Highly Efficient Photodecomposition of Ammonia by a Nanoporous Semiconductor Photoanode and an O2-Reducing Cathode with Internal Quantum Efficiency over 300 (=3 x 104 %)

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Abstract

UV light-activated and highly efficient photodecomposition of an ammonia aqueous solution was achieved to produce dinitrogen (N_2) by a Biophotochemical Cell (BPCC) comprised of a nanoporous semiconductor film photoanode and an O_2-reducing cathode with high internal quantum efficiency over 300 (= 3 x 10^4 %). It was shown that a BPCC composed of a photoanode/cathode unit and a large volume reaction chamber is effective as an efficient cell. When the reaction chamber volume was increased, the total decomposition increased to a great deal, almost linearly with the cell volume. Major decomposition reaction was concluded to be dark auto-oxidation of the activated ammonia by the bulk O_2 into N_2, and its internal quantum efficiency, i.e., quantum efficiency of the NH_3 decomposition versus the UV light-activated NH_3, exceeded 300. Even based on the total incident UV light, the photodecomposition quantum yield reached 40 (=4000%).

Key Words: Ammonia photodecomposition, Nanoporous titanium dioxide, Dioxgen-reducing cathode, Quantum efficiency, Dinitrogen formation

1. Introduction

Photoelectrocatalytic reactions at semiconductor electrodes were investigated before the 1960s [1], and a crystalline n-TiO_2 photoanode to decompose water by UV light attracted a great attention [2]. Organic compounds have also been decomposed by crystalline TiO_2 photoanodes [3] [4]. An n-type semiconductor forms a kind of Schottky junction at the aqueous electrolyte interface, the photogenerated holes can oxidize organic compounds or water on the semiconductor surface, and the photogenerated electrons reduce protons to produce H_2 at a counter electrode. However, without applied potentials the photoelectrochemical reactions were not efficient enough, so that they have mostly been investigated under applied potential conditions. In the beginning of the 1990's, a nanoporous TiO_2 thin film was applied to a dye-sensitized solar cell (DSSC) [5], for which the nanoporous TiO_2 film works only in an organic liquid electrolytes solution, while working as both electron acceptor and conductor rather than as a liquid-junction semiconductor. The photoreactivity of a nanoporous TiO_2 film has been an interesting issue towards applications, but the details have not been investigated. From the beginning of the 1990's powders and coatings of semiconductors were used to photodecompose and clean environmental pollutants and dirty/harmful compounds [6]. However, their activity was not high enough, so that high concentration and a large volume of biomass wastes, serious pollutants in the world, have not been photocleaned. The reasons for the low activity of conventional UV region powder photocatalysts were: (1) The semiconductor powders need to be loaded on some carrier to separate afterwards, which hinders light absorption and activity. (2) The incident light has

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to reach the catalyst after passing the pollutant solution, through which the light is absorbed by the solutes (pollutants), making light intensity on the catalysts insufficient. It has been difficult for powder-based-photocatalysts to clean concentrated, colored, and/or solid suspended pollutant solution due to the strong absorption of UV light by the carrier, solutes and/or suspended materials. To our knowledge, quantum efficiency over 2 (current doubling effect) has not been reported in photocatalytic decomposition of organic and biological compounds. In order to increase photocatalysts' activity, narrow bandgap semiconductors capable of using visible light have been developed and achieved some success, but still the activity was not high enough for concentrated and a large amount pollutants. Such environmental pollution especially by organic materials and biowastes is becoming more and more a serious issue all over the world [7].

The present authors have reported a Biophotochemical Cell (BPCC) composed of a nanoporous semiconductor photoanode and an O_2-reducing cathode that can photocatalytically decompose biomass, its wastes and also suspended materials in water, generating simultaneously electrical power [8]~[11]. In the BPCC the semiconductor thin film photoanode is exposed directly to the incident light, so that light absorption by concentrated solutes, colored compounds and solid suspension is negligible allowing sufficient light irradiation on the semiconductor surface. However, details of photodecomposition and cleaning of high concentration ammonia have been open to further research. As for pollutants, ammonia is one of the serious ones to be cleaned, but there has not been any good process to decompose ammonia into harmless compounds such as N_2: in most cases NH_3 decomposition leads to the formation of nitrogen oxides such as nitrates and nitrites that cause serious eutrophication all over the world [7]. We have reported that NH_3 was photodecomposed only to N_2 [8]~[10] and not to N oxides, and that nitrates and nitrites were reduced to N_2 in the presence of NH_3 in the BPCC [12]. In the present paper we will report remarkably enhanced photodecomposition of NH_3 by the BPCC reaching internal quantum efficiency over 300 enabling photodecomposition of concentrated ammonia wastes over 10^3 to 10^5 ppm in water.

2. Experimental

2.1 Materials and Electrode Preparation

Ti-nanoxide T/SP paste was purchased from Solaronics Co.Ltd. and F-doped SnO_2 conductive glass (FTO, surface resistance 10Ω/sq) from AGC Fabritec Co.Ltd. A nanoporous TiO_2 film was prepared as before by a squeeze coating method,

for which an adhesive tape (thickness about 70μ m) was used as a spacer to adjust the TiO_2 film thickness obtained after calcination. The film was finally calcined at 450 ℃ for 30 min to attain around 10 μ m thickness whose roughness factor was nearly 10^3. As an O_2 reduction cathode, Pt-black was deposited electrochemically from $K_2[PtCl_6]$ on a Pt foil. Another cathode used for the Cell 3 was composed of stainless steel mesh (5 x 5 cm^2, 100 mesh) coated at first by a thin layer of Nafion (cation exchange resin) and then Pt-black was electrodeposited on the Nafion (designated SUS mesh/Pt black). All the chemicals used were of commercially available purest grade and used as received. As for the sample, ammonia was mainly used. A black-colored mixture of pig urine/wash water = 1/4 was also used by obtaining from a livestock breeding farmer house in Ibaraki prefecture, Japan.
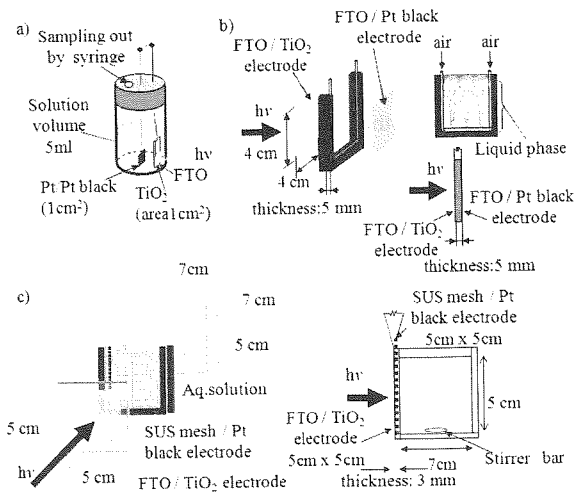
2.2 Cell Fabrication

Fig.1 a) Cylindrical cell (Cell 1). (b) Thin layer cell (Cell 2). (c) Combination cell (Cell 3) comprised of a photoanode /cathode unit and a large reaction chamber. Charge collectors made of SUS foil and placed between FTO conducting glass and spacer are not shown for the Cells 2 and 3.

The most important point for the enhancement of the photodecomposition efficiency was the structure of the cell. At first an airtight cylindrical cell (Cell 1, Fig.1 a) was used in which three electrodes (TiO_2 photoanode, O_2-reducing cathode and Ag-AgCl reference electrode) are inserted, cyclic voltammogram (CV) can be measured, and the gases evolved were analyzed by sampling out the gas by a syringe from the rubber septum equipped on the top of the cell.

A thin layer type cell (Cell 2, Fig.1 b) was designed in order to minimize the solution resistance between the TiO_2 photoanode and Pt-coated O_2-reducing cathode, e.g., the solution layer thickness was usually 1 to 5 mm between the 5

cm x 5 cm size photoanode and cathode [10]. The efficient Cell 3 (Fig. 1 c) was designed and fabricated by combining the fundamental thin layer Cell 2 structural unit with a large volume of solution chamber where auto-oxidation of the activated substrate radicals formed on the TiO_2 takes place.

2.3 Irradiation and Product Analysis

The UV-A (290-390nm) region light intensity was measured by a UV light meter (model UV-340, CUSTOM Co. Ltd.). The TiO_2 film was in most cases irradiated at the irradiance of $100 mWcm^{-2}$ with a 500 W xenon lamp through an IR-cutoff filter (HA-50), UV-A light intensity being 8 mW cm^{-2}. This UV intensity was the same as that from a solar simulator (PEC-L10 from Peccell Technologies, Inc.) at the irradiance of AM 1.5 G and 100 $mWcm^{-2}$, where AM (Ari Mass) 1 means that sun is irradiated vertically on a sea surface, so that AM 1.5 means that the solar irradiation passed through 1.5 times thicker air layer. G means that the spectrum of the solar simulator is adjusted by using filter(s) and mirror(s) so that the irradiated light spectrum is close to that of the solar irradiation. As a reference, the UV irradiance on a sunny day of Oct.28th at 14:50 in our campus was 4.5 $mWcm^{-2}$ when the total solar irradiance was 100 $mWcm^{-2}$.

Formed gases were analyzed by a gas chromatograph [8]. NH_4^+ was analyzed either by an ion chromatograph (Dionex Dx-AQ) by using a cation exchange column (Ion Pac CS12A) with an eluate CH_3SO_3H and an electric conductance detector, or by DR2800 analyzer from Hach Company, Germany.

3. Results and Discussion

3.1 Photodecomposition of ammonia and urine aqueous solution in a cylindrical cell (Cell 1) and a thin layer cell (Cell 2)

The nanostructured semiconductor thin film of 10 μm thickness was estimated to have a roughness factor of about 1000, meaning that active surface area is 1000 times as large as its apparent surface area. The photodecomposition of many biorelated organic compounds in the BPCC to produce CO_2 and N_2 have been established in our previous papers [8]~[10]. As a typical example, the cyclic voltammogram of a 10M ammonia aqueous solution (17000ppm, pH = 12) in the dark and under irradiation measured in a cylindrical cell (Cell 1) is shown in Fig. 2. The photocurrent started to increase at -1.0 V vs. Ag-AgCl that is -0.78 V vs. SHE (at pH=12), i.e., -0.07 V vs. SHE at pH=0. This value is close to the conduction band edge potential (-0.06 V vs. SHE at pH=0) of a nanoporous TiO_2 film reported [13]. After the first scan the photocurrent showed enhanced current and reached a steady state. The clear anodic photocurrent curves in the Fig. 2 exhibit

unambiguously that the nanoporous n-type semiconductor film forms a kind of Schottky junction (called a liquid-junction in the present case) at the water interface, typical for an n-type semiconductor. In a liquid-junction n-semiconductor photoelectrochemical system [1]~[3], excitation of electrons from the valence band (VB) to the conduction band (CB) takes
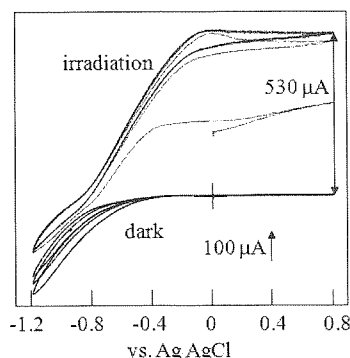

Fig. 2 Cyclic voltammogram of 10M NH_3 (pH=12) at nanoporous TiO_2 photoanode (1cm x 1cm) measured in the Cell 1 under O_2 at the light intensity 505 $mWcm^{-2}$. Scan rate 20 mV s^{-1}.

place by irradiation of the semiconductor with the light whose energy is larger than the bandgap of the semiconductor, forming separated electrons (in the CB) and holes (in the VB) (later shown in Eq.4), and thus separated charges can induce oxidation and reduction reactions at the photoanode and the cathode, respectively.

A 10 M (170000 ppm) ammonia aqueous solution (+ 0.1 M Na_2SO_4, 5mL) was photodecomposed under O_2 in the Cell 1 under 505 $mWcm^{-2}$ irradiation producing 410 μL N_2 with 11.0 C charges passed at the outer circuit, showing that the charges for the decomposition was approximately the same (88%) as the charges passed. This result demonstrated that the degree of decomposition could be monitored by the charges passed during the photodecomposition. Quantitative formation of N_2 from the photodecomposition of NH_3 in the BPCC was also established in our previous papers [8][14].

Livestock waste especially pig urine is a serious pollutant all over the world. The photodecomposition of urea $(NH_2)_2C=O$, the main component of urine, was investigated in an airtight cylindrical cell (Cell 1) with a 1 cm x 1cm nanoporous TiO_2 photoanode and a Pt-black coated Pt plate (1 cm x 1 cm) O_2-reducing cathode using a 0.4 M (= mol dm^{-3})(=24000 ppm) urea aqueous solution (5 ml) irradiated with a xenon lamp at 100 $mWcm^{-2}$ intensity (UV light 8 $mWcm^{-2}$), showing that almost quantitative $CO_2/N_2 = 1/1$ was formed.

Since urea in urine is rapidly decomposed to ammonia (NH_3) due to the presence of urease in nature, photodecomposition of ammonia (170 mM aqueous solution = 2890 ppm NH_3) was investigated in a thin layer cell (Cell 2) (solution layer thickness 3 mm, volume 4 mL) under air at the

white light intensity of 100 mWcm^{-2}. Since it is difficult to analyze the evolved gaseous products in the thin layer Cell 2 due to the open air cell structure needed to supply O_2 from air, the decomposition of NH_3 was monitored by the decrease of NH_4^+. It had been confirmed by another experiment that disappearance of NH_4^+ is always accompanied by N_2 formation. A mixture of pig urine/wash water = 1/4 (vol.) containing 191 mM ammonia (= 3450 ppm) was photodecomposed in a Cell 2 (solution layer thickness 1 mm, volume 2 mL). After 18 h, 71 % ammonia (=0.271 mmol) was decomposed and 57.0 C charges passed meaning that the ratio of the charges for the decomposition/photocurrent = 1.4, i.e., nearly the same amount (negative) charges were donated into the outer circuit as those used for the oxidative decomposition of the ammonia in the Cell 2. It is estimated that more than 5 days' solar irradiation would be needed to completely clean the wastes, but it is no problem if enough volume cell is used for the wastes treatment. In the paper published recently (15) we estimated required area for the cells for three kinds of wastes including pig urine, confirming that the needed area is reasonable.

3.2 Cell design (Cell 3) to enhance the quantum efficiency of the photodecomposition

A Cell 3 was designed so as to provide a large volume chamber in combination of a TiO_2 photoanode (5cm x 5cm)/O_2-reducing cathode (SUS mesh/Pt black) unit (with a 3 mm spacer between the two electrodes) capable of photoactivating substrate compounds. In changing the chamber volume to 13, 67.5, 124, 180, and 240 mL by using a neoprene rubber plate as shown in Fig. 3, the photodecomposition of a 79.6 mM NH_3 aqueous solution (1353 ppm) was investigated in the Cell 3 under air with 54 mW cm^{-2} xenon lamp irradiation (UV intensity 3.5 mWcm^{-2}, corresponding to 1 sum conditions). As an example, the photocurrent-photovoltage (I-V) characteristics of the cell with 180 mL volume at irradiation start and after 6 h are shown in Fig. 4. The I-V characteristics degraded only slightly after 6 h's continuous irradiation. The total decomposed NH_3 against the solution volume are shown in Fig. 5. It was surprising that the total decomposed NH_3 increased linearly with the solution volume, which is unusual since the photodecomposition has been regarded to take place on the TiO_2 photoanode that limits all the photodecomposition yield. The Fig.5 results demonstrate clearly that the main decomposition reaction took place in the large volume chamber independent of the photoirradiation.

It has been considered that in a semiconductor powder-based photodecomposition of organic compounds, auto-oxidation of activated compound by O_2 might take place, but it has been difficult to prove that quantum efficiency of

photodecomposition can exceed 1 by an auto-oxidation mechanism. One of the merits of the present BPCC is that the quantum efficiency of the photodecomposition can be estimated, since the charges used for the decomposition can be obtained from the charges passed at the outer circuit as mentioned in the last section. In TiO_2 powder systems, photoelectrochemically separated electrons diffuse to the surface of the semiconductor to reduce O_2 into O_2^- and/or HO_2^- However, in the BPCC, natural positive potential is applied from the cathode due to the O_2/H_2O redox couple making the band bending large, which facilitates electron diffusion into the inside of the TiO_2 film after charge separation and
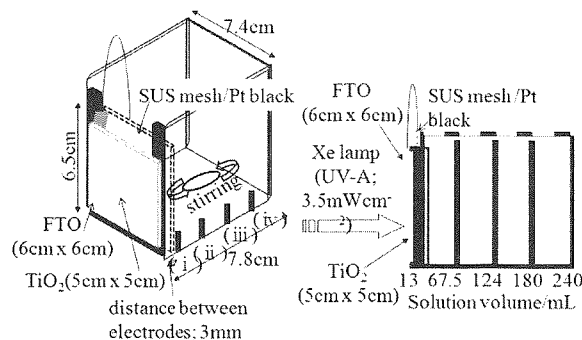
Fig.3 Combination cell composed of a TiO_2 photoanode/O_2-reducing cathode unit and a changeable-volume reaction chamber. Irradiation 6 h with stirring + dark 18h without stirring.
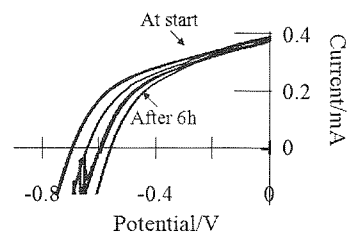
Fig.4 I-V characteristics for a 79.6 mM (1353 ppm) ammonia aqueous solution measured in the cell shown in Fig. 3 with a solution volume of 180 mL. After 6 h's irradiation the photopotential decreased slightly, but the photocurrent kept its initial value.
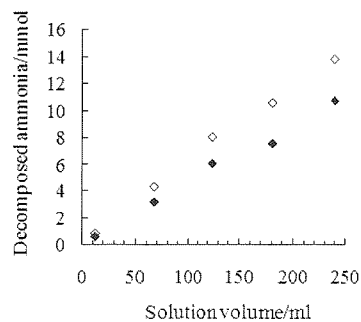
Fig. 5 Photodecomposed NH_3 (mmol) against cell volume (mL) under 6's irradiation with stirring (lower plots) and 18 h's dark reaction without stirring after 6's irradiation (higher plots). 79.6 mM ammonia aqueous solution under 54 mWcm^{-2} xenon lamp irradiation (UV intensity 3.5 mWcm^{-2}).

therefore most of the electrons would flow towards cathode via outer circuit as demonstrated already. Under these circumstances the (negative) charges passed in the outer circuit are the same amount as the (positive) charges used effectively for substrate oxidation at TiO_2. The internal quantum efficiency for the decomposition (= η') could then be defined as the ratio of the total decomposition number against photon number effectively used for activating the substrate (Eq.1), where the denominator can be estimated from the charges passed at the outer circuit in the BPCC.

In the above ammonia photodecomposition, the total decomposed amount of NH_3 in 6 h, the charges passed during this time, and the calculated internal quantum efficiency (η') are shown in Table 1. As expected, the η' increased as the solution volume increased showing clearly that auto-oxidation of the activated NH_3 takes place in the large volume chamber. Moreover, it should be noted that after stopping the irradiation, the decomposition proceeds in the dark about 30% of that under irradiation (Fig. 5), also supporting auto-oxidation of the activated ammonia independent of photoexcitation.

In addition to the internal quantum efficiency (η'), external quantum efficiency (η) that is quantum efficiency of the reaction number based on total incident UV photon number, was obtained by using the IPCE (incident photon to current efficiency) (Eq.2) when approximating that IPCE does not depend on the effective UV wavelength. The intrinsic quantum efficiency (η''), quantum efficiency of the reaction number against the UV photon number absorbed by the TiO_2 film, was obtained by measuring the UV photon number absorbed by TiO_2 film (Eq.3).

Internal quantum efficiency, η' = decomposed mol of substrate x number of electron involved in one molecular decomposition / photon mol effectively used for activating substrate (1)

External quantum efficiency $\eta = \eta'$ x IPCE (2)

Intrinsic quantum efficiency η'' = decomposed mol of substrate x number of electron involved in one molecular decomposition / absorbed photon mol by TiO_2 (3)

The IPCE value for the photodecomposition of the 65 mM NH_3 aqueous solution was 13.7 % (=0.137) measured by a monochromatic light of 350 nm. It was approximated that this IPCE value is applicable to all the incident effective UV light wavelengths. The FTO conducting glass transmitted 60 % of the incident UV light, and the absorption by the TiO_2 film was measured to be 88 % of the UV light transmitted through the FTO, so that the TiO_2 film alone absorbed 53 % (=60% x 88%) of the total incident UV light. Therefore, APCE (=absorbed photon to current efficiency) = IPCE / 0.53, so that

η'' is represented by η' x APCE = η' x (IPCE / 0.53). Therefore, when η' was 344 (for the 240 mL case in the Table 1), η was calculated to be 344 x 0.137 = 47.1, and η'' to be 344 x 0.137 / 0.53 = 88.9. These results demonstrate that the conversion efficiency for the decomposition based on the total incident UV light (η) was 47.1, while the intrinsic quantum efficiency (η'') 88.9. The photodecomposition quantum efficiency thus exceeded 40 (= 4×10^3 %) even based on the total incident UV light.

Table 1 Decomposed amount of NH_3 and its quantum efficiency (q.e.) (η' η'' and η) for the photodecomposition in the cell shown in Fig. 6. A 79.6 mM (1353 ppm) ammonia aqueous solution was used with different cell volumes under 54 mWcm⁻² xenon lamp irradiation (UV intensity 3.5 mWcm⁻²) for 6 h under stirring.

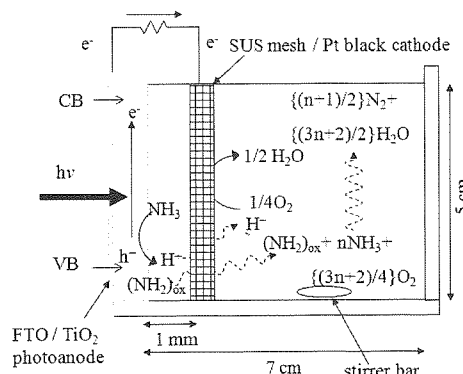| Cell volue/mL	Decomposed NH_3/mmol	Coulombs passed/C	Internal q.e. (η')	Intrinsic q.e. (η'')	External q.e. (η)
13	0.58	10	16.8	4.34	2.30
67.5	3.17	20	45.9	11.9	6.29
124	6.05	16	109	28.2	14.9
180	7.54	9	243	62.8	33.3
240	10.7	9	344	88.9	47.1

Fig.6 Photodecomposition mechanism of ammonia in the Cell 3 composed of a TiO_2 photoanode / O_2-reducing cathode unit and a large reaction chamber. The mechanism comprises activation of ammonia by UV light at the photoanode/cathode unit and auto-oxidation of the activated ammonia by O_2 (main decomposition) in the large chamber.
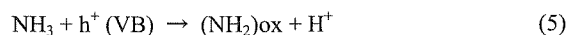
3.3 Mechanism of UV-Light Activated Photodecomposition

The present highly efficient UV-light activated decomposition of ammonia could be represented by the Eqs. from 4 to 7.
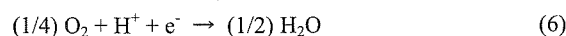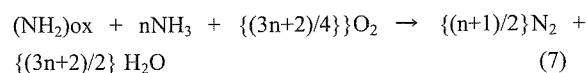
(At photoanode):

TiO_2 + UV light $\rightarrow$ e⁻ (CB) + h⁺ (VB) (4)
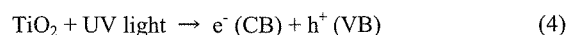
Activation of ammonia at photoanode:

NH_3 + h⁺ (VB) $\rightarrow$ (NH_2)ox + H⁺ (5)

(O_2 reduction at cathode):

(1/4) O_2 + H⁺ + e⁻ $\rightarrow$ (1/2) H_2O (6)

Auto-oxidative chain reaction of (NH_2)ox with NH_3 and O_2 in the bulk chamber:

(NH_2)ox + nNH_3 + {(3n+2)/4}}O_2 $\rightarrow$ {(n+1)/2}N_2 + {(3n+2)/2} H_2O (7)

The nanostructured TiO_2 film photoanode forms a kind of Schottky junction with the ammonia aqueous solution, which induced charge separation by absorbing the UV light whose wavelength is shorter than 390 nm (Eq.4). Ammonia is oxidized by the hole in the valence band (VB) to form an unstable oxidized intermediate $(NH_2)ox$ (Eq. 5). The $(NH_2)ox$ would be oxidized rapidly with O_2 by a chain auto-oxidation mechanism, during which n x NH_3 molecules would be activated by active intermediate by a kind of chain reaction mechanism (Eq.7) where η' is equal to 3(n+1). The structure of $(NH_2)ox$ is not known yet, but it can be hydrazine $(H_2N=NH_2)$ and/or hydroxyl amine (NH_2OH) that are highly reactive with O_2. The chain auto-oxidation mechanism involving $(NH_2)ox$, NH_3, and O_2 is also not yet known; it is the subject to be investigated further. The electrons in the conduction band is transported to the cathode where it is accepted by O_2 to directly form H_2O or via H_2O_2 to finally form H_2O (Eq. 6). Such efficient photodecomposition of ammonia in the Cell 3 can be represented by Fig. 6. It is important that in the Cell 3, the major decomposition reaction is dark auto-oxidation of the activated ammonia by the bulk O_2 whose internal quantum efficiency can exceed 300 $(=3x10^4 \%)$.

4. Conclusion

To conclude, UV light-activated and highly efficient decomposition of high concentration $(> 10^{3\sim5}$ ppm) ammonia was successfully achieved by a Biophotochemical Cell (BPCC) comprised of a nanoporous semiconductor film photoanode and an O_2-reducing cathode proving high internal quantum efficiency over 300 by using a combination cell (Cell 3) of photoanode/cathode unit with a large volume auto-oxidation chamber. The major decomposition reaction was dark auto-oxidation of the activated ammonia intermediate by the dissolved O_2 in water. This can lead to photodecomposition/cleaning of a highly concentrated and a large volume of ammonia based wastes in the near future.

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