Photoelectrochemical conversion of NO_3^- to N_2 by using a photoelectrochemical cell composed of a nanoporous TiO_2 film photoanode and an O_2 reducing cathode

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Photoelectrochemical conversion of nitrate anions into dinitrogen was successfully achieved by using a photoelectrochemical cell composed of a nanoporous TiO_2 film photoanode and an O_2 reducing cathode in the presence of NH_3, which can be regarded as a model of denitrification and is of importance for environmental cleaning.

Photoelectrochemical reactions at semiconductor electrodes were investigated before the 1960s,[1] and the work on a crystalline n-TiO_2 photoanode to photodecompose water by UV light attracted a great deal of attention.[2] Organic compounds have also been photodecomposed by TiO_2.[3,4] The crystalline n-TiO_2 semiconductor forms a kind of Schottky junction at the TiO_2/aqueous electrolyte interface; the photogenerated holes oxidize water or organic compound on the TiO_2 surface, and the photogenerated electrons reduce protons to produce H_2 at a counter-electrode. However, the photoelectrochemical reactions were not efficient enough without an applied potential, so that these reactions have mostly been investigated under applied potential conditions. At the beginning of the 1990s, a nanoporous TiO_2 thin film was successfully applied to fabricate a dye-sensitized solar cell (DSSC) without applied potentials.[5] The photoreactivity of a nanoporous semiconductor film having a large area of effective interface with water phase is an interesting and important issue towards applications, but the details have been open to further investigations. We have reported a biophotochemical cell (BPCC) composed of a nanoporous semiconductor photoanode and an O_2-reducing cathode that can photodecompose various biomass wastes generating simultaneously electrical power. Using this BPCC, highly concentrated ammonia solutions (>1000 ppm) could be photodecomposed to N_2,[6] and at the same time O_2 was reduced to H_2O at a Pt cathode. Another important merit of the BPCC is that separation of the semiconductor catalyst from the cleaned water is remarkably easy and simple.

The nitrogen in an organic compound is often converted to nitrogen oxides by biological,[7] catalytic[8] and electrocatalytic[9] decomposition. Nitrogen has several oxidation states (−3 to +5), which is the reason of its high ability to exchange electrons with other elements, producing nitrates (NO_3^-) and nitrites (NO_2^-). Such nitrogen oxide ions cause an eutrophication phenomena,[10] so that it is important that N compounds are decomposed not to nitrogen oxides but rather to N_2, that is compatible with the nitrogen cycle in nature. As for the N_2 formation from NH_3 by the photoexcited TiO_2, hydrazine $H_2N–NH_2$ would at first be formed by oxidation of two molecules of NH_3 at the neighboring sites of TiO_2, and the formed reactive hydrazine would be rapidly further oxidized to N_2. Photocatalytic reduction of 100 ppm nitrate over metal modified TiO_2 powders was successfully achieved by using hole scavengers such as formic acid and acetic acid.[11]

In wastewater containing biomass wastes such as livestock, human or industrial wastes, concentration of nitrate anions are high, often more than hundreds of ppm. In our investigations using the above BPCC it was found that highly concentrated NO_3^- of >6000 ppm can be photoelectrochemically reduced to N_2, which can be regarded as a denitrification model and is important for environmental cleaning; the first preliminary results are reported here.

Titanium dioxide (P-25, particle size, *ca.* 21 nm; specific surface area, 50 ± 15 m^2 g^{-1}) was purchased from Japan Aerosil Co. Ltd., and potassium nitrate (purity >99.0%) and ammonia aqueous solution (purity 28.0–30.0% NH_3) from Kanto Kagaku Co. Ltd. Lead(II) acetate trihydrate (purity >99.9%) and potassium hexachloroplatinate(IV) (purity >99.0%) were from Wako Pure Chemical Co. Ltd. Triton X-100 and acetylacetone (purity >99.0%) were from Kishida Chemical Co. Ltd., and Ar gas from Nippon Sanso Corp. F-doped SnO_2 conductive glass (FTO, surface resistance, 10 Ω/(sq)) was purchased from AGC Fabritec Co. Ltd, and Pt plate from Furuya Metal Co. Ltd.

A nanoporous TiO_2 film coated on an FTO electrode was used as a photoanode by preparing as follows. 3 g TiO_2 and acetylacetone (0.1 ml) were mixed well in a mortar while adding 3 ml water slowly during 2 h. Triton X-100 (0.1 ml) detergent was added and mixed well with the TiO_2 slurry, and then the mixture was sonicated. This mixture was spin-coated (2000 rpm) on an FTO electrode (2×1 cm) for about 10 s to obtain a 1×1 cm area of a nanoporous TiO_2 film, and the film was dried at 100 °C for 30 min. This procedure was repeated until the film thickness reached 10 μm, and then the film was calcined at 450 °C for 30 min giving the photoanode denoted as FTO/TiO_2. A cathode was prepared from a Pt plate (1 cm × 1 cm) coated with Pt black by electrodeposition in a

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H_2PtCl_6 aqueous solution containing $Pb(CH_3COO)_2 \cdot 3H_2O$ to give the cathode denoted as Pt/Pt black.

The FTO/TiO_2 and Pt/Pt black electrodes were soaked in 5 ml of 1.0 mM NH_3 aqueous solution containing 0.1 M KNO_3 in a 10 ml cylindrical cell made of Pyrex glass. In this cell air leakage was negligible. Ar gas was bubbled into the solution for 20 min and the FTO/TiO_2 was irradiated with a 500 W xenon lamp (500 mW cm^{-2}, UV-A region *ca.* 20 mW cm^{-2}).

The time dependence of the short circuit photocurrent was measured by a potentiostat/galvanostat and function generator (Hokuto Denko). The cylindrical cell was sealed with a rubber septum, through which the gas phase was sampled by a syringe. The gases were analyzed by a gas chromatograph (Shimadzu GC2014) with a molecular sieve 5A column at 40 °C using Ar carrier gas.
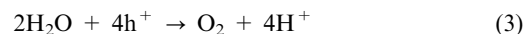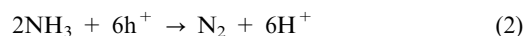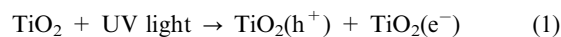
In the photoelectrochemical decomposition of ammonia by the BPCC, oxidative potential was generated by the holes at the nanoporous TiO_2 and reductive potential at the cathode as shown later in Fig. 3. We attempted nitrate reduction by this BPCC using NH_3 in the presence of excess nitrate (NH_3 = 1 mM, NO_3^- = 100 mM, 6200 ppm). In the photodecomposition of ammonia on the photoanode, cathodic reaction was investigated under Ar atmosphere. As mentioned in the introductory section, ammonia can be oxidatively decomposed to dinitrogen gas (N_2) quantitatively at a TiO_2 thin film photoanode.[6] If a 1 mM NH_3 aqueous solution (5 mL) (NH_3 = 5 μmol) was completely photodecomposed, 2.5 μmol N_2 should be produced from NH_3. The gases evolved under Ar are shown in Fig. 1. As reported earlier, by using platinized TiO_2 powders or BPCC with ammonia solutes without NO_3^-, N_2 and H_2 were photoelectrochemically evolved under Ar atmosphere at the molar ratio of nearly 1 : 3.[12,13] However, it is evident from Fig. 1 that, when nitrate anions were present (NO_3^-/NH_3 = 100), H_2 did not evolve, but N_2 was evolved in excess over the calculated value from the NH_3 (broken line in Fig. 1). The only possible interpretation would be that the nitrate anions were reduced to N_2 at the cathode. Additionally, it was also important that oxygen was evolved due to the water oxidation at the TiO_2 photoanode donating reduction power to the cathode. It should be noted that the evolved O_2 reached a maximum and then decreased, which can be interpreted by reduction of the formed O_2 producing H_2O at the cathode as reported before in our previous paper.[6] Water oxidation is a four-electron process and N_2 production from two molecules of NH_3 is a six-electron process. In addition, it is of importance that oxygen was not evolved when the
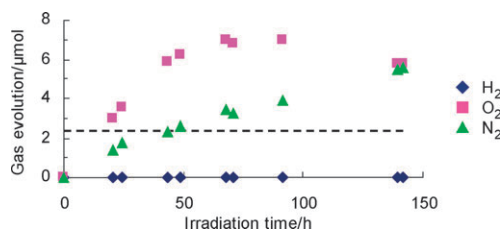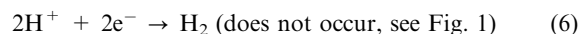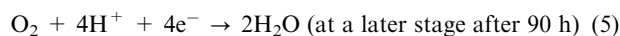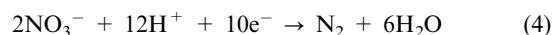

Fig. 1 Time dependence of the formed gases in NH_3 (1 mM)–KNO_3 (100 mM, NO_3^- 6200 ppm)–water (5 mL) under Ar at pH 9.74. Broken line, theoretical amount (2.5 μmol) of evolved N_2 by complete decomposition of 5 μmol NH_3 (1 mM, 5 mL).

photodecomposition was performed under a high ammonia concentration (1 M) as proved by another experiment, showing that oxidations of water and NH_3 are competitive. The reactions at the photoanode and cathode in the BPCC can be summarized as follows (refer also Fig. 3):

Photoanodic reactions:

$$TiO_2 + \text{UV light} \rightarrow TiO_2(h^+) + TiO_2(e^-) \qquad (1)$$

$$2NH_3 + 6h^+ \rightarrow N_2 + 6H^+ \qquad (2)$$

$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+ \qquad (3)$$

Cathodic reactions:

$$2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O \qquad (4)$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \text{ (at a later stage after 90 h)} \quad (5)$$

$$2H^+ + 2e^- \rightarrow H_2 \text{ (does not occur, see Fig. 1)} \qquad (6)$$

By excitation of TiO_2 by UV irradiation whose energy is larger than the bandgap of the semiconductor, charge separation takes place producing electrons in the conduction band (CB) and holes in the valence band (VB) (eqn (1)). The NH_3 and H_2O molecules react with holes on the TiO_2 to produce N_2 and O_2, respectively (eqn (2) and (3)). The electrons left in the CB (eqn (1)) are transported to the Pt/Pt black cathode *via* outer circuit, and NO_3^- would be reduced there to produce N_2 (eqn (4)). At a later stage after 90 h, the formed O_2 is partially reduced at the cathode to H_2O (eqn (5)). If there were no electron acceptor in the cell, proton reduction to H_2 would take place, but H_2 was not formed.

Thus, when NH_3 was present (Fig. 1), NO_3^- was photochemically reduced to N_2 (eqn (2) and (4)). After 142 h, the total evolved N_2 was 5.6 μmol, and the total O_2 5.7 μmol. Since the formed O_2 produced a reduction power of 4 mol e$^-$/mol O_2 reducing $2NO_3^-$ to N_2 by a 10 e$^-$ process, it is calculated that 2.3 μmol N_2 (= 5.7 μmol × (4 e$^-$/10 e$^-$)) came from NO_3^- reduction by electrons donated from H_2O. The remainder, 3.3 (= 5.6–2.3) μmol N_2 is calculated to come from NH_3 oxidation (eqn (2)) + NO_3^- reduction (eqn (4)), to which it is calculated that 4.1 μmol NH_3 contributed; from this, NH_3 decomposition yield was calculated to be 82% (= (4.1/5) × 100) after 142 h, as summarized in Table 1.

The same photoelectrochemical reaction as Fig. 1 was conducted in the absence of ammonia and O_2 (under Ar), and the results are shown in Fig. 2. In this case H_2 was formed in addition to N_2 and O_2. When the holes formed by UV light excitation (eqn (1)) were used for water oxidation evolving O_2 (eqn (3)), the electrons left in the CB are transported to the cathode and then reduce NO_3^- and H^+ forming N_2 (eqn (4)) and H_2 (eqn (6)), respectively. From the above-mentioned reactions of O_2 formation (4e$^-$ process), proton reduction to H_2 (2e$^-$ process), and $2NO_3^-$ reduction to N_2 (10e$^-$ process), the amount of the evolved N_2 was calculated from the evolved O_2 and H_2. After 48 h the formed N_2 (1.6 μmol) was much less than the calculated value (2.6 μmol), which could be interpreted by slow reduction of NO_3^- to gaseous N_2. After 96 h the formed N_2 (2.9 μmol), in contrast, exceeded the calculated value (2.1 μmol). We have reported that TiO_2 can produce reduction power also through oxidation of Ti^{4+} to Ti^{5+}

Table 1 Evolved N_2 shown in Fig. 1 after 142 h. Total evolved $N_2 = 5.6$ µmol. Of the total N_2, 2.3 µmol N_2 is calculated to come from NO_3^- reduction by electrons donated by H_2O producing O_2, and 3.3 µmol N_2 is calculated to come from NH_3 (eqn (2)) as well as from NO_3^- reduction by electrons donated by NH_3 oxidation (eqn (2))

Total N_2 evolved after 142 h	5.6 µmol
1. Calculated N_2 from NO_3^- via O_2 (= 5.7 µmol) formation Anodic reaction: $2H_2O + 4h^+ \rightarrow O_2 + 4H^+$ Cathodic reaction: $2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O$	2.3 µmol (= 5.7 µmol × 4/10) ($4e^-$ is liberated; evolved O_2 after 142 h = 5.7 µmol) (calculated $N_2 = 2.28$ µmol (= 5.7 µmol × 4/10))
2. Calculated N_2 via NH_3 (= 4.1 µmol) oxidation Anodic reaction: $NH_3 + 3h^+ \rightarrow (1/2) N_2 + 3H^+$	2.1 µmol (= 4.1 µmol × 3/6) ($3e^-$ is liberated; calculated $N_2 = 2.1$ µmol (= 4.1 µmol × 3/6))
3. Calculated N_2 from NO_3^- via NH_3 (= 4.1 µmol) oxidation to N_2 Cathodic reaction: $2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O$	1.2 µmol (= 4.1 µmol × 3/10) (calculated $N_2 = 1.2$ µmol (= 4.1 µmol × 3/10))
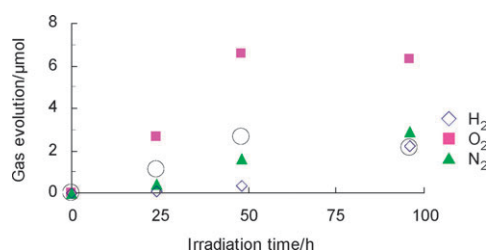
Fig. 2 Time dependence of evolved gases using KNO_3 (100 mM, $NO_3^- = 6200$ ppm) aqueous solution (5 mL) in BPCC under Ar. The pH of 5.67 changed to 9.80; (○) Calculated N_2 value based on the evolved O_2 and H_2.
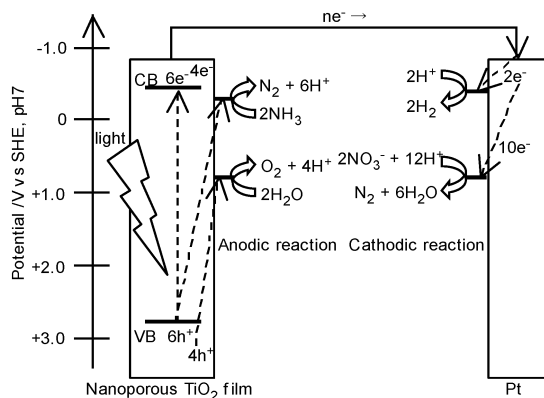
Fig. 3 Photoelectrochemical denitrification of NO_3^- to N_2 using NH_3 and H_2O as electron donors in a biophotochemical cell (BPCC) under Ar.

instead of oxidizing water.[14] One possible explanation for the above excess N_2 formation could be this side reaction, but the details require future investigation. Another explanation could be the formation of surface peroxide species on the TiO_2.

The present photoelectrochemical denitrification of NO_3^- to N_2 by using NH_3 and H_2O as electron donating compounds at a nanoporous TiO_2 photoanode in a BPCC can be summarized by Fig. 3. By excitation of TiO_2 by UV irradiation whose energy is larger than the bandgap of the semiconductor, charge separation takes place producing electrons in the conduction band (CB) and holes in the valence band (VB) (eqn (1)). NH_3 and H_2O molecules react with holes on the

TiO_2 to produce N_2 and O_2, respectively (eqn (2) and (3)). The electrons left in the CB are transported to the Pt/Pt black cathode via the outer circuit, and reduce NO_3^- and H^+ forming N_2 (eqn (4)) and H_2 (eqn (6)), respectively.

It was confirmed by another experiment that nitrite ion (NO_2^-) was also reduced to N_2 by NH_3 in the same BPCC and procedure. In a BPCC a 32 mL mixture of pig urine/wash water (= 1/4) containing NH_4^+, NO_3^- and NO_2^- was photodecomosed under aerobic conditions with 100 mW cm^{-2} white light (UV-A region = 8 mW cm^{-2}). After 24 h, NH_4^+-N decreased from 2580 to 166 ppm, NO_3^--N from 18.6 to 17.0 ppm, and NO_2^--N from 4.84 to 3.17 ppm. By another experiment it was confirmed that NH_4^+ was converted to N_2. In this experiment it is important that oxidative photodecomposition of NH_4^+ to N_2 in the BPCC did not increase NO_3^- or NO_2^-.

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