

Artificial photochemical nitrogen cycle to produce nitrogen and hydrogen from ammonia by platinumized TiO₂ and its application to a photofuel cell

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Photochemical artificial nitrogen cycle was reported to produce dinitrogen and dihydrogen by photodecomposing ammonia with platinumized TiO₂, and its application to a photofuel cell with a nanoporous TiO₂ film electrode, a new concept of a fuel cell to photochemically produce electricity and H₂ from ammonia, was proposed.

The treatment of livestock waste is becoming more and more a serious problem. Especially, the excess amount of nitrogen compounds in the waste are difficult to treat or decompose for the purpose of discarding into the environment or recycling as useful compounds. In Nature the carbon/nitrogen cycle maintains material balance. Carbon waste can be converted into methane (fuel) by methane fermentation, which is regarded as one of the promising methods to create renewable energy from biomass waste. However, nitrogen compounds contained in the livestock waste are now becoming a serious pollutant for the environment, which should be solved urgently. Since nitrogen compounds can be converted finally to ammonia by enzymes such as urease in livestock wastes, if ammonia is converted to harmless or useful compounds, it can solve the livestock waste problem. In addition to this, ammonia is now attracting a great deal of attention as an energy storage material for H₂ fuel cells instead of H₂ that requires high pressure and large volume for storage.

TiO₂ photoanode was found to photoelectrochemically decompose water under UV light irradiation,¹ and since then many organic and inorganic compounds have been decomposed by this photocatalyst.^{2–4} Photodecomposition of ammonia has also been reported, but the products were not N₂/H₂. The photodecomposition of ammonia in neutral water has been reported by using TiO₂-supported Pt or Pd catalyst, but only N₂ and nitrogen oxides were obtained.⁵ TiO₂/Pt decomposed aqueous ammonia into N₂, while pure TiO₂ decomposed NH₃ into nitrite and nitrate.⁶ In these reports hydrogen formation was not reported. Some reports are found on photodecomposition of ammonia with TiO₂ in a gas phase.^{7,8} However, to our knowledge, photochemical conversion of aqueous ammonia into N₂/H₂ has not been reported yet. The present authors have found that an aqueous solution of ammonia can be photochemically converted into N₂/H₂ if reacted under alkaline conditions and in a stoichiometric 1:3 (N₂:H₂) molar ratio by using platinumized titanium dioxide (TiO₂) suspension. This could lead to a future artificial nitrogen cycle driven by solar irradiation. Very interestingly, our further investigation showed that the system can lead to a new concept of a photofuel cell in which ammonia

serves as a fuel, the light irradiation induces decomposition of the fuel, and so photocurrent is produced in addition to the N₂/H₂ production. The first fundamental results are reported in this paper.

TiO₂ (ST-01, average size 7 nm, from Ishihara Sangyo Co.Ltd.) was platinumized by photochemically reducing tetrachloroplatinate in a TiO₂-water suspension in the presence of 2 wt% methanol. The platinumized TiO₂ powders (TiO₂-Pt) (10 mg) with 1 wt% Pt were suspended in a 5 ml aqueous solution of 1 wt% ammonia (pH 12.3) in a 10 ml cylindrical cell. The cell was sealed after bubbling argon gas into the water for 30 min, and then the suspension was irradiated with a 500 W xenon lamp (intensity 102 or 469 mW cm⁻²). The products were analyzed by a gas chromatograph (Shimadzu, GC4C-PT) with a 13X-D molecular sieve column at 80 °C using argon carrier gas. N₂ and H₂ were produced by irradiation with nearly in the stoichiometric 3:1 ratio (H₂/N₂ = 3.4/1 molar ratio) with a slight excess of H₂. The slight excess of H₂ formation would be ascribable to photochemical proton reduction to generate H₂ by the TiO₂-Pt that has been reported earlier.⁹ The effect of pH is shown in Table 1.

The decrease of the solution pH to 9.18, 6.93 and 0.97 by adding HNO₃ remarkably reduced the photodecomposition rate. Since the pK_a value for the dissociation of NH₄⁺ to NH₃(+H⁺) is 9.24, the trend of N₂ formation on pH should show that the dissociated NH₃ is more effective for the photodecomposition than NH₄⁺. However, the trend for H₂ formation is not simple; at pH 6.93 the amount H₂ formed increased slightly, which should be investigated in more detail in future. The TiO₂ powders without deposited Pt did not show any appreciable activity.

The photodecomposition yield (%) of NH₃ was examined by changing its concentration (1, 0.1 and 0.01 wt%), and the results are shown in Table 2. When the concentration was decreased, the decomposition yield (%) increased (85.4% for 0.01 wt% NH₃ after 20 h). After prolonged irradiation this value approached nearly 100% decomposition.

Table 1 N₂ and H₂ evolution by photochemical decomposition of 1 wt% NH₃ aqueous solution (5 ml) in the presence of suspended TiO₂-Pt (0.01 g) in 3 h. Light intensity, 102 mW cm⁻²

pH	H ₂ (μl)	N ₂ (μl)	Mol. ratio (H ₂ /N ₂)
12.3	47.8	13.9	3.4
9.18 ^a	Trace	10.3	0
6.93 ^a	3.6	6.6	0.6
0.97 ^a	Trace	6.8	0

^a pH was adjusted by adding HNO₃.

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Table 2 N₂/H₂ evolution and ammonia photodecomposition yield (%) of different concentrations NH₃ aqueous solution (5 ml) in the presence of suspended TiO₂-Pt (0.02 g) in 20 h. Light intensity, 469 mW cm⁻²

NH ₃ conc. (wt%)	pH	H ₂ (μl)	N ₂ (μl)	Mol. ratio (H ₂ /N ₂)	Decom. yield (%)
1	11.9	2111	663	3.2	7.5
0.1	12.2	979	296	3.3	33.7
0.01	12.1	409	75	5.4	85.4

^a pH was adjusted by adding NaOH.

A nanoporous TiO₂ film was prepared that was reported to fabricate a dye-sensitized solar cell.¹⁰ 12 g TiO₂ (P-25, received from Japan Aerosil Co.Ltd.) and acetylacetone (0.4 ml) were mixed well in a mortar while adding 4 ml water slowly during 2 h. Triton X-100 (0.2 ml) was added and further mixed well with the TiO₂ slurry, and then the mixture was sonicated. This mixture was spin-coated (2000 rpm) on a FTO glass (2 cm × 1 cm) for about 10 s to obtain 1 cm × 1 cm area of a nanoporous TiO₂ 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 calcinated at 450 °C for 30 min. The quality of the TiO₂ nanoporous film was proved by using this film for a dye-sensitized solar cell¹⁰ by using the well-known *cis*-bis(isothiocyanato)-bis(4,4'-dicarboxyl-2,2'-bipyridine)-ruthenium(II), Ru(dcbpy)₂(NCS)₂ (called N3) dye with a conventional I₃⁻/I⁻ redox electrolyte solution giving the light-to-electrical power conversion efficiency of around 7%.¹¹

A cyclic voltammogram was measured with this TiO₂ film as working electrode, Ag-AgCl as a reference electrode, and a platinum foil as a counter electrode in a pH 14.1 aqueous solution of 10 M NH₃ containing 0.1 M KNO₃ electrolyte. The CVs under dark and under illumination in an Ar atmosphere are shown in Fig. 1. Clear photoanodic currents were observed showing that the TiO₂ works as a photoanode in the presence of NH₃. This system induced photoanodic currents also in the absence of NH₃ under the same pH conditions, but the photocurrent density was less than 1/40 in comparison with the Fig. 1 showing evidently that NH₃ works as a donor for the photoelectrochemical event.

Although the photocurrents in Fig. 1 tended to decrease with repeated scanning, it approached a saturated value of around 0.5 mA cm⁻² after 3 to 4 hours. The generated H₂ and N₂ after repeated scanning for 2 hours are shown in Table 3.

The obtained H₂/N₂ ratio was 2.6/1 under Ar. The smaller amount of H₂ than the 3:1 ratio could be ascribable to the consumption of the photogenerated electrons by the leaked O₂ from air since for this three electrodes system the cell was not tight enough against air leakage. This was supported by the remarkable smaller H₂/N₂ ratio (0.6) obtained under O₂ atmosphere as shown in Table 3. The use of K₂SO₄ instead of KNO₃ as an electrolyte gave almost the same results as Table 3, indicating that NO₃⁻ anion is not involved in the photoelectrochemical reaction. By using the nanoporous TiO₂ film electrode and a Pt foil counter electrode, photoelectrochemical reaction was carried out (10 M NH₃ at pH 14.1 and 0.1 M KNO₃) under short circuit conditions without any bias potential. For this system the cell was tight enough against air leakage as the cell used for the TiO₂-Pt suspension systems. This system produced 150 μA cm⁻² photocurrent, and the H₂ and N₂ produced in 2 h were 194 μl and 63 μl, respectively, with the H₂/N₂ ratio of 3.08/1 nearly in the theoretical

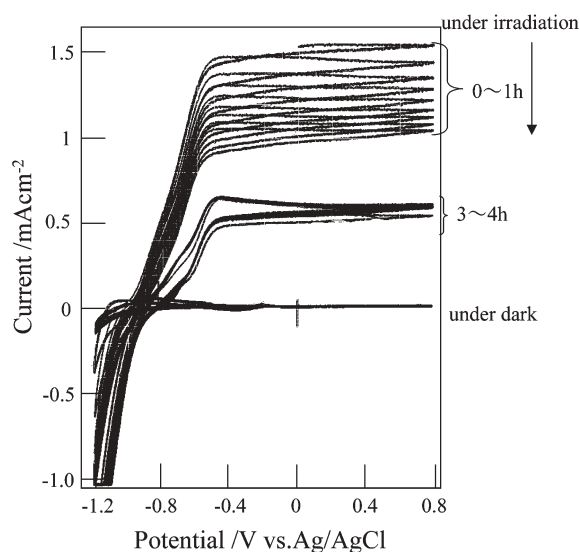


Fig. 1 Repeated cyclic voltammograms under dark and irradiation at a TiO₂ nanoporous electrode soaked in an aqueous solution of NH₃ (10 M) and KNO₃ (0.1 M) at pH = 14.1, with a Pt foil as a counter and a Ag/AgCl as a reference electrode, measured at the scan rate of 20 mV s⁻¹ under Ar atmosphere. Light intensity, 505 mW cm⁻².

3/1 ratio. The use of a TiO₂ nanoporous film with deposited Pt did not show activity for the NH₃ photodecomposition. These results show that irradiation of the TiO₂ film by UV light created electrons and holes, the ammonia is oxidized by the holes to N₂ and protons, and then the electrons in the conduction band of the TiO₂ moved to the counter Pt electrode to reduce protons to H₂.

Ammonia was thus photochemically decomposed into H₂ and N₂ by using TiO₂-Pt in an aqueous solution, and this photocatalytic system was successfully applied to fabricate a photofuel cell, a new concept of fuel cell, by which NH₃ is used as a fuel assisted by photocatalysis to generate photocurrent as well as H₂ and N₂. The present photolysis of ammonia would not only lead to a future artificial solar nitrogen cycle, but also could lead to a future photofuel cell energy system using ammonia as an energy transporting and storing material.

Table 3 H₂ and N₂ generated during irradiation for 2 hours under similar conditions to those in Fig. 1 using 10 M NH₃ and 0.1 M KNO₃ aqueous solution (pH 14.1) under Ar or O₂ atmosphere. Light intensity, 505 mW cm⁻²

Atmosphere	H ₂ (μl)	N ₂ (μl)	H ₂ /N ₂ Molar ratio
Ar	568	220	2.6
O ₂	143	225	0.6

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