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Highly effective photocatalytic system comprising semiconductor photocatalyst and supported bimetallic non-photocatalyst for selective reduction of nitrate to nitrogen in water

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ABSTRACT

Photocatalytic reduction of NO$_3^-$ under UV irradiation in the presence of ethanol was carried out in the presence of semiconductor photocatalyst Pt/TiO$_2$ and supported bimetallic non-photocatalyst Sn-Pd/Al$_2$O$_3$, which were dispersed in water. This system effectively and selectively promoted the photocatalytic reduction of NO$_3^-$ to N$_2$, whereas Pt/TiO$_2$ or Sn-Pd/Al$_2$O$_3$ alone showed no or little activity under the reaction conditions. The decomposition rate of NO$_3^-$ and selectivity to gaseous nitrogen compounds (mainly N$_2$) for the present photocatalytic system were higher than those for TiO$_2$ photocatalyst directly-modified with Sn-Pd particles.

Keywords:

Photocatalytic nitrate reduction; Groundwater remediation; Titanium oxide; Bimetallic palladium catalyst
1. Introduction

Pollution of groundwater with nitrate (NO$_3^-$) is a widespread problem because excess intake of NO$_3^-$ is harmful for humans, especially infants [1,2]. Since Cu-Pd/Al$_2$O$_3$ was found to promote the reduction of NO$_3^-$ with H$_2$ in water (Eq. 1) [3], the reaction over supported bimetallic catalysts has been actively investigated as a promising technology to remediate NO$_3^-$-polluted groundwater [4–25].

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

Thus far, a few bimetallic Pd and bimetallic Pt catalysts showing high activity and high selectivity to N$_2$ have been developed [4–18]. However, using gaseous H$_2$ as a reducing agent is a serious issue because handling the flammable gas at high pressures is difficult. Therefore, an alternative technology that does not use gaseous H$_2$ is highly desired for practical use.

A potential method to overcome this issue is photocatalytic reduction of NO$_3^-$. In recent years, selective photocatalytic reduction of NO$_3^-$ in water over noble metal modified semiconductor photocatalysts has been reported [26–34]. Among the semiconductor
photocatalysts, TiO$_2$ has one of the highest potentials for practical applications because of its chemical stability, nontoxicity, and low cost. The photocatalytic activity of TiO$_2$ has been increased by modifying it with noble metals [26, 29, 33]. Zhang et al. have reported that TiO$_2$ modified with a homogeneous dispersion of Ag clusters with small sizes shows extremely high activity for the photocatalytic reduction of NO$_3^-$ in water in the presence of formic acid as a hole scavenger and that NO$_3^-$ is selectively reduced to N$_2$ [29]. However, the selectivity significantly decreases from >99% to 20% when ethanol is used as a hole scavenger [29]. Gao et al. have demonstrated that bimetal-modified TiO$_2$, Cu-Pd/TiO$_2$, which is prepared by using a conventional impregnation method, shows photocatalytic activity for the conversion of NO$_3^-$ under UV irradiation in the presence of oxalic acid, whereas unmodified TiO$_2$ shows low photocatalytic activity [33]. Kominami et al. have reported that NO$_3^-$ is effectively and selectively reduced to N$_2$ in the presence of Cu-Pd/TiO$_2$, which is prepared by using a photodeposition method, in the presence of oxalic acid as a hole scavenger under basic conditions [27]. However, this is unsuitable for drinking water purification due to the basic reaction conditions (pH ≈ 11).

The materials used as a catalyst support strongly affect the catalytic performance for the conventional non-photocatalytic reduction of NO$_3^-$ with H$_2$ in water over supported bimetallic-Pd catalysts [9, 16, 24]. Among the catalyst supports, Al$_2$O$_3$ is one of the best because bimetallic-Pd
assemblies active towards selective hydrogenation of NO$_3^-$ to N$_2$ readily form on Al$_2$O$_3$. On the other hand, TiO$_2$ is considered to be rather unsuitable for use as a support due to its low N$_2$ selectivity [35]. Thus, for the photocatalytic reduction of NO$_3^-$ in water, if Al$_2$O$_3$ is utilized as a support for an active bimetal component, the photocatalyst should be highly effective. However, Al$_2$O$_3$ itself does not show any photocatalytic activity, meaning that it must be modified in order to use it.

Herein we report a photocatalytic reaction system comprising a semiconductor photocatalyst (Pt/TiO$_2$) and a supported bimetallic non-photocatalyst (Sn-Pd/Al$_2$O$_3$) dispersed in water. This system effectively and selectively promoted the photocatalytic reduction of NO$_3^-$ to N$_2$ under UV irradiation in the presence of ethanol, whereas Pt/TiO$_2$ or Sn-Pd/Al$_2$O$_3$ alone showed no or little activity under the reaction conditions. The decomposition rate of NO$_3^-$ and selectivity to N$_2$ for the present photocatalytic system were higher than those for TiO$_2$ photocatalyst directly-modified with Sn-Pd particles.

2. Experimental

2.1. Preparation of catalysts

0.5 wt% Pt/TiO$_2$ was prepared by using a photodeposition method. TiO$_2$ (2 g, Degusa, P-25,
50 m² g⁻¹), ultrapure water (140 cm³) which was obtained by treating distilled water with a Millipore filtration system (Milli-Q Element), methanol (15.6 cm³, Wako Pure Chem. Ind., Ltd.), and H₂PtCl₆·6H₂O (0.265 cm³, Wako Pure Chem. Ind., Ltd.) were placed in a quartz glass cell. After bubbling Ar gas (100 cm³ min⁻¹) into the reaction solution for 30 min in the dark, the solution was irradiated with UV light from a Xe lamp (200 W) at 293 K for 1.5 h. The resulting suspension was centrifuged to separate the catalyst powder. The supernatant solution was replaced with ultrapure water (100 cm³), and then the resulting suspension was centrifuged again. This process was repeated three times. Finally, the catalyst powder was dried in vacuo at 353 K overnight.

4.6 wt% Sn-2.0 wt% Pd/Al₂O₃ (denoted to Sn-Pd/Al₂O₃), in which the Sn/Pd molar ratio was 2, was prepared by using an incipient wetness method. Al₂O₃ (AEROSIL Alu C, 100 m² g⁻¹) was calcined in air at 523 K for 4 h in advance. An aqueous solution of PdCl₂ (3.3 cm³, 0.115 mol dm⁻³, Wako Pure Chem. Ind., Ltd.) was dropped onto Al₂O₃ (2.0 g), and then the resulting wet solid was dried in air at 353 K overnight, followed by calcination in air at 523 K for 1 h. An aqueous solution of SnCl₂ (8.5 cm³, 0.0917 mmol dm⁻³, Wako Pure Chem. Ind., Ltd.) was dropped onto the resulting solid, and then the wet solid was dried in air at 353 K overnight, followed by calcination in air at 523 K for 1 h.
Just before the photocatalytic and non-photocatalytic reactions, Sn-Pd/Al₂O₃ was reduced with NaBH₄. Powder Sn-Pd/Al₂O₃ was dispersed into ultrapure water (50 cm³). NaBH₄ (mole ratio of NaBH₄/(Sn + Pd) = 5) was added to the suspension, and the suspension was stirred at room temperature for 30 min. The catalyst powder was filtered and washed with ultrapure water (ca. 100 cm³).

Sn-Pd/TiO₂ with different metal loadings was prepared by using a procedure similar to that for Sn-Pd/Al₂O₃. The loading amount of metals was in the range of 0.055–6.6 wt%, whereas the molar ratio of Sn/Pd was 2, regardless of the loading amount. 0.61 wt% Sn-0.27 wt% Pd/0.5 wt% Pt/TiO₂ was prepared from 0.5 wt% Pt/TiO₂, which was prepared in advance, and aqueous solutions of PdCl₂ and SnCl₂ by using an incipient impregnation method similar to that for Sn-Pd/TiO₂.

2.2 Characterization

Specific surface areas were estimated by using the Brunauer-Emmett-Teller (BET) equation with an adsorption isotherm of N₂ at 77 K, which was taken on a Belsorp-mini instrument (BEL Japan Inc.). Powder X-ray diffraction (XRD) was performed using an X-ray diffractometer (Rigaku Mini Flex) with Cu Kα radiation (\(\lambda = 0.154 \text{ nm}\)). Metal dispersion was estimated from
adsorption amount of CO at 323 K, which was taken on a BEL-CAT instrument (BEL Japan Inc.)

The stoichiometry of CO to metal was assumed to be one.

2.3. Photocatalytic reduction of NO$_3^-$ in water

Photocatalytic reduction of NO$_3^-$ in water was conducted in a batch reactor equipped with a stirrer and whose upper side was opened to the air. Before initiating the reaction, Pt/TiO$_2$ (150 mg) and Sn-Pd/Al$_2$O$_3$ (20 mg), an aqueous KNO$_3$ solution (10 cm$^3$, 10 mmol dm$^{-3}$), and ethanol (1.0 mmol) were loaded into the reactor. Then the reactor tube was photoirradiated at 380 nm with an LED (8 W) to start the photocatalytic reaction. During photoirradiation, the temperature of reaction solution was kept at 306 K by soaking the reactor tube in a water bath to avoid any thermal reactions. Concentrations of NO$_3^-$, NO$_2^-$, and NH$_4^+$ in the reaction solution were determined by using two ion-chromatographs (Tosoh Co. Ltd., IC-2001). A column containing an anion-exchange resin (TSK gel Super IC-AZ, Tosoh) and an aqueous solution of NaHCO$_3$ (2.9 mmol dm$^{-3}$) and Na$_2$CO$_3$ (3.1 mmol dm$^{-3}$) were used as a stationary and mobile phases, respectively, for anion analysis. For cation analysis, a column containing an cation-exchange resin (IC-Cation 1/2 HR, Tosoh) and an aqueous solution of HNO$_3$ (2.0 mmol dm$^{-3}$) and histidine (1.0 mmol dm$^{-3}$) were used as a stationary and mobile phases, respectively. Since the gas phase
was not analysed, the selectivity for the gaseous nitrogen compounds was calculated by subtracting the selectivity for products in the liquid phase ($\text{NO}_2^-$ and $\text{NH}_4^+$) from 100%.

Normally, the solutions were not degassed before the reaction, but for experiments to analyze the gaseous products, degassing treatment was performed.

2.4. Analysis of gaseous products formed during the photocatalytic reduction of $\text{NO}_3^-$

In order to analyze the gaseous products, the photocatalytic reduction of $\text{NO}_3^-$ in water was carried out in a batch reactor connected to a closed gas circulation system with an online gas chromatograph equipped with Molesieve 5A and PLOT-U columns (Agilent Technology Co. Ltd, 3000 A Micro GC). An experimental setup is illustrated in Fig. A1 (Supplementary data). After Pt/TiO$_2$ (150 mg), Sn-Pd/Al$_2$O$_3$ (20 mg), an aqueous KNO$_3$ solution (10 cm$^3$, 10 mmol dm$^{-3}$), and ethanol (1.0 mmol) were loaded into the reactor, the suspension was degassed by using a vacuum-freeze method. Then the reaction tube was irradiated at 380 nm with an LED (8 W) for 24 h. After the reaction, the gaseous products were analyzed by using the online gas chromatograph.
2.5. Non-photocatalytic hydrogenation of NO$_3^-$ with gaseous H$_2$ in water

Catalytic reduction of NO$_3^-$ with gaseous H$_2$ in water was carried out in a batch reactor at 298 K in the dark. After Sn-Pd/Al$_2$O$_3$ (20 mg) and ultrapure water (90 cm$^3$) were loaded into the reactor, a mixed gas composed of equimolar H$_2$ and CO$_2$ was bubbled at a rate of 3 cm$^3$ min$^{-1}$ for 30 min and then an aqueous KNO$_3$ solution (10 cm$^3$, 100 mmol dm$^{-3}$) was added to start the reaction with the gas flow. An aqueous phase was periodically analyzed by the ion-chromatographs.

3. Results and discussion

Specific surface areas of Pt/TiO$_2$ and Sn-Pd/Al$_2$O$_3$ were 49 and 94 m$^2$ g$^{-1}$, respectively. Pt/TiO$_2$ gave an XRD pattern assignable to anatase and rutile phases as reported (Fig. A2 in Supplementary data). From the adsorption amount of CO (2.9 $\mu$ mol g$^{-1}$), particle size of Pt was estimated to be 9.9 nm. Sn-Pd/Al$_2$O$_3$ showed an XRD pattern identical to $\gamma$-Al$_2$O$_3$ (Fig. A2 in Supplementary data). However, no diffraction line due to Pd-Sn alloy as well as Pd and Sn particles was observed, because of high dispersion. If it was assumed that CO adsorbed only on Pd atom, dispersion of Pd estimated from the adsorption amount of CO (29 $\mu$mol g$^{-1}$) was 16%.
Table 1 summarizes the results of the photocatalytic reduction of NO$_3^-$ at 4 h in the presence of various catalysts. The reaction did not take place at all in the presence of Pt/TiO$_2$ alone (Entry 1) under the present reaction conditions. Sn-Pd/Al$_2$O$_3$ alone exhibited only low catalytic activity (Entry 2). Because a similar conversion was obtained under dark conditions in the presence of Sn-Pd/Al$_2$O$_3$, the results in Entry 2 were due to the non-photocatalytic reaction, that is, NO$_3^-$ reduction with ethanol via a thermochemical reaction over Sn-Pd/Al$_2$O$_3$. On the other hand, when the reaction was conducted in the presence of both catalysts (Entry 3), a high NO$_3^-$ conversion was obtained. In a separate experiment, we analyzed the gaseous nitrogen compounds under reaction conditions similar to those for Entry 3 and found that 99% or more of the gaseous nitrogen products was N$_2$. In addition, we confirmed from ICP-AES analysis that the leaching of metals (Pt, Pd, and Sn) during the reaction in Entry 3 was negligible (Supplementary data). As shown in Fig. 1, NO$_3^-$ conversion increased with the reaction time, and complete conversion was obtained after 16 h. Over the entire reaction, no NO$_2^-$ formed, and the formation of NH$_4^+$, which is undesirable for drinking water, was suppressed (10%).

Even when the reaction was carried out in the presence of both catalysts, NO$_3^-$ conversion did not proceed without ethanol (Entry 4). In addition, under dark conditions, a low conversion comparable to that for Sn-Pd/Al$_2$O$_3$ alone (Entry 2) was obtained (data not shown). When
Sn-Pd/SiO$_2$ was used (Entry 5) instead of Sn-Pd/Al$_2$O$_3$, the NO$_3^-$ conversion was about half of that for Entry 3. When Sn-Pd/active carbon was employed instead of Sn-Pd/Al$_2$O$_3$, no reaction occurred (Entry 6) undoubtedly due to strong absorption of UV light by active carbon.

From the results in Entries 1 and 3, it is thought that the catalyst on which NO$_3^-$ is actually converted is Sn-Pd/Al$_2$O$_3$, not Pt/TiO$_2$. On the other hand, comparing Entries 2 and 3 indicates that the photoexcited electrons generated on Pt/TiO$_2$ by UV light contributed to the reduction of NO$_3^-$. Thus, in the present photocatalytic system, some species must be present to facilitate electron transfer or transfer of the reducing agent from Pt/TiO$_2$ to Sn-Pd/Al$_2$O$_3$ for the photocatalytic reduction of NO$_3^-$. One possibility is an O$_2$-derived species, like O$_2^-$, or partially-oxidized derivatives of ethanol because we normally carried out the photocatalytic reduction of NO$_3^-$ with O$_2$ in the reaction solution due to the open glass tube reactor. The other one was H$_2$ evolved by the photoreduction of water over Pt/TiO$_2$ with ethanol as a hole scavenger.

In order to verify this, we carried out the photocatalytic reduction of NO$_3^-$ under reaction conditions similar to those in Entry 3; however, O$_2$ gas or N$_2$ gas was bubbled (5 cm$^3$ min$^{-1}$) into the reaction solution during the photocatalytic reaction. As shown in Table A1 (Supplementary data), the conversion of NO$_3^-$ decreased to about one-sixth of that without gas bubbling. On the other hand, when N$_2$ gas was bubbled into the reaction solution, the conversion and selectivity
were similar to those without gas bubbling. These results suggested that the former mechanism was improbable. Therefore, H₂ evolved by photoreduction of water over Pt/TiO₂ was concluded to be the courier between the Pt/TiO₂ and Sn-Pd/Al₂O₃. In fact, a substantial amount of H₂ was detected in the gas phase during the photocatalytic reduction of NO₃⁻ in the presence of Pt/TiO₂ and Sn-Pd/Al₂O₃. We separately carried out the photocatalytic reaction under reaction conditions similar to those shown in Fig. 1, but without NO₃⁻, and determined the amount of H₂ in the gas phase. After 24 h, the amount of H₂ in the gas phase was determined to be 0.21 mmol. The amount of H₂ detected was consistent with the amount of H₂ consumed during the photocatalytic reaction (0.27 mmol), calculated from the conversion of NO₃⁻ and the selectivities shown in Fig. 1. Therefore, we concluded that the H₂ that formed on Pt/TiO₂ acted as the reductant for the NO₃⁻ conversion reaction at the Sn-Pd/Al₂O₃ catalyst, but further investigations are needed.

Next we compared the performance of the present photocatalytic system with Sn-Pd/TiO₂. Since the loading amount of the noble metal in TiO₂ strongly affects the photocatalytic activity, the loading amount of Sn-Pd on TiO₂ was optimized (Fig. A3 in Supplementary data). As a result, 0.88 wt% Sn-Pd/TiO₂ (Sn/Pd molar ratio = 2) exhibited the highest photocatalytic activity for the photocatalytic reduction of NO₃⁻ in water (Entry 7), where the amounts of TiO₂ and Sn-Pd introduced in the reaction tube were almost the same as those for Entry 3. A comparison between
Entries 3 and 7 clearly shows that the present photocatalytic system is superior to Sn-Pd/TiO$_2$ in activity and selectivity for N$_2$. In addition, the activity and selectivity of the present photocatalytic system is much higher than those of Sn-Pd modified Pt/TiO$_2$ (Entry 8).

In order to understand why the present system showed high photocatalytic performance, we investigated the evolution of H$_2$ from the photocatalytic reduction of water in the presence of ethanol but in the absence of NO$_3^-$ using the present system (Pt/TiO$_2$ + Sn-Pd/Al$_2$O$_3$) and Sn-Pd/TiO$_2$. As shown in Fig. 2, the amount of H$_2$ evolved was similar for both (Pt/TiO$_2$ + Sn-Pd/Al$_2$O$_3$) and Sn-Pd/TiO$_2$. Since it was speculated that the non-photocatalytic reduction of NO$_3^-$ with H$_2$ strongly affected the photocatalytic reduction of NO$_3^-$, we carried out the non-photocatalytic reduction of NO$_3^-$ with H$_2$, that is, catalytic hydrogenation of NO$_3^-$ with H$_2$ gas, in water in the absence of ethanol over Sn-Pd/Al$_2$O$_3$ and Sn-Pd/TiO$_2$ in the dark. Fig. 3 shows the reaction time dependence of the conversion and selectivity for the reduction of NO$_3^-$ with H$_2$ over Sn-Pd/Al$_2$O$_3$ and Sn-Pd/TiO$_2$, where the amounts of Sn and Pd in the reaction tube were almost the same. As shown in Fig. 3, the activity and selectivity for the gaseous compounds were much higher over Sn-Pd/Al$_2$O$_3$ than those over Sn-Pd/TiO$_2$, indicating that the Sn-Pd sites on Al$_2$O$_3$ are more active and selective toward the formation of the gaseous compounds from NO$_3^-$ than those on TiO$_2$ are. Thus, we concluded that this was the reason for the high photocatalytic
ability of the present system for the photocatalytic reduction of NO$_3^-$ in water.

4. Conclusion

The photocatalytic system comprising Pt/TiO$_2$ and Sn-Pd/Al$_2$O$_3$ dispersed in water effectively and selectively promoted the photocatalytic reduction of NO$_3^-$ in the presence of ethanol under UV irradiation. Hydrogen (H$_2$) formed by photoreduction of water over Pt/TiO$_2$ acted as the reductant for NO$_3^-$ conversion reaction over Sn-Pd/Al$_2$O$_3$. The photocatalytic activity and selectivity to gaseous nitrogen compounds for the system were higher than those for the Sn-Pd directly-modified TiO$_2$. This was due to the high catalytic performance for Sn-Pd/Al$_2$O$_3$ in the non-photocatalytic reduction of NO$_3^-$ with H$_2$.

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Appendix A. Supplementary data
Supplementary data to this article can be found online at doi: ???????????.
References


### Table 1
Photocatalytic reduction of nitrate in water in the presence of various catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion [%]</th>
<th>Selectivity [%]</th>
<th>NO$_2$</th>
<th>NH$_4^+$</th>
<th>gas$^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pt/TiO$_2$ $^a$</td>
<td>0</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>2</td>
<td>Sn-Pd/Al$_2$O$_3$ $^b$</td>
<td>2</td>
<td>0</td>
<td>31</td>
<td>69</td>
<td>---</td>
</tr>
<tr>
<td>3</td>
<td>Pt/TiO$_2$ $^a$ + Sn-Pd/Al$_2$O$_3$ $^b$</td>
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<td>0</td>
<td>10</td>
<td>90</td>
<td>---</td>
</tr>
<tr>
<td>4$^c$</td>
<td>Pt/TiO$_2$ $^a$ + Sn-Pd/Al$_2$O$_3$ $^b$ w/o ethanol</td>
<td>0</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>5</td>
<td>Pt/TiO$_2$ $^a$ + Sn-Pd/SiO$_2$ $^b$</td>
<td>23</td>
<td>0</td>
<td>12</td>
<td>88</td>
<td>---</td>
</tr>
<tr>
<td>6</td>
<td>Pt/TiO$_2$ $^a$ + Sn-Pd/active carbon$^b$</td>
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<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>7</td>
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<td>0</td>
<td>23</td>
<td>77</td>
<td>---</td>
</tr>
<tr>
<td>8</td>
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<td>23</td>
<td>0</td>
<td>24</td>
<td>76</td>
<td>---</td>
</tr>
</tbody>
</table>

Reaction conditions: catalyst weight, Pt/TiO$_2$ 150 mg, Sn-Pd/Al$_2$O$_3$ 20 mg; reactant NO$_3^-$ 10 cm$^3$, (10 mmol dm$^{-3}$ aqueous KNO$_3$); ethanol/NO$_3^-$ = 10; and UV irradiation (8 mW LED) for 4 h.

$^a$0.5 wt% Pt/TiO$_2$.  $^b$4.6 wt% Sn-2.0 wt% Pd/Al$_2$O$_3$.  Sn/Pd molar ratio was 2.0.  "Photocatalytic reduction of NO$_3^-$ was conducted in the absence of ethanol.  Other reaction conditions were the same as those for Entry 3.  $^c$0.61 wt% Sn-0.27 wt% Pd/TiO$_2$.  The catalyst weight was 150 mg, and thus, the amounts of Sn, Pd, and TiO$_2$ introduced in the reaction tube were almost the same as those for Entry 3.  $^d$0.61 wt% Sn-0.27 wt% Pd/active carbon$^b$.  The catalyst weight was 150 mg, and thus, the amounts of Sn, Pd, Pt, and TiO$_2$ introduced in the reaction tube were almost the same as those for Entry 3.  $^e$Gaseous nitrogen compounds.
Figure captions

**Fig. 1.** Time courses for (●) conversion of NO$_3^-$ and selectivities for (○) gaseous nitrogen compounds, (□) NH$_4^+$, and (△) NO$_2^-$ in the photocatalytic reduction of NO$_3^-$ in the presence of Pt/TiO$_2$ and Sn-Pd/Al$_2$O$_3$ under UV irradiation. Pt/TiO$_2$, 150 mg; Sn-Pd/Al$_2$O$_3$, 20 mg; reactant NO$_3^-$, 10 cm$^3$ (10 mmol dm$^{-3}$ aqueous KNO$_3$); ethanol/NO$_3^-$ = 10; and UV irradiation (8 mW LED).

**Fig. 2.** Time courses for the amount of H$_2$ evolved by photocatalytic reduction of water in the presence of (●) Pt/TiO$_2$ and Sn-Pd/Al$_2$O$_3$ and (○) Sn-Pd/TiO$_2$. Reaction conditions: catalyst weight, Pt/TiO$_2$, 150 mg; Sn-Pd/Al$_2$O$_3$, 20 mg; Sn-Pd/TiO$_2$ 150 mg; water, 10 cm$^3$; ethanol, 1 mmol; and UV irradiation (8 mW LED).

**Fig. 3.** Time courses for (●, ○) conversion of NO$_3^-$ and selectivities for (■, □) gaseous nitrogen compounds and (▲, △) NH$_4^+$ over 6.6 wt% Sn-Pd/Al$_2$O$_3$ (closed symbol) and 0.88 wt%
Sn-Pd/TiO₂ (open symbol) for non-photocatalytic hydrogenation of NO₃⁻ with H₂ gas in water.

Catalyst weight, 20 mg for 6.6 wt% Sn-Pd/Al₂O₃ and 150 mg for 0.88 wt% Sn-Pd/TiO₂; reactant
NO₃⁻, 100 cm³ (10 mmol dm⁻³ aqueous KNO₃); gas composition, H₂/CO₂ = 1/1; gas flow rate, 3 cm³ min⁻¹; and reaction temperature, 298 K.
Fig. 1

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Fig. 2

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Fig. 3

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