Highly Efficient Photoelectrochemical Decomposition of Aqueous Ammonia by a Mesoporous TiO$_2$ Thin Film Closely Correlated with Evaporation

Masao Kaneko[a*], Rie Saito[b], Hirohito Ueno[a], Junichi Nemoto[a], Yuki Fujii[a], Akira Izuoka[b]

Abstract

UV light-activated and highly efficient photoelectrochemical decomposition of an aqueous ammonia to N$_2$ by a mesoporous TiO$_2$ thin film photoanode was investigated in relevance to ammonia evaporation. The cells fabricated were; (a) closed cell without ammonia trap, (b) closed cell with inside ammonia trap containing dilute aqueous H$_2$SO$_4$, (c and d) quasi-open cell connected with outside ammonia trap operated under air flow, and (e) open-air cell without ammonia trap. It was found that ammonia photodecomposition is closely correlated with its evaporation. The ratio of the photodecomposition/ evaporation and the external quantum (η, based on incident UV photons) and internal (η', based on activating photons) quantum efficiencies (QEs) for the photodecomposition were estimated. The activity order of the cells was; (a) < (b) < (c, d) ～ (e), supporting the importance of the cell structure. After subtracting evaporated ammonia, η exceeded 1 (= 100%) for the cell (c) with η' = 8, and η was 2.5 with η' = 18 for the cell (d). When air was bubbled into the open cell (e) by changing the flow rate, η' increased with the increase of the evaporation, but photodecomposition decreased after passing an optimum point (η' = 9.5), and finally stopped under higher air flow rate. Such strange behavior was interpreted by two conflicting factors. A positive factor would be either or both the efficient O$_2$ supply for the oxidative photodecomposition, or/and efficient transport of the product N$_2$ from water phase into air by increasing the air flow rate, shifting the equilibrium towards the product. A negative factor under high air flow rate could be quenching of intermediate radical species by excess supply of O$_2$ working as a radical scavenger.

Key Words : mesoporous titanium dioxide thin film / O$_2$-reducing cathode/ photodecomposition / ammonia aqueous solution / ammonia evaporation / quantum efficiency

1. Introduction

Photoelectrochemical reactions at semiconductor electrodes were investigated from before 1960s [1-3], and a crystalline n-TiO$_2$ photoanode to decompose water by UV light attracted a great attention [4]. Organic compounds have also been decomposed [5,6]. A nanoporous TiO$_2$ thin film was applied to a dye-sensitized solar cell (DSSC)[7] in which a nanoporous TiO$_2$ film works in an organic liquid electrolytes solution while working as an electron acceptor and conductor rather than as a liquid-junction semiconductor. The photoreactivity of a nanoporous TiO$_2$ film has been an important issue towards applications in an aqueous phase.

As an application powders and coatings of semiconductors were used to photodecompose and clean environmental pollutants and dirty materials [8]. Since such so-called photocatalyst powders have to be adsorbed or coated onto a proper carrier material for practical use, their photocatalytic activity has not been high (usually limited to photodecompose less than 100 to 1000 ppm pollutants) due to the hindrance against UV irradiation on TiO$_2$ by the carrier materials as well as by the wastes. It has been not easy for conventional powder-based-photocatalysts utilizing only UV-light to clean a large volume of highly concentrated and colored pollutant solution due to the strong absorption of UV light by the carrier, solutes and solid suspensions. In order to increase

*a   The Institute of Biophotochemonics Co.Ltd.
  (2-1-1 Bunkyo, Mito, Ibaraki 310-8512, Japan,
  e-mail：kaneko@biophotochem.co.jp
*b   Faculty of Science, Ibaraki University
  (2-1-1 Bunkyo, Mito, Ibaraki 310-8512, Japan)
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photocatalyst's activity, narrow bandgap semiconductors capable of using visible light have been developed and achieved some success, but still the activity is not satisfactory enough.

Environmental pollution by biowastes is becoming more and more a serious issue [9], and among the pollutants, concentrated ammonia is one of the most serious industrial and biomass wastes, since ammonia is the second largest chemical products in the world. Moreover, livestock wastes such as pig urine that is quickly converted to ammonia by urease abundant in nature are also serious pollutants. The present authors reported a Biophotochemical Cell (BPCC) composed of a nanoporous semiconductor photoanode such as TiO_2 and an O_2-reducing cathode that can photocatalytically decompose biomass and its wastes in water [10-13]. In the BPCC a nanoporous semiconductor thin film is exposed directly to the incident light, so that irradiation hindrance by concentrated solutes, colored compounds and suspended solids is almost negligible. We succeeded in remarkably enhancing the BPCC activity for ammonia photodecomposition with a nanoporous TiO_2 film photoanode attaining high internal quantum efficiency (QE based on activating phtons) over 10 ($=10^3$%), exhibiting that the major decomposition of ammonia takes place by O_2 oxidation of the UV-activated NH_3 by a kind of chain auto-oxidation mechanism [14,15], which enabled photodecomposition of concentrated NH_3 pollutants over 10^4 ppm. It should be noted that NH_3 oxidation with O_2 is an exergic process allowing in principle spontaneous reaction, but activation is actually needed like combustion of fuels. In our ammonia photodecomposition system UV-photon is used to activate NH_3, and afterwards auto-oxidative chain reaction, a kind of combustion, takes place in water to produce N_2 with high efficiency. In this system, the activating UV photon can be regarded as a "lighter" or "igniter". It is also important to add here that our oxidative ammonia photodecomposition produces mainly N_2 and not nitrogen oxides. Nitrogen oxides are serious pollutants, but many of oxidative ammonia decomposition systems produce nitrogen oxides. Since ammonia gas is inflammable, i.e., combustible, it is usually oxidatively decomposed by combustion with O_2 under air producing nitrogen oxides as N products.

Photodecomposition of other electron-donating compounds such as agricultural wastes [14], ethanol [16], etc. is also an important relevant research area.

In our further investigations an interesting phenomenon was found that the present photoelectrochemical decomposition of aqueous ammonia and its physicochemical evaporation are closely correlated. Since it is of importance to study ammonia evaporation with respect to its photodecomposition, the correlation was investigated and the first results will be reported here.

2. Experimental

2.1. Materials

Ti-nanoxide T/SP (average particle size, 13nm; surface area, $\sim$ 120 m^2g^{-1}, anatase > 90%) was purchased from Solaronix Co. Ltd. Lead acetate trihydrate (purity > 99.0%) and hydrogen hexachloroplatinate (IV) hexahydrate (purity > 98.5%) were from Wako Pure Chemical Co. Ltd. F-doped SnO_2 conductive glass (FTO, surface resistance 10Ω/ (sq)) was purchased from AGC Fabritec Co. Ltd.,Japan. As for the sample solution, an ammonia aqueous solution (the highest concentration is 28.0 % NH_3) was used.

2.2. Electrode preparation

A nanoporous TiO_2 film coated on an FTO electrode (FTO/TiO_2) was prepared with Ti-nanoxide T/SP paste as before by a squeeze coating method, for which an adhesive tape (thickness about $70\mu m$) was used as a spacer to adjust the TiO_2 film thickness obtained after calcinations [17]. The TiO_2 film was at first dried at 100 ℃ for 30 min and then calcined at 450℃ for 30min giving about $10\mu m$ thick film the roughness factor of which was nearly 10^3 with respect to the apparent surface area. An O_2 reduction cathode connected with a TiO_2 photoanode was either a Pt-black-coated Pt foil (1cm x 1cm), or a stainless steel mesh (100mesh, size 2 cm x 2cm or 5cm x 5 cm) coated at first by a thin layer of Nafion (cation exchange resin composed of sulfonated perfluoroalokyl polymer) and Pt black was electrodeposited thereafter from hydrogen hexachloroplatinate (IV) hexahydrate (designated as SUS mesh/Pt-black).

2.3. Cell design and fabrication (Fig.1 (a) ～ (e))

A closed cell (Fig.1 (a), volume 60 mL) was used to detect and analyze N_2 formation by ammonia photodecomposition. The product gas was sampled out from the top of the cell to analyze by a gas chromatograph. In order to investigate the amount of evaporated ammonia, an airtight photoelectrochemical reaction cell (60mL) was fabricated installing 2cm x 2cm area TiO_2 thin film coated on FTO and SUS mesh cathode (1cm x 1cm) coated with Pt-black. The cell installing inside an ammonia trap (see Fig. 1 (b)) contains a tube involving 9 mL of 0.1 M H_2SO_4 (pH 0.8) to trap the evaporated ammonia as

ammonium sulfate; it was confirmed that the evaporated ammonia can be trapped quantitatively. The same size cell (60mL) was connected by using a plastic tube with a same size cell for ammonia trap containing 50 mL of 0.4 M H_2SO_4 (pH 0.4) (see Fig.1 (c)), and air (or O_2) was bubbled into the aqueous ammonia solution from the top of the photoreaction cell at a constant flow rate, and the introduced air (or O_2) was transported to the ammonia trap and then exit into the open air. This type cell is regarded as a quasi-open cell, by which evaporated ammonia can be trapped quantitatively, but the product gas (N_2) escapes into open air with the introduced air (or O_2).

In order that this quasi-open cell resembles the open-air cell (sample volume = 250mL) shown later as (e), two larger bottles of 500mL were connected instead of the cells (60mL) in (c) by using a plastic tube (see Fig. 1 (d)), one bottle for photodecomposition, and another for ammonia trap. The gas phase above the aqueous ammonia sample solution is 250mL, much larger volume than that of the cell (c) (20mL). The cell (e) was used for photodecomposition under open air as reported earlier by us [14,15,18], by which formed N_2 can escape into air easily shifting the equilibrium between starting ammonia and product N_2 towards N_2. For this cell (e) ammonia was easily evaporated. An FTO anode was 5 cm x 5 cm = 25 cm^2, combined with a Pt-black coated SUS-mesh cathode (5 cm x 5 cm = 25 cm^2); this cell (e) was used with magnetic stirring under open air.

2.4. Irradiation and measurements

The UV-A region light intensity was measured by a UV light meter (model UV-340, CUSTOM Co. Ltd.). The TiO$_2$ film was irradiated at 100mWcm^{-2} white light with a 500W xenon lamp through an IR-cutoff filter (HA-50), which contained UV-A (290-390nm) region light with the intensity of 3.5 mWcm^{-2} (1 sun condition), 5.0 mWcm^{-2} or 10 mWcm^{-2}. The incident photon (on the FTO) to current conversion efficiency (IPCE) was measured by the Fig. 1 (a) type photoelectrochemical reaction cell under irradiation by monochromatic light using a Shimadzu-Bausch & Lomb monochrometer.

The N_2 formed in the closed cylindrical cell (Fig.1 (a) and (b)) was analyzed by a gas chromatograph (Shimadzu, GC-8A and GC-2014) with a molecular sieve 5A column at 30℃ using Ar carrier gas. All the photoelectrochemical reactions were performed at the room temperature 25℃. NH_4^+, NO_2^- and NO_3^- were analyzed by a DR2800 analyzer from Hach Company, USA.
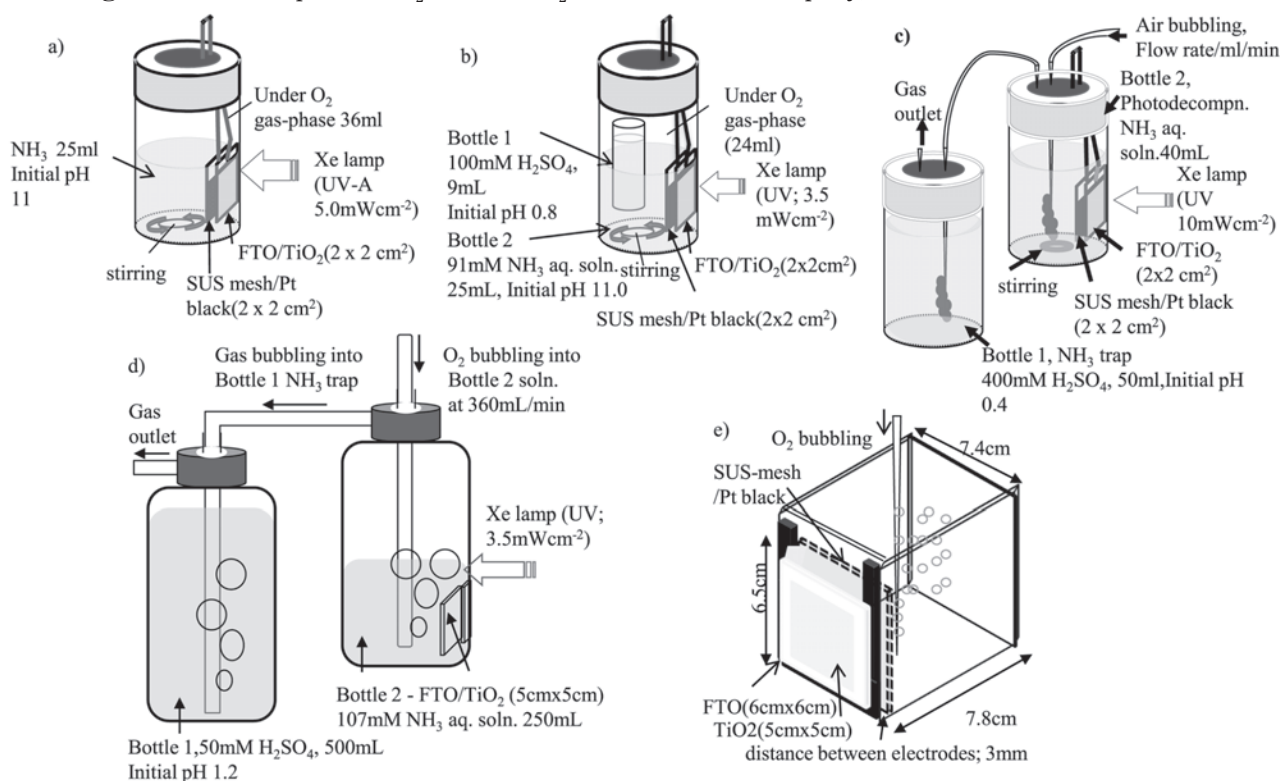

Fig.1 Cells for the photodecomposition:
a) Closed cell (60mL) for gaseous products analysis operated under 1 atm O_2
b) Closed cell (60mL) with an inside NH_3 trap tube (10mL) containing dilute H_2SO_4 aq.soln. operated under 1 atm O_2.
c) Quasi-open cell (60mL) with an ammonia trap (60mL) containing dilute H_2SO_4 aq.soln. operated under air flow.
d) Quasi-open cell (250mL) with an ammonia trap (250mL) containing dilute H_2SO_4 aq.soln. operated under air flow.
e) Open cell (250mL) operated under air.

During the photoelectrochemical reactions, time dependence of the short circuit photocurrent was measured by a potentiostat/galvanostat (HA-301, Hokuto Denko), a function generator (HB-104, Hokuto Denko) and a coulomb/amperehour meter (HF-201, Hokuto Denko).

3. Results and Discussion

Photoelectrochemical decomposition of ammonia has been investigated in a BPCC composed of a nanoporous semiconductor photoanode and an O_2-reducing cathode producing mainly N_2 with a small amount of NO_2^- and NO_3^- [10-13]. The product (N_2) was analyzed by conducting the decomposition using a closed cell under 1 atom O_2, but in a closed cell the photodecomposition efficiency was not high, the internal quantum efficiency ($=\eta'=$ number of NH_3 decomposition per activating UV photon number) having been usually only 1. It should be noted here that when one ammonia molecule was decomposed to N_2, the number of decomposition is 3. When the photodecomposition was conducted in an open cell under aerobic conditions, the decomposition numbers were determined by the decreased ammonia due to the open cell system. With this open air cell, NH_3 evaporation blank was estimated by measuring the decreased ammonia under dark conditions amounting to 10 to 15 % of the total decreased ammonia under irradiated conditions under which photodecomposition takes place. However, it was found thereafter that evaporated ammonia amount is higher when the photodecomposition is conducted under irradiation (without TiO_2) by which ammonia photodecomposition does not occur but only evaporation occurs. Interestingly, it was further found that photochemical ammonia decomposition and its physicochemical evaporation are closely correlated, so that the following experiments were conducted.

3.1 Determination of evaporated ammonia and quantum efficiency in an open cell (Fig.1 (e)):

As mentioned before, the efficiency of ammonia photodecomposition was not high in a closed cell system probably due to the inefficient transportation of formed N_2, we have carried out such photodecomposition in an open cell shown in Fig. 1 (e) [15,18].

In such open-air systems ammonia evaporation is a problem, which should be determined exactly, but it has not been easy to determine evaporated ammonia. We have therefore conducted blank experiment by which photodecomposition does not occur, but evaporation takes place. At first

evaporated ammonia was measured by the decreased amount of ammonia in the cell simply by switching off the irradiation; evaporated ammonia was not large, only around 10% of the photodecomposed ammonia. However, in further experiments it was found that, due to the liquid temperature increase by the irradiation, the ammonia evaporation is much more during irradiation. Therefore, evaporated ammonia blank was measured during irradiation without TiO_2 film using only FTO glass by which photodecomposition does not occur.

Photodecomposition (Photodecomp.) and evaporation (Evaporn.) of aqueous ammonia in an open-air photoelectrochemical cell (Fig. 1 (e)) comprising only a mesoporous TiO_2 photoanode (or with Pt cathode) were measured for 6 h under irradiation of 5 mWcm^{-2} (UV-A region) with magnetic stirring under ambient air, and the results are shown in Table 1.

In a conventional photochemistry, blank experiment should usually be conducted without irradiation while keeping other conditions the same as those under irradiation since changing other conditions can bring about some other unexpected effects on the whole process. Therefore, we have adopted simply dark conditions to measure evaporation as shown in Table 1. Evaporation was measured by two kinds of blank experiments : one is without irradiation (under dark) with TiO_2, and another is under irradiation without TiO_2 using only FTO as shown in the upper part of Table 1. For measuring blank ammonia evaporation in the present paper, we adopted two systems for the photodecomposition; one is with TiO_2 photoanode plus Pt-cathode, and another is with only a TiO_2 photoanode. Photodecomposition after subtraction blank ammonia evaporation was much more efficient with TiO_2/Pt-cathode (60% NH_3 decrease by photodecomposition) than that with only TiO_2 (33% NH_3 decrease by photodecomposition). Blank evaporation under dark conditions was 6 % (this value is the same for both the systems), resulting in that the ratio of Photodecomposition/Evaporation is 10 for the TiO_2 anode /Pt-cathode system, and 5.5 without Pt-cathode. These results show that, even though evaporation is not very few, the major process is still photodecomposition.

However, the situation was quite different for the blank evaporation measured without TiO_2 using only FTO while keeping irradiation, as shown in the lower part of Table 1. The ratio of photodecomposition/evaporation was 1.2 showing that evaporation takes place nearly the same as the photodecomposition, which is ascribed to temperature increase to 28 ~ 29℃ under

irradiation. It should be noted here that temperature increase under irradiation without TiO_2 was a little bit higher $(1 \sim 2℃)$ than that under irradiated photodecomposition conditions using TiO_2 since TiO_2 absorbs and scatters some part UV-light irradiated, so that ammonia evaporation can be overestimated under irradiated conditions. In spite of this problem we have to be careful of course that ammonia evaporation is not negligible for the photodecomposition when considering the low ratio of the photodecomposition/evaporation nearly 1.2 even if the ammonia evaporation is overestimated. It is important to add that, even if evaporation takes place to considerable extent accompanying photodecomposition, collection and circulation of the evaporated ammonia to repeat photodecomposition are not difficult by using for example a dilute aqueous H_2SO_4 trap.

We have reported that ammonia photodecomposition in our system proceeds at high quantum efficiencies [14,15,18]. At first quantum efficiencies are briefly summarized as follows. The external $(=$ overall$)$ quantum efficiency (QE) $(=$ $\eta)$, quantum efficiency of the decomposition number based on the total incident UV photon number, was obtained by the eq. (1). The internal quantum efficiency for the decomposition $(= \eta')$ is designated as the quantum efficiency for the decomposition against photon numbers activating ammonia $(eq.$ $(2))$. In the present Biophotochemical Cell $(BPCC)$, since the TiO_2 thin film forms a clear Schottky-type junction with an aqueous ammonia solution, the e^- passed through the external circuit can be regarded nearly equal to the amount of the h^+ used effectively for ammonia activation at TiO_2 [14,15].

Therefore, when IPCE is defined to be incident photon-to-current efficiency, η is equal to η' x IPCE, which leads to the eq.2.

External quantum efficiency, $\eta =$
decomposed mol of ammonia x number of electron involved in one molecular decomposition / total incident UV photon mol (1)

Internal quantum efficiency, $\eta' =$
decomposed mol of ammonia x number of electron involved in one molecular decomposition / photon number in mol effectively used for activating ammonia $= \eta$ / IPCE (2)

The QE's of an aqueous ammonia photodecomposition were investigated by subtracting evaporated ammonia while changing the blank evaporation conditions. In the Table 1 when Pt was used in addition to the TiO_2 photoanode, the external QE $(\eta) = 8.08$ $(=808\%)$, and the internal QE $(\eta') = 59.0$ was calculated by measuring photocurrent to give IPCE $= 0.137$ [18], high η' value even after subtracting the evaporated blank ammonia, which was interpreted by the chain oxidative decomposition of the ammonia intermediates formed by activation with holes formed on the TiO_2 by UV excitation [18]. When Pt cathode was not used, the efficiency of photodecomposition was less than that with Pt cathode, so that QE values $(\eta = 4.42$ and $\eta' = 32.3)$ were about half of those in the presence of Pt cathode, but still high QE values for the photodecomposition.

When blank experiment was conducted during irradiation without TiO_2, by which ammonia photodecomposition does not take place, blank ammonia evaporation (18%) was nearly the same

Table 1 photodecomposition (Photodecomp.), evaporation (Evaporn.) and quantum efficiencies (QE) of aqueous ammonia in an open-type photoelectrochemical cell (Fig. 1 (e), 250mL) comprising only a mesoporous TiO_2 photoanode (or with Pt cathode), for 6 h under irradiation of 5mWcm^{-2} (UV-A region) with magnetic stirring under ambient air. Evaporated ammonia was estimated from the total ammonia decrease in the cell and the blank ammonia decrease either under dark (with TiO_2) or irradiation (without TiO_2). Note, NH$_3$1000ppm=58.8mM, IPCE=0.137.

Init.NH$_3$ conc./ppm	Conditions	TiO$_2$ photoanode	Irradi- ation	NH$_3$ Decrease /%	Net photodecomp. /%	Photodecomp. /Evaporn. ratio	QE/ External η	QE/ Internal η'	Note
2.4x1000 (141mM)	Photo- decomp.+ Evaporn.	Yes (with Pt cathode)	Yes	66	60 (21.2mmol)	10	8.08	59.0	Evaporn.(Blank) measured under dark with TiO$_2$
		Yes	Yes	39	33 (11.6mmol)	5.5	4.42	32.3	η=8.08 means 808%
	Evaporn. (Blank)	Yes	No	6	-	-	-		
1.1x1000 (64.7mM)	Photo- decomp.+ Evaporn.	Yes	Yes	39	21 (3.4mmol)	>1.2	>1.30	>9.5	Evaporn.(Blank) Measured under irradian. without TiO$_2$ (Evapn. may be overestimated)
	Evaporn. (Blank)	No (only FTO)	Yes	18	-	-	-		

as the photodecomposition (21%), the QE's for the photodecomposition being $\eta > 1.30$ and $\eta' > 9.5$ (lower part of Table 1).
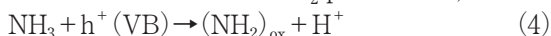
3.2 Determination of quantum efficiency in closed cells (Fig.1 (a) and (b)) :

As mentioned before, the internal quantum efficiency (η') of ammonia photodecomposition was not high in a closed cell system. This could be ascribed to the dynamic equilibrium of the ammonia photodecomposition represented by the eqs. (3) $\sim$ (7), i.e., since the photodecomposition should be in an dynamic equilibrium state, it would be important to shift this equilibrium to the right side by transporting the produced N_2 into the gas phase (see eq. (8)).
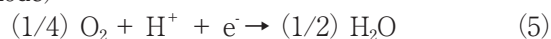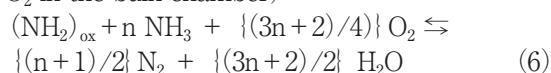
(At photoanode, Excitation of TiO_2) :
$$TiO_2 + UV\text{-light} \rightarrow e^-(CB) + h^+(VB) \qquad (3)$$
(Activation of ammonia at TiO_2 photoanode) :
$$NH_3 + h^+(VB) \rightarrow (NH_2)_{ox} + H^+ \qquad (4)$$
(O_2 reduction at Pt cathode; at TiO_2 without Pt cathode) :
$$(1/4)\ O_2 + H^+ + e^- \rightarrow (1/2)\ H_2O \qquad (5)$$
(Auto-oxidative chain reaction of $(NH_2)_{ox}$ with NH_3 and O_2 in the bulk chamber) :
$$(NH_2)_{ox} + n\ NH_3 + \{(3n+2)/4)\}\ O_2 \leftrightarrows$$
$$\{(n+1)/2\}\ N_2 + \{(3n+2)/2\}\ H_2O \qquad (6)$$
(Overall photodecomposition process) :
$$2\ NH_3 + 3/2\ O_2\ (\text{in } H_2O) \leftrightarrows (N_2)_{aq} + 3\ H_2O \qquad (7)$$
(Transport of formed N_2 from aqueous solution into air) :
$$(N_2)_{aq} \leftrightarrows (N_2)_{air} \qquad (8)$$
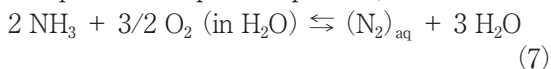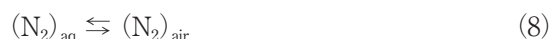
If these processes were conducted in a closed system, it would be difficult to shift the equilibrium of the eq. (8) to the right side since the main product N_2 is accumulated inside the closed cell. However, in order to avoid the ammonia evaporation problem, closed cells (Fig.1 (a) and (b)) were adopted now, and it was tried to increase and determine η' values based on the formed N_2.

A 93mM (1600 ppm) ammonia aqueous solution (25mL, pH = 11) was photodecomposed by using an FTO/TiO_2 thin film (2x2 = 4cm^2) and a SUS mesh/Pt-black (2x2 = 4cm^2) in a 60mL cylindrical cell (60mL) (Fig.1 (a)) under 1 atm O_2 and 5mW cm^{-2} UV-light intensity with magnetic stirring. After 24 h 28.5% ammonia was decomposed to N_2, which corresponds to external quantum efficiency (η = number of decomposition based on the total incident UV light) of 0.39 (=39%) (Table 2), fairly high for this type of photocatalysis. In this photodecomposition system it was measured by another experiment that IPCE (= incident photon-to-photocurrent conversion efficiency) is 0.137, so

that internal quantum efficiency (η'), represented by $\eta' = \eta$/IPCE, was calculated to be 2.8 (Exp.1 in Table 2). Although this efficiency is not high in comparison to those obtained in an open cell system mentioned in Table 1, this value of nearly 3 demonstrates that when ammonia was activated by one photon, the activated ammonia can undergo at least further two-electrons oxidation by O_2 (dark process) present in the liquid to be decomposed finally to N_2 that is totally a six-electrons process for two ammonia molecules by using two UV photons.

In a same closed cell (60mL), it was tried to trap the evaporated ammonia in a small bottle containing an acidic sulfate aqueous solution (9 mL) put inside the cell (see Fig. 1 (b)), and QE was measured for the photodecomposition of a 93mM ammonia aqueous solution (25mL) for 6 h at the 3.5 mA cm^{-2} irradiance under the same conditions as the above. The η and η' values were 0.65 and 4.8 (Exp.3 in Table 2), respectively, exhibiting clearly that another ammonia molecule is also activated when one ammonia molecule is activated.

3.3. Determination of quantum efficiency in quasi open cells (Fig.1 (c) and (d)) :

In order to measure the amount of evaporated ammonia, quasi-open cells were fabricated and used that can trap evaporated ammonia as shown in Fig. 1 (c) and (d). In these cell systems two cells (either 60 mL or 500 mL volume) are connected by a plastic tube and the whole system was made airtight; one cell (Bottle 2) for photochemical ammonia decomposition and another cell (Bottle 1) containing dilute hydrogen sulfate aqueous solution (0.4 M in 50 mL or 0.05M in 500 mL) for trapping evaporated ammonia. Air was bubbled into the aqueous ammonia solution and the evaporated ammonia was introduced into the Bottle 1 to trap ammonia. It should be noted that the gas phase between the Bottles 2 and 1 is not open to ambient air but closed, so that the cells are a kind of quasi-open systems

At first it was confirmed by using only an aqueous ammonia solution without TiO_2 that evaporated ammonia can be trapped quantitatively in the Bottle 1 in both the cells (c) and (d). A 162mM (2750 ppm, pH 11.5) ammonia aqueous solution was photodecomposed in the cell (c) by using a TiO_2 photoanode and a Pt cathode under air bubbling and magnetic stirring for 3 h. In this cell the amount of blank evaporated ammonia can be determined quantitatively from the decreased amount of ammonia in the photodecomposition bottle 2 under the irradiated conditions without TiO_2. The photodecomposed ammonia can then be estimated under the irradiated conditions with TiO_2, by subtracting the evaporated ammonia as well as a small amount of formed NO_2^-

and NO_3^- from the decreased ammonia in the Bottle 2. The η and η' values for the photodecomposition were 1.1 and 8.0 (Exp.5 in Table 2), respectively, the efficiency being nearly the same as the Exp.4 using a closed cell (b). It should be noted that the amount of evaporated ammonia was fairly high for the cells (b) and (c), the ratio of Photodecomposition / Evaporation being 0.22 ～ 0.56.

In order to try to increase the quantum efficiency in the quasi-open cell system, the cell volume and the sample volume were increased in the cell (d) about 4 times those of the cell (c). An aqueous ammonia (107 mM, 250 mL) was photodecomposed in the cell (d), and the results are shown as Exp.6 in Table 2. By using this quasi-open cell (d), the η and η' values for the photodecomposition were 2.5 and 18, more than twice enhanced than those of the cell (c) (Exp.5). The η' value of 18 means that once ammonia was activated by one UV photon, 18 times dark decomposition takes place, i.e., 6 molecules of ammonia are decomposed by one photon activation, showing that dark decomposition of ammonia to N_2 represented by the eq. (6) is the major process for the photodecomposition. This result shows also that, in spite of the photodecomposition process for which the reaction rate should be limited by the incident photon numbers, the reaction can be applied to a much large scale cell since dark reaction is the major process as reported previously [18] .

In the last column of Table 2 the results of open cell system (e) was added by citing from Table 1 for comparison purpose. It is not the aim of this table to compare and discuss detailed reaction conditions affecting the photoreactivity, but the results of Table 2 can be summarized as follows :
1) The cell becomes more efficient for the photodecomposition in the order of the cells;
[closed (a) < closed with inside NH_3 trap (b) < quasi-open with outside NH_3 trap (c,d) ～ open-air (e)]

It would not be adequate to give a final conclusion from the above results, but, since ammonia evaporation increases roughly with this photodecomposition order, it is suggested that ammonia evaporation might be an important factor for conducting photodecomposition. This will be investigated and discussed in the next section 3.4.
2) The external QE (η) can exceed 1 (= 100%) for the cells b ～ e, and internal QE (η') exceeds 18 for the cell (d) showing that dark oxidation of a photo-activated ammonia to N_2 is the major process for the present ammonia photodecomposition process.

3.4 Effect of air flow rate in ammonia photodecomposition and evaporation -Correlation between photochemical decomposition and physicochemical evaporation-

Based on the results of the last section for the quasi-open cells (c) and (d), the air (or O_2) flow

Table 2 Quantum efficiencies of ammonia photodecomposition dependent on evaporation using FTO/TiO$_2$ photoanode and SUS-mesh/P-black cathode (each area, 2cmx2cm=4cm^2 for Exp.1~4, and 5cmx5cm=25cm^2 for Exp.6 and 7) with various cells a ～ e in Fig.1. UV-A light intensity = 3.5, 5 or 10 mWcm^{-2}. Evaporation was measured under irradiation without FTO/TiO$_2$ photoanode. Quantum efficiencies (QE's) are external (η) and internal (η') ones.

Exp	Cell in Fig.1 (Structure)	Soln.mL (Conc.M)	React.time/h (UV intensity)	Init. NH$_3$ /mmol	Products / mmol			Evaporated NH$_3$ /mmol	Photo Decomp /Evaprn	QE/—		Note
					N$_2$-N	NO$_3^-$	NO$_2^-$			η	η'	
1	a (Closed,O$_2$)	25 mL (93mM)	24 (5.0mWcm^{-2})	2.33	0.66	0.087	0.067	Not measured	-	0.39	2.8	
2	b (Closed with inside NH$_3$ trap, under O$_2$ or air)	25 mL (91mM)	6 (3.5mWcm^{-2})	2.27	0.14	0.016	0.040	0.25	0.56	0.48	3.5	Under O$_2$
3		20 mL (197mM)	6 (3.5mWcm^{-2})	3.94	0.19	0.019	0.047	0.85	0.22	0.65	4.8	Under O$_2$
4		20 mL (190mM)	6 (3.5mWcm^{-2})	3.80	0.29	0.005	0.010	0.91	0.32	1.0	7.3	Under air
5	c (Outside NH$_3$ trap, air flow 40 mL min^{-1})	40 mL (162mM)	3 (10 mWcm^{-2})	6.46	0.44	0.007	0.005	0.83	0.53	1.1	8.0	From N$_2$ peak in Fig.3
6	d (Outside NH$_3$ trap,O$_2$ flow 360 mL min^{-1})	250 mL (107mM)	6 (3.5mWcm^{-2})	26.7	4.34	0	0.118	6.44	0.67	2.5	18	Without Pt cathode
7	e (Open air)	250 mL (63.0mM)	6 (5.0 mWcm^{-2})	15.8	3.32	-	-	< 2.8	>1.2	>1.3	>9 .5	From Table1

rate must be an important factor for the photodecomposition and evaporation. Therefore, by changing the air flow rate from 20 to 160 ml min^{-1} in the cell (c) with the same conditions as the Exp.5 in Table 2, the photodecomposition and evaporation of ammonia were measured and the results are shown in Fig. 2. Since minor amounts of NO_2^- and NO_3^- were also formed as decomposition products (e.g., 0.81 ～ 0.42% and 0.74 ～ 0.18% of the initial ammonia, respectively), so that these values were also subtracted from the reduced ammonia to estimate net produced N_2. The estimated conversion to N_2 (% based on the initial NH_3 concentration) and the evaporated ammonia (%) were plotted against the air flow rate in this Fig.2.

It would be a natural consequence that the evaporated ammonia increased with the increase of the air flow rate. However, it is important that the ammonia photodecomposition to N_2 at first increased with the flow rate, but after passing a maximum point at 40 mL min^{-1}, it decreased gradually with the flow rate increase. The first rise of the photodecomposition to N_2 in accord with the ammonia evaporation was expected from the results of Table 2. However, the latter suppression of ammonia photodecomposition was not expected. An explanation for this behavior could be given and summarized as follows :

1) The first part increase of the photodecomposition with the air flow rate might be interpreted by either or both the following two reasons :

1-1) Efficient O_2 supply for the oxidative decomposition by the bubbling air.
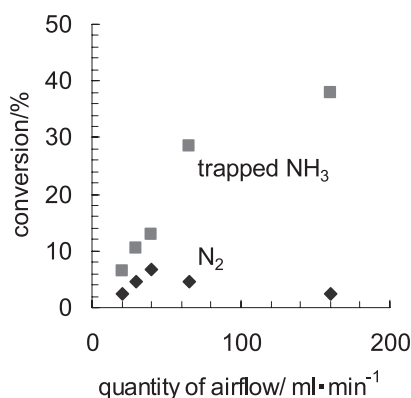

Fig. 2 Evaporated ammonia and produced N_2 vs. air flow rate during 3h, in the photodecomposition of a 190mM ammonia aq. solution using the Fig.1c) cell connected with an ammonia trap, irradiated by Xe lamp (UV 10mWcm^{-2}). Produced N_2 was estimated from the decreased ammonia, trapped ammonia and products NO_2^-, NO_3^-. For instance, at 40 mLmin^{-1}, NO_2^- formed was 0.42%, and NO_3^- 0.50% of the initial NH_3 concentration.

1-2) Intrinsic mechanism for the photodecomposition : It is important that ammonia photodecomposition by the present system was indicated to be a first order process with respect to its concentration against time [14]. This first order decrease of ammonia indicates that the rate-determining step for the ammonia photodecomposition is also first order for which transport of formed N_2 from water into air phase (see eq. (8)) is the most probable candidate. When considering the dynamic equilibrium of the ammonia photodecomposition shown as eqs. from (6) to (8), the transport of the formed N_2 from the liquid phase into gas phase represented by eq. (8), a first order physicochemical process, would be rate-determining in the whole photodecomposition processes.

2) The later decrease of the photodecomposition with air flow rate might be ascribed to some hindrance by excess supply of O_2 that is known as a radical scavenger, deactivating radical type intermediates of ammonia decomposition due to triplet ground state O_2.

3) It should be noted here that ammonia decomposition is a photochemical process, but evaporation is a physicochemical one, so that both the processes should be independent generally. However, the Fig. 2 shows that both the processes look like to be closely correlated.

To discuss the item 3) problem, the correlation between the photodecomposed % against evaporated ammonia (%) was plotted from Fig.2, and is shown in Fig. 3.

The sharp change of photodecomposition increase at the first stage and its sudden decrease at the later stage in Fig. 3 would show most probably that both the processes are originated from different reasons as discussed above, supporting that the above interpretation could be applied to the present photodecomposition of ammonia.

Low temperature photodecomposition was investigated at 0 ℃ by using a floating TiO_2 thin film/ FTO on an aqueous ammonia solution to suppress ammonia evaporation as much as possible, but ammonia vaporization could not be suppressed much.

Finally it should be added that, when enhancing the photodecomposition QE, evaporation also increases, the ratio of the photodecomposition/ evaporation being about 0.5 ～ 1 (Table 2). For a practical system it is strongly suggested that trap and circulation of the evaporated ammonia into the photoreaction cell for further photodecomposition would be a realistic way to completely decompose NH_3 into N_2.

4. Conclusions

UV light-activated and highly efficient photoelectrochemical decomposition of an aqueous ammonia to N_2 by a mesoporous TiO_2 thin film photoanode was investigated in relevance to ammonia evaporation. The cells fabricated were; (a) closed cell without ammonia trap, (b) closed cell with inside ammonia trap containing dilute aqueous H_2SO_4, (c and d) quasi-open cell connected with outside ammonia trap operated under air flow, and (e) open-air cell without ammonia trap. It was found that ammonia photodecomposition is closely correlated with its evaporation. The ratio of the [photodecomposition/evaporation] and the external (η, based on total incident UV photons) and internal (η', based on activating photons) quantum efficiencies (QEs) for the photodecomposition were estimated. The activity order of the cells was; (a) < (b) < (c, d) ∼ (e), supporting the importance of the cell structure. After subtracting evaporated ammonia, η exceeded 1 (= 100%) for the cell (c) with η' = 8, and η was 2.5 with η' = 18 for the cell (d). When air was bubbled into the open cell (e) by changing the flow rate, η' increased with the increase of the evaporation, but photodecomposition decreased after passing an optimum point (η' = 9.5), and finally stopped under higher air flow rate. Such strange behavior was interpreted by two conflicting factors. A positive factor would be either or both the efficient O_2 supply for the oxidative photodecomposition, or/and efficient transport of the product N_2 from water into air by increasing the air flow rate, shifting the equilibrium towards the product. A negative factor under high air flow rate could be quenching of intermediate radical species by excess supply of O_2 working as a radical scavenger. Trap and recycling of evaporated ammonia are suggested for a practical photodecomposition system.

5. References

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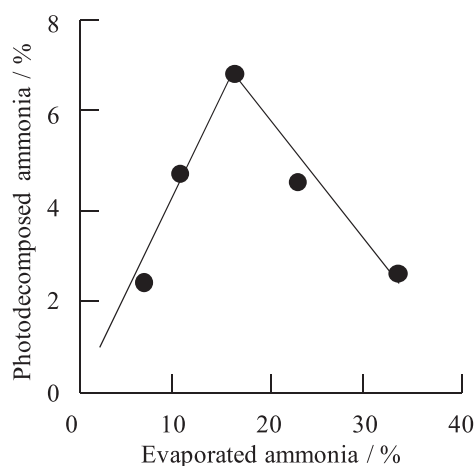
Fig. 3 Correlation of ammonia photodecomposition (%) against evaporation (%) based on initial ammonia concentration (188mM, 3200ppm) in 3 h irradiated by 10 mWcm^{-2} UV-light under stirring and air flow (from the first closed circle at the left hand side, 20,30,40,65, and 160 mL min^{-1}) using a quasi-open cell (c) composed of a photoreactor and an outside ammonia trap (0.4M H_2SO_4).