Journal of Photochemistry and Photobiology A: Chemistry xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Invited paper

# Effect of proton concentration upon two-electron oxidation of water to hydrogen peroxide using $Ge^{IV}$-porphyrin-sensitized photovoltaic cell

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ARTICLE INFO

*Article history:*
Received 31 July 2017
Received in revised form 11 October 2017
Accepted 18 October 2017
Available online xxx

*Keywords:*
Artificial photosynthesis
Water oxidation
Hydrogen peroxide
Geranium porphyrin
Photovoltaic cell
Visible-light

ABSTRACT

The dependence of proton concentration (pH) in aqueous electrolyte solution upon two-electron oxidation of water to form hydrogen peroxide ($H_2O_2$) was investigated in a photovoltaic cell (PVC) composed of an FTO electrode coated by $Ge^{IV}$-porphyrin complexes having a phenyl boronic acid groups (**1**)-adsorbed titanium oxide ($TiO_2$) particles as an anode (**1**/$TiO_2$/FTO) and a Pt electrode as a cathode. The short-circuit photocurrent density (*J*), amount of $H_2O_2$ and faradaic efficiency FE strongly depended on pH, respectively. Both *J* and amount of $H_2O_2$ decreased with the increase of pH simply in the range from pH = 2 to pH = 10, suggesting that the photoinduced electron transfer (PET) from excited **1** to $TiO_2$ conduction band (CB) should be suppressed due to the negative shift of CB by the increase of pH. On the other hand, the recovers of both *J* and amount of $H_2O_2$ were observed in **1**-PVC system at pH = 13. Especially, the FE of **1b** became 91%, although it was 60% at pH = 6. These results indicate an existence of different species with **1** under basic condition. The chemical species can be **4**, in which a proton of axial ligand in **1** is dissociated under strong basic condition on the $TiO_2$ surface. **4** can have a lower oxidation potential than that of **1**, because **4** has a negative charge by the proton dissociation. Therefore, the observed recovers can be explained by both promotion of PET from excited **4** to $TiO_2$ and the direct formation of Ge-oxyl complex from the PET of **4**, which is a key intermediate for a two-electron activation of water to form hydrogen peroxide, not through a proton dissociation process of axial hydroxo ligand.


## 1. Introduction

Recently, the development of water oxidation systems is desirable in the studies of artificial photosynthesis [1–5]. Especially, much attention is focused on how a water molecule can be incorporated into the oxidation terminal end of photoredox system. As for the water oxidation processes using metal complexes as a catalyst, the studies on the electrochemical oxidation of water to molecular oxygen through four-electron transfer processes have been reported mainly [6–14]. Unfortunately, it is difficult to achieve the photochemical oxidation of water through the four-electron transfer [15], because a period of time of the order of seconds is required to achieve the stepwise four-electron oxidation of a metal complex in the photochemical process, owing to the rarity of photon-flux density in natural sunlight [16]. Therefore, the unstable highly oxidized state of the metal complex must survive during the second-order timescale in order to induce the four-electron transfer with a photochemical process. This problem is referred to as the "photon-flux-density problem" [16].

On the other hand, we have focused on the two-electron oxidation of water using metal complexes as an alternative pathway for water activation and found that the oxygenation of alkenes to form epoxides can be sensitized by metalloporphyrins such as di(hydroxo)porphyrininato $Sb^V$ [13], $Sn^{IV}$ complexs [17–20], carbonyl-coordinated ruthenium porphyrin complex [21–24] or, aluminum porphyrin complex [25] in the presence of water as both an electron and oxygen atom donor. In this system, a key intermediate capable of activating the water molecule is thought to be a metal-oxo complex formed by photoinduced electron transfer (PET) to an electron acceptor and the subsequent proton dissociation of the axial hydroxo ligand. We elucidated that these reactions proceed with a two-electron oxidation process using the energy of one photon, so that they are free from the "photon-flux-density problem". Accordingly, it can be expected that it would be possible to achieve the two-electron oxidation of water to form hydrogen peroxide ($H_2O_2$) [26], if a photochemical water oxidation system were properly fabricated using a metal complex.

Recently, we focused on the photocatalytic reaction using $Ge^{IV}$-porphyrin complexes as a sensitizer because the photochemical

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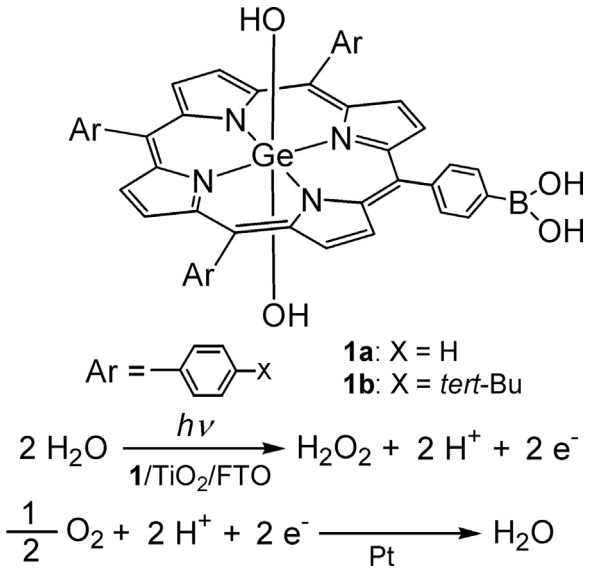
https://doi.org/10.1016/j.jphotochem.2017.10.032
1010-6030/

properties of them are unknown [27,28]. We found that visible-light driven two-electron oxidation of water to hydrogen peroxide ($H_2O_2$) using a photovoltaic cell (PVC) system fabricated with an FTO electrode coated by di(hydroxo)tetrakis-(4-carboxylphenyl) porphyrinatogermanium(IV) (Getcpp)-adsorbed titanium oxide ($TiO_2$) particles as an anode (Getcpp/$TiO_2$/FTO) and a Pt electrode as a cathode [29]. In this PVC system, it was elucidated that Ge-oxyl complex, formed by PET from the excited singlet state of Getcpp to $TiO_2$ and the following proton dissociation of axial hydroxo ligand, is a key intermediate capable of activating water molecule. Therefore, the promotion of both proton dissociation of axial hydroxo ligand and the nucleophilic attack of $H_2O$ to Ge-oxyl complex can be necessary to induce the effective formation of $H_2O_2$. Accordingly, it is desirable that the photoreaction is carried out under a basic aqueous condition. However, the photooxidation of water by Getcpp/$TiO_2$/FTO have failed under a basic condition, because Getcpp was quickly desorbed from $TiO_2$ into an aqueous solution under basic condition, indicating that a carboxyl group should be a weak linker to $TiO_2$ in a basic aqueous solution. So, we found that $Ge^{IV}$-porphyrin complexes (**1**) having a phenyl boronic acid groups, which is known as a good linker to $TiO_2$ [30], kept on adsorbing into $TiO_2$ even under strong basic condition (pH = 13). Here, we report on the effect of proton concentration (pH) upon the formation of $H_2O_2$ sensitized by **1**/$TiO_2$/FTO electrode under visible light irradiation (Scheme 1).

## 2. Experimental

### 2.1. Materials and instruments

$H_2O_2$ aqueous solution, tetraethylammonium tetrafluoroborate ($Et_4N^+BF_4^-$), germanium tetrachloride ($GeCl_4$) and organic solvents were purchased from Wako Pure Chemical Industries as guaranteed reagent grade (GR) and used without further purification. Oxo [5,10, 15, 20-tetra(4-pyridyl)porphyrinato]titanium(IV) was purchased from Tokyo Kasei as GR reagent for the quantitative analysis of the produced hydrogen peroxide. UV–vis absorption of the solutions was obtained on a JASCO V-500 spectrophotometer. The short-circuit current of the PVC experiment was measured by a microammeter (8340A, ADC Corporation, Japan). LED light (>400 nm; 14 mW $cm^{-2}$) was irradiate toward an anode. (L12194, Hamamatsu Photonics K. K, Japan).




**Scheme 1.** **1**-sensitized oxidation of water to form $H_2O_2$.

### 2.2. Synthesis of *1*

The synthesis of **1** was carried out as follows (Scheme 2). **2** was prepared using pyrrole, 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl) benzaldehyde and benzaldehyde or *p-tert*-butyl-benzaldehyde as an starting material by Lindsey's method [31]. The synthesis of **3** was performed by the reaction of **2** (0.08 g) with $GeCl_4$ (0.16 g) in water-free quinoline (15 $cm^3$) at 150 °C for 24 h under $N_2$ atmosphere. The reaction mixture was poured into hexane to give the precipitate of crude **3**. The resulting precipitate was solved in $CHCl_3$ and washed with aqueous HCl solution and aqueous NaOH solution to remove quinoline. During the follow-up process, two axial chloro ligands turned to two hydroxo ligands. After evaporation, **3** was isolated by column chromatography in silica gel (Fuji Silysia BW-300) using $CHCl_3$-MeOH (100:1 v/v) as an eluent. Finally, **1** was obtained by the hydrolysis of boronate in **3** under strong basic condition. The aqueous ethanol solution (10 $cm^3$) including **3** (0.04 g) and tetraethylammonium hydroxide (10% in water) (1.5 $cm^3$) was refluxed for 8 h under $N_2$ atmosphere. The reaction mixture was poured into hexane to give the precipitate of crude **1**. The resulting precipitate was solved in $CHCl_3$ and washed with water. After evaporation, **1** was isolated by column chromatography in silica gel (Fuji Silysia BW-300) using $CHCl_3$-MeOH (30:1 v/v) as an eluent.

**1a**: Yield 20% from **2a**; MS(MALDI-MS): *m/z* 764.166 (calcd. for $C_{44}H_{31}N_4O_4BGe$ 764.165); $^1H$ NMR (400 MHz; $CDCl_3$; $Me_4Si$) $\delta_H$, ppm 7.81–7.74 (9H, m), 8.27–8.26 (6H, m), 8.28 (2H, d, *J* = 9.2 Hz), 8.29 (2H, d, *J* = 9.2 Hz), 9.05 (8H, m). **3a**: Yield 22% from **2a**; MS (MALDI-MS): *m/z* 832.229 (calcd. for $C_{49}H_{39}N_4O_4BGe$ 832.227); $^1H$ NMR (400 MHz; $CDCl_3$; $Me_4Si$) $\delta_H$, ppm 1,18 (6H, s), 3.94 (s 4H), 7.78–7.75 (9H, m), 7.26–7.79 (6H, m), 8.27 (2H, d, *J* = 7.6 Hz), 8.28 (2H, d, *J* = 7.6 Hz), 9.05(2H, d, *J* = 2.4 Hz), 9.07 (4H, s), 9.08 (2H, d, *J* = 2.4 Hz). **1b**: Yield 9% from **3b**; MS(MALDI-MS): *m/z* 929.3659 (calcd. for $C_{56}H_{52}N_4O_4BGe$ 929.3528); $^1H$ NMR (400 MHz; $CDCl_3$; $Me_4Si$) $\delta_H$, ppm 1.62 (27H, s), 7.78–7.72 (6H, m), 8.17 (2H, d, *J* = 2.5 Hz), 8.21 (2H, d, *J* = 2.5 Hz), 8.18-8.23 (6H, m), 9.13 (8H, m).

### 2.3. Photovoltaic cell

Transparent FTO glass electrodes (160 mm × 80 mm × 3.2 mm) coated with $TiO_2$ particles (0.8 $cm^2$ of the coating area) were purchased from Dyesol Industries Pty. Ltd. (Australia). The preparation of **1**/$TiO_2$/FTO was performed by a dipping $TiO_2$/FTO for 2 h in a methanol solution of **1**. The amount of adsorbed **1** was estimated to be $5.1 \times 10^{-8}$ mol $cm^{-2}$. The area of **1**-modified $TiO_2$ electrode used for the photoreaction was 0.8 $cm^2$. The PVC was composed of **1**/$TiO_2$/FTO as an anode, Pt wire as a cathode, and aqueous solution (12 $cm^3$) of $Et_4N^+BF_4^-$ (0.1 M) as an electrolyte. The anode and cathode chambers were separated by a glass filter, as shown in Fig. 1.

### 2.4. Photoreaction

The short-circuit photocurrent was normally measured under irradiation of the anode with LED light (>400 nm) under air or argon atmospheres at 20 °C. The identification and quantitative analysis of $H_2O_2$ was carried out for the irradiated solution in the anode chamber by absorption spectrophotometry using a Ti-oxo porphyrin complexing reagent. [32]

## 3. Results

Fig. 2 shows the time-course plot for the production of $H_2O_2$ from water in the **1a**-PVC system. $H_2O_2$ was produced in amounts that increased nearly linearly vs. irradiation time, without an induction period. The turnover number (TON) for the formation of

Please cite this article in press as: J. Uchida, T. Shiragami, Effect of proton concentration upon two-electron oxidation of water to hydrogen peroxide using $Ge^{IV}$-porphyrin-sensitized photovoltaic cell, J. Photochem. Photobiol. A: Chem. (2017), https://doi.org/10.1016/j.jphotochem.2017.10.032