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Photodecomposition of ammonia to dinitrogen and dihydrogen on platinized TiO_2 nanoparticules in an aqueous solution

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Abstract

By using suspended platinized titanium dioxide (Pt-TiO_2) as a photocatalyst in an NH_3 aqueous solution, NH_3 was photodecomposed into H_2 and N_2. The amount of loaded Pt was changed between 0 and 2.0 wt% and the reaction was conducted under irradiation in an Ar atmosphere. In the Pt loading between 0 and 0.5 wt% the H_2 and N_2 evolution increased linearly with the Pt amount and the H_2/N_2 molar ratio was about 3:1. The evolution of H_2 and N_2 reached a maximum at 0.5 wt% Pt, and then decreased probably due to a filter effect by the Pt. The effect of pH on the photodecomposition of NH_3 in the presence of Pt-TiO_2 under Ar was investigated at pH from 0.68 to 13.7. The evolution of H_2 increased steeply at the pH from 9 to 10 showing that the dissociation of NH_4^+ to free NH_3 is important for the photodecomposition (pK_a of NH_4^+/NH_3 is 9.24). The time-course of H_2 and N_2 evolution in a 59 mM NH_3 aqueous solution during 53 h irradiation gave the photodecomposition yield of 21.6%. The effect of RuO_2 loading as a co-catalyst for the TiO_2 or Pt-TiO_2 was investigated showing that the RuO_2 does not work as a H^+ reduction catalyst. The activity of $SrTiO_3$ used instead of TiO_2 was only small, and the H_2/N_2 ratio (0.64) was very small showing that the Pt-$SrTiO_3$ is not a good photocatalyst to decompose NH_3. A TiO_2/FTO nanoporous film photoanode was used in combination with a Pt counter electrode instead of the Pt-TiO_2 photocatalyst, leading also to photodecomposition of NH_3 to produce H_2 and N_2 at 3:1 ratio.

Keywords: Nanoporous TiO_2; Ammonia; Photodecomposition; Nitrogen and hydrogen evolution

1. Introduction

The worldwide eutrophication on lands, in lakes and rivers is causing environmental problems such as species reduction [1,2]. For instance, the increase in nitrogen and phosphorus compounds in wastewater, including industrially discharged water, is creating serious eutrophication problems all over the world. In relevance to such eutrophication problems, the treatment of livestock waste is becoming more and more an important issue attracting a great deal of attention. Especially, nitrogen compounds contained in the livestock waste are difficult to treat for the purpose of discarding them into the environment, or recycling as useful compounds. Since nitrogen compounds can finally be converted to ammonia by enzymes such as urease in livestock wastes, if ammonia is converted to a harmless or even useful compound, it can solve the livestock waste problem concerning nitrogen. Similarly, treatment of NH_3-containing wastewater from many factories such as fertilizer, dye, metal-plating, semiconductor, and liquid crystal factories into harmless compound is very important to protect against environmental destruction. The ammonia contained in wastewater can be treated by either biological or artificial process. The biological process is composed of nitrification and denitrificaiton processes, by which ammonia can be converted finally into dinitrogen (N_2) gas via NO_2^- and NO_3^-. Among the biological processes the nitrification is a rate-determining slow process; such that the biological process requires a larger system, a longer time, and a higher cost than an artificial system such as catalytic decomposition. Recently, electrochemical treatment of wastewater is attracting attention because it is comparatively economical and the efficiency is high [1]. By using the electrochemical process, nitrogen can be converted into N_2 and nitrogen oxide.

TiO_2 photoanode was found to decompose water photoelectrochemically under UV light irradiation [3]. Since then, many organic and inorganic compounds have been decomposed by this

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photocatalyst [4–6]. Photodecomposition of ammonia has also been reported, but the products were not H_2/N_2. The photodecomposition of ammonia in water has been reported by using TiO_2-supported Pt or Pd catalyst, but N_2 and nitrogen oxides were obtained [7]. TiO_2/Pt decomposed aqueous ammonia at a low concentration (0.1 mM) into N_2, while pure TiO_2 decomposed NH_3 into nitrite and nitrate [8]. In these reports hydrogen formation was not reported. Some findings were reported on the photodecomposition of ammonia with TiO_2 in a gas phase [9,10]. However, to our knowledge, photochemical conversion of aqueous ammonia into H_2/N_2 has not been reported yet, except in our recent communication [11]. The present authors have found that an aqueous solution of ammonia can be converted photochemically into H_2/N_2 in a nearly stoichiometric 3:1 (H_2:N_2) molar ratio if reacted under alkaline conditions by using platinized titanium dioxide (Pt-TiO_2) suspension, showing that this photochemical reaction can not only treat the hazardous ammonia into harmless N_2 and H_2, but also produce H_2 capable of generating electricity with a fuel cell. Dinitrogen/dihydrogen production from NH_3 is also important, since ammonia is now attracting a great deal of attention as an energy storage material for H_2–O_2 fuel cells instead of H_2 that requires high pressure, large volume for stock, and safe supply system [12,13].

In our previous paper, we published for the first time the photodecomposition of an aqueous NH_3 solution into N_2 and H_2 under limited conditions. In the present paper, we investigated and report the details of the photodecomposition as follows: (1) in the Pt-loaded TiO_2 suspension system we investigated various reaction conditions such as various Pt amount loaded on TiO_2, dependence of N_2 and H_2 evolution on pH or reaction time, and the effect of co-catalyst on the photodecomposition. (2) In the photoelectrocatalytic system consisting of a TiO_2/FTO nanoporous film photoanode and a Pt counter electrode, we investigated the effect of Pt loading on TiO_2/FTO nanoporous film.

2. Experimental

2.1. Materials

Titanium oxide (ST-01, anatase 100%, average size 7 nm) was purchased from Ishihara Sangyo Co. Ltd., potassium chloroplatinate (K_2PtCl_6) from Mitsuwa Chemical Co. Ltd., and chloroplatinic acid (H_2PtCl_6) from Kishida Chemical Co. Ltd. Ammonia aqueous solution (30%) was from Kanto Chemical Co. Ltd., and Pt-black from Kojima Chemical Reagents, Inc. Ar gas with >99% purity was obtained from Nippon Sanso Corp. All the solutions were prepared using ion-exchanged and distilled water. All the chemicals were commercially available purest grade and used as received.

A Quartz cell was purchased from Mito Rika Glass Co. Ltd., a nonluminesent glass from Matsunami Glass Ind. Co. Ltd., and the reaction cell from Tokyo Glass Kikai Co. Ltd. The cell used for photolysis and analysis was a cylindrical shaped vessel (diameter 24 mm and height 48 mm with a volume of nearly 11 ml) made by Pyrex glass. The reaction solution was usually 5 ml for photolysis. The cell glass transmits the light over 300 nm wavelength.

2.2. Preparation of metallized TiO_2

Platinization of TiO_2 was carried out using a photodeposition method by irradiating (with a 200 W high-pressure mercury lamp) an aqueous suspension of TiO_2 (1.0 g/l) for 7 h in the presence of 1 M methanol and 0.1 mM potassium chloroplatinate (K_2PtCl_6). After irradiation, the filtered Pt/TiO_2 sample was collected and washed with distilled water. A RuO_2 (0.25–0.50 wt%)-loaded on TiO_2 was used also in the reaction. Loading of RuO_2 onto the powdered TiO_2 was conducted using a 1 ml of 1 wt% $RuCl_3$ (Aldrich) aqueous solution by adding to TiO_2 (1.0 g). After adsorbing the $RuCl_3$ onto TiO_2, it was oxidized in a muffle furnace at 500 °C for 1 h.

2.3. Preparation of nanoporous TiO_2 film

A nanoporous TiO_2 film was prepared by modifying the reported procedure for fabricating a dye-sensitized solar cell [14]. Twelve grams TiO_2 (P-25, received from Japan Aerosil Co. Ltd.) and acetylacetone (0.4 ml, Kishida Chemical Co. Ltd.) were mixed well in a mortar while adding 4 ml water slowly during 2 h. Triton X-100 (0.2 ml, Kishida Chemical Co. Ltd.) was added and the mixture was sonicated. This mixture was spin-coated (2000 rpm) on a FTO (fluorine-doped tin oxide) glass (2 cm × 1 cm, resistivity 9.0 $\Omega/\square$) for about 10 s to obtain 1 cm × 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 becomes 10 μm, and then the film was calcinated at 450 °C for 30 min.

2.4. Preparation of Pt loaded nanoporous TiO_2 film coated on FTO (Pt-TiO_2/FTO)

Platinization of nanoporous TiO_2 film (TiO_2/FTO) was carried out using an electrodeposition method in an aqueous solution consisting of 2 mM lead (II) acetate ($Pb(OCOCH_3)_2$) and 10 mM chloroplatinic acid (H_2PtCl_6) with a small amount of H_2SO_4. A three-electrodes system was fabricated with TiO_2/FTO as an anode, Ag/AgCl as a reference and Pt plate as a counter electrode, by which electrodeposition was carried out by galvanostat conditions at 30 mA cm^{-2}.

2.5. Photolysis and analysis

Neat or metallized TiO_2 suspensions were usually prepared in water at a concentration of 0.02 g/l. An NH_3 aqueous solution (16.5 M) was added to the suspensions to make the desired concentration (typically 0.59, 0.059 and 0.0059 M), and then the pH of the suspensions was adjusted by adding NaOH. The solution (5 ml) was purged with Ar gas for 30 min, and then the photoirradiation was carried out using a 500 W Xenon (Xe)-lamp with the light intensity from 469 to 515 mW cm^{-2} under magnetic stirring. A high-pressure Hg lamp was used for the Pt-$SrTiO_3$ system.

The cylindrical reactor was sealed with a rubber septum, through which the gas phase can be sampled out by a syringe. A sample aliquot of 100 μl gas was taken out with a 100 μl syringe for the analysis by a gas chromatograph. Analysis of the nitrogen and hydrogen gases evolved was carried out by using a gas chromatograph, Shimadzu GC4C-PT or GC-8A at 40 °C or 80 °C, respectively, with a 5 Å molecular sieve column using Ar carrier gas.

3. Results and discussion

The absorption and transmission of an aqueous ammonia and the cell glass were investigated and the results are shown in Fig. 1. The present Pyrex glass cell and a nonluminesent glass do not transmit the light below the wavelength of 300 nm. By using a quartz cell (transparent up to 200 nm), we have confirmed that a direct excitation of NH_3 caused some complicated and undesired side reactions, so that the evolution of both H_2 and N_2 gases did not occur. Therefore, we adopted the present Pyrex glass cell to avoid direct excitation of NH_3. When using a quartz cell, we can use a nonluminesent glass filter to inhibit direct excitation of NH_3 as shown in Fig. 1.

Our preliminary investigation has shown that an NH_3 aqueous solution can photochemically be decomposed into H_2 and N_2 gases by using suspended platinized titanium dioxide (Pt-TiO_2) if reacted at pH over 10, and that the evolved H_2/N_2 molar ratio was nearly stoichiometric value (3:1) [11]. By using the Pt-TiO_2 (0.02 g) as a photocatalyst in an NH_3 aqueous solution (0.59 M, 5 ml), the amount of loaded Pt was changed between 0 and 2.0 wt% and the reaction was conducted for 6 h under irradiation at pH 10.7 in an Ar atmosphere. The dependence of Pt amount/TiO_2 on the evolution of H_2 and N_2 gases is shown in Fig. 2. In the Pt amount between 0 and 0.5 wt% the H_2 and N_2 evolution increased linearly with the Pt amount and the H_2/N_2 molar ratio was nearly 3:1 except 0.1 wt% Pt amount giving H_2/N_2 ratio around 4. The evolution of H_2 and N_2 reached a maximum at 0.5 wt% Pt, and looks like to be roughly constant in between 0.75 and 1.2 wt% followed by clear decrease at 2.0 wt%. It means that the increase of Pt amount on TiO_2 causes both a promoting effect and an inhibiting effect (filter effect), so that these two effects are competitively working for the photodecomposition. The decrease is ascribable to the filter effect by the black-colored Pt loaded on TiO_2.

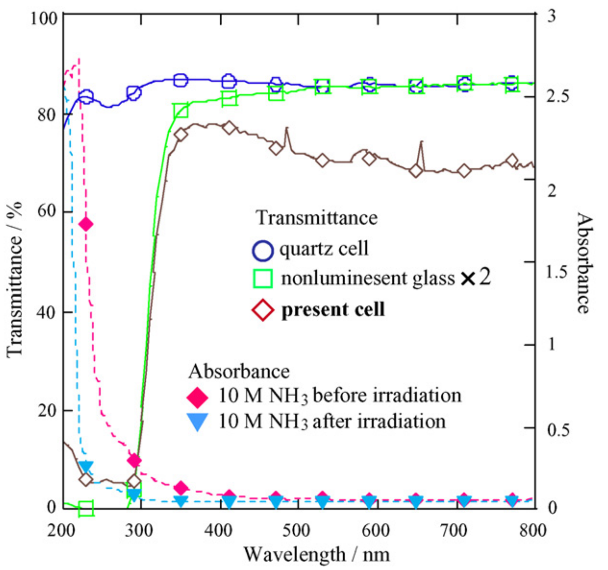

Fig. 1. Transmittance of various cell substances, and spectrum change of 10 M NH_3 aqueous solution by Xe lamp irradiation for 1 h (505 mW cm^{-2}).

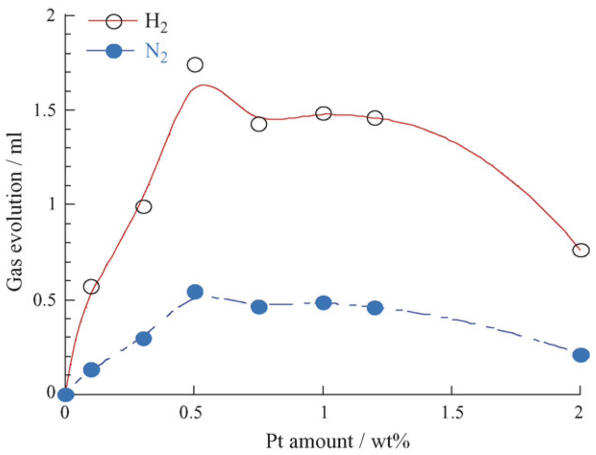

Fig. 2. Dependence of H_2 and N_2 evolution on Pt loading from 0.59 M NH_3 solution (5 ml) at pH 10.7, irradiated by Xe lamp (515 mW cm^{-2}).

The effect of pH on the photodecomposition of NH_3 (0.59 M of solution) in the presence of Pt-TiO_2 (Pt, 0.5 wt%) for 3 h under Ar is shown in Fig. 3. The photolysis experiments were carried out at pH from 0.68 to 13.7. The H_2/N_2 ratio observed was almost 3 in the pH region over 10. The decrease of the solution pH reduced remarkably the photodecomposition rate. The evolution of H_2 increased steeply at the pH from 9 to 10 showing that the dissociation of NH_4^+ to free NH_3 is important for the photodecomposition (pK_a of NH_3 is 9.24). The evolved H_2 and N_2 decreased over pH 11. As we mentioned later in Fig. 6, in the mechanism of NH_3 photodecomposition by irradiation on the Pt-TiO_2 powder system, the charge separation produces electrons (e^-) and holes (h^+) in the TiO_2 powder resulting in the oxidation of NH_3 by h^+ followed by the reduction of proton on

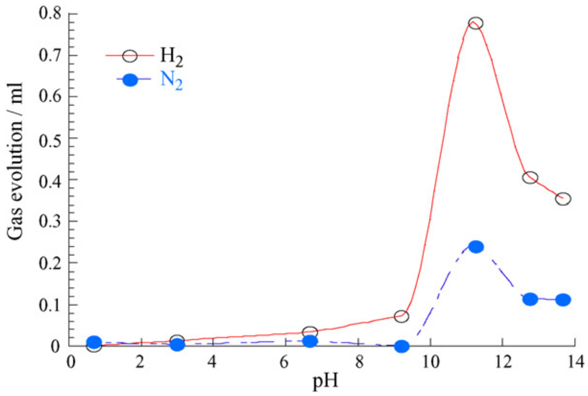

Fig. 3. Dependence of H_2 and N_2 evolution on pH from 0.59 M NH_3 solution (5 ml), irradiated by Xe lamp (515 mW cm^{-2}) for 3 h under Ar. 0.5 wt% Pt was loaded on TiO_2. pH below 9 was adjusted by adding HCl aqueous solution.

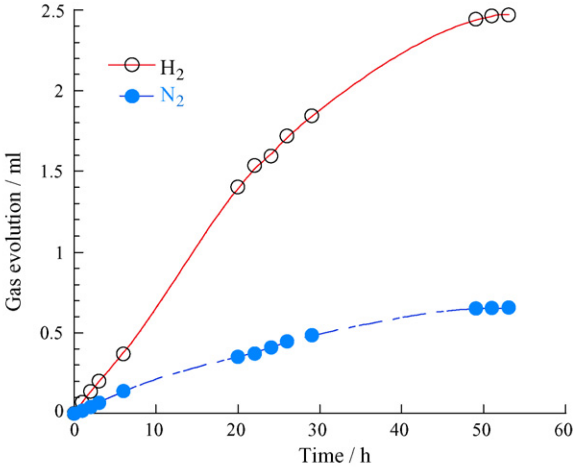

Fig. 4. Time-course of the volume of N_2 and H_2 gases in the photocatalytic reaction of NH_3 solution (59 mM, pH 11.9, 5 ml), irradiated by Xe lamp (469 mW cm^{-2}) under Ar. 1.0 wt% Pt was loaded on TiO_2 (0.02 g).

the Pt site. Since the proton concentration in the high pH region is low, the electrons would accumulate in the TiO_2 so that the possibility of recombination between electrons and holes would become high. As a consequence, the oxidation of NH_3 would be suppressed in high pH region.

The time-course of H_2 and N_2 evolution in an NH_3 solution (59 mM, pH 11.9) during 53 h irradiation in the presence of Pt-TiO_2 (1.0 wt% Pt) under Ar is shown in Fig. 4. The H_2/N_2 molar ratio was in the initial stage lower than 3/1, but in the later stage it tended to be constant with a slight excess of H_2 ($H_2/N_2 = 2.67$–4.11). In our earlier study [15] of water photodecomposition by using a platinized TiO_2 powder susupension, only H_2 was evolved without giving any oxidized product such as O_2 showing that the TiO_2 itself was oxidized. However, the oxidation of TiO_2 does not mean its dissolution. As we mentioned in the paper [15], we can ascribe the TiO_2 oxidation to the oxidation of Ti(IV) to Ti(V) in the nanoporous film. In the present photolysis of NH_3, such side reaction might also have taken place resulting in higher H_2/N_2 ratio. The decomposition yield of NH_3 (59 mM) was 21.6% after 53 h. The photochemical reaction yield depends on the number of the irradiated photon, so that if the number of photon is constant, the lower substrate concentration causes higher reaction yield. In suspension systems, it is impossible to measure the intensity of the really absorbed light, so that the quantum yield could not be determined. Instead of the quantum yield, the reaction yield based on all the incident photon numbers of the monochromatic light (340 nm) was estimated as 5.1%. The lower H_2/N_2 ratio in the initial stage could be ascribed to that the injected e^- would be consumed to occupy the electron trap sites, and hence the amount of H_2 evolution would be lower in the initial stage.

Because RuO_2 is known as an oxidation catalyst, we investigated its effect on the oxidation of NH_3 by using as a co-catalyst for the TiO_2 or Pt-TiO_2. Table 1 shows the effect of co-catalyst RuO_2 on the photochemical decomposition of NH_3 (0.59 M, pH 11.6) in a 8 h irradiation under Ar. For all the samples the N_2 evolved was similar, but the H_2 evolved was very different depending on the catalyst. For the standard photocatalyst of Pt-TiO_2, the H_2/N_2 molar ratio was 2.31, less than a stoichiometric value under this condition, which is ascribed to the reason mentioned above. For the photocatalyst of Pt-RuO_2-TiO_2, the N_2 evolved was similar as in the Pt-TiO_2 but the H_2/N_2 molar ratio was small (0.41). For the RuO_2-TiO_2, H_2 did not form. These results show that the RuO_2 cannot work as a H^+ reduction catalyst; the RuO_2 would be reduced by the electrons. Similar results were found in our earlier study of the decomposition of water in which the H_2 evolved by RuO_2-TiO_2 was much smaller than that by Pt-TiO_2 [15].

Table 1
Effect of ruthenium dioxide co-deposited on platinized TiO_2 for the photochemical H_2/N_2 evolution from 0.59 M NH_3 aqueous solution (5 ml, pH 11.6) by Pt-RuO_2-TiO_2 (0.03 g with 0.5 wt% Pt and 0.25 wt% RuO_2) and their blank experiments in 8 h under Ar, irradiated by Xe lamp through TND-30 neutral density filter (102 mW cm^{-2})

Photocatalyst	H_2 (μl)	N_2 (μl)	Molar ratio (H_2/N_2)
Pt-TiO_2	79.8	34.6	2.31
RuO_2[a]-TiO_2	0.1	31.9	0.003
Pt-RuO_2[a]-TiO_2	20.0	48.4	0.41

[a] RuO_2 content: 0.5 wt%.

The effect of other catalyst ($SrTiO_3$) on the photochemical decomposition of NH_3 (0.59 M, pH 11.9) by 6 h irradiation under Ar is shown in Table 2. In the Pt-$SrTiO_3$ system, the evolved H_2 and N_2 gases were much lower than those in the Pt-TiO_2, and the H_2/N_2 ratio (0.64) was very small. The band gap of TiO_2 and $SrTiO_3$ is 3.1 and 3.2 eV, respectively, and the bottom of the conduction band of the latter is slightly more negative than that of the former. For this reason, it is difficult to explain the difference of gas evolution between Pt-TiO_2 and Pt-$SrTiO_3$ by the band structure and redox potential. Therefore, we could infer that there is a difference of NH_3 adsorption between two semiconductors, or in the Pt-$SrTiO_3$ system, charge recombination might be easier after charge separation to inhibit the following reaction. It should be noted here that in dye-sensitized solar cells, $SrTiO_3$ does not give good performance.

The present Pt-TiO_2 phtocatalyst system was extended to a TiO_2 photoanode/Pt cathode photoelectorchemical system to photodecompose NH_3 as reported also in our earlier communication [11]. Now, we investigated the effect of Pt loaded on the nanoporous TiO_2 film/FTO photoanode on the photochemical decomposition of an NH_3 solution, and the results are shown in Table 3. In the case of using TiO_2/FTO as a photoanode and Pt as a cathode, the NH_3 photodecomposition takes place stoichiometrically. On the contrary, the same reaction does not easily

Table 2
Effect of platinized TiO_2 and $SrTiO_3$ (0.02 g with 1.0 wt% Pt) for the photochemical H_2/N_2 evolution from 0.59 M NH_3 aqueous solution (5 ml) and their blank experiments in 6 h under Ar, irradiated by high-pressure Hg lamp

Photocatalyst	pH	H_2 (μl)	N_2 (μl)	Molar ratio (H_2/N_2)
Pt-TiO_2	11.8	699.0	289.5	2.41
Pt-$SrTiO_3$[a]	11.8	5.6	23.8	0.24
Pt-$SrTiO_3$[b]	11.9	26.3	41.1	0.64

[a] Nanosize $SrTiO_3$.

[b] $SrTiO_3$ particle size < 10 μm.

Table 3
Effect of Pt loading on the TiO_2/FTO photoanode used with a Pt cathode for the photoelectrochemical H_2/N_2 evolution from 10 M NH_3 aqueous solution (5 ml, pH 14) in 2 h under Ar, irradiatied by Xe lamp (500 mW cm^{-2})

Electrode	H_2 (μl)	N_2 (μl)	Molar ratio (H_2/N_2)
TiO_2/FTO	194.1	63.0	3.08
Pt-TiO_2/FTO	16.2	13.4	1.21

occur in the case of using Pt-TiO_2/FTO as a photoanode. We can say that in the former case the oxidation and reduction take place on the anode and on the cathode, respectively. On the other hand, the photodecomposition in the latter case (Pt-TiO_2/FTO) does not easily occur mainly because both oxidation site (TiO_2) and reduction site (Pt) coexist in the same photoanode, which would make the photodecomposition difficult. It is difficult to clarify the reason because there can be various reasons such as the possibility of acceleration for e^-/h^+ recombination by the back conductive FTO, etc. Although the Pt-TiO_2/FTO should work as a photocatalyst by itself for the NH_3 decomposition without Pt cathode, such a film system is concluded to be unsuitable as a photocatalyst.

The mechanism of the NH_3 photodecomposition by irradiation on TiO_2 photoanode could be represented as Fig. 5. In the TiO_2 the photoinduced charge separation produces electron (e^-) in the conduction band and hole (h^+) in the valence band, and then the NH_3 molecule adsorbed on the TiO_2 reacts with h^+ to produce N_2 and proton (H^+) via some oxidized intermediate $(NH_3)ox$ (2). The electrons are transported to the Pt cathode via outer circuit, and then H^+ is reduced by the electrons there to produce H_2 (3 and 4), and so the total reaction is represented by Eq. (5).

$$TiO_2 + h\nu \rightarrow e^- + h^+ \qquad (1)$$

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

$$e^- + Pt \rightarrow Pt(e^-) \qquad (3)$$

$$6H^+ + 6Pt(e^-) \rightarrow 3H_2 + 6Pt \qquad (4)$$

$$2NH_3 \rightarrow N_2 + 3H_2 \qquad (5)$$

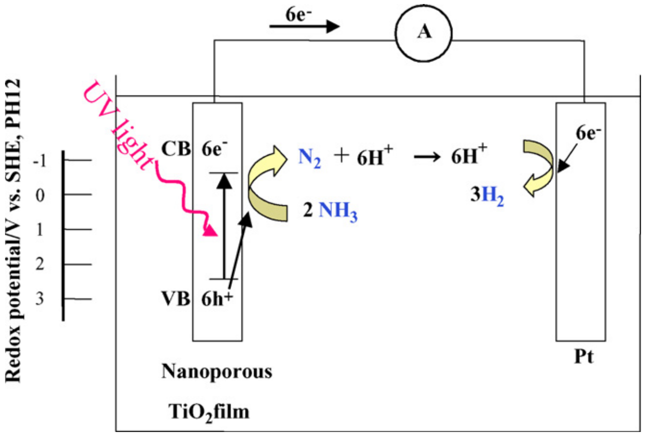

Fig. 5. Scheme of photodecomposition of ammonia on nanoporous TiO_2 film anode.

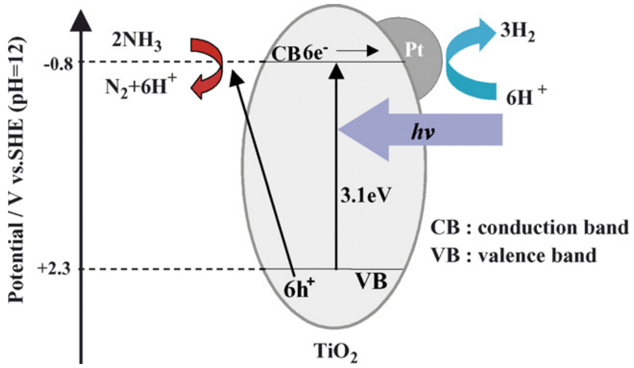

Fig. 6. Photochemical mechanism of NH_3 photodecomposition in the presence of Pt-TiO_2 suspension in water.

The structure of the $(NH_3)ox$ cannot be determined at present, but a possible candidate could be hydrazine or hydroxylamine.

Since free NH_3 is mainly active for the photodecomposition, the electron donation from the lone pair of the NH_3 to the electron-deficient TiO_2 site would be principally of importance rather than NH_3 adsorption onto the TiO_2 which should be much more favorable for the $NH_4{}^+$ than the free NH_3. The same mechanism can be applied to the Pt-TiO_2 powder system as shown in the Fig. 6.

4. Conclusions

Ammonia was thus photochemically decomposed into H_2 and N_2 by using Pt-TiO_2 powder suspension in an NH_3 aqueous solution. The highest evolution of both gases was obtained at pH about 11. It is necessary to keep pH over 10 for decomposing NH_3 solution. The H_2/N_2 molar ratios obtained were about 3/1 stoichiometric value. It was found that Pt amount loaded on TiO_2 gave the best result at 0.5 wt% loading for decomposition of NH_3. This photocatlyst was successfully applied to a noanoporous TiO_2 film photoanode/Pt cathode photoelectrochemical system, for which platinization of the TiO_2 film reduced drastically the photocatalytic activity. The present photolysis of ammonia could lead to a future artificial photochemical nitrogen cycle not only to convert biohazardous NH_3 into a safe N_2, but also to produce H_2 energy from NH_3.

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