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# PHOTOINDUCED WATER OXIDATION BY POLYMERIC IRON CYANIDE COMPLEX

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Abstract : It was found that photoelectrochemical water oxidation takes place at a polynuclear iron-cyanide complex-coated electrode called Berlin Brown (BB ; $Fe_4^{III}[Fe^{III}(CN)_6]_3^{3-}$ $3X^-$). The electrode-coated BB showed electrocatalytic activity for water oxidation to produce $O_2$ not only in the dark but also under illumination to result in photoinduced water oxidation. The amount of the photoelectrochemically produced $O_2$ increased with the thickness of the BB film, indicating that the BB works as a bulk catalyst.

## INTRODUCTION

In view of the basic science and new energy resource, it is of importance to construct an artificial photosynthetic system which utilizes solar energy and water. Water oxidation by four-electron transfer is one of the most important reactions in a photosynthetic system. However, only very few catalysts have been reported with high activity (Refs. 1-6). The present authors have reported recently that trinuclear Ru-amine complex (so called Ru-red) incorporated into a Nafion® membrane has a high activity to oxidize water (Refs. 1-4). Such a polynuclear complex can be a promissing candidate for a four-electron water oxidation catalyst.

In the modeling of a photosynthetic system, it is an important subject to induce oxidation/reduction reactions by utilizing solar energy such as photosystems I and II in nature. In our earlier work, photoresponsive electrode of a bilayer system composed of $Ru(bpy)_3^{2+}$ and a polynuclear iron-cyanide complex called Prussian Blue (PB, $Fe_4^{III}[Fe^{II}(CN)_6]_3$ (unit cell structure)) was studied (Ref. 7). The result showed that not only $Ru(bpy)_3^{2+}$ but also PB is photoresponsive, showing that PB has a photosensitizing effect. In the following investigations it has been found that the oxidized form of PB called Berlin Brown (BB, $Fe_4^{III}[Fe^{III}(CN)_6]_3^{3-}$ $3X^-$ (unit cell structure)) can work not only as a dark catalyst for water oxidation but also as a photocatalyst. In the present work, photoelectrochemical water oxidation, which corresponds to a photosystem II model, will be reported with BB coated on an indium-tin oxide (ITO) electrode.

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## EXPERIMENTAL

### *Materials and Photoelectrochemistry*

The same volumes of a 5 mM potassium hexacyanoferrate(III) and a 5 mM iron(III) chloride aqueous solution were mixed to obtain a water-soluble BB ($Fe^{III}[Fe^{III}(CN)_6]$) solution as reported previously (Ref. 8). The water-insoluble $Fe^{III}$-$Fe^{II}$ complex called Prussian Blue (PB ; $Fe_4^{III}[Fe^{II}(CN)_6]_3$), which is a reduced species of the BB, was prepared from the BB solution by depositing electrochemically on an ITO electrode under cathodic polarization (+0.6 V vs. Ag/AgCl, a saturated KCl aqueous solution was empolyed as the inner liquid). The PB-coated ITO electrode was rinsed repeatedly with water. An electrochemical cell was equipped with the PB-coated ITO working (effective area : ca. 1 $cm^2$), spiral Pt wire counter, and a Ag/AgCl reference electrode. A tungsten-halogen lamp (100 V, 100 W) was used as a light source, and the coated BB was irradiated from the back side of the ITO. The potentiostatic electrolysis was carried out in a pH 5.5 aqueous solution containing 0.1 M $KNO_3$ electrolyte for 1 hour under argon. The amount of the gaseous $O_2$ produced was analyzed by a gas chromathograph (Hitachi 165) with a molecular sieve 5Å column and argon carrier gas.

### *Measurements of action spectrum and absorption spectrum*

A visible absorption spectrum of the BB coated on an ITO electrode was measured by a spectrophotometer (Otsuka Denshi, IMUC-7000). For the action spectrum, the photocurrent density of the ITO/BB system was measured at +1.30 V (vs. Ag/AgCl). The incident light intensity was measured by an irradiation intensity meter (type CA1 from Kipp & Zonen).

## RESULTS AND DISCUSSION

A typical cyclic voltammogram (CV) of the coated polynuclear iron-cyanide complex (Refs. 8-11) is shown in Fig. 1(a). The CV shows two couples of reversible redox waves for Prussian white (PW, $Fe_4^{II}[Fe^{II}(CN)_6]_3^{4-}$)/PB couple at +0.2 V (vs. Ag/AgCl) and for PB/BB couple at +0.8 V. The CV scan up to +1.5 V was also carried out at both the BB-coated ITO system (denoted as ITO/BB) and a bare ITO, and is shown in Fig. 1(b). Almost no anodic current at a bare ITO system was observed in the dark as well as under illumunation. At the BB-coated ITO anodic current was observed in the dark, and under illumination much higher anodic current was observed than in the dark. It is expected that not only dark oxidation reaction but also photoinduced oxidation by the BB film takes place.

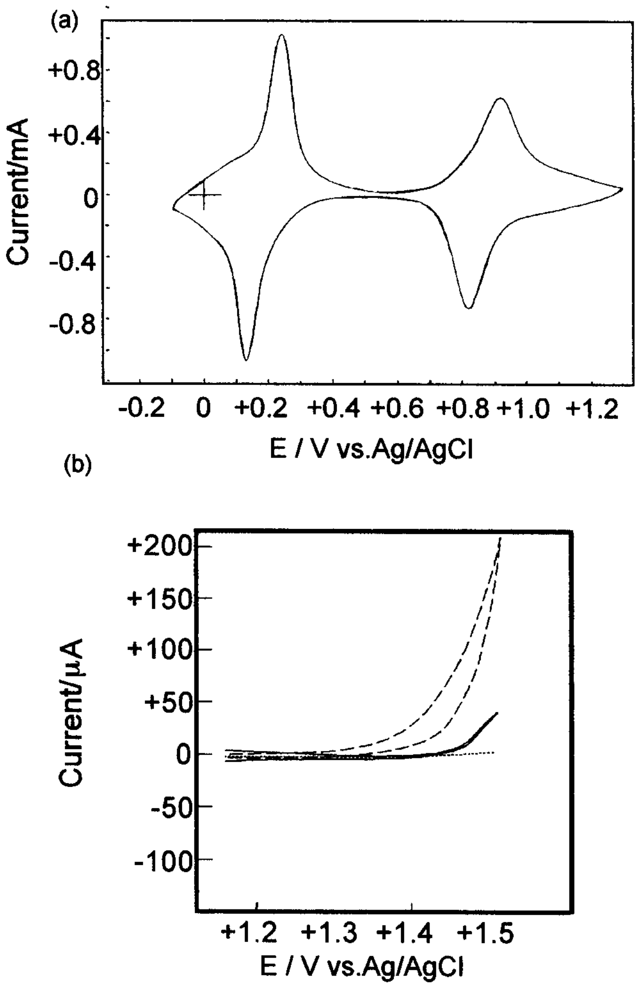

Fig.1 Typical CV ( Scan rate : 20 $mVs^{-1}$) at ITO electrode coating the polynucler iron-cyanide complex in a $KNO_3$ electrolyte solution (pH5.5)(a). CV scaning up to + 1.5V vs. Ag/AgCl at the BB-coated ITO electrode (Scan rate : 5$mVs^{-1}$) (b). _ _ _ , ITO/BB under illumination ; ____ , ITO/BB under dark; ..... , a bare ITO in the dark and illumination.

Fig. 2 shows the typical results of potentiostatic electrolyses at an ITO/BB and a bare ITO in the dark as well as under illumination. Almost no $O_2$ was observed in the dark as well as under illumination at a bare ITO. At ITO/BB $O_2$ was produced in the dark. The amount of $O_2$ produced at the ITO/BB under illmination was remarkably higher than that in the dark. The ITO/BB system brought about photoinduced $O_2$ production even at +1.3 V. The turnover number (TN) of the catalyst for photoinduced $O_2$ production based on the total amount of the coated BB unit ($1.2 \times 10^{-8}$ mol) was 78 $h^{-1}$ at +1.5 V. The dissolved $O_2$ in the aqueous phase was measured by an $O_2$ senser, and Faradaic efficiency (F. E.) for the total $O_2$ produced was calculated ; the average F. E. exceeded 80 %.

In order to investigate the photocurrent generation which induces water oxidation in the ITO/BB system, the action spectrum for the photocurrent was measured at +1.3 V, and the results are shown in Fig. 3 compared with the absorption spectrum of the BB film. The action spectrum shows the photon-to-current conversion efficency ( $\eta$ , %) on the irradiated wavelength (Ref. 12). The action spectrum was in accord with the absorption spectrum of the BB, so that the light absorption by the BB species is responsible for the photoinduced process.

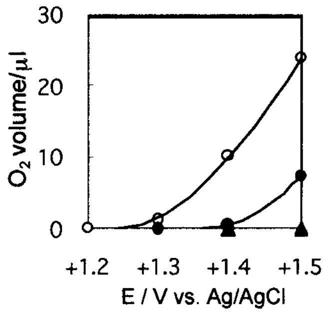

Fig. 2 Result of typical electrolysis data at the BB-coated ITO and a bare ITO.
Total coated amount of the BB is $1.2 \times 10^{-8}$ mol $cm^{-2}$. ○, ITO/BB under irradiation ; ●, ITO/BB under dark; ; ▲,a bare ITO under both dark and illumination..

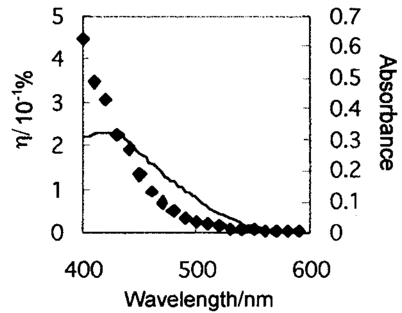

Fig.3 Comparison of action spectrum for photocurrent in ITO/BB system(◆) with absorption spectrum of BB film.

The photocatalytic activity for water oxidation was studied as a function of the total amount of the BB on the ITO as shown in Fig. 4. The amount of the $O_2$ produced increased with the coated amount of BB up to ca. $1.0 \times 10^{-8}$ $molcm^{-2}$ and tended to approach a saturation, showing that the BB works as a bulk photocatalyst for the water oxidation. The TN value of the catalyst per unit cell of the total coated BB decreased with the coated BB amount. This would be ascribed to the charge transport from the electrode to the coated BB as well as to the filter effect of the BB.

A longer-term electrolysis in the ITO/BB system was carried out, and the result is shown in Fig. 5. The amount of the $O_2$ produced increased almost linearly with the reaction time.

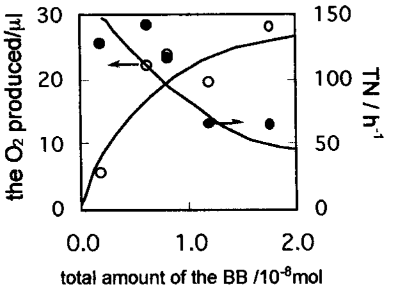

Fig. 4 Dependence of the amount of the $O_2$ produced and the turnover number of a BB unit cell with the coated amount of BB.

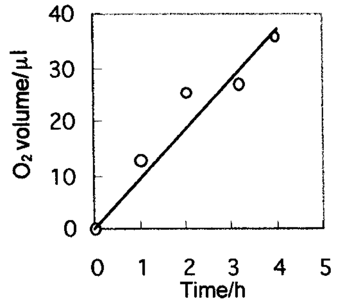

Fig.5 A longer-term electrolysis data at ITO/BB (applied potential,+1.4V vs. Ag/AgCl). Total coated amount of BB is 3.5 x$10^{-8}$ mol $cm^{-2}$

The mechanism of the photoelectrocatalysis in the ITO/BB system is shown in Scheme 1. The BB species works as a photoexcitation center, and the oxidative quenching of the photoexcited BB by electron transfer to the ITO electrode would take place under applied potentials. The BB thus oxidized can catalyze water oxidation under photoelectrochemical conditions.

$$\mathrm{BB} \xrightarrow{h\nu} \mathrm{BB}^*$$

$$\mathrm{BB}^* \xrightarrow{\text{electrode}} \mathrm{BB}^+ + e^-$$

$$4\mathrm{BB}^+ + 2\mathrm{H_2O} \longrightarrow 4\mathrm{BB} + \mathrm{O_2}$$

Scheme 1 The proposed mechanism of the photoelectrocatalytic water oxidation

REFERENCES

(1) I. Ogino, K. Nagoshi, M. Yagi, M. Kaneko, *J. Chem. Soc. FARADAY TRANS.*, **92(18)**, 3431(1996).

(2) M. Yagi, K. Kinoshita, M. Kaneko, *J. Phys. Chem.*, **100**, 11098(1996).

(3) M. Yagi, S. Tokita, K. Nagoshi, I. Ogino, M. Kaneko, *J. Chem. Soc. FARADAY TRANS.*, **92(13)**, 2457(1996).

(4) M. Yagi, I. Ogino, A. Miura, M. Kaneko, *Chem. Lett.*, 863(1995).

(5) Y. Naruta, M. Sasayama, T. Sasaki, *Angew. Chem. Int. Engl.*, **33**, 1839(1994).

(6) J. A. Gilbert, D. S. Eggleston, W. R. Murphy, Jr., D. A. Geselowitz, S. W. Gersten, D. J. Hodgson, T. J. Meyer, *J. Am. Chem. Soc.*, **107**, 3855(1985).

(7) M. Kaneko, A. Yamada, *Electrochimica Acta*, **31**, 273(1986).

(8) M. Kaneko, S. Hara, A. Yamada, *J. Electroanal. Chem.*, **194**, 165(1985).

(9) K. Itaya, T. Ataka, S. Toshima, *J. Am. Chem. Soc.*, **104**, 4767(1982).

(10) K. Itaya, T. Ataka, S. Toshima, T. Shinohara, *J. Phys. Chem.*, **86**, 2415(1982).

(11) D. Ellis, M. Eckhoff, V. D. Neff, *J. Phys. Chem.*, **85**, 1225(1981).

(12) K. Kalyanasundaram, N. Vlachopoulos, V. Krishnan, A. Monnier, M. Grätzel, *J. Phys. Chem.*, **91**, 2342(1987).