, Japan). These chemicals were used without purification. SrTiO$_3$ nanoparticles were supplied by Toda Kogyo Co., Ltd., and calcined at 600°C for 2 h before use.

2.2. Synthesis of Photocatalyst

A carbon nitride nanosheet was prepared following a method given in a previous study [34]. Urea was calcined at 600°C in a crucible with a cover (heating rate: 5°C/min) in order to obtain the bulk g-C$_3$N$_4$. The bulk C$_3$N$_4$ powder was washed with 0.1 M HNO$_3$ and distilled water, followed by drying at 70°C for 12 h. The powder was dispersed into a 15% HCl aqueous solution (150 mL). The resulting suspension was sonicated for 1 h and was then magnetically stirred for 24 h. The suspension was transferred to Teflon-lined stainless steel autoclaves and heated to 110°C for 5 h. The obtained suspension was pump filtrated and washed at least five times to remove HCl and agglomerate the C$_3$N$_4$. To achieve g-C$_3$N$_4$ nanosheet dispersion, the wet product was dispersed into 100 mL distilled water.

The calcined SrTiO$_3$ (0.3 g) was dispersed into 100 mL distilled water, followed by sonification for 10 min. The g-C$_3$N$_4$ nanosheet dispersion was dropped into the SrTiO$_3$ dispersion under vigorous stirring. The amount of the dropped g-C$_3$N$_4$ nanosheet dispersion was varied in the range of 10 to 30 mL. The resulting suspension was stirred at room temperature for 1 h, and left without stirring for 3 h. The obtained sedimentation was centrifugated and dried at 110°C overnight. The resulting powder was calcined at 600°C for 5 h in flowing N$_2$. The doped sample was abbreviated as SrTiO$_3$-Dx (x is volume of added g-C$_3$N$_4$ nanosheet dispersion).
2.3. Characterization

The crystal structures of the samples were determined using an X-ray diffraction (XRD) diffractometer (Rigaku, SmartLab, Tokyo, Japan) with monochromated Cu Kα radiation (40 kV, 30 mA). X-ray fluorescence (XRF; Horiba, XGT-7200, Tokyo, Japan) analysis was used to obtain the chemical composition of the samples. For the samples, the microstructures were observed and local elemental analysis was conducted using field emission scanning electron microscopy (FE-SEM) with energy-dispersive X-ray analysis (EDX, Hitachi S-4800, Tokyo, Japan). Diffuse reflectance absorption spectra were recorded using a UV-Vis spectrometer (Shimadzu, UV-3100PC, Kyoto, Japan) to determine the optical band gap energy.

2.4. Photocatalytic Reaction

The photocatalytic reaction was conducted in an external-irradiation quartz cell connected to a closed gas-circulating system. The photocatalyst (0.1 g) was suspended in 50% methanol aqueous solution (150 mL) in the cell. The rate of H₂ evolution was determined via gas chromatography (Shimadzu GC-8A, TCD, Ar carrier, MS-5A) under irradiation from a 500 W Xe lamp (light density at 420 nm: 0.23 W/cm², illuminated area: 78.5 cm², distance between light source and cell: 10 cm). The light wavelength was controlled using a cut-off filter (Sigma Koki, Saitama, Japan). Additionally, the photocatalytic reaction was carried out after Pt photodeposition.

3. Results and Discussion

3.1. Characterization of Doped SrTiO₃

A nanosheet will have an unstable surface compared to bulk material because of its high surface energy. Therefore, a g-C₃N₄ nanosheet will strongly adsorb SrTiO₃ nanoparticles to form the precursor material for a doped sample. The doped sample can be synthesized by a solid state reaction between the g-C₃N₄ nanosheet and SrTiO₃ owing to strong interaction. To optimize the amount of adsorbed g-C₃N₄ nanosheet in the precursor material, we synthesized the doped sample by changing the volume of g-C₃N₄ nanosheet dispersion. The crystal structures of the as-prepared samples were examined via XRD. Figure 1 shows the XRD patterns of pristine SrTiO₃, g-C₃N₄ nanosheet, and the doped samples. The XRD pattern of the pure g-C₃N₄ nanosheet exhibited two diffraction peaks at 13.2° and 27.6°, which corresponded to the (100) and (002) diffraction planes, respectively [25,29,35]. These were attributed to the characteristic in-plane and inter-planar stacking peaks of the aromatic system in graphite-like carbon nitride, respectively [29]. The pristine SrTiO₃ exhibits five distinct peaks at 22.66°, 32.27°, 39.79°, 46.28°, 52.11°, and 57.53°, which can be attributed to the (100), (110), (111), (200), (210), and (211) crystal planes, respectively. The doped samples were not observed as having the peaks owing to the g-C₃N₄; only the peaks ascribed to SrTiO₃. It is suggested that this sample was not a simple composite of g-C₃N₄ and SrTiO₃ nanoparticles. However, the diffraction peaks at 32.34° for the (110) planes of the doped samples (SrTiO₃-D15) exhibited a slightly higher shift than that of pristine SrTiO₃ (32.27°), which indicated that nitrogen or carbon was doped into SrTiO₃, resulting in lattice distortion. The shift was also observed on other doped samples (Table S1).

The morphologies of the doped samples were examined via FE-SEM (Figure 2). As shown in Figure 2a, uniform spherical nanoparticles with grain sizes of approximately 30 nm could be observed. The g-C₃N₄ nanosheet particles (Figure 2b) had a thin lamellar shape and obvious particle aggregation was observed. Nanosheet aggregation may occur during the drying process. In the FE-SEM image (Figure 2c) of the calcination product from the SrTiO₃/g-C₃N₄ composite, g-C₃N₄ nanosheet particles were not observed, which made it difficult to differentiate pristine SrTiO₃ from the doped sample. From the energy dispersed X-ray spectroscopy (EDX) analysis results for pristine SrTiO₃ and SrTiO₃-D15 (Figure 3), it can be seen that the content of the C element in the doped sample is notably higher than that of pristine SrTiO₃. In addition, the presence of the N element was observed in the doped sample, indicating that C and N were successfully doped into the lattice of SrTiO₃.
We attempted to perform an X-ray photoelectron spectroscopy (XPS) analysis of the doped samples to elucidate the chemical state of C and/or N. However, we could not sufficiently obtain the XPS spectra because of low concentration.

![XRD patterns](image1)

**Figure 1.** X-ray diffraction (XRD) patterns of (a) pristine SrTiO$_3$, (b) SrTiO$_3$-D10, (c) SrTiO$_3$-D15, (d) SrTiO$_3$-D20, (e) SrTiO$_3$-D25, (f) SrTiO$_3$-D30, and (g) C$_3$N$_4$.

![SEM images](image2)

**Figure 2.** Scanning electron microscopy (SEM) images of (a) pristine SrTiO$_3$, (b) pristine g-C$_3$N$_4$, and (c) SrTiO$_3$-D15.

![EDX spectra](image3)

**Figure 3.** Energy-dispersive X-ray (EDX) spectra of (a) pristine SrTiO$_3$ and (b) SrTiO$_3$-D15.

The diffuse reflectance absorption spectra were used to study the optical properties of the doped samples. Figure 4 shows the diffuse reflectance UV-Vis absorption spectra of the doped samples. The doped samples exhibited a longer light absorption edge compared to pristine SrTiO$_3$, indicating that C or N doping was an efficient alternative for expanding light absorption by SrTiO$_3$. Moreover,
an obvious red shift was observed in the absorption edge of the doped samples. We also observed color change of samples from white to light yellow after doping (Figure S1). Figure 4b shows the Tauc plots obtained from the UV-vis absorption spectra by transformation based on the Kubelka–Munk function versus the energy of light. The transformation was conducted according to the formula: \((ahv)^2 = A(hv - E_g)\), where \(a\), \(v\), \(A\), and \(E_g\) are the absorption coefficient, light frequency, proportionality constant, and band gap, respectively [36]. As shown in Table 1, the band gaps of the doped samples were smaller than that of pristine SrTiO\(_3\) and decreased with increasing g-C\(_3\)N\(_4\) nanosheet dispersion during the preparation of the precursor to the doped samples. It is suggested that the g-C\(_3\)N\(_4\) nanosheet can directly contribute to doping.

![Figure 4](https://via.placeholder.com/150)

**Figure 4.** Diffuse reflectance UV-Vis absorption spectra (a) of SrTiO\(_3\), C\(_3\)N\(_4\), and the doped samples, and their Tauc plots (b).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Band Gap/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrTiO(_3)</td>
<td>3.21</td>
</tr>
<tr>
<td>C(_3)N(_4) nanosheet</td>
<td>2.78</td>
</tr>
<tr>
<td>SrTiO(_3)-D10</td>
<td>3.17</td>
</tr>
<tr>
<td>SrTiO(_3)-D15</td>
<td>3.02</td>
</tr>
<tr>
<td>SrTiO(_3)-D20</td>
<td>2.81</td>
</tr>
<tr>
<td>SrTiO(_3)-D25</td>
<td>2.74</td>
</tr>
<tr>
<td>SrTiO(_3)-D30</td>
<td>2.42</td>
</tr>
</tbody>
</table>

**3.2. The Photocatalytic Property of Doped SrTiO\(_3\)**

At first, the photocatalytic activities of the doped samples were evaluated by considering the hydrogen evolution in the presence of methanol as a sacrificial agent. Figure 5 shows the hydrogen evolution rate for the doped samples synthesized using different amounts of g-C\(_3\)N\(_4\) nanosheet dispersion. From the results of the UV-vis absorption analysis, it can be seen that the amount of dopant increased with increasing g-C\(_3\)N\(_4\) nanosheet dispersion during the preparation of the precursor materials. The hydrogen evolution rate increased with increasing dopant concentration; however, excess increase of dopant makes the recombination center between the photogenerated electrons and holes increase [17]. SrTiO\(_3\)-D15 prepared using 15 mL C\(_3\)N\(_4\) nanosheet dispersion, therefore, showed maximum photocatalytic activity. The hydrogen evolution rate of SrTiO\(_3\)-D15 was higher than those of pristine g-C\(_3\)N\(_4\) and SrTiO\(_3\) nanoparticles (Figure 6), suggesting that the photocatalytic activity of SrTiO\(_3\)-D15 increased due to a synergistic effect between SrTiO\(_3\) and the dopant. To enhance the photocatalytic activity, Pt was loaded onto the SrTiO\(_3\)-D15 as a co-catalyst. The Pt loading sample showed photocatalytic activity under visible light irradiation (\(\lambda > 420\) nm) (Figure S2). The 5-h photocatalytic test under UV irradiation using the Pt loaded sample could be repeated two times without noticeable deactivation (Figure S3). Figure 7 shows the effect of photocatalytic activity on Pt loading. The photocatalytic H\(_2\) evolution rate showed maximum value at 0.2 wt% loading.
The photo-formed electron transfers to the Pt nanoparticle owing to a high work function, and proton reduction can efficiently take place over the Pt nanoparticles.

**Figure 5.** Photocatalytic H$_2$ evolution over the doped SrTiO$_3$ synthesized using different amounts of g-C$_3$N$_4$ nanosheet dispersion under UV light irradiation. The photocatalytic reaction was performed in an external-irradiation quartz cell under irradiation from a 500 W Xe lamp, 150 mL of a 50% methanol solution, and 0.1 g of a photocatalyst.

<table>
<thead>
<tr>
<th>Amount of added C$_3$N$_4$ / mL</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$ evolution rate / μmol·h$^{-1}$</td>
<td>0</td>
<td>2</td>
<td>4</td>
<td>6</td>
<td>8</td>
<td>10</td>
<td>12</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 6.** Comparison of photocatalytic activity under UV light irradiation between SrTiO$_3$-D15 and pristine SrTiO$_3$ and C$_3$N$_4$.

**Figure 7.** The effect of Pt loading on the photocatalytic H$_2$ evolution rate over SrTiO$_3$-D15 under visible light irradiation. The photocatalytic reaction was performed in an external-irradiation quartz cell under irradiation from a 500 W Xe lamp with a cut-off filter ($\lambda > 420$ nm), 150 mL of 50% methanol solution, and 0.1 g of photocatalyst.
4. Conclusions

We demonstrate a new doping method using g-C$_3$N$_4$ nanosheets. C$_3$N$_4$ nanosheets reacted with SrTiO$_3$ nanoparticles via a strong adsorption interaction to form the doped sample. The doped sample shows light absorption in a longer wavelength region ($\lambda > 420$ nm) compared to SrTiO$_3$. The photocatalytic activity of the doped sample under UV irradiation was higher than those of both pristine g-C$_3$N$_4$ and SrTiO$_3$ nanoparticles owing to their synergistic effect, and was enhanced by Pt loading. Moreover, the doped sample can operate under visible light irradiation. This doping method can applied to a broad range of oxide-based photocatalysts. We investigated the photocatalytic properties of various doped samples prepared by this method. However, the photocatalytic H$_2$ evolution reaction in the doped sample cannot proceed without a sacrificial agent under visible light irradiation. Therefore, the overall water splitting under visible light irradiation should be investigated in the Z-scheme reaction system formed by combination with O$_2$ evolution photocatalysts.

Supplementary Materials: The following are available online at http://www.mdpi.com/2571-6131/3/1/3/s1, Figure S1: The photograph of samples, Figure S2: Time course of H$_2$ evolution reaction over 0.2 wt% Pt loaded SrTiO$_3$-D15, Figure S3: The repeated photocatalytic test, Table S1: The peak position and d-spacing in XRD of doped samples.

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Conflicts of Interest: The authors declare no conflict of interest.

References
24. Ong, W.-J.; Tan, L.-L.; Ng, Y.H.; Yong, S.-T.; Chai, S.-P. Graphitic carbon nitride (g-C₃N₄) and its hybrids with enhanced photoactivity. *RSC Adv.* 2016, 6, 13063–13071. [CrossRef]


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