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Combining the Photocatalyst Pt/TiO_2 and the Nonphotocatalyst SnPd/Al_2O_3 for Effective Photocatalytic Purification of Groundwater Polluted with Nitrate

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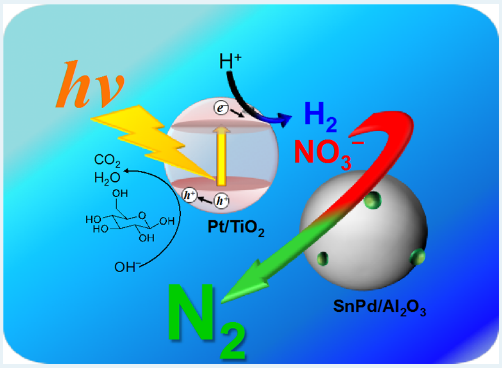
S Supporting Information

ABSTRACT: We investigated photocatalytic reduction of NO_3^- in real groundwater in the presence of the photocatalyst Pt/TiO_2 and the nonphotocatalyst SnPd/Al_2O_3, which were dispersed in the groundwater, under irradiation at $\lambda > 300$ nm, with glucose as a hole scavenger. In this system, photocatalytic H_2 evolution ($2H^+ + 2e^- \rightarrow H_2$) proceeded over Pt/$TiO_2$, and nonphotocatalytic, that is, conventional catalytic, reduction of NO_3^- with H_2 ($NO_3^- + 5/2H_2 \rightarrow 1/2N_2 + 2H_2O + OH^-$) occurred over SnPd/$Al_2O_3$. NO_3^- (1.0 mmol dm^{-3}) in the groundwater completely and selectively decomposed to N_2 (yield 83%) after 120 h with a 300 W Xe lamp ($\lambda > 300$ nm) over the Pt/TiO_2−SnPd/Al_2O_3 system in combination with photooxidative pretreatment of the groundwater over Pt/TiO_2 to decompose organic compounds. The decomposition rate of NO_3^- in the groundwater was still slower than that in an aqueous NO_3^- solution even after the pretreatment of the groundwater. The lower photocatalytic performance was due to poisoning of Pt/TiO_2 with sulfate and silicate ions and poisoning of SnPd/Al_2O_3 with polymerized silicate ions. On the other hand, cations, including Na^+, K^+, Mg^{2+}, and Ca^{2+}, in the groundwater did not affect the photocatalytic and catalytic performances of the system. Sulfate ions adsorbed on the Pt sites on Pt/TiO_2, where H_2 evolution occurs, and silicate ions deactivated the oxidation sites on TiO_2 by reacting with the surface hydroxyl groups, leading to a decline in the photocatalytic performance of Pt/TiO_2.



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INTRODUCTION

Pollution of groundwater with nitrate (NO_3^-) as a result of intensive agricultural activities using nitrogen fertilizers, human sewage, and industrial effluents is a serious global problem.[1] NO_3^- is reduced to nitrite (NO_2^-) in the human body, which causes methemoglobinemia in infants (i.e., blue-baby syndrome) and is a possible precursor of carcinogenic nitrosamine.[2] Thus, the World Heath Organization recommends that the concentration of NO_3^- in drinking water should be below 0.8 mmol dm^{-3}, which corresponds to 50 mg dm^{-3}.[3] Since groundwater is an important fresh water resource that is indispensable to human society, NO_3^- needs to be removed from polluted groundwater.

In recent years, photocatalytic reduction of NO_3^- in water has been extensively investigated as a promising technology to remediate NO_3^--polluted groundwater.[4−19] Guan's group[9] and Kominami's group[10] have reported that Ag/TiO_2 and CuPd/TiO_2, respectively, show high selectivity to N_2 in the photocatalytic reduction of NO_3^- in aqueous NO_3^- solutions under UV irradiation in the presence of a hole scavenger. However, there are only a few reports on the photocatalytic reduction of NO_3^- in real groundwater. Westerhoff et al. first reported the photocatalytic reduction of NO_3^- in groundwater in 2012.[15] They use TiO_2 to photocatalytically reduce NO_3^- in groundwater under UV irradiation. Although NO_3^- decomposes in the presence of formic acid, the conversion decreases from 51% in aqueous NO_3^- solution to 37% in groundwater. To the best of our knowledge, the photocatalytic reduction of NO_3^- to N_2 with high selectivity in real groundwater has not been reported so far.

Photocatalytic reactions over semiconductor photocatalysts, such as TiO_2 and WO_3, proceed via three sequential reactions:[20,21] (1) photoexcited electrons (e^-) and positive holes (h^+) are produced in the bulk of the semiconductor photocatalyst by photoabsorption, (2) e^- and h^+ migrate to the surface, (3) e^- and h^+ undergo reduction and oxidation, respectively, with the substrates adsorbed on the surface, and (4) unreacted e^- and h^+ recombine, which does not cause any

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chemical reactions to occur with the substrates. Observed rates of the chemical reactions, i.e., rates of reactant consumption and of product formation, depend on the rates of these three reactions. The reaction rates of (1) and (3) positively influence the observed rate, whereas the reaction rate of (4) negatively influences it.

Generally, semiconductor photocatalysts themselves, i.e., unmodified bare photocatalysts, show low photocatalytic activities. However, the photocatalytic activity is dramatically increased when a small amount of metal is added.[14,22] There are a few reasons for the increase in the photocatalytic activity. One reason is that e^- are trapped on the modified metal, leading to elongation of the charge-separated state of e^- and positive holes, which decreases the rate of (4). Another reason is that the modified metal becomes an adsorption site for the reactants, resulting in an increase in the rate of (3). However, addition of metal into the photocatalyst may increase the rate of (4) because the excess metal acts as recombination sites for e^- and h^+.[7,9] Therefore, an optimal balance among the loading amount, kind, crystalline structure, location, and particle size of the metal must be obtained to afford high-performance photocatalysts.

In some photocatalytic reactions, not only the loading amount and particle size but also the elemental species of metal strongly affect the photocatalytic performance. Photocatalytic reduction of NO_3^- in water over a semiconductor photocatalyst is a quite typical case that the elemental species of metal strongly affects the photocatalytic performances. Semiconductor photocatalysts modified with silver and Cu–Pd particles have high activity and high selectivity to N_2 in the photocatalytic reduction of NO_3^-,[9,10,14] but Pt- and Rh-modified ones show extremely low activities in the photocatalytic reduction of NO_3^-,[5,14] because Ag and Cu–Pd form adsorption sites for NO_3^-, which become activated. Since the metal particles activate NO_3^- via adsorption, they must have a high surface area for high photocatalytic activity. In addition, the modified metal must help in the charge separation of the e^-–h^+ pairs. If the two functions are maximized simultaneously by optimizing the loading amount, elemental species, crystalline structure, location, and particle size of the metals, extremely high-performance semiconductor photocatalysts can be obtained. However, it is usually difficult to achieve this with semiconductor photocatalysts modified directly with metals, because excess metal provides the recombination sites for e^- and h^+.

Recently, reaction systems in which various catalytic functions are distributed to separate catalysts present in the same solution have been actively investigated to maximize the performance of catalysts. Artificial Z-scheme-type photocatalytic water splitting, which affords H_2 and O_2, is an example of function-distribution on separate catalysts. In the artificial Z-scheme photocatalytic system, O_2 and H_2 evolution sites are built on separate semiconductor photocatalysts (e.g., WO_3 for O_2 evolution and TaON for H_2 evolution), and two catalysts are added to the reaction solution with a redox shuttle between the two catalysts.[23−27] The combination of a biocatalyst and a conventional catalyst (metal complexes and precious metal-supported catalysts are examples for the latter) has been reported to be a highly efficient system.[28,29] In this reaction system, the biocatalyst promotes difficult reactions with high chemo-, regio-, and stereoselectivities, and conventional catalysts perform relatively simple reactions with high reaction rates. However, the biocatalysts and conventional catalysts perform their reactions successively.

We have previously reported that the photocatalytic reduction of NO_3^- in an aqueous NO_3^- solution is effectively and selectively promoted under light irradiation in the presence of a photocatalyst (Pt/TiO_2[17] or $Pt/SrTiO_3$:Rh[18]) and a nonphotocatalyst ($SnPd/Al_2O_3$). In this photocatalytic system, H_2 is formed by a photocatalytic reaction over Pt/TiO_2 (eq 1), and the formed H_2 thermally reduces NO_3^- in water over $SnPd/Al_2O_3$ (eq 2):

$$2H^+ + 2e^- \rightarrow H_2 \qquad (1)$$

$$NO_3^- + 5/2H_2 \rightarrow 1/2N_2 + 2H_2O + OH^- \qquad (2)$$

The combined photocatalytic system shows much better photocatalytic performance in terms of both activity and selectivity than does TiO_2 directly modified with Sn–Pd particles. The photocatalyst (Pt/TiO_2) and nonphotocatalyst ($SnPd/Al_2O_3$) can be designed separately to maximize their performance levels for the photocatalytic (eq 1) and nonphotocatalytic (eq 2) reactions, respectively.

In the present study, we investigated the photocatalytic reduction of NO_3^- in real groundwater in the presence of both the photocatalyst Pt/TiO_2 and the nonphotocatalyst $SnPd/Al_2O_3$ under light irradiation ($\lambda > 300$ nm). We chose glucose as a hole scavenger for the photocatalytic reaction because it is a readily available organic compound and has a high efficiency of H_2 production by photocatalysis. Moreover, the effects of compounds in the groundwater on the photocatalytic and nonphotocatalytic performance levels over Pt/TiO_2 and $SnPd/Al_2O_3$, respectively, were systematically investigated, and we have proposed a guideline for the remediation of real groundwater by photocatalytic reduction of NO_3^-.

EXPERIMENTAL METHODS

Preparation of Catalysts. AEROXIDE TiO_2 P25 (Evonik) was used as a TiO_2 photocatalyst. TiO_2 was modified with 0.5 wt % Pt by using photodeposition. TiO_2 (2 g) was dispersed in distilled water (135 cm^3), and then CH_3OH (15 cm^3, Wako Pure Chem., Ind., Ltd.) and $H_2PtCl_6 \cdot 6H_2O$ (1.25 cm^3, 0.04 mol dm^{-3}, Wako Pure Chem., Ind., Ltd.) were added to the suspension. The suspension, which was 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 ($\lambda > 300$ nm, USHIO Inc., Optical Modulex) for 3 h with stirring. The suspension was centrifuged to separate the catalyst powder, and the resulting supernatant solution was replaced with distilled water (200 cm^3). The suspension was stirred for a few minutes and centrifuged again. This process was repeated three times. Finally, the catalyst powder was dried in air at 333 K overnight. The obtained catalyst is denoted as Pt/TiO_2.

The nonphotocatalytic catalyst, 2.3 wt % Sn-4.2 wt % Pd/Al_2O_3 (molar ratio of Sn/Pd was 0.5, denoted as $SnPd/Al_2O_3$), was prepared by using an incipient wetness method. Al_2O_3 (AEROXIDE, Alu C, Evonik) was heated in air at 523 K for 4 h before use. An aqueous solution of $PdCl_2$ (7.38 cm^3, 0.112 mol dm^{-3}, Wako Pure Chem., Ind., Ltd.) was dropped onto the Al_2O_3 (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 $SnCl_2 \cdot 2H_2O$ (2.31 cm^3, 0.172 mol dm^{-3}, Wako Pure Chem., Ind., Ltd.) 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. TiO_2

Table 1. Concentrations of the Components Contained in the Groundwater and Reaction Solutions Used in this Study

		concentration/mmol dm^{-3}									
reaction solution	initial pH	NO_3^-	Cl^-	SO_4^{2-}	SiO_x^{n-}	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	TOC[i]
GW[a]	8.1	1.0	0.5	1.1	1.1	<0.01	1.0	0.1	0.7	1.6	3.3
GW-Ox[b]	8.1	1.0	0.5	1.1	0.7	<0.01	1.0	0.1	0.7	1.6	0.2
GW-Ox-Cation-removal[c]	7.8	1.0	0.5	1.1	0.7	0	0	3.0	0	0	0.2
GW-Ox-Anion-removal[d]	5.3	1.0	0	0	0	<0.01	1.0	1.1	0.7	1.6	0.2
KNO_3-aq[e]	5.5	1.0	0	0	0	0	0	1.0	0	0	0
KNO_3-Cl^--aq[f]	5.4	1.0	1.0	0	0	0	0	2.0	0	0	0
$KNO_3-SO_4^{2-}$-aq[g]	5.5	1.0	0	1.0	0	0	0	3.0	0	0	0
$KNO_3-SiO_3^{2-}$-aq[h]	9.8	1.0	0	0	1.0	0	0	3.0	0	0	0

[a] Groundwater obtained from a well in Kitami, Hokkaido, Japan. [b] GW treated with photocatalytic oxidation in the presence of Pt/TiO_2. [c] GW from which cations were removed by passing GW through a cation-exchange resin, followed by treatment with photocatalytic oxidation to decompose organic matter. [d] GW from which anions were removed by passing GW through an anion-exchange resin, followed by treatment with photocatalytic oxidation to decompose organic matter. After treatment, KNO_3 was added to the water to adjust the concentration of NO_3^- to 1.0 mmol dm^{-3}. [e] Aqueous KNO_3 solution. [f] Aqueous KNO_3 solution with KCl. [g] Aqueous KNO_3 solution with K_2SO_4. [h] Aqueous KNO_3 solution with K_2SiO_3. [i] Total organic carbon (ppm).

modified with 2.3 wt % Sn and 4.2 wt % Pd was prepared by using a procedure similar to that for $SnPd/Al_2O_3$ and is denoted as $SnPd/TiO_2$.

Just before the photocatalytic and nonphotocatalytic reactions, $SnPd/Al_2O_3$ was reduced with $NaBH_4$ (Wako Pure Chem, Ind., Ltd.). $NaBH_4$ (molar ratio of $NaBH_4/(Sn + Pd) = 10$) was added to an aqueous suspension (30 cm^3) of $SnPd/Al_2O_3$, and the suspension was stirred at room temperature for 30 min. The catalyst powder was filtered and washed with distilled water (~200 cm^3) to afford the reactants. $SnPd/TiO_2$ was reduced by using a procedure similar to that for $SnPd/Al_2O_3$.

Component Analysis of Groundwater. Groundwater polluted with NO_3^- was obtained from a well in Kitami, Hokkaido, Japan (denoted as GW). Concentrations of the anions and cations in the groundwater were determined by using two ion-chromatographs (Tosoh Co., IC-2001). Analytical conditions are described in detail in our previous report.[18] The concentrations of Si species in the groundwater were determined by using inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Shimadzu ICPS-7000. The Si species present in the groundwater were anions (silicate ion, SiO_x^{n-}) because no Si was detected in the groundwater that was treated with an anion-exchange resin. The amounts of the organic compounds in the groundwater were measured by using a total organic carbon (TOC) analyzer (Shimadzu Co., TOC-5000A). Components contained in the groundwater (GW) are listed in Table 1.

Reaction Solutions. The reaction solutions and their compositions are listed in Table 1. GW-Ox stands for GW pretreated with photocatalytic oxidation in the presence of Pt/TiO_2 (500 mg dispersed in 300 cm^3 of GW) to decompose the organic compounds. The suspension in a Pyrex glass cell was purged with a stream of air (100 cm^3 min^{-1}) and then irradiated with a 300 W Xe lamp for 24 h. The catalyst was separated from the suspension by filtration. TOC decreased from 3.3 in GW to 0.2 ppm in GW-Ox by the treatment. The concentrations of the other components besides SiO_x^{n-} were not affected by the treatment. The concentration of SiO_x^{n-} decreased from 1.1 to 0.7 mmol dm^{-3}.

The cations were removed by passing GW through a glass column with a cation-exchange resin (ORGANO Co., AMBERLYST 70), followed by addition of KOH to adjust the pH of the solution to 7.8 (GW-Ox-Cation). The obtained solution was further treated with the photocatalytic oxidation, like GW-Ox was. The anions were removed from GW (GW-Ox-Anion) by using a procedure similar to that for GW-Ox-Cation, but an anion exchange resin (ORGANO Co., AMBERLITE IRA410 OH AG) and CO_2 were used instead of the cation-exchange resin and KOH, respectively. To adjust the concentration of NO_3^- to 1.0 mmol dm^{-3}, KNO_3 (Wako Pure Chem, Ind., Ltd.) was added to the solution.

KNO_3 was dissolved in distilled water to afford KNO_3-aq. The concentration of NO_3^- in the solution was adjusted to 1.0 mmol dm^{-3}. KNO_3-Cl^--aq, $KNO_3-SO_4^{2-}$-aq, and $KNO_3-SiO_3^{2-}$-aq were prepared by adding KCl (Wako Pure Chem., Ind., Ltd.), K_2SO_4 (Wako Pure Chem., Ind., Ltd.), and K_2SiO_3 (Wako Pure Chem., Ind., Ltd.), respectively, to KNO_3-aq.

Photocatalytic Reduction of NO_3^- in Water. Photocatalytic reduction of NO_3^- in water was carried out in a Pyrex reaction vessel connected to a closed gas circulation system. Pt/TiO_2 and $SnPd/Al_2O_3$ were suspended in the reaction solution (250 cm^3, $[NO_3^-] = 1.0$ mmol dm^{-3}) containing glucose (1.0 mmol dm^{-3}, Wako Pure Chem., Ind., Ltd.), and the suspension was stirred using a magnetic stirrer. The reaction suspension was thoroughly degassed and then exposed to He (101.3 kPa). A 300 W Xe lamp covered with Pyrex glass ($\lambda > 300$ nm) was used as the light source. The evolved gases were analyzed using an online gas chromatograph (Agilent Technology Inc., 3000 A Micro GC, He carrier) with columns of molecular sieves (for H_2, O_2, and N_2) and Porapak Q (for N_2O). The concentrations of NO_3^-, NO_2^-, and NH_4^+ in the reaction solution were determined by using two ion chromatographs.

Nonphotocatalytic (conventional catalytic) Reduction of NO_3^- with H_2 in Water. Nonphotocatalytic reduction, that is, conventional catalytic reduction, of NO_3^- with H_2 in water was carried out in a batch reactor at 298 K in the dark. The reaction solution (250 cm^3, $[NO_3^-] = 1.0$ mmol dm^{-3}, 14 mg N dm^{-3}) containing $SnPd/Al_2O_3$ (10 mg) was purged with a stream of He (30 cm^3 min^{-1}) for 30 min. Then the gas was changed to a mixture of H_2 (0.5 atm) and CO_2 (0.5 atm) to start the reaction. A small portion of the reaction solution was periodically withdrawn and analyzed by using two ion chromatographs to determine the concentrations of NO_3^-, NO_2^-, and NH_4^+.

Photocatalytic H_2 and O_2 Evolutions. Photocatalytic H_2 evolution from the reaction solution with glucose over Pt/TiO_2 was carried out by using a procedure similar to that for the

Table 2. Photocatalytic Reduction[a] of NO_3^- in Groundwater (GW) under Light Irradiation

				selectivity [%]			
entry	catalyst	glucose	conversion [%]	NO_2^-	NH_4^+	N_2	amnt of H_2 detected in gas phase/μmol
1	Pt/TiO_2	absence	<1	–	–	–	60
2	Pt/TiO_2	presence	<1	–	–	–	227
3	SnPd/Al_2O_3	presence	0	–	–	–	n.d.[d]
4	Pt/TiO_2+SnPd/Al_2O_3	presence	23	3	22	75	18
5	Pt/TiO_2+SnPd/Al_2O_3[b]	presence	0	–	–	–	n.d.[d]
6	Pt/TiO_2+SnPd/Al_2O_3	absence	<1	–	–	–	n.d.[d]
7	SnPd/TiO_2[c]	presence	5	0	38	62	21

[a] Reaction conditions: catalyst weight, Pt/TiO_2, 500 mg and SnPd/Al_2O_3, 100 mg; reactant NO_3^-, 1.0 mmol dm^{-3} with 1.0 mmol dm^{-3} glucose; reaction volume, 250 cm^3; light irradiation ($\lambda > 300$ nm) and reaction time, 12 h. [b] Under dark conditions. [c] 2.3 wt % Sn-4.2 wt % Pd/TiO_2. The amount of the catalyst loaded in the reactor was 500 mg. [d] Not detected.

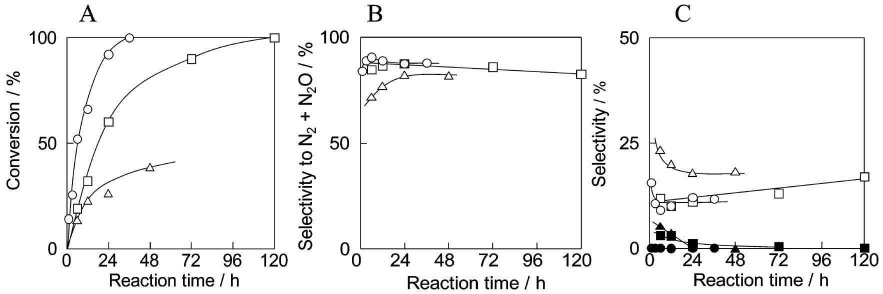

Figure 1. Time courses for photocatalytic reduction of NO_3^- in (Δ) GW, (□) GW-Ox, and (○) KNO_3-aq in the copresence of Pt/TiO_2 and SnPd/Al_2O_3. (A) Conversion of NO_3^-, (B) selectivity to $N_2 + N_2O$, and (C) selectivities to NO_2^- (closed symbols) and NH_4^+ (open symbols). Reaction conditions: catalyst weight, Pt/TiO_2, 500 mg and SnPd/Al_2O_3, 100 mg; reactant NO_3^- (from KNO_3), 1.0 mmol dm^{-3} with 1.0 mmol dm^{-3} glucose; reaction volume, 250 cm^3; light irradiation ($\lambda > 300$ nm).

photocatalytic reduction of NO_3^- in water, as described above, but in the absence of SnPd/Al_2O_3. In addition, photocatalytic O_2 evolution from the reaction solution with $AgNO_3$ (10 mmol dm^{-3}, Wako Pure Chem., Ind., Ltd.) was conducted by using a procedure similar to that for the photocatalytic H_2 evolution. To prevent the formation of silver colloid, the pH of the reaction solution was adjusted to 8.0 by adding HNO_3 to the solution with $AgNO_3$ and K_2SiO_3.

Adsorption Measurement. The amount of adsorption of SiO_3^{2-} on Pt/TiO_2 at 303 K was measured as follows. Pt/TiO_2 (30 mg) was added to an aqueous SiO_3^{2-} solution (10 cm^3), which was prepared from K_2SiO_3, and the suspension was heated at 303 K with stirring. After 24 h, Pt/TiO_2 was filtered off, and the concentration of SiO_3^{2-} in the filtrate was determined using ICP-AES. The initial concentrations of SiO_3^{2-} were varied from 0.1 to 8.0 mmol dm^{-3}. Adsorption reached equilibrium within several hours.

■ RESULTS AND DISCUSSION

Photocatalytic Reduction of NO_3^- in Groundwater (GW). Table 2 summarizes the data from the photocatalytic reduction of NO_3^- in groundwater (GW) samples under light irradiation for 12 h. Pt/TiO_2 alone in the absence of glucose (entry 1) showed negligible activity for the decomposition of NO_3^-, whereas H_2 was produced. The H_2 evolution under light irradiation was due to a photocatalytic reaction over Pt/TiO_2 (eq 1) consuming organic substances (3.3 ppm TOC), which were originally present in GW (Table 1) and acted as a hole scavenger because the amount of CO_2 in the gas phase increased with an increase in the reaction time (data not shown). Pt/TiO_2 alone hardly decomposed NO_3^- even in the presence of glucose (entry 2), but the amount of H_2 evolved in the gas phase was larger than that for entry 1. SnPd/Al_2O_3 alone (entry 3) showed no photocatalytic or catalytic activity for the decomposition of NO_3^- or for the evolution of H_2 even under light irradiation.

On the other hand, relatively high NO_3^- conversion was obtained when both Pt/TiO_2 and SnPd/Al_2O_3 (Pt/TiO_2–SnPd/Al_2O_3) were dispersed in the reaction solution in the presence of glucose (entry 4). In addition, the formation of undesirable NO_2^- was greatly suppressed (3% selectivity), and desired N_2 selectively formed (75% selectivity at 23% conversion of NO_3^-), though the selectivity may change with further conversion. At the time, only N_2 formed as a gaseous nitrogen-containing product. When the reaction was conducted in the dark, the conversion of NO_3^- was negligible even using Pt/TiO_2–SnPd/Al_2O_3 (entry 5). Thus, photocatalysis is responsible for the decomposition of NO_3^- in entry 4. When the reaction was conducted in the absence of glucose under light irradiation (entry 6), NO_3^- did not decompose, and no H_2 evolved in the gas phase. Although H_2 evolved during the photocatalytic reaction over Pt/TiO_2 even in the absence of glucose (entry 1), no photocatalytic reactions, including the decomposition of NO_3^- and H_2 evolution, occurred when Pt/TiO_2 and SnPd/Al_2O_3 were copresent in GW (entry 6). This is probably because the organic compounds are removed from GW by adsorption on SnPd/Al_2O_3, which consequently quenches the photocatalytic H_2 evolution over Pt/TiO_2.

TiO_2 directly modified with SnPd particles exhibited photocatalytic activity for the decomposition of NO_3^- (entry 7). However, it was much less active than the Pt/TiO_2–SnPd/Al_2O_3 system was under the same reaction conditions. Since H_2 evolution, as well as NO_3^- decomposition, occurred over SnPd/TiO_2 under light irradiation, photoexcited e^- formed in SnPd/TiO_2 were consumed for the reduction of NO_3^- (NO_3^-

$+ 6H^+ + 5e^- \rightarrow 1/2N_2 + 3H_2O$) and for H_2 evolution ($2H^+ + 2e^- \rightarrow H_2$). We calculated the number of e^- consumed during the reaction in entry 7 to be 116 μmol. On the other hand, that calculated for the reaction in entry 4 (the $Pt/TiO_2-SnPd/Al_2O_3$ system), in which H_2 evolved and NO_3^- decomposed, was 369 μmol. A comparison of the amount of consumed e^- in entries 4 and 7 clearly indicates that the photocatalytic performance of the $Pt/TiO_2-SnPd/Al_2O_3$ system is much higher than that of $SnPd/TiO_2$. In addition, $SnPd/TiO_2$ is less active toward the nonphotocatalytic reduction of NO_3^- ($NO_3^- + 5/2H_2 \rightarrow 1/2N_2 + 2H_2O + OH^-$) than $SnPd/Al_2O_3$ is because a similar amount of H_2 formed over both $SnPd/TiO_2$ and $Pt/TiO_2-SnPd/Al_2O_3$. On the other hand, in the case of the $Pt/TiO_2-SnPd//Al_2O_3$ system, the photocatalytic function on Pt/TiO_2 and nonphotocatalytic function on $SnPd/Al_2O_3$ can be individually optimized. Therefore, we concluded that this reaction system showed superior activity for the decomposition of NO_3^- under light irradiation than $SnPd/TiO_2$ did.

Figure 1 shows time courses for the conversion of NO_3^- and selectivities to $N_2 + N_2O$, NO_2^-, and NH_4^+ for the photocatalytic reduction of NO_3^- in GW, GW-Ox, and KNO_3-aq over the $Pt/TiO_2-SnPd/Al_2O_3$ system. The conversion of NO_3^- increased as the reaction progressed up to 12 h in GW but only slightly increased after that (Figure 1A: Δ). That is, the catalytic activity in GW was less than that in KNO_3-aq. Since GW contained various compounds (Table 1), these compounds must have a negative effect on the activities over Pt/TiO_2, $SnPd/Al_2O_3$, or both.

In order to clarify the influence of the compounds in GW, we conducted the photocatalytic reduction of NO_3^- with the $Pt/TiO_2-SnPd/Al_2O_3$ system in KNO_3-aq, which did not contain any cations other than K^+, anions other than NO_3^- ions, and organic compounds other than glucose. NO_3^- in KNO_3-aq decomposed more rapidly than it did in GW, and the conversion of NO_3^- reached 100% at 36 h (Figure 1A: ○) without any catalyst deactivation. At 100% conversion, the selectivity to $N_2 + N_2O$ was 88% (Figure 1B: ○). From these results, it was concluded that the compounds in GW decreased the photocatalytic or catalytic performances (activity and selectivity) of the $Pt/TiO_2-SnPd/Al_2O_3$ system. During the initial 24 h of the reaction in KNO_3-aq, N_2O formed in addition to N_2 but was completely transformed to N_2 at 36 h (shown in Figure S1 in the Supporting Information [SI]).

To investigate the effects of the organic compounds in GW on the photocatalytic performance of the $Pt/TiO_2-SnPd/Al_2O_3$ system, we treated GW with photocatalytic oxidation in the presence of Pt/TiO_2 to decompose the organic compounds (see Experimental Methods) and conducted the photocatalytic reduction of NO_3^- in the treated solution (GW-Ox, Table 1) over the $Pt/TiO_2-SnPd/Al_2O_3$ system. The decomposition rate of NO_3^- in GW-Ox was nearly twice that in GW, and NO_3^- was completely decomposed at 120 h (Figure 1A: □). At 100% conversion (120 h), the selectivity to $N_2 + N_2O$ was 83% (Figure 1B: □), which was almost the same as that in KNO_3-aq. Thus, removing the organic compounds from GW makes it possible to decompose NO_3^- selectively to N_2 and N_2O. However, the reaction rate for NO_3^--decomposition in GW-Ox was slower than that in KNO_3-aq (Figure 1A), indicating that compounds other than the organic ones in GW negatively affected the catalytic performance of the $Pt/TiO_2-SnPd/Al_2O_3$ system. This will be discussed later.

In order for the water obtained by the photocatalytic decomposition of NO_3^- to be used as drinking water, glucose and its partially oxidized compounds must ultimately be removed from the water. Figure 2 shows time courses for TOC during the photocatalytic reduction of NO_3^- in GW-Ox over the $Pt/TiO_2-SnPd/Al_2O_3$ system. The initial TOC was 73 ppm, and it decreased as the reaction progressed, reaching 59 ppm at 120 h, at which time NO_3^- was completely decomposed. To completely decompose the organic compounds in the reaction solution, the catalyst powder ($Pt/TiO_2-SnPd/Al_2O_3$ mixture) was separated from the reaction solution at 120 h, and fresh Pt/TiO_2 was added to the solution, followed by light irradiation with a stream of air flowing into the reactor (100 cm^3 min^{-1}). After an additional 24 h, the organic compounds in the reaction solution were completely decomposed. In other words, glucose added in GW and its partially oxidized compounds can be easily decomposed so that the groundwater can be used as drinking water.

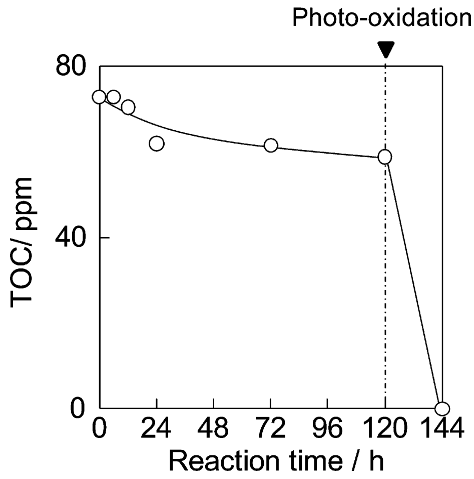

Figure 2. Changes in the concentration of total organic compounds (TOC) during the photocatalytic reduction of NO_3^- in GW-Ox in the presence of Pt/TiO_2 and $SnPd/Al_2O_3$. Reaction conditions ($t \leq 120$ h): catalyst weight, Pt/TiO_2, 500 mg and $SnPd/Al_2O_3$, 100 mg; reactant NO_3^- (from KNO_3), 1.0 mmol dm^{-3} with 1.0 mmol dm^{-3} glucose; reaction volume, 250 cm^3; light irradiation ($\lambda > 300$ nm). The catalyst powder ($Pt/TiO_2-SnPd/Al_2O_3$ mixture) was separated from the reaction solution at 120 h and fresh Pt/TiO_2 (500 mg) was added to the solution, followed by light irradiation ($\lambda > 300$ nm) with a flow of air to decompose the organic matter in the solution by photocatalytic oxidation. Reaction conditions ($t > 120$ h): catalyst weight, Pt/TiO_2, 500 mg; reactant concentration, 1.0 mmol dm^{-3}; reaction volume, 250 cm^3; air flow rate, 100 cm^3 min^{-1}; light irradiation ($\lambda > 300$ nm).

Effects of the Compounds in the Groundwater (GW) on Photocatalytic and Catalytic Performance. Figure 3a shows the conversion of NO_3^- and selectivity for $N_2 + N_2O$ in the photocatalytic reduction of NO_3^- using the $Pt/TiO_2-SnPd/Al_2O_3$ system in the various reaction solutions under light irradiation for a period of 12 h with an initial concentration of NO_3^- of 1.0 mmol dm^{-3} in each reaction solution. Although the pH of the solutions was different in each case, as shown in Table 1, it barely affected the photocatalytic performance (Figure S2A in the SI).

As was described above, compounds other than the organic compounds still caused the NO_3^--decomposition activity of the $Pt/TiO_2-SnPd/Al_2O_3$ system to decrease. Thus, cations and

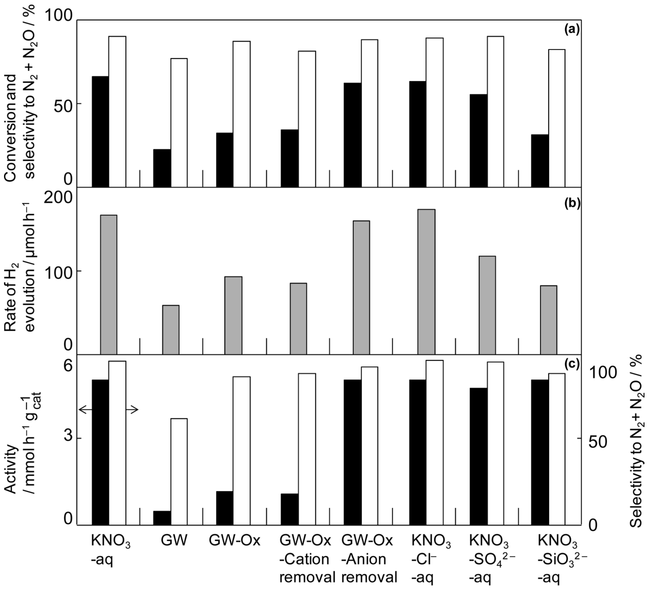

Figure 3. Effects of different compounds in the groundwater on photocatalytic and catalytic performances. (a) Photocatalytic reduction of NO_3^- in water in the copresence of Pt/TiO_2 and $SnPd/Al_2O_3$ under light irradiation. (■) Conversion of NO_3^-, and (□) selectivity to N_2 + N_2O. Reaction conditions: catalyst weight, Pt/TiO_2, 500 mg and $SnPd/Al_2O_3$, 100 mg; concentration of NO_3^-, 1.0 mmol dm^{-3}; concentration of glucose, 1.0 mmol dm^{-3}; volume of reaction solution, 250 cm^3; light irradiation ($\lambda > 300$ nm). (b) Photocatalytic hydrogen evolution over Pt/TiO_2 under light irradiation. Reaction conditions: catalyst weight, Pt/TiO_2, 500 mg; concentration of glucose, 1.0 mmol dm^{-3}; volume of reaction, 250 cm^3; light irradiation ($\lambda > 300$ nm). (c) Nonphotocatalytic reduction of NO_3^- with H_2 in water over $SnPd/Al_2O_3$ under the dark conditions. (■) Conversion of NO_3^-, and (□) selectivity to N_2 + N_2O. Reaction conditions: catalyst weight, $SnPd/Al_2O_3$, 10 mg; concentration of NO_3^-, 1.0 mmol dm^{-3}; volume of reaction solution, 250 cm^3; gas composition, H_2/CO_2 = 1/1; gas flow rate, 30 cm^3 min^{-1}.

anions were removed from GW by passing it through ion-exchange resins, followed by photocatalytic oxidation over Pt/TiO_2. The solutions obtained from GW by passing through a cation- and an anion-exchange resins are denoted as GW-Ox-Cation-removal and GW-Ox-Anion-removal, respectively. The conversion of NO_3^- and the selectivity to N_2 + N_2O in GW-Ox-Cation-removal were almost the same as those in GW-Ox, indicating that the cations in GW did not affect the photocatalytic and nonphotocatalytic performance levels of the Pt/TiO_2−$SnPd/Al_2O_3$ system. However, in GW-Ox-Anion-removal, the conversion of NO_3^- and the selectivity to N_2 + N_2O were recovered, being almost the same as those in KNO_3-aq. The results clearly indicate that the anions in GW render the Pt/TiO_2−$SnPd/Al_2O_3$ system ineffective.

Next, we investigated the influence of each anion (Cl^-, SO_4^{2-}, and SiO_3^{2-}), which is contained in GW, on the photocatalytic performance of the Pt/TiO_2−$SnPd/Al_2O_3$ system toward the reduction of NO_3^- by using aqueous NO_3^- solutions that contained each anion separately. Cl^- in KNO_3−Cl^--aq did not affect the conversion of NO_3^- and selectivity to N_2 + N_2O (Figure 3a). On the other hand, when SO_4^{2-} or SiO_3^{2-} was present in the solution, the conversion of NO_3^- decreased. In particular, the decrease in the conversion was most notable in KNO_3−SiO_3^{2-}-aq.

Since the photocatalytic reduction of NO_3^- over Pt/TiO_2−$SnPd/Al_2O_3$ proceeded with photocatalytic H_2 evolution over Pt/TiO_2 and nonphotocatalytic (conventional catalytic) reduction of NO_3^- with H_2 over $SnPd/Al_2O_3$, both reaction rates affect the overall reaction rate of the NO_3^- decomposition and the selectivities. Thus, to clarify the influence of the organic and anionic compounds in GW on the performance of the Pt/TiO_2−$SnPd/Al_2O_3$ system, their effects on the photocatalytic performance of Pt/TiO_2 toward H_2 evolution and the catalytic performance of $SnPd/Al_2O_3$ for the reduction of NO_3^- with H_2 must be individually investigated.

Figure 3b shows the photocatalytic H_2 evolution rate over Pt/TiO_2 in the presence of glucose but the absence of $SnPd/Al_2O_3$ in various reaction solutions. The H_2 evolution rate (μmol h^{-1}) was estimated from the amount of H_2 formed in 1 h from the beginning of the reaction. Although the pH values of the reaction solutions were different, as shown in Table 1, the pH had little impact on the photocatalytic performance of Pt/TiO_2 (shown in Figure S2B in the SI). The H_2 evolution rate was 167 μmol h^{-1} in KNO_3-aq, whereas it was only 59 μmol h^{-1} in GW. The H_2 evolution rate was 93 μmol h^{-1} in GW-Ox, indicating that H_2 evolution over Pt/TiO_2 was inhibited by the organic compounds in GW. However, the H_2 evolution rate in GW-Ox was still slower than that in KNO_3-aq. The effects of the cations and anions in GW on the H_2 evolution rate over Pt/TiO_2 were investigated in both GW-Ox-Cation-removal and GW-Ox-Anion-removal. It was found that the cations in GW had no impact on the H_2 evolution rate, whereas the anions in GW inhibited the photocatalytic H_2 evolution over Pt/TiO_2. In KNO_3−Cl^--aq, the H_2 evolution rate was the almost same as that in KNO_3-aq. In contrast, when either SO_4^{2-} or SiO_3^{2-} was present in KNO_3-aq, the H_2 evolution rate was significantly slower than that in KNO_3-aq. In particular, SiO_3^{2-} dramatically inhibited H_2 evolution. From these results, it was concluded that the organic compounds, SO_4^{2-}, and SiO_x^{n-} in GW decreased the photocatalytic performance of Pt/TiO_2, following the trend organic compounds > SiO_3^{2-} > SO_4^{2-}, which also corresponds to the photocatalytic performance of the Pt/TiO_2−$SnPd/Al_2O_3$ system toward NO_3^- decomposition (Figure 3a). The mechanism for the inhibition of the photocatalytic reaction over Pt/TiO_2 by SO_4^{2-} and SiO_3^{2-} will be discussed in detail later.

Next, we investigated the influence of the compounds in GW on the catalytic performance of $SnPd/Al_2O_3$. Figure 3c shows the decomposition rate of NO_3^- and selectivity for N_2 + N_2O in the nonphotocatalytic reduction of NO_3^- with H_2 over $SnPd/Al_2O_3$ in the absence of Pt/TiO_2 in the dark. The decomposition rate of NO_3^- in KNO_3-aq was 5.2 mmol h^{-1} g_{cat}^{-1}, and the selectivity for N_2 + N_2O was 97%. Since the amount of N_2O was negligible due to very low selectivity (less than 1%), the formation of N_2O did little harm to the environment. In the case of GW, the decomposition rate of NO_3^- was much slower than that in KNO_3-aq, with a value of 0.5 mmol h^{-1} g_{cat}^{-1}, and the selectivity for N_2 + N_2O was only 63%. The decomposition rate of NO_3^- in GW-Ox was still about a quarter of that in KNO_3-aq, and the selectivity for N_2 + N_2O was 88%, indicating that the organic compounds in GW significantly affected the nonphotocatalytic reduction of NO_3^- with H_2 over $SnPd/Al_2O_3$. Since the activity and selectivity in GW-Ox-Cation-removal were similar to those in GW-Ox, the cations in GW did not affect the catalytic performance of $SnPd/Al_2O_3$. On the other hand, in GW-Ox-Anion-removal, the decomposition rate of NO_3^- and selectivity to N_2 + N_2O were the same as those in KNO_3-aq. Thus, the anions in GW inhibited the catalytic performance of $SnPd/Al_2O_3$. However,

Table 3. Catalytic Reduction[a] of NO_3^- in the Dark in an Aqueous KNO_3 Solution over $SnPd/Al_2O_3$ in the Presence of K_2SiO_3, KCl, and K_2SO_4

entry	anion	activity/mmol h^{-1} g_{cat}^{-1}	selectivity/[%] NO_2^-	NH_4^+	$N_2 + N_2O$[b]	absorbance @ 440 nm[c]
1	NO_3^-	5.2	0	3	97	–
2	NO_3^-, SiO_3^{2-}, Cl^-, SO_4^{2-}	1.7	1	7	92	0.38
3	NO_3^-, Cl^-, SO_4^{2-}	5.2	0	4	96	–
4	NO_3^-, SiO_3^{2-}, SO_4^{2-}	5.2	1	6	93	0.46
5	NO_3^-, SiO_3^{2-}, Cl^-	3.9	<1	5	95	0.43
6	NO_3^-, SiO_3^{2-}	5.1	1	8	91	0.47

[a] Reaction conditions: catalyst weight, $SnPd/Al_2O_3$, 10 mg; reactant NO_3^- (from KNO_3), 1.0 mmol dm^{-3}; reaction volume, 250 cm^3; gas composition, H_2/CO_2 = 1/1; gas flow rate, 30 cm^3 min^{-1}. Initial concentrations of K_2SiO_3, KCl, and K_2SO_4 were 1.1, 0.5, and 1.1 mmol dm^{-3}, respectively. [b] Selectivity to $N_2 + N_2O$ was calculated by subtracting the selectivities of NO_2^- and NH_4^+ from 100%. [c] Determined by using a molybdenum yellow method.[30]

when the anions, including Cl^-, SO_4^{2-}, and SiO_x^{n-}, were individually present in KNO_3-aq, the decomposition rate of NO_3^- by the catalytic reduction with H_2 over $SnPd/Al_2O_3$ and the selectivity for $N_2 + N_2O$ were almost the same as those in KNO_3-aq.

Thus, we thought that the anions (Cl^-, SO_4^{2-}, and SiO_x^{n-}) only had a significant effect on the catalytic performance of $SnPd/Al_2O_3$ when a combination of these anions was present. Therefore, we determined the catalytic performance of $SnPd/Al_2O_3$ for the reduction of NO_3^- with H_2 in solutions containing different combinations of Cl^-, SO_4^{2-}, and SiO_x^{n-}. Table 3 summarizes the results for the catalytic reduction of NO_3^- with H_2 over $SnPd/Al_2O_3$ without irradiation in reaction solutions containing Cl^-, SO_4^{2-}, and SiO_3^{2-} in the same concentrations (0.5, 1.1, and 1.1 mmol dm^{-3}, respectively) as those in GW. In the reaction in entry 2, the decomposition rate of NO_3^- was significantly slower in comparison with that in KNO_3-aq (entry 1). On the other hand, the decomposition rates of NO_3^- in the solutions containing SO_4^{2-} and Cl^- (entry 3) and SO_4^{2-} and SiO_3^{2-} (entry 4) were comparable to that in KNO_3-aq (entry 1). In contrast, in a solution containing SiO_3^{2-} and Cl^- (entry 5), the decomposition rate of NO_3^- decreased to 3.9 mmol h^{-1} g_{cat}^{-1}, which was slower than that in KNO_3-aq (5.2 mmol h^{-1} g_{cat}^{-1}). A possible reason for the deactivation of $SnPd/Al_2O_3$ with SiO_3^{2-} in solutions that also contained Cl^- or Cl^--SO_4^{2-} is that SiO_3^{2-} polymerizes in the presence of Cl^- and SO_4^{2-}, after which the formed silicate oligomers are adsorbed on $SnPd/Al_2O_3$.

Thus, the amount of SiO_3^{2-} monomer in each reaction solution was determined by using a molybdenum yellow method,[30] where Mo^{6+} is added to the solution and reacts with monomeric silicate ions to form a heteropolyanion ($[SiMo_{12}O_{40}]^{4-}$). The amount of $[SiMo_{12}O_{40}]^{4-}$ in the solution is determined from the absorbance at 440 nm in a UV−vis spectrum of the solution. Therefore, if the intensity of the absorbance at 440 nm decreases, then the amount of silicate oligomers has increased. Table 3 lists the absorbances at 440 nm in the reaction solutions after 1 h of the catalytic reduction of NO_3^- with H_2 over $SnPd/Al_2O_3$.[31] The absorbance in entry 4 (A_{440} = 0.46) was almost the same as that in entry 6 (A_{440} = 0.47). On the other hand, the absorbances in entries 2 and 5 (A_{440} = 0.38 and 0.43, respectively), in which the catalytic performance was smaller, were lower than that in entry 6. In particular, the absorbance in entry 2 was much smaller than that in entry 5. The results indicate that a larger amount of silicate ions was polymerized in the reaction solution in entry 2 than it was in entry 6. The catalytic activity correlated with the absorbances (Table 3). This correlation clearly indicates that the polymerized silicate ions deactivate $SnPd/Al_2O_3$ in the nonphotocatalytic reduction of NO_3^- with H_2.

From the results mentioned above, we concluded that K_2SO_4, K_2SiO_3, and organic compounds in GW decreased the photocatalytic performance of Pt/TiO_2 and that the organic compounds and polymerized silicate ions in GW lowered the nonphotocatalytic performance of $SnPd/Al_2O_3$. Thus, the decomposition rate of NO_3^- and selectivity to $N_2 + N_2O$ by the Pt/TiO_2−$SnPd/Al_2O_3$ system also decreased for the photocatalytic reduction of NO_3^- in GW and GW-Ox.

Mechanism for Deactivation of Pt/TiO_2 by K_2SO_4 and K_2SiO_3. As described above, SO_4^{2-} and SiO_x^{n-} in GW decreased the photocatalytic activity of Pt/TiO_2 (Figure 3b). Possible reasons for the deactivation of Pt/TiO_2 by SO_4^{2-} and SiO_x^{n-} are poisoning of the reduction sites (Pt_e^-), oxidation sites (TiO_2_h^+), or both on Pt/TiO_2 with SO_4^{2-} and SiO_x^{n-} (Figure S3 in the SI). In order to clarify which sites were poisoned by SO_4^{2-} and SiO_x^{n-}, we investigated the influence of the concentrations of both compounds on the photocatalytic performance for H_2 evolution ($2H^+ + 2\,(Pt\_e^-) \rightarrow H_2 + 2Pt$) from an aqueous glucose solution over Pt/TiO_2 and for the O_2 evolution ($2H_2O + 4\,(TiO_2\_h^+) \rightarrow O_2 + 4H^+ + 4TiO_2$) from an aqueous $AgNO_3$ solution over bare TiO_2. The former reaction can be used to estimate the level of poisoning of Pt_e^- sites due to these compounds, and the latter one can be used to estimate the level of poisoning of TiO_2_h^+ sites.

The H_2 evolution rate over Pt/TiO_2 under photocatalytic conditions was 298 μmol h^{-1} in the absence of K_2SO_4 (Figure S4 in the SI). When 0.1 mmol dm^{-3} of K_2SO_4 was added to the solution, the H_2 evolution rate decreased to 245 μmol h^{-1}. Further addition of K_2SO_4 did not change the H_2 evolution rate. Since a small amount of K_2SO_4 had a substantial effect on the H_2 evolution rate over Pt/TiO_2, we concluded that SO_4^{2-} was strongly adsorbed on the H_2 evolution sites on Pt/TiO_2, i.e., Pt atoms exposed on the surface of the Pt particles, resulting in the deactivation of Pt/TiO_2. In contrast to the H_2 evolution rate, the presence of SO_4^{2-} in the solution did not cause a decrease in the O_2 evolution rate over the bare TiO_2, indicating that SO_4^{2-} did not poison the TiO_2_h^+ sites on TiO_2 (Figure S4 in the SI).

Figure 4 shows the effects of the concentration of K_2SiO_3 on the H_2 evolution rate from the photocatalytic reaction over Pt/TiO_2 in an aqueous glucose solution and on the O_2 evolution rate from the photocatalytic reaction over bare TiO_2 in an aqueous $AgNO_3$ solution. The H_2 evolution rate did not change with the concentration of K_2SiO_3 up to 0.5 mmol dm^{-3},

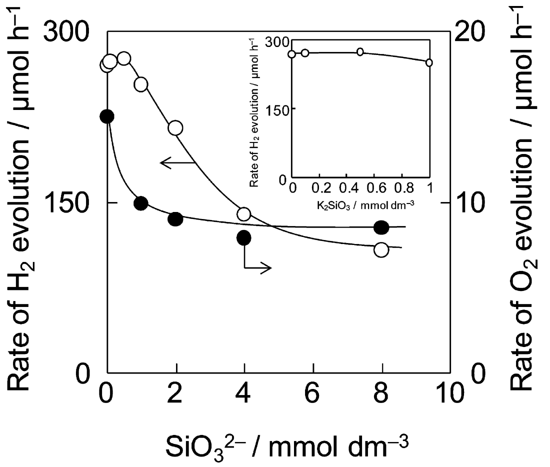

Figure 4. Effects of the concentration of SiO_3^{2-} on the rates of (○) H_2 evolution for the photocatalytic reactions in an aqueous glucose solution over Pt/TiO_2 and (●) O_2 evolution for the photocatalytic reaction in an $AgNO_3$ solution over TiO_2. Reaction conditions for H_2 evolution: catalyst weight, Pt/TiO_2, 500 mg; reactant glucose, 100 mmol dm^{-3}; reaction volume, 250 cm^3; and light irradiation ($\lambda > 300$ nm). Reaction conditions for O_2 evolution: catalyst weight, TiO_2, 500 mg; initial pH, 9.8; reactant $AgNO_3$, 10 mmol dm^{-3}; reaction volume, 250 cm^3; and light irradiation ($\lambda > 300$ nm).

although the total amount of SiO_3^{2-} (125 μmol) in the 0.5 mmol dm^{-3} K_2SiO_3 solution was much larger than the number of exposed Pt sites on the surface (3 μmol), which was estimated from the adsorption amount of CO at 323 K.[32] Therefore, the adsorption of SiO_3^{2-} on the surface of the Pt particles was very weak. On the other hand, the O_2 evolution rate significantly decreased, even in the presence of a small amount of K_2SiO_3 (1.0 mmol dm^{-3}). These results clearly indicated that TiO_2_ h^+ sites on TiO_2 were deactivated with K_2SiO_3. Although the rate-limiting step for the H_2 evolution reaction from the aqueous glucose solution over Pt/TiO_2 was the H_2 evolution reaction from the Pt_e^- sites and SiO_3^{2-} deactivated TiO_2_h^+ sites on TiO_2, the H_2 evolution rate decreased when an excess amount of K_2SiO_3 (>1.0 mmol dm^{-3}) was added. This is probably because the rate-limiting step for the H_2 evolution reaction from the aqueous glucose solution changed from the consumption of Pt_e^- to form H_2 to that of TiO_2_h^+ due to the poisoning of most of the TiO_2_h^+ sites with SiO_3^{2-} when excess SiO_3^{2-} was present in the reaction solution.

Figure 5 shows an adsorption profile for SiO_3^{2-} on Pt/TiO_2 at 303 K. The dashed line in Figure 5 represents the number of surface hydroxyl groups on Pt/TiO_2 (295 μmol g^{-1}), which was calculated from the surface area of the Pt/TiO_2 and the density of surface hydroxyl groups (3.3 OH nm^{-2}).[32] The adsorption amount of SiO_3^{2-} increased with an increase in the concentration of SiO_3^{2-} and saturated at ~350 μmol g^{-1}, which was approximately equal to the number of surface hydroxyl groups (295 μmol g^{-1}). This result implies that SiO_3^{2-} stoichiometrically reacted with the surface hydroxyl groups in a 1:1 ratio (Ti−O−Si−OH) and supports the hypothesis that the TiO_2_h^+ sites were poisoned by SiO_3^{2-}.

CONCLUSIONS

Nitrate in real groundwater was decomposed mainly into N_2 with an 83% selectivity by using a photocatalytic reaction system composed of the photocatalyst Pt/TiO_2 and the nonphotocatalyst $SnPd/Al_2O_3$, which were dispersed in the groundwater, irradiated at $\lambda > 300$ nm in the presence of glucose as a hole scavenger. However, pretreatment of the groundwater by photooxidation with Pt/TiO_2 was necessary to remove the organic compounds from the groundwater because they poisoned both Pt/TiO_2 and $SnPd/Al_2O_3$. The decomposition rate of NO_3^- and the selectivity to $N_2 + N_2O$ in the photocatalytic reduction of NO_3^- in the groundwater were lower than those in an aqueous solution of KNO_3. The lower photocatalytic performance of the Pt/TiO_2−$SnPd/Al_2O_3$ system in the groundwater was due to sulfate and silicate ions and the organic compounds in the groundwater. Sulfate and silicate ions deactivated Pt_e^- and TiO_2_h^+ sites, respectively, on the Pt/TiO_2 surface by adsorption, causing a decrease in the photocatalytic performance toward H_2 evolution. In addition, polymerized silicate ions in the groundwater decreased the catalytic performance of $SnPd/Al_2O_3$ for the hydrogenation of NO_3^- with H_2.

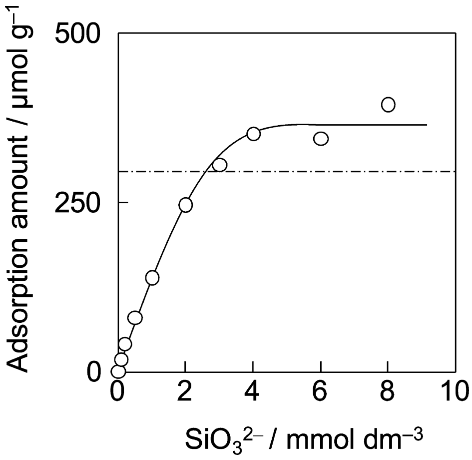

Figure 5. Adsorption of SiO_3^{2-} on Pt/TiO_2. Adsorption conditions: weight of Pt/TiO_2, 30 mg; initial concentration of SiO_3^{2-} (from K_2SiO_3), 0.1−8.0 mmol dm^{-3}; temperature, 303 K; and volume of solution, 10 cm^3.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Time courses for the photocatalytic reduction of NO_3^-, influence of pH on the photocatalytic reduction of NO_3^-, and dependences of concentrations of glucose and $AgNO_3$ on the rates of H_2 and O_2 evolutions, respectively, as mentioned in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(31) Two cubic centimeters of a 10% (w/v) aqueous $(NH_4)_6Mo_7O_{24}$ solution and 1 cm^3 of hydrochloric acid (6 mol dm^{-3}) were added to 50 cm^3 of the reaction solution (entries 2 and 4−6 in Table 3). The solution was allowed to stand for 5 min at 293 K, and then the absorbance of the solution at 440 nm was measured on a spectrophotometer to estimate the amount of $[SiMo_{12}O_{40}]^{4-}$ in the solution.

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