**Supplementary data for**

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

**1. Analysis of gaseous products formed during the photocatalytic reduction of NO3–**

An experimental setup is illustared in Fig. A1.



Fig. A1 Experimental setup for gaseous product analysis

**2. Powder XRD patters of Pt/TiO2 and Sn-Pd/Al2O3**

Fig. A2 shows powder XRD patterns of Pt/TiO2 and Sn-Pd/Al2O3. Pt/TiO2 gave an XRD pattern assignable anatase and rutile phases as reported (Fig. A2(a)), but no diffraction line due to platinum particles was observed because of low loading amount. Sn-Pd/Al2O3 showed an XRD pattern identical to γ–Al2O3 (Fig. A2(b)). However, no diffraction line due to Pd-Sn alloy as well as Pd and Sn particles was observed, probably because of high dispersion.



Fig. A2 Powder XRD patterns of (a) Pt/TiO2 and (b) Sn-Pd/Al2O3.

**3. Determination of the metals leached into the reaction solution during the photocatalytic reduction of NO3– in the presence of Pt/TiO2 and Sn-Pd/Al2O3**

After the reaction in Entry 3 in Table 1, the concentrations of Sn, Pd, and Pt in the reaction solution were determined by using an inductively-coupled plasma atomic emission spectrometer (ICP-AES, Shimadzu ICPS-8000). The concentration of each element in the reaction solution was below the detection limit of the ICP-AES.

**4. Photocatalytic reduction of NO3– in the presence of Pt/TiO2 and Sn-Pd/Al2O3 with continuous bubbling of O2 and N2**

Photocatalytic reductions of NO3– in water in the presence of Pt/TiO2 and Sn-Pd/Al2O3 were carried out in a batch reactor with continuous bubbling of O2 or N2 gas. After Pt/TiO2 (150 mg), Sn-Pd/Al2O3 (20 mg), an aqueous KNO3 solution (10 cm3, 10 mmol dm–3), and ethanol (5.0 mmol) were loaded into the reactor, O2 or N2 gas was bubbled at a rate of 5 cm3 min–1 for 15 min into the reaction suspension in the dark, where the amount of O2 dissolved in water was determined to be ≥20 or 0.3 ppm, whereas the amount of O2 without gas bubbling was 7.6 ppm. Then the reaction tube was irradiated at 380 nm with an LED (8 W) for 4 h with continuous bubbling of O2 or N2 gas (5 cm3 min–1). After the reaction (4 h), the concentrations of NO3–, NO2–, and NH4+ in the liquid phase were determined by using two ion-chromatographs (Tosoh Co. Ltd., IC-2001). The concentration of ethanol in the liquid phase was determined by using a gas chromatograph equipped with a flame-ionization detector (Shimadzu GC-2010).

Table A1 lists the photocatalytic results. When the reaction was conducted with continuous bubbling of O2, the conversion of NO3– decreased to about one-sixth of that without gas bubbling, whereas the conversion of ethanol was about double that without gas bubbling. On the other hand, when the photocatalytic reaction was carried out with N2 bubbling, the conversion and selectivities were almost the same as those without gas bubbling.

**Table A1**

Influence of gas bubbling on the photocatalytic reduction of NO3– in the presence of Pt/TiO2 and Sn-Pd/Al2O3 under UV irradiation

|  |  |  |  |
| --- | --- | --- | --- |
| Gas bubbling | NO3– conv. | Selectivity/% | Ethanol conv. |
|  | /% | NO2– | NH4+ | gasb | /% |
| w/o gas bubblinga | 49  | 4 | 2 | 94  | 8  |
| O2 | 8  | 0 | 0 | 100  | 18  |
| N2 | 43  | 5 | 3 | 92  | 8  |

Reaction conditions: catalyst weight, Pt/TiO2 150 mg; Sn-Pd/Al2O3 20 mg; reactant NO3–, 10 cm3 (10 mmol dm–3 aqueous KNO3); ethanol/NO3–, 50; and UV irradiation (LED, 8 W) for 4 h.

aNo gas was bubbled into the reaction solution during the photocatalytic reduction of NO3–.

bGaseous nitrogen-derived compounds.

**5. Dependence of the loading amount of Sn-Pd on the photocatalytic reduction of NO3– in the presence of Sn-Pd/TiO2**

Fig. A3 shows the dependence of the loading amount of Sn-Pd on the conversion and selectivities toward the photocatalytic reduction of NO3– in water over Sn-Pd/TiO2 under UV irradiation.



Fig. A3 Dependence of the loading amount of metals in Sn-Pd/TiO2 on the conversion and selectivities toward the photocatalytic reduction of NO3– in water over Sn-Pd/TiO2 under UV irradiation. (●) Conversion of NO3– and selectivities to (□) NH4+ and (▽) gaseous nitrogen compounds. NO2– was not detected regardless of the metal loading. Reaction conditions: catalyst weight, 150 mg; reactant NO3–, 10 cm3 (10 mmol dm–3 aqueous KNO3 solution); ethanol/NO3–, 10; UV irradiation (8 mW LED); and reaction time, 4 h.

Unmodified TiO2 exhibited only low photocatalytic activity. Modification of TiO2 with a small amount of Sn-Pd significantly enhanced the photocatalytic activity, and 0.88 wt% Sn-Pd/TiO2 exhibited the highest activity. Moreover, the selectivities changed depending on the metal loading, but 0.88 wt% Sn-Pd/TiO2 showed decent selectivity toward gaseous nitrogen-derived compounds. Therefore, we determined that 0.88 wt% loading was optimal for the photocatalytic reduction of NO3– in water over Sn-Pd/TiO2 under UV irradiation.