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Combinational effect of Pt/SrTiO$_3$:Rh photocatalyst and SnPd/Al$_2$O$_3$ non-photocatalyst for photocatalytic reduction of nitrate to nitrogen in water under visible light irradiation

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Abstract

Photocatalytic reduction of nitrate in water in the co-presence of Pt/SrTiO$_3$:Rh and SnPd/Al$_2$O$_3$ under visible light irradiation ($\lambda > 420$ nm) was investigated. This reaction system efficiently and selectively promoted the photocatalytic reduction of nitrate to nitrogen, whereas Pt/SrTiO$_3$:Rh or SnPd/Al$_2$O$_3$ alone showed little activity under the reaction conditions. The selectivity to N$_2$ was 94% under the optimum reaction conditions, where the amounts of Pt/SrTiO$_3$:Rh and SnPd/Al$_2$O$_3$ loaded in the reaction system were 500 mg and 150 mg, respectively. This reaction system showed a superior nitrate decomposition rate and superior selectivity to nitrogen compared with SrTiO$_3$:Rh directly modified with SnPd bimetal. From analysis of the reaction mechanism, hydrogen formed by photoreduction of water over Pt/SrTiO$_3$:Rh acted as the reductant for a non-photocatalytic nitrate conversion reaction over SnPd/Al$_2$O$_3$. Moreover, the products, including formaldehyde and formic acid, formed by photo-oxidation of methanol over Pt/SrTiO$_3$:Rh acted as reductants for nitrate over SnPd/Al$_2$O$_3$.

Keywords

Nitrate reduction, Photocatalyst, Groundwater purification, Tin-palladium bimetal
1. Introduction

Pollution of groundwater with nitrate (NO$_3^-$) as a result of agricultural activity, human sewage, and industrial effluents is a serious global problem. Since groundwater is an important fresh water resource that is indispensable to human society, NO$_3^-$ needs to be removed from polluted groundwater.

Since the discovery by Vorlop and co-workers in 1989 that Cu-Pd/Al$_2$O$_3$ promoted the reduction of NO$_3^-$ with H$_2$ to N$_2$ (Eq. (1)) in water [1], the reaction over supported bimetallic catalysts has been the subject of intense investigation as a method of removing NO$_3^-$ from groundwater. However, in the catalytic reduction, the formation of ammonia (NH$_3$) and ammonium ion (NH$_4^+$) (Eq. (2)) is a critical problem, because the allowable level of NH$_4^+$ in drinking water is 0.5 mg dm$^{-3}$, which is recommended by the WHO.

\[
\text{NO}_3^- + \frac{5}{2}\text{H}_2 \rightarrow \frac{1}{2}\text{N}_2 + 2\text{H}_2\text{O} + \text{OH}^- \quad (1)
\]

\[
\text{NO}_3^- + 4\text{H}_2 \rightarrow \text{NH}_4^+ + \text{H}_2\text{O} + 2\text{OH}^- \quad (2)
\]

Thus far, high selectivity to N$_2$ and high catalytic activity have been achieved with supported bimetallic catalysts composed of Pd and a base metal, such as Cu, Sn, or In.
However, using gaseous H\textsubscript{2} as a reductant is a serious issue because handling this flammable gas at high pressure is difficult. Therefore, for practical use, there is great demand for an alternative technology that does not use gaseous H\textsubscript{2}.

As a potential method to overcome this issue, photocatalytic reduction of NO\textsubscript{3} has attracted much attention. Kudo and co-workers first reported the photocatalytic reduction of NO\textsubscript{3} in 1987 \[18\]. They employed Pt-modified TiO\textsubscript{2} for the reaction under UV light irradiation. However, their target was evolution of NH\textsubscript{3} and O\textsubscript{2} by photocatalytic reaction of NO\textsubscript{3} with H\textsubscript{2}O, rather than purification of NO\textsubscript{3}-polluted groundwater, and thus NH\textsubscript{3} was selectively formed. Research aiming at the purification of NO\textsubscript{3}-polluted groundwater by a photocatalytic reaction was first reported by Schlögl et al. in 1999 \[19\]. They focused on TiO\textsubscript{2} as a photocatalyst and humic acid as a hole scavenger. Although NO\textsubscript{3} was decomposed under UV irradiation, a large amount of nitrite (NO\textsubscript{2}%), which is more toxic than NO\textsubscript{3}, was formed.

In 2005, Guan’s group \[20\] and Kominami’s group \[21\] reported photocatalysts showing high selectivity to N\textsubscript{2} for the photocatalytic reduction of NO\textsubscript{3} in water under UV light irradiation in the presence of sacrificial compounds. Guan and co-workers developed Ag/TiO\textsubscript{2} prepared by a pH-controlled photocatalytic process and found that this showed extremely high selectivity to N\textsubscript{2} (> 99%) in the presence of formic acid as a
hole scavenger under UV irradiation [20]. Kominami et al. have reported that NO$_3^-$ is reduced to N$_2$ with high selectivity over TiO$_2$ modified with Pd-Cu in the presence of oxalic acid as a hole scavenger under basic conditions and UV irradiation [21].

In contrast to the reaction using UV light as a light source, there are only a few reports on the photocatalytic reduction of NO$_3^-$ under visible light irradiation [22, 23]. Tawkaew et al. first reported the use of CdS pillared-layered compounds, including H$_2$Ti$_4$O$_9$/CdS and H$_4$Nb$_6$O$_{17}$/CdS, as visible-light-active photocatalysts for the photocatalytic reduction of NO$_3^-$ in water [22]. While the photocatalytic reduction of NO$_3^-$ proceeded in the presence of methanol as a hole scavenger under visible light irradiation ($\lambda > 400$ nm), NO$_2^-$ and NH$_3$ mainly formed. Hamanoi and Kudo have reported that a Ni-doped ZnS photocatalyst shows photocatalytic activity for the reduction of NO$_3^-$ in the presence of methanol under visible light irradiation ($\lambda > 420$ nm) [23], however, the selectively to N$_2$ was not so high. To the best of our knowledge, a photocatalyst or photocatalytic reaction system showing high selectively to N$_2$ under visible light irradiation has not been reported so far.

Generally, modification of semiconductor photocatalysts with precious metals is indispensable for enhancing the photocatalytic performance [24]. The photocatalytic performance of precious-metal-modified semiconductor photocatalysts is
determined by the kind, crystalline structure, location on the semiconductor photocatalyst, and particle size of the modifying metals. Since bare semiconductor photocatalysts like TiO$_2$, ZnS, and CdS are basically inactive for the photocatalytic reduction of NO$_3^-$, to make them show photocatalytic activity, these photocatalysts should be modified with one or more metals, including Ru, [25] Ag [20, 26], Ni [27, 28], Ni-Cu [29], Pt-Cu [30], Pd-Cu [21, 31], and Sn-Pd [32], which are active for thermochemical, that is, non-photocatalytic, reduction of NO$_3^-$. For a precious-metal-modified semiconductor photocatalyst, photogenerated electrons in the semiconductor photocatalyst should be transferred to the metal particles on the semiconductor photocatalyst, where they then reduce NO$_3^-$ with H$^+$, which are adsorbed on the surface of the metal particles. According to this mechanism, the metal particles should have the ability to show high photocatalytic performance, that is to say, (i) to smoothly transfer the photogenerated electrons from the semiconductor photocatalyst to the metal particles, (ii) to stably reserve the electrons on them, and (iii) to selectively activate NO$_3^-$ and H$^+$. However, it is hard for the metal particles to satisfy these three abilities simultaneously. Therefore, in practice, to develop a photocatalyst that is active and selective for the photocatalytic reduction of NO$_3^-$ in water, the properties relevant to the modifying metal particles (kind, crystalline structure, location, and
particle size) should be optimized to balance these abilities.

To overcome this issue, we have previously developed a photocatalytic reaction system in which a separately prepared photocatalyst (Pt/TiO$_2$) and non-photocatalyst (SnPd/Al$_2$O$_3$) are dispersed in water containing NO$_3^-$.

This photocatalytic system effectively and selectively promoted the photocatalytic reduction of NO$_3^-$ to N$_2$ under UV irradiation [32]. In this photocatalytic system, H$_2$ was formed by a photocatalytic reaction over Pt/TiO$_2$ (Eq. (3)), and the formed H$_2$, which was dissolved in water, was used as a reductant for non-photocatalytic, namely thermocatalytic, reduction of NO$_3^-$ over SnPd/Al$_2$O$_3$ (Eq. (1)). In the photocatalytic system, two reactions, shown in Eqs. 1 and 3, continuously take place under UV irradiation over SnPd/Al$_2$O$_3$ and Pt/TiO$_2$, respectively.

\[
2H^+ + 2e^- \rightarrow H_2 \quad (3)
\]

We found that the photocatalytic performance of this system was much better than that of TiO$_2$ directly modified with Sn-Pd bimetal (SnPd/TiO$_2$). In the system, the photocatalyst (Pt/TiO$_2$) and non-photocatalyst (SnPd/Al$_2$O$_3$) can be designed separately to show the optimal performance for the photocatalytic and non-photocatalytic reactions.
individually.

In the present study we expanded the photocatalytic system to NO$_3^-$ reduction driven by visible light. We report the photocatalytic reduction of NO$_3^-$ in water in the co-presence of Pt/SrTiO$_3$:Rh photocatalyst and SnPd/Al$_2$O$_3$ non-photocatalyst (denoted as a Pt/SrTiO$_3$:Rh–SnPd/Al$_2$O$_3$ system) under visible light irradiation ($\lambda > 420$ nm). The reaction system effectively and selectivity promoted the photocatalytic reduction of NO$_3^-$ under visible light irradiation, whereas Pt/SrTiO$_3$:Rh or SnPd/Al$_2$O$_3$ alone showed only low activity. It should be noted that this reaction system showed superior NO$_3^-$ decomposition rate and superior N$_2$ selectivity compared with SrTiO$_3$:Rh directly modified with Sn-Pd bimetal. We also investigated the reaction mechanism over the Pt/SrTiO$_3$:Rh–SnPd/Al$_2$O$_3$ system and found that NO$_3^-$ was reduced over SnPd/Al$_2$O$_3$ with methanol (CH$_3$OH), formaldehyde (H$_2$CO), and formic acid (HCO$_2$H), in addition to H$_2$, where the H$_2$CO, HCO$_2$H, and H$_2$ were formed on Pt/SrTiO$_3$:Rh by photocatalytic reactions. The reduction of NO$_3^-$ with HCO$_2$H over SnPd/Al$_2$O$_3$ contributed largely to the decomposition rate of NO$_3^-$, which was the reason for the high efficiency of the Pt/SrTiO$_3$:Rh–SnPd/Al$_2$O$_3$ system in the photocatalytic reduction of NO$_3^-$ in water.
2. Experimental

2.1. Preparation of catalysts

SrTiO$_3$ doped with 1 mol% Rh relative to Ti (denoted SrTiO$_3$:Rh) was prepared according to the literature procedure [33] by a solid state reaction. Starting materials SrCO$_3$ (3.432 g, Kanto Chemicals), TiO$_2$ (1.838 g, Soekawa Chemicals), and Rh$_2$O$_3$ (0.030 g, Wako Pure Chemicals) were mixed with a small amount of methanol in an agate mortar so that the chemical formula was SrTi$_{0.99}$Rh$_{0.01}$O$_3$. The mixture was calcined at 1273 K for 10 h in air. The obtained solid was confirmed to be SrTiO$_3$:Rh by X-ray diffraction (Rigaku; MiniFlex, Cu Kα) and UV–vis diffuse reflectance spectroscopy (JASCO, V-650,) as shown in Fig. A1 in Supplementary data.

Modification of SrTiO$_3$:Rh with 0.1 wt.% Pt was conducted by photodeposition. Two grams of SrTiO$_3$:Rh was dispersed in distilled water (225 cm$^3$), and then CH$_3$OH (25 cm$^3$, Wako Pure Chemicals) and H$_2$PtCl$_6$·6H$_2$O (0.25 cm$^3$, 0.04 mol dm$^{-3}$, Wako Pure Chemicals) were added to the suspension. The suspension, in a Pyrex glass cell, was purged with a stream of N$_2$ (15 cm$^3$ min$^{-1}$) for 30 min and then irradiated using a 300 W Xe lamp (USHIO, Optical Modulex) for 3 h. The solid was filtered from the suspension, washed with distilled water (ca. 500 cm$^3$), and dried in air at 333 K overnight. The obtained catalyst is denoted as Pt/SrTiO$_3$:Rh.
Al₂O₃ modified with 2.3 wt.% Sn and 4.2 wt.% Pd (Sn/Pd molar ratio of 0.5, denoted as SnPd/Al₂O₃) was prepared by an incipient wetness method. Al₂O₃ (AEROSIL Alu C) was heated in air at 523 K for 4 h before use. An aqueous solution of PdCl₂ (7.38 cm³, 0.112 mol dm⁻³, Wako Pure Chemicals) was dropped onto Al₂O₃ (2.0 g), and then the resulting wet solid was dried in air at 373 K overnight, followed by calcination in air at 523 K for 3 h. An aqueous solution of SnCl₂·2H₂O (2.31 cm³, 0.172 mol dm⁻³, Wako Pure Chemicals) was dropped onto the resulting solid, and then the wet solid was dried in air at 373 K overnight, followed by calcination in air at 523 K for 3 h. From X-ray photoelectron spectroscopy analysis, the Sn/Pd atomic ratio on the surface was determined to be 1.0 before the reaction (Fig. A2 in Supplementary data). SrTiO₃:Rh modified with 2.3 wt.% Sn and 4.2 wt.% Pd was prepared by a similar procedure to that for SnPd/Al₂O₃ and is denoted as SnPd/SrTiO₃:Rh.

Just before the photocatalytic and non-photocatalytic reactions, SnPd/Al₂O₃ and SnPd/SrTiO₃:Rh were reduced with NaBH₄ (Wako Pure Chemicals). NaBH₄ (molar ratio of NaBH₄/(Sn+Pd)=10) was added to the aqueous suspension (30 cm³) in which the catalyst powder was dispersed, and the mixture was stirred at room temperature for 30 min. The catalyst powder was filtered and washed with distilled water (ca. 200 cm³) before it was used for the photocatalytic and non-photocatalytic
2.2. Photocatalytic reduction of $\text{NO}_3^-$ in water

Photocatalytic reduction of $\text{NO}_3^-$ in water was carried out in a Pyrex reaction vessel connected to a closed gas circulation system (Fig. 1). Pt/SrTiO$_3$:Rh and SnPd/Al$_2$O$_3$ were suspended in an aqueous KNO$_3$ solution (250 cm$^3$, 0.8 mmol dm$^{-3}$, Wako Pure Chemicals) containing 10 vol% methanol ($6 \times 10^3$ µmol), and the suspension was stirred using a magnetic stirrer. The reaction suspension was thoroughly degassed and then exposed to He (101.3 kPa). The light source was the 300 W Xe lamp fitted with a cutoff filter (AGC Techno Glass, L–42) to select only light at visible wavelengths ($\lambda > 420$ nm). During photoirradiation, the temperature of the reaction solution was kept at 298 K by immersing the reactor in a water bath. The evolved gases were analyzed using an on-line gas chromatograph (Agilent Technology, 3000 A Micro GC, He carrier) equipped with Molecular sieve 5A and Plot U columns. The concentrations of $\text{NO}_3^-$, $\text{NO}_2^-$, $\text{HCO}_2^-$, and $\text{NH}_4^+$ in the reaction solution were determined by using two ion-chromatographs (Tosoh, IC-2001). For anion analysis, a column containing an anion-exchange resin (TSK gel Super IC-AZ, Tosoh) was used as a stationary phase, and an aqueous solution of NaHCO$_3$ (2.9 mmol dm$^{-3}$, Wako Pure
Chemicals) and Na$_2$CO$_3$ (3.1 mmol dm$^{-3}$, Wako Pure Chemicals) was used as a mobile phase. For cation analysis, a column containing a cation-exchange resin (TSK gel IC-Cation 1/2 HR, Tosoh) was used as a stationary phase, and an aqueous solution of methanesulfonic acid (2.2 mmol dm$^{-3}$, Wako Pure Chemicals) and 18-crown-6 (1.0 mmol dm$^{-3}$, Wako Pure Chemicals) was used as a mobile phase.

The amount of H$_2$CO in the reaction solution was determined by an iodometric titration method. The iodometric titration was conducted as follows. Iodine solution (25 cm$^3$, 0.05 mol dm$^{-3}$, Junsei Chemicals) and KOH (10 cm$^3$, 1.2 mol dm$^{-3}$, Wako Pure Chemicals) were added to the reaction solution, from which the catalyst powder was removed in advance. The solution was left to stand at room temperature for 15 min, and then dilute sulfuric acid (7.5 cm$^3$, 10 vol%, Wako Pure Chemicals) was added to the solution. Finally, the solution was titrated with Na$_2$S$_2$O$_3$ solution (0.06 mol dm$^{-3}$, Wako Pure Chemicals) using starch as an indicator to determine the amount of I$_2$, which corresponds to the amount of H$_2$CO initially present in the solution.

2.3. Non-photocatalytic reduction of NO$_3^-$ with reductant (CH$_3$OH, H$_2$CO, HCO$_2$H) in water

Non-photocatalytic reduction, namely conventional catalytic reduction, of NO$_3^-$
with reductants, including $\text{CH}_3\text{OH}$, $\text{H}_2\text{CO}$, and $\text{HCO}_2\text{H}$ (Wako Pure Chemicals), in water was carried out in a batch reactor at 298 K in the dark. An aqueous KNO$_3$ solution (250 cm$^3$, 0.8 mmol dm$^{-3}$) containing reductants was purged with a stream of He (30 cm$^3$ min$^{-1}$) for 30 min, and then SnPd/Al$_2$O$_3$ (150 mg) was added to the solution to start the reaction. A small portion of the reaction solution was periodically withdrawn and was analyzed by using the two ion-chromatographs and the iodometric titration to determine the concentrations of NO$_3^-$, NO$_2^-$, HCO$_2^-$, NH$_4^+$, and H$_2$CO.

3 Results and discussion

3.1. Photocatalytic reduction of NO$_3^-$ in water in the presence of both Pt/SrTiO$_3$:Rh and SnPd/Al$_2$O$_3$ under visible light irradiation

Table 1 summarizes the data of the photocatalytic reduction of NO$_3^-$ in water under visible light irradiation for 6 h. Pt/SrTiO$_3$:Rh alone (Entry 1), although it is a visible light-active photocatalyst [33], showed negligible activity. This is because SrTiO$_3$:Rh itself and Pt metal do not have any ability to activate NO$_3^-$. SnPd/Al$_2$O$_3$ alone showed only low catalytic activity (Entry 2). The conversion in Entry 2 was due to non-photocatalytic reduction of NO$_3^-$ with methanol over the SnPd bimetal because a similar conversion to that in Entry 2 was obtained for the reaction in the presence of
only SnPd/Al₂O₃ under dark conditions. In contrast to these, high conversion was obtained when both Pt/SrTiO₃:Rh and SnPd/Al₂O₃ were dispersed in the reaction solution (Entry 3). In addition to the high conversion, formation of undesirable NH₄⁺ was suppressed to a low level (6% selectivity). When the reaction was conducted under dark conditions, the conversion was low even in the presence of both catalysts (Entry 4). Thus, the photocatalysis accounts for the enhanced activity shown in Entry 3. The catalyst in which SrTiO₃:Rh was directly modified with SnPd bimetal was much less active than the Pt/SrTiO₃:Rh–SnPd/Al₂O₃ system (Entry 5). As a separate experiment, we confirmed that SnPd/SrTiO₃:Rh did not produce H₂ at all in the absence of NO₃⁻ even though visible light was irradiated and methanol was present. In other words, SnPd/SrTiO₃:Rh had no function in the photocatalytic reaction, probably due to the incident light shielding effect and the formation of a number of recombination sites by the SnPd bimetal particles. Therefore, the activity in Entry 5 was due to non-photocatalytic reduction of NO₃⁻ with methanol over the SnPd bimetal particles. The conversion in Entry 5 was higher than those in Entries 2 and 4, but this was because a large amount of the catalyst (500 mg) was loaded in the reactor for the reaction in Entry 5 compared with those in Entries 2 and 4.

The photocatalytic reduction of NO₃⁻ in the Pt/SrTiO₃:Rh–SnPd/Al₂O₃ system
was strongly influenced by the balance of the reaction rates between the photocatalytic reaction over Pt/SrTiO$_3$:Rh and the thermochemical, that is, non-photocatalytic, reduction of NO$_3^-$ over SnPd/Al$_2$O$_3$. Thus, we optimized the amounts of both catalysts loaded in the reactor. Fig. 2 shows the dependence of the H$_2$ evolution rate over Pt/SrTiO$_3$:Rh from 10 vol% CH$_3$OH solution under visible light irradiation on the weight of Pt/SrTiO$_3$:Rh loaded in the reactor. The rate of H$_2$ evolution was estimated from the amount of H$_2$ formed in 1 h from the beginning of the reaction. This experiment was conducted in the absence of SnPd/Al$_2$O$_3$ as well as NO$_3^-$. The H$_2$ evolution rate increased with an increase in the amount of Pt/SrTiO$_3$:Rh up to 500 mg, and reached a constant (27 $\mu$mol h$^{-1}$). Further addition of Pt/SrTiO$_3$:Rh did not enhance the H$_2$ evolution rate. At Pt/SrTiO$_3$:Rh amounts less than 500 mg, the number of photons absorbed by the reaction system increased with an increase in the amount of Pt/SrTiO$_3$:Rh, resulting in an increased H$_2$ evolution rate. On the other hand, when the amount of Pt/SrTiO$_3$:Rh was more than 500 mg, the amount of catalyst relative to the incident light level was excessive, resulting in a constant H$_2$ evolution rate. From these results, we decided that the optimum amount of Pt/SrTiO$_3$:Rh to be loaded in the reactor was 500 mg for the Pt/SrTiO$_3$:Rh–SnPd/Al$_2$O$_3$ system.

In Fig. 3, conversion of NO$_3^-$, selectivities for NH$_4^+$ and N$_2$, and the amount of
H₂ detected in the gas phase in the photocatalytic reduction of NO₃⁻ under visible light irradiation by the Pt/SrTiO₃:Rh–SnPd/Al₂O₃ system are plotted against the weight of SnPd/Al₂O₃ loaded in the reactor. The weight of Pt/SrTiO₃:Rh loaded in the reactor was fixed at 500 mg. The conversion of NO₃⁻ linearly increased with an increase in the amount of SnPd/Al₂O₃ and reached a maximum at around 150 to 200 mg. Since only a negligible amount of NO₃⁻ was converted in the absence of SnPd/Al₂O₃, some substances, like H₂, acted as a reductant for non-photocatalytic reduction of NO₃⁻ over SnPd/Al₂O₃, and such substances were formed by a photocatalytic reaction over Pt/SrTiO₃:Rh in the presence of methanol. In fact, H₂ was detected in the gas phase when the amount of SnPd/Al₂O₃ loaded in the reactor was less than 150 mg (Fig. 3(b)). When the amount of SnPd/Al₂O₃ loaded in the reactor exceeded 200 mg, the conversion of NO₃⁻ noticeably decreased, probably due to shielding of Pt/SrTiO₃:Rh from incident light by SnPd/Al₂O₃.

The amount of SnPd/Al₂O₃ also had an impact on the selectivity. When only a small amount of SnPd/Al₂O₃ was loaded, like 25 or 50 mg, undesirable NH₄⁺ formation was dominant. In contrast, desirable N₂ was selectively formed with high selectivity when the amount of SnPd/Al₂O₃ was 125 mg or more. NO₂⁻ was not detected at all regardless of the amount of SnPd/Al₂O₃. No gaseous
nitrogen-containing product other than N₂ was formed. From these results, we concluded that the optimum amount of SnPd/Al₂O₃ was 150 mg for the Pt/SrTiO₃:Rh–SnPd/Al₂O₃ system.

Fig. 4 shows repeated use of the catalysts (Pt/SrTiO₃:Rh–SnPd/Al₂O₃ mixture) for the photocatalytic reduction of NO₃⁻ under the optimal reaction conditions. For the first run, the conversion of NO₃⁻ increased linearly with the reaction time up to 6 h. However, the reaction rate decreased after 12 h, even though the conversion was not so high and a large amount of CH₃OH remained. There are two possibilities for the decrease of the reaction rate. One is that Pt/SrTiO₃:Rh or SnPd/Al₂O₃, or both, was deactivated due to changes in their structures, or due to possible poisoning by the products formed during the reaction. To clarify which was plausible, the catalyst powder (Pt/SrTiO₃:Rh–SnPd/Al₂O₃ mixture) was separated from the reaction suspension at 24 h and washed with distilled water (ca. 300 cm³), and then the catalyst was used for the reaction again with fresh reaction solution to avoid possible poisoning by the products. As Fig. 4 demonstrates, the initial rate of the NO₃⁻ conversion reaction was completely recovered by such treatment. After 48 h, the catalyst was separated again, washed, and was used for a third run, and the catalytic activity was recovered. Thus, possible poisoning of the catalysts by the products is a more
plausible explanation for the decrease of the reaction rate.

On the other hand, the selectivity for N\textsubscript{2} was gradually decreased with repeated use. For the first run, the N\textsubscript{2} selectivity was about 90% but decreased to about 75% in the third run. The decrease of the N\textsubscript{2} selectivity suggested that the alloy structure of SnPd bimetal changed during the reaction. To examine the change of the SnPd alloy structure, powder XRD patterns of the catalysts were taken before and after the reaction. Diffraction patterns due to Pd, Sn, and SnPd particles were not observed before or after the reaction. Since the amount of SnPd bimetal was small because of the amounts of Pt/SrTiO\textsubscript{3}:Rh (500 mg) and SnPd/Al\textsubscript{2}O\textsubscript{3} (150 mg) used, XRD patterns due to the metal particles were not observed. At the present stage, though it is hard to discuss the difference of the SnPd alloy structure before and after the reaction, it is plausible that the structure of SnPd alloy particles on Al\textsubscript{2}O\textsubscript{3} changed to preferentially form NH\textsubscript{4}\textsuperscript{+} during the photocatalytic reduction of NO\textsubscript{3}\textsuperscript{−} under visible light irradiation.

3.2. Relationship between amount of H\textsubscript{2} evolved and amount of NO\textsubscript{3}\textsuperscript{−} converted by photocatalytic reaction

As we previously reported [32], in the photocatalytic reduction of NO\textsubscript{3}\textsuperscript{−} in water under UV irradiation by the reaction system comprising Pt/TiO\textsubscript{2} and SnPd/Al\textsubscript{2}O\textsubscript{3}, H\textsubscript{2}
was formed by a photocatalytic reaction over Pt/TiO₂, and non-photocatalytic reduction of NO₃⁻ proceeded with H₂ dissolved in water over SnPd/Al₂O₃ (Fig. 5 (a)). In fact, the amount of H₂ needed in the reaction, which was calculated from the amounts of converted NO₃⁻, produced NH₄⁺, and N₂, was approximately equal to the amount of H₂ evolved by the photocatalytic reaction over Pt/TiO₂ under reaction conditions similar to those for NO₃⁻ reduction but without NO₃⁻ [32].

We investigated whether the photocatalytic reduction of NO₃⁻ in the Pt/SrTiO₃:Rh–SnPd/Al₂O₃ system proceeded through a similar reaction mechanism to that in the Pt/TiO₂–SnPd/Al₂O₃ system, that is, whether only H₂ acted as a reductant for NO₃⁻ over SnPd/Al₂O₃. The number of electrons consumed for H₂ evolution in the absence of NO₃⁻ was compared with that consumed for NO₃⁻ reduction and H₂ formation in the presence of NO₃⁻ in the Pt/SrTiO₃:Rh–SnPd/Al₂O₃ system under visible light irradiation for 6 h. The former was calculated from Eq. (4) and is denoted as N(e⁻)ₜₐₜ. The latter was calculated from Eq. (5) and is denoted as N(e⁻)ₜₚ.

\[
N(e^-)_{t_{0}} [\mu \text{mol}] = (\text{Amount of H}_2 \text{detected in the gas phase in the absence of NO}_3^-) \times 2 \quad (4)
\]

\[
N(e^-)_{t} [\mu \text{mol}] = (\text{Amount of H}_2 \text{detected in the gas phase in the presence of NO}_3^-) \times 2 + (\text{Amount of...}
\]
\[ \text{NO}_3^- \text{ converted to N}_2 \times 5 + (\text{Amount of NO}_3^- \text{ converted to NH}_4^+) \times 8 \]  

(5)

In Fig. 6, \( N(e^-)_{w/o} \) and \( N(e^-)_w \) are plotted against the weight of SnPd/Al\(_2\)O\(_3\) loaded in the reactor. Figures in parentheses in Fig. 6 are the fraction (%) of \( N(e^-)_w \) consumed for \( \text{NO}_3^- \) reduction; if this is less than 100%, some of \( N(e^-)_w \) were consumed for \( \text{H}_2 \) evolution even in the presence of \( \text{NO}_3^- \).

When SnPd/Al\(_2\)O\(_3\) was absent, \( N(e^-)_{w/o} \) was large (194 \( \mu \)mol), but drastically decreased with an increase in the amount of SnPd/Al\(_2\)O\(_3\) loaded in the reactor. This was due to shielding of Pt/SrTiO\(_3\):Rh from light irradiation by SnPd/Al\(_2\)O\(_3\). However, it is noted that \( N(e^-)_{w/o} \) did not drop to zero even when an excess amount of SnPd/Al\(_2\)O\(_3\) was loaded in the reactor, but became nearly constant at 75 \( \mu \)mol in the presence of more than 75 mg of SnPd/Al\(_2\)O\(_3\). Since \( \text{H}_2 \) was not formed at all over SnPd/Al\(_2\)O\(_3\) regardless of whether light irradiation was present or not (data not shown), photocatalytic \( \text{H}_2 \) evolution over Pt/SrTiO\(_3\):Rh took place to some extent even if excess SnPd/Al\(_2\)O\(_3\) was present in the reactor. In the reaction system, Pt/SrTiO\(_3\):Rh was certainly exposed to some light even if an excess amount of SnPd/Al\(_2\)O\(_3\) was co-present in the reactor. Hence, the \( \text{H}_2 \) evolution, that is, \( N(e^-)_{w/o} \), did not drop to zero.

As for \( N(e^-)_w \), the maximum was obtained in the absence of SnPd/Al\(_2\)O\(_3\), but
electrons were exclusively consumed for the H₂ evolution, because Pt/SrTiO₃:Rh is inactive for NO₃⁻ reduction. \( N(e^-)_w \) increased with an increase in the amount of SnPd/Al₂O₃ in the range of 25 to 200 mg and reached a maximum at around 150 to 200 mg. Under such conditions, H₂ was not detected in the gas phase at all, and thus, all electrons were consumed to reduce NO₃⁻; the fraction of \( N(e^-)_w \) consumed for NO₃⁻ reduction was 100%. In the reaction where the amount of SnPd/Al₂O₃ was 25 mg, \( N(e^-)_w \) was basically equal to \( N(e^-)_{w/o} \), indicating that H₂ evolution by the photocatalytic reaction over Pt/SrTiO₃:Rh balanced out NO₃⁻ reduction with H₂ over SnPd/Al₂O₃. Contrary to this, \( N(e^-)_w \) was much larger than \( N(e^-)_{w/o} \) with 75 mg or more of SnPd/Al₂O₃. The difference between \( N(e^-)_w \) and \( N(e^-)_{w/o} \) showed a maximum when the amount of SnPd/Al₂O₃ was 150 mg. Under these conditions, \( N(e^-)_w \) was about three-times larger than \( N(e^-)_{w/o} \). The difference between \( N(e^-)_w \) and \( N(e^-)_{w/o} \) indicated that some substances other than H₂, which were formed by the photocatalytic reaction over Pt/SrTiO₃:Rh, acted as reductants for NO₃⁻ reduction over SnPd/Al₂O₃. It can be estimated from the difference that the contribution to the NO₃⁻ reduction by the reductants other than H₂ was about twice that by H₂. When a semiconductor photocatalyst dispersed in aqueous methanol solution is irradiated with light having an energy higher than the semiconductor band gap, the photoexcited electrons in the
conduction band of the photocatalyst reduce water, leading to H₂ evolution, if the bottom of the conduction band is more negative than the reduction potential of water (Eq. (3)). In this process, holes (h⁺) formed in the valence band of the photocatalyst oxidize methanol as well as water, leading to the formation of H₂CO, HCO₂H, and also carbon oxides (Eqs. (6–9)) [34].

\[
\text{H}_2\text{O} + h^+_{\text{VB}} \rightarrow \cdot\text{OH} + H^+ \quad (6)
\]

\[
\text{CH}_3\text{OH} + 2\cdot\text{OH} (\text{or } h^+_{\text{VB}}) \rightarrow \text{H}_2\text{CO} + 2\text{H}_2\text{O} (\text{or } H^+) \quad (7)
\]

\[
\text{H}_2\text{CO} + 2\cdot\text{OH} (\text{or } h^+_{\text{VB}}) \rightarrow \text{HCO}_2\text{H} + \text{H}_2\text{O} (\text{or } H^+) \quad (8)
\]

\[
\text{HCO}_2\text{H} + 2\cdot\text{OH} (\text{or } h^+_{\text{VB}}) \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} (\text{or } H^+) \quad (9)
\]

In fact, during the NO₃⁻ reduction in the Pt/SrTiO₃:Rh–SnPd/Al₂O₃ system, H₂CO and HCO₂H were formed by visible light irradiation in the presence of methanol.

Fig. 7 shows changes in the amounts of H₂CO and HCO₂H formed in the reaction solution versus reaction time for the photocatalytic reduction of NO₃⁻ by the Pt/SrTiO₃:Rh–SnPd/Al₂O₃ system in the presence of methanol under visible light irradiation. The amounts of both substances increased with increasing reaction time, and the amount of H₂CO formed was much greater than the amount of HCO₂H. At 6 h,
the amounts of $\text{H}_2\text{CO}$ and $\text{HCO}_2\text{H}$ were 448 and 58 µmol, respectively. That is, when the photocatalytic reaction steadily proceeded in the Pt/SrTiO$_3$:Rh–SnPd/Al$_2$O$_3$ system, $\text{H}_2\text{CO}$ and $\text{HCO}_2\text{H}$ were present in the reaction solution, in addition to methanol and $\text{H}_2$. Thus, these could act as reductants for $\text{NO}_3^-$ over SnPd/Al$_2$O$_3$. This will be investigated in the next section (Section 3.3). The amount of CO$_2$ in the gas phase was only 0.6 µmol even at 6 h. More CO$_2$ was probably formed and dissolved in the reaction solution. However, it was unable to determine quantity, because an aqueous solution of NaHCO$_3$ and Na$_2$CO$_3$ was used as a mobile phase for the ion chromatography.

3.3. $\text{CH}_3\text{OH}, \text{H}_2\text{CO},$ and $\text{HCO}_2\text{H}$ as reductants for $\text{NO}_3^-$ reduction over SnPd/Al$_2$O$_3$

We investigated whether $\text{CH}_3\text{OH}$, $\text{H}_2\text{CO}$, and $\text{HCO}_2\text{H}$ acted as reductants for non-photocatalytic reduction of $\text{NO}_3^-$ over SnPd/Al$_2$O$_3$ by separately adding them to the reaction solution in the presence of SnPd/Al$_2$O$_3$. First, we conducted non-photocatalytic reduction of $\text{NO}_3^-$ with $\text{H}_2$, $\text{CH}_3\text{OH}$, $\text{H}_2\text{CO}$, and $\text{HCO}_2\text{H}$ over Pt/SrTiO$_3$:Rh in the absence of SnPd/Al$_2$O$_3$ under dark conditions. Only negligible conversions below 1% were obtained for all reactions. Therefore, the contribution of the non-photocatalytic reduction over Pt/SrTiO$_3$:Rh was very small. In other words,
the function of Pt/SrTiO$_3$:Rh in the Pt/SrTiO$_3$:Rh–SnPd/Al$_2$O$_3$ system was forming H$_2$ by photocatalytic reduction and causing H$_2$CO and HCO$_2$H evolution by photocatalytic oxidation.

Next, we conducted non-photocatalytic reduction of NO$_3^-$ with CH$_3$OH, H$_2$CO, and HCO$_2$H in the presence of SnPd/Al$_2$O$_3$ under dark conditions. Table 2 summarizes the data of the catalytic reduction of NO$_3^-$ over SnPd/Al$_2$O$_3$ under dark conditions for 6 h in the presence of CH$_3$OH, H$_2$CO, or HCO$_2$H individually, or a mixture of them, but in the absence of Pt/SrTiO$_3$:Rh. In these reactions, the amounts of CH$_3$OH, H$_2$CO, and HCO$_2$H added in the reaction solution were $615\times10^3$, 440, and 60 µmol, respectively, which corresponded to those present in the reaction solution for the photocatalytic reduction of NO$_3^-$ by the Pt/SrTiO$_3$:Rh–SnPd/Al$_2$O$_3$ system at 6 h. In the reaction where CH$_3$OH, H$_2$CO, and HCO$_2$H were added together (Entry 1), the conversion was 17%, which was almost the same as the conversion for the photocatalytic reduction of NO$_3^-$ in the Pt/SrTiO$_3$:Rh–SnPd/Al$_2$O$_3$ system (Entry 3 in Table 1). After 6 h, the amounts of H$_2$CO and HCO$_2$H in the reactor were changed to 518 and 17 µmol, respectively. The amount of H$_2$CO at 6 h increased compared with the initial amount (440 µmol), whereas that of HCO$_2$H decreased from 60 µmol (initial) to 17 µmol at 6 h. H$_2$CO was oxidized with NO$_3^-$ to HCO$_2$H, and HCO$_2$H was oxidized to CO$_2$. Since
the amount of HCO$_2$H decreased by the reaction for 6 h, it is reasonable that the reaction rate of HCO$_2$H oxidation to CO$_2$ was faster than that of H$_2$CO oxidation to HCO$_2$H. In fact, as shown in Fig. 8(a), which shows the time course changes in the amounts of H$_2$CO and HCO$_2$H in the reaction solution for the reaction of Entry 1 in Table 2, the amount of HCO$_2$H considerably decreased within 1 h. To demonstrate more clearly the contribution of each substrate as a reductant, the catalytic reductions of NO$_3^-$ over SnPd/Al$_2$O$_3$ were conducted by separately adding each reductant (Entries 2–4).

 Whereas the initial amount of CH$_3$OH was extremely large compared with the amounts of H$_2$CO and HCO$_2$H, the reduction rate of NO$_3^-$ was very low (Entry 2). In contrast, high conversions comparable to that in Entry 1 were obtained when H$_2$CO (Entry 3) and HCO$_2$H (Entry 4) were used as reductants, namely, 16% and 13%, respectively. The conversion in Entry 4 was lower than that in Entry 3, but this was because all HCO$_2$H was consumed within 1 h (Fig. A3 in Supplementary data). Thus, we compared the initial rates of NO$_3^-$ reduction, which were estimated from the conversion at 1 h, and found that the initial rate of NO$_3^-$ reduction with HCO$_2$H was about twice as high as that with H$_2$CO (Entries 3 and 4). From these results, we concluded that the abilities of CH$_3$OH, H$_2$CO, and HCO$_2$H to serve as reductants for


\[ \text{NO}_3^- \text{ reduction over SnPd/Al}_2\text{O}_3 \text{ were in the order } \text{HCO}_2\text{H} > \text{H}_2\text{CO} >> \text{CH}_3\text{OH}, \text{ if they were used independently.} \]

However, in the actual reaction in the Pt/SrTiO$_3$:Rh–SnPd/Al$_2$O$_3$ system, CH$_3$OH, H$_2$CO, and HCO$_2$H simultaneously existed in the reaction solution, and CH$_3$OH was present in a large quantity, which might inhibit H$_2$CO and HCO$_2$H from acting as reductants due to adsorbed inhibition. Thus, we investigated the inhibition effect of CH$_3$OH on the reactions with H$_2$CO or HCO$_2$H by conducting NO$_3^-$ reduction over SnPd/Al$_2$O$_3$ in the presence of CH$_3$OH with H$_2$CO or HCO$_2$H. When CH$_3$OH was co-present in the reaction solution in addition to H$_2$CO (Entry 5), the initial rate of NO$_3^-$ reduction dropped to half of that without CH$_3$OH (Entry 3), indicating that H$_2$CO was inhibited by CH$_3$OH from acting as a reductant for NO$_3^-$. In contrast, in the case where H$_2$CO and CH$_3$OH were present together (Entry 6), the initial rate was almost the same as that without CH$_3$OH (Entry 4), suggesting that HCO$_2$H strongly adsorbed on the SnPd bimetal surface, and thus acted as a reductant even though a large amount of CH$_3$OH was present in the reaction solution. We also measured the initial reaction rate of NO$_3^-$ reduction and those of H$_2$CO and HCO$_2$H consumption for the reaction where H$_2$CO and HCO$_2$H were present together. The initial rate of NO$_3^-$ reduction was 28 $\mu$mol h$^{-1}$ (Entry 7). This rate was lower than the sum of the initial rates (36 $\mu$mol h$^{-1}$)
of NO₃⁻ reduction for the reactions where H₂CO and HCO₂H were added independently (Entries 3 and 4), suggesting that the ability of one of them to act as a reductant was lowered by the other. Fig. 8(b) shows the time course changes in the amounts of H₂CO and HCO₂H in the reaction solution for the reaction of Entry 7. As demonstrated in Fig. 8(b), HCO₂H was preferentially consumed at the initial stage of the reaction, and the initial rates of H₂CO and HCO₂H consumption were estimated to be 38 and 50 µmol h⁻¹, respectively. Thus, it can be concluded that HCO₂H had a greater ability to act as a reductant than H₂CO for the NO₃⁻ reduction over SnPd/Al₂O₃.

3.4. Reaction mechanism of photocatalytic reduction of NO₃⁻ in the Pt/SrTiO₃:Rh–SnPd/Al₂O₃ system

Since H₂ was not detected at all in the gas phase during the photocatalytic reduction of NO₃⁻ by the Pt/SrTiO₃:Rh–SnPd/Al₂O₃ system under the optimum reaction conditions, all H₂ formed by the photocatalytic reaction over Pt/SrTiO₃:Rh was consumed to reduce NO₃⁻ over SnPd/Al₂O₃. As Fig. 6 indicates, the number of electrons consumed for H₂ formation in the absence of NO₃⁻ (N(e⁻)w/o) was 60 µmol under the optimum reaction conditions, where the amount of SnPd/Al₂O₃ was 150 mg. On the other hand, the number of electrons consumed for NO₃⁻ reduction in the
presence of \( \text{NO}_3^- \) (\( N(e^-)_w \)) was 166 µmol. From these values, the fraction of the reduction of \( \text{NO}_3^- \) with \( \text{H}_2 \) over \( \text{SnPd/Al}_2\text{O}_3 \) can be estimated to be about 36% relative to the whole \( \text{NO}_3^- \) reduction. Thus, the contribution of the reduction of \( \text{NO}_3^- \) with \( \text{CH}_3\text{OH}, \text{H}_2\text{CO}, \) and \( \text{HCO}_2\text{H} \) was estimated to be 64%. As was discussed in Section 3.3, \( \text{CH}_3\text{OH} \) was almost completely ineffective as a reductant for \( \text{NO}_3^- \) reduction, although it was abundantly present in the reaction solution. Mainly \( \text{H}_2\text{CO} \) and \( \text{HCO}_2\text{H} \), in addition to \( \text{H}_2 \), acted as reductants for \( \text{NO}_3^- \) reduction. As discussed earlier, \( \text{HCO}_2\text{H} \) acted as a reductant more effectively than \( \text{H}_2\text{CO} \) for \( \text{NO}_3^- \) reduction. Based on these findings, we propose a reaction mechanism illustrated in Fig. 5(b). However, during the photocatalytic reduction of \( \text{NO}_3^- \) in the \( \text{Pt/SrTiO}_3: \text{Rh–SnPd/Al}_2\text{O}_3 \) system, oxidations of \( \text{CH}_3\text{OH}, \text{H}_2\text{CO}, \) and \( \text{HCO}_2\text{H} \) with \( h^+ \) formed on \( \text{Pt/SrTiO}_3: \text{Rh} \) took place in parallel with the reduction with \( \text{NO}_3^- \) over \( \text{SnPd/Al}_2\text{O}_3 \). Thus, it is difficult to estimate the contribution of each reductant in the reduction of \( \text{NO}_3^- \) over \( \text{SnPd/Al}_2\text{O}_3 \). Further investigation of kinetics analysis will be needed, and this will be the topic of future work.

4. Conclusions

The photocatalytic reaction system comprising \( \text{Pt/SrTiO}_3: \text{Rh} \) and \( \text{SnPd/Al}_2\text{O}_3 \)
dispersed in water efficiently and selectively promoted the photocatalytic reduction of NO$_3^-$ in the presence of CH$_3$OH under visible light irradiation. The selectivity to N$_2$ was 94% under the optimum reaction conditions, where the amounts of Pt/SrTiO$_3$:Rh and SnPd/Al$_2$O$_3$ loaded in the reaction system were 500 and 150 mg, respectively. Hydrogen (H$_2$) formed by photoreduction of water over Pt/SrTiO$_3$:Rh acted as a reductant for the non-photocatalytic NO$_3^-$ conversion reaction over SnPd/Al$_2$O$_3$, and the reduction of NO$_3^-$ with H$_2$ accounted for 36% of the whole NO$_3^-$ conversion reaction. The rest of the NO$_3^-$ conversion reaction was due to the non-photocatalytic NO$_3^-$ conversion reaction over SnPd/Al$_2$O$_3$ mainly with H$_2$CO and HCO$_2$H as reductants, which were formed by photo-oxidation of CH$_3$OH over Pt/SrTiO$_3$:Rh. Pt/SrTiO$_3$:Rh was inactive for both the photocatalytic and non-photocatalytic NO$_3^-$ conversion reactions, and the function of this catalyst in the present reaction system was to generate H$_2$ by photoreduction of water and to generate H$_2$CO and HCO$_2$H by photo-oxidation of CH$_3$OH.
References


678–679.


<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion [%]</th>
<th>Selectivity [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pt/SrTiO$_3$:Rh$^b$</td>
<td>&lt; 1</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>SnPd/Al$_2$O$_3$</td>
<td>3</td>
<td>35</td>
</tr>
<tr>
<td>3</td>
<td>Pt/SrTiO$_3$:Rh$^b$+SnPd/Al$_2$O$_3$</td>
<td>16</td>
<td>6</td>
</tr>
<tr>
<td>4$^a$</td>
<td>Pt/SrTiO$_3$:Rh$^b$+SnPd/Al$_2$O$_3$</td>
<td>5</td>
<td>9</td>
</tr>
<tr>
<td>5</td>
<td>SnPd/SrTiO$_3$:Rh$^d$</td>
<td>8</td>
<td>16</td>
</tr>
</tbody>
</table>

Reaction conditions: catalyst weight, Pt/SrTiO$_3$:Rh, 500 mg; SnPd/Al$_2$O$_3$, 150 mg; reactant NO$_3^-$ (from KNO$_3$), 0.8 mmol dm$^{-3}$ with 10 vol% CH$_3$OH, 250 cm$^3$; visible light irradiation ($\lambda > 420$ nm), and reaction time, 6 h.

$^a$ Under dark conditions.

$^b$ 0.1 wt.% Pt/SrTiO$_3$:Rh.

$^c$ 2.3 wt.% Sn-4.2 wt.% Pd/Al$_2$O$_3$. Sn/Pd molar ratio was 0.5.

$^d$ 2.3 wt.% Sn-4.2 wt.% Pd/SrTiO$_3$:Rh. The amount of catalyst loaded in the reactor was 500 mg.
Table 2 Catalytic reduction of NO$_3^-$ under dark conditions in water over SnPd/Al$_2$O$_3$ in the presence of various reductants.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reductant</th>
<th>Initial amount / µmol</th>
<th>Conversion [%]</th>
<th>Initial rate of NO$_3^-$ reduction µmol h$^{-1}$</th>
<th>Selectivity [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH$_3$OH + H$_2$CO + HCO$_2$H</td>
<td>615 × 10$^3$</td>
<td>60</td>
<td>17</td>
<td>24</td>
</tr>
<tr>
<td>2</td>
<td>CH$_3$OH</td>
<td>615 × 10$^3$</td>
<td>440</td>
<td>2</td>
<td>0.7</td>
</tr>
<tr>
<td>3</td>
<td>H$_2$CO</td>
<td></td>
<td>440</td>
<td>16</td>
<td>12</td>
</tr>
<tr>
<td>4</td>
<td>HCO$_2$H</td>
<td></td>
<td>60</td>
<td>13</td>
<td>24</td>
</tr>
<tr>
<td>5</td>
<td>CH$_3$OH + H$_2$CO</td>
<td>615 × 10$^3$</td>
<td>440</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>6</td>
<td>CH$_3$OH + HCO$_2$H</td>
<td>615 × 10$^3$</td>
<td>60</td>
<td>14</td>
<td>18</td>
</tr>
<tr>
<td>7</td>
<td>H$_2$CO + HCO$_2$H</td>
<td></td>
<td>440</td>
<td>19</td>
<td>28</td>
</tr>
</tbody>
</table>

Reaction conditions: catalyst weight, Sn-Pd/Al$_2$O$_3$, 150 mg; reactant NO$_3^-$ (from KNO$_3$), 0.8 mmol dm$^{-3}$, 250 cm$^3$, He 30 cm$^3$ min$^{-1}$, and reaction time, 6 h.

$^a$ Selectivity to gaseous compounds was calculated by subtracting NH$_4^+$ selectivity from 100%.
Figure Captions

**Fig. 1** Schematic illustration of the photocatalytic reaction system.

**Fig. 2** Dependence of H$_2$-evolution rate over Pt/SrTiO$_3$:Rh under visible light irradiation ($\lambda > 420$ nm) on weight of Pt/SrTiO$_3$:Rh loaded in the reactor. The rate of H$_2$ evolution was estimated from the amount of H$_2$ formed in 1 h from the beginning of the reaction. Reaction conditions: reaction solution, 10 vol% aqueous CH$_3$OH solution (250 cm$^3$), and light source, 300 W Xe lamp with cutoff filter ($\lambda > 420$ nm). SnPd/Al$_2$O$_3$ was not loaded in the reactor, and NO$_3^-$ was absent.

**Fig. 3** Dependences of (a) conversion of NO$_3^-$ (●), selectivities for NH$_4^+$ (□) and N$_2$ (△), and (b) amount of H$_2$ detected in the gas phase (○) in the photocatalytic reduction of NO$_3^-$ in water in the co-presence of Pt/SrTiO$_3$:Rh and SnPd/Al$_2$O$_3$ on weight of SnPd/Al$_2$O$_3$ loaded in the reactor. The weight of Pt/SrTiO$_3$:Rh loaded in the reactor was fixed at 500 mg. Reaction conditions: reaction solution, reactant NO$_3^-$ (from KNO$_3$), 0.8 mmol dm$^{-3}$ with 10 vol% CH$_3$OH; light source, 300 W Xe lamp with cutoff filter ($\lambda > 420$ nm); and reaction time, 6 h.
Fig. 4  Repeated use of the catalysts for the photocatalytic reduction of NO$_3^-$ in water in the co-presence of Pt/SrTiO$_3$:Rh and SnPd/Al$_2$O$_3$ under visible light irradiation. Time courses for (a) conversion of NO$_3^-$ (●), and (b) selectivities for NH$_4^+$ (□) and N$_2$ (Δ). Reaction conditions: catalyst weight, Pt/SrTiO$_3$:Rh, 500 mg; SnPd/Al$_2$O$_3$, 150 mg; reactant NO$_3^-$ (from KNO$_3$), 0.8 mmol dm$^{-3}$ containing 10 vol% CH$_3$OH, 250 cm$^3$; and visible light irradiation (λ > 420 nm).

Fig. 5  Schematic illustrations of the photocatalytic reduction of NO$_3^-$ in water in the co-presence of photocatalyst and non-photocatalyst.  (a) Pt/TiO$_2$–SnPd/Al$_2$O$_3$ system: H$_2$ is formed by photocatalytic reaction over Pt/TiO$_2$ under UV irradiation. H$_2$ is successively consumed as a reductant for non-photocatalytic reduction of NO$_3^-$ over SnPd/Al$_2$O$_3$.  (b) Pt/SrTiO$_3$:Rh–SnPd/Al$_2$O$_3$ system: H$_2$ is formed by photocatalytic reaction over Pt/SrTiO$_3$:Rh under visible light irradiation. H$_2$, methanol, and products formed by photo-oxidation of methanol, including formaldehyde and formic acid, were successively consumed as reductants for non-photocatalytic reduction of NO$_3^-$ over SnPd/Al$_2$O$_3$.

Fig. 6  Influence of weight of SnPd/Al$_2$O$_3$ on the number of electrons consumed for H$_2$
formation in the absence of NO$_3^-$ ($N(e^-)_{w/o}$) under visible light irradiation (●), and the number of electrons consumed for NO$_3^-$ reduction and H$_2$ formation in the presence of NO$_3^-$ ($N(e^-)_w$) under visible light irradiation (▽) in the Pt/SrTiO$_3$:Rh–SnPd/Al$_2$O$_3$ system. The figures in parenthesis are the fraction (%) of $N(e^-)_w$ consumed for the NO$_3^-$ reduction. The weight of Pt/SrTiO$_3$:Rh loaded in the reactor was fixed at 500 mg.

Reaction conditions: (●): 10 vol% aqueous CH$_3$OH solution (250 cm$^3$); reaction time, 6 h; and light source, 300 W Xe lamp with cutoff filter ($\lambda > 420$ nm). (▽) : 10 vol% CH$_3$OH with 0.8 mmol dm$^{-3}$ NO$_3^-$; light source, 300 W Xe lamp with cutoff filter ($\lambda > 420$ nm); and reaction time, 6 h.

**Fig. 7** Amounts of H$_2$CO (▽) and HCO$_2$H (□) in the reaction solution during the photocatalytic reduction of NO$_3^-$ in the co-presence of Pt/SrTiO$_3$:Rh and SnPd/Al$_2$O$_3$ under visible light irradiation. Reaction conditions: catalyst weight, Pt/SrTiO$_3$:Rh, 500 mg; SnPd/Al$_2$O$_3$, 150 mg; reactant NO$_3^-$ (from KNO$_3$), 0.8 mmol dm$^{-3}$ containing 10 vol% CH$_3$OH, 250 cm$^3$; and visible light irradiation ($\lambda > 420$ nm).

**Fig. 8** Amounts of H$_2$CO (▽) and HCO$_2$H (□) in the reaction solution during non-photocatalytic reduction of NO$_3^-$ over SnPd/Al$_2$O$_3$ in the dark in the presence of (a)
CH₃OH, H₂CO, and HCO₂H, and (b) H₂CO and HCO₂H. Reaction conditions: catalyst weight, SnPd/Al₂O₃, 150 mg; reactant NO₃⁻ (from KNO₃), 0.8 mmol dm⁻³, 250 cm³; and He 30 cm³ min⁻¹.
Fig. 1
Fig. 2

Rate of \( \text{H}_2 \) evolution / \( \mu \text{mol h}^{-1} \)

Weight of Pt/SrTiO\(_3\):Rh / mg
Fig. 3

Amount of $H_2$ detected in gas phase / µmol

Conversion / %

Selectivity / %

Weight of SnPd/Al$_2$O$_3$ / mg

(a)

(b)

Amount of H$_2$ detected in gas phase / µmol

Weight of SnPd/Al$_2$O$_3$ / mg

Fig. 3
Fig. 4

Plot showing conversion and selectivity over reaction time.

- Conversion / %
- Selectivity / %
- Reaction time / h

Legend:
- Conversion: [●] 1st, [●] 2nd, [●] 3rd
- Selectivity: [▲] 1st, [▲] 2nd, [▲] 3rd

Wash. marks after each cycle.
Fig. 5
Fig. 6
Fig. 7
Fig. 8

Amounts of $\text{H}_2\text{CO}$ and $\text{HCO}_2\text{H}$ / µmol vs. Reaction time / h