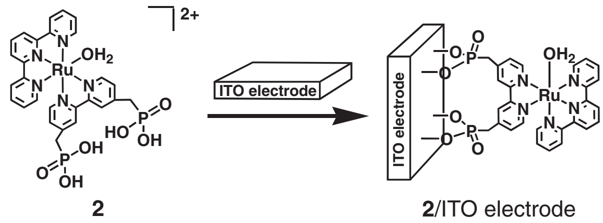
doi:10.1246/cl.2010.1146

Electrocatalytic O_2 Evolution from Water at an ITO Electrode Modified with $[Ru(terpy)\{4,4'-(CH_2PO_3H_2)_2-2,2'-bpy\}(OH_2)]^{2+}$: Evidence for a Unimolecular Pathway

Josaku Kiyota,[1] Junpei Yokoyama,[1] Masaki Yoshida,[1] Shigeyuki Masaoka,*[1,2] and Ken Sakai*[1]
[1]*Department of Chemistry, Faculty of Science, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581*
[2]*PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012*

(Received August 2, 2010; CL-100667; E-mail: ksakai@chem.kyushu-univ.jp, masaoka@chem.kyushu-univ.jp)

An ITO (indium tin oxide) electrode modified with $[Ru(terpy)\{4,4'-(CH_2PO_3H_2)_2-2,2'-bpy\}(OH_2)]^{2+}$ was prepared to gain insight into the mechanism of O_2 evolution from water catalyzed by a series of mononuclear aquaruthenium complexes, such as $[Ru(terpy)(bpy)(OH_2)]^{2+}$. The modified ITO electrode showed a clear decrease in overpotential for O_2 evolution (1.35 V in an aqueous 0.1 M Na_2SO_4/H_2SO_4 solution, pH 4.0), indicating that the O_2 evolution proceeds in a unimolecular fashion without having any intermolecular associations.



Scheme 1.

Life on earth largely relies on O_2 evolution from water with the aim of uptaking electrons to generate high energy molecules, like sugar, even though the O_2 evolved is a mere waste product. Nature uses a tetramanganese cluster[1] to effectively catalyze the four-electron one-step redox transformation ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$), while chemists have paid great attention to dinuclear metal complexes in hopes to facilitate the reaction through the coupling of two active centers, i.e., through a combination of two sets of two-electron redox processes.[2] In spite of such a widely accepted direction toward the development of highly active O_2-evolving molecular catalysts, we *accidentally* discovered the fact that a mononuclear aquaruthenium(II) complex $[Ru(terpy)(bpy)(OH_2)]^{2+}$ (**1**) is a highly active catalyst toward O_2 evolution from water.[3,4] Several other researchers also started to pay attention to the same topic.[5] Further, efforts have also been made in our group to clarify the structure–activity relationship as well as the mechanism of O_2 evolution catalyzed by such mononuclear aquaruthenium catalysts.[6,7]

Our studies on the O_2-evolving catalysis of **1** have revealed the following aspects: (i) the rate law of O_2 evolution obeys $d[O_2]/dt = k[\text{catalyst}][Ce^{4+}]$, revealing the operation of a unimolecular rate-determining step with regard to the catalyst molecule;[7] (ii) the $Ru^V{=}O$ species is an intermediate in the highest oxidation level, which was spectrophotometrically detected in our recent studies;[8] (iii) a radical coupling between the $Ru^V{=}O$ species and the radical-like O(hydroxide) atom of hydroxocerium(IV) species plays a crucial role in the O–O bond formation.[7]

In order to further gain evidence for the unimolecular path to the O_2 evolution *with no cooperation of two catalyst molecules through the overall process*, here we develop an ITO electrode modified with a $[Ru(terpy)(bpy)(OH_2)]^{2+}$ derivative to examine the O_2-evolving characteristics by means of electrochemical techniques. Under the appropriate conditions, intermolecular interactions can be effectively excluded. Even if the molecules are densely packed over the electrode surface, neighboring molecules cannot have flexible motions to *cooperatively* catalyze O_2 evolution in a bimolecular fashion. With these factors in mind, we decided to prepare the ITO electrode modified with $[Ru(terpy)\{4,4'-(CH_2PO_3H_2)_2-2,2'-bpy\}(OH_2)]^{2+}$ (**2**) (Scheme 1).

Before examining the ITO system modified with **2**, the basic features of the O_2 evolution from water catalyzed by **2** in an aqueous acetate buffer solution (pH 5.0) were investigated (Figure S1a).[9] **2** displays two redox couples at $E_{1/2} = 0.58$ V vs. SCE ($Ru^{II}–OH_2/Ru^{III}–OH$) and 1.03 V vs. SCE ($Ru^{III}–OH/Ru^{IV}{=}O$) (hereafter all potentials will be given in volt vs. SCE). Under the same experimental conditions, the redox potential of the $Ru^{II}–OH_2/Ru^{III}–OH$ couple of **2** is close to that of **1** ($E_{1/2} = 0.61$ V), while the potential for the $Ru^{III}–OH/Ru^{IV}{=}O$ couple of **2** is largely shifted to the higher potential in comparison with that of **1** ($E_{1/2} = 0.72$ V) (Figure S1b).[9] In addition, the cyclic voltammogram of **2** exhibits a large irreversible anodic current at more positive potential, which is attributed to the electrocatalytic oxidation of water into O_2. The potential, at which the catalytic current becomes 20 μA, for **2** is shifted to higher potential by 0.04 V; O_2 evolution occurs at 1.31 V for **1**, and 1.35 V for **2**. In order to prepare ITO electrodes favorable for surface modification, hydrophilic treatment was conducted by heating the ITO electrodes at 80 °C for 30 min in a 1:1:5 (v/v/v) mixture of an aqueous 28% NH_3 solution, an aqueous 35% H_2O_2 solution, and water. The electrodes were then washed with pure water and dried under Ar atmosphere. Finally, thus treated ITO electrodes were immersed in a methanolic solution of **2** (0.1 mM) for 24 h followed by washing them with absolute methanol.

The anchoring of **2** over the ITO surface was first confirmed spectrophotometrically, in which the so-called metal-to-ligand charge-transfer (MLCT) band of **2**, consistent with that for an aqueous solution of **2**, was observed at 498 nm (Figure S3).[9] In order to further ensure the adsorption of **2** over the ITO surface, the X-ray photoelectron spectrum (XPS) of the **2**/ITO electrode was measured (Figures S4 and S5b).[9] The Ru $3d_{5/2}$ peak observed as a singlet at 280.8 eV (fwhm = 1.33 eV) further supports the presence of **2** loaded over the ITO surface (fwhm = full width at half maximum height). This binding

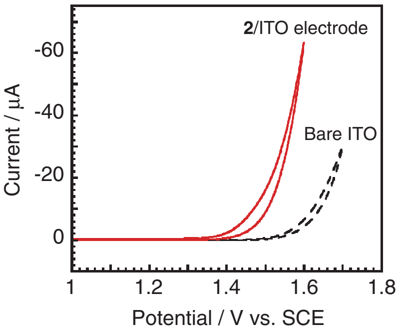


Figure 1. Cyclic voltammograms of the **2**/ITO electrode and a bare ITO in an aqueous 0.1 M Na_2SO_4/H_2SO_4 solution (pH 4.0) at a scan rate of $20\,mV\,s^{-1}$ under Ar atmosphere. The net area of ITO surface was $0.352\,cm^2$. The counter and reference electrodes were a Pt wire and a saturated calomel electrode, respectively.

energy is quite consistent with that observed for the powder sample of **2** (280.5 eV, fwhm = 2.07 eV; Figure S5a).[9] These results reveal that the ITO surface has been successfully modified with complex **2**. To examine the O_2 evolution from water catalyzed by the **2**/ITO electrode, cyclic voltammogram in an aqueous 0.1 M Na_2SO_4/H_2SO_4 solution (pH 4.0) was measured. As shown in Figure 1, there is a clear decrease in the overpotential for O_2 evolution upon loading **2** over the electrode surface. The O_2-evolution potential for the **2**/ITO electrode is by ca. 150 mV shifted to the cathodic side in comparison with that of the bare ITO electrode. Moreover, the potential at which water oxidation occurs (1.35 V vs. SCE) is consistent with that observed for **2** in solution (Figure S1a).[9]

On the other hand, Figure 2a shows the cyclic voltammograms of the **2**/ITO electrode measured at various scan rates. The redox peaks at $E_{1/2} = 0.66$ V, corresponding to the Ru^{II}–OH_2/Ru^{III}–OH couple, are reasonably symmetric and exhibit a bell-shape characteristic for adsorbed redox species. A linear dependence of the anodic (and also cathodic) peak current on the scan rate reconfirms that **2** is adsorbed over the electrode surface (Figure 2b). The slope of the regression line is estimated to be $I_p/v = 5.46 \times 10^{-6}$ [AV^{-1}], where I_p is a peak current (A) and v is a scan rate ($V\,s^{-1}$). From this value, the surface coverage of **2** over the ITO electrode can be derived according to the following equation,

$$\Gamma = \frac{I_p}{v}\frac{4RT}{n^2F^2A} \tag{1}$$

where Γ is the surface coverage ($mol\,cm^{-2}$), and n is the number of electrons transferred in this electrode reaction. In the present case, the surface coverage can be estimated as $\Gamma = 1.62 \times 10^{-11}$ $mol\,cm^{-2}$ by applying $n = 1$ based on the Ru^{II}–OH_2/Ru^{III}–OH couple.

Next, we conducted another XPS measurement to ascertain the stability of the complex during the electrocatalytic O_2 evolution with use of the **2**/ITO system. In this experiment, only one cycle of cyclic voltammetric sweep was carried out in the potential range 0–1.60 V using a freshly prepared **2**/ITO electrode (the voltammetric sweep shown in Figure 1 was conducted exactly one cycle). After this procedure, the XPS measurement was carried out to confirm that the Ru $3d_{5/2}$ peak (281.0 eV, fwhm = 1.54 eV), consistent with that observed before the electrolysis, can be observed without any sign attributable to decomposition of the complex (Figure S5c).[9] The stability of the **2**/ITO electrode was further examined by comparing the surface coverage of **2** determined before and after the voltammetric sweep in the potential range 0–1.50 V. Consequently, the surface coverage redetermined had a value of $\Gamma = 1.46 \times 10^{-11}$ $mol\,cm^{-2}$ (Figure S6),[9] revealing that 90% of molecular catalyst remained undesorbed over the electrode surface after the electrolysis. It is noteworthy that the experiments by employing carboxylate anchors were not successful since considerable desorption was observed after the measurements. Some reports also show much more stable phosphonate-anchored systems.[10]

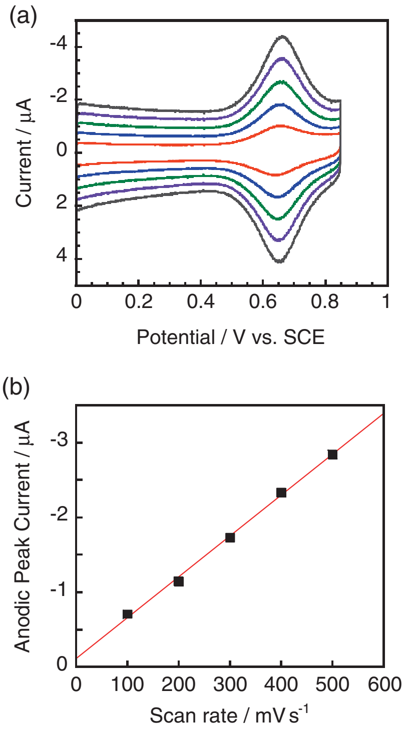


Figure 2. (a) Cyclic voltammograms of the ITO electrode modified with **2** at various scan rates (100, 200, 300, 400, and $500\,mV\,s^{-1}$), measured in an aqueous 0.1 M Na_2SO_4/H_2SO_4 solution (pH 4.0), using a Pt wire as a counter electrode and a saturated calomel electrode as a reference electrode. (b) Plot of anodic peak currents at 0.66 V vs. SCE as a function of the scan rate.

To better understand the manner in which the molecular catalysts are loaded over the ITO surface, the molecular structure of **2** was first computed using molecular mechanics calculations (MM3[11] and SCIGRESS Ver 2.0[12]) (the details in Supporting Information).[9] Here we suppose that both of the phosphonate groups are anchored over the surface with the bipyridyl plane located perpendicular to the ITO surface (Figure 3a). The space filling model of the complex viewed perpendicular to the ITO surface shows that a molecule occupies an area having a shape of an ellipse with the major and minor axis lengths being 11.5 and 10.5 Å, respectively (Figure 3b). Consequently, the molecular area is roughly estimated to be $9.48 \times 10^{-15}\,cm^2$ per molecule, leading to an estimate that about 9.2% of the surface area is covered by molecules under $\Gamma = 1.62 \times 10^{-11}\,mol\,cm^{-2}$. This modeling study also reveals that the aqua ligand is well exposed to the bulk (Figure 3a). Next, supposing that the

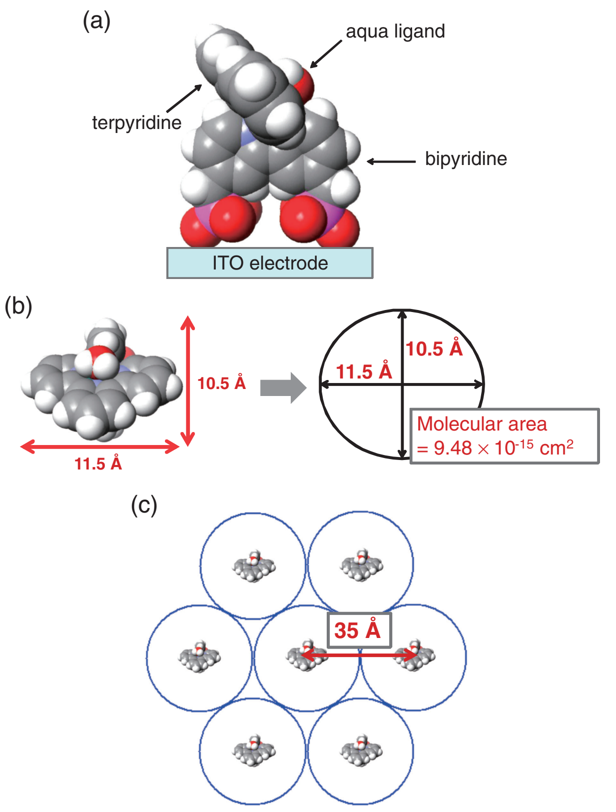


Figure 3. (a) The space filling model of **2** on the ITO electrode (side view). The molecular structure of **2** was optimized by MM3. The two phosphonate groups are assumed to be anchored on the ITO surface. (b) The space filling model of **2** viewed perpendicular to the ITO surface (top view). The molecular area is roughly estimated as 9.48×10^{-15} cm^2 per molecule. (c) A possible molecular arrangement over the ITO surface, where the molecules are positioned supposing a regular 2-D hexagonal close-packed model of circles.

molecules are positioned in a regular fashion with a 2-D hexagonal close-packed model of circles, a possible molecular arrangement may be proposed as illustrated in Figure 3c. The average separation between the closest couple of molecules can be estimated to be 35 Å, supposing that adsorption of molecules over the surface merely obeys a simple statistical law. If there is any minor contribution of a bimolecular path, the apparent electrode reaction rate must exhibit special acceleration at the higher surface coverage due to the higher probability of affording a special geometry where two catalyst molecules can work together to evolve O_2. In other words, a sort of quadratic dependence of the O_2 evolution current on the surface coverage must be observed. To answer this question, the catalytic current at the **2**/ITO electrode was examined as a function of the surface coverage (Γ; Figure S7b),[9] where various **2**/ITO electrodes were separately prepared by changing the immersion time for anchoring the complex, and their surface coverage (Γ) was also determined individually. The observed linear relationship between the catalytic current and the surface coverage (Figure S7b)[9] clearly indicates that the intermolecular interactions leading to the bimolecular activation are extremely unfavorable in the present **2**/ITO system. In other words, the rate of electrocatalytic water oxidation into O_2 is proportional to the surface coverage of the mononuclear aquaruthenium site. This leads to our conclusion that the present electrocatalytic water oxidation proceeds at a single Ru center without having any intermolecular associations among the catalyst molecules.

In the present study, a $[Ru(terpy)(bpy)(OH_2)]^{2+}$ derivative tethered to phosphonate anchors has been successfully loaded over an ITO electrode with the average closest intermolecular separation longer than 35 Å. This system does not allow two or more ruthenium centers to engage in the same O_2-evolving event, and hence the electrocatalytic O_2 evolution from water promoted with this system can be fully attributable to an O_2-evolving event at a single aquaruthenium site. Although the present O_2-evolving catalysis cannot proceed through the radical–radical coupling of the $Ru^V{=}O$ and the $Ce^{IV}(OH)$ species proposed in our recent study,[7] this is an important evidence revealing that the O–O bond formation can also take place by the direct attack of a water molecule, as pointed out by Hurst et al.,[13] even though their system also involved a $Ce^{IV}(OH)$ species. Attempts to further clarify the detailed mechanisms of these catalytic processes are still in progress in our laboratory.

The present work was supported by PRESTO, Japan Science and Technology Agency (JST). This work was also in part supported by a Grant-in-Aid for Young Scientists (B) (No. 21750065), and a Grant-in-Aid for the Global COE Program ("Science for Future Molecular Systems") from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References and Notes

1 a) G. W. Brudvig, R. H. Crabtree, *Prog. Inorg. Chem.* **1989**, *37*, 99. b) T. J. Meyer, *Acc. Chem. Res.* **1989**, *22*, 163. c) W. Rüttinger, G. C. Dismukes, *Chem. Rev.* **1997**, *97*, 1. d) M. Yagi, M. Kaneko, *Chem. Rev.* **2001**, *101*, 21.

2 a) S. W. Gersten, G. J. Samuels, T. J. Meyer, *J. Am. Chem. Soc.* **1982**, *104*, 4029. b) T. Wada, K. Tsuge, K. Tanaka, *Angew. Chem., Int. Ed.* **2000**, *39*, 1479. c) Y. Shimazaki, T. Nagano, H. Takesue, B.-H. Ye, F. Tani, Y. Naruta, *Angew. Chem., Int. Ed.* **2004**, *43*, 98. d) R. Zong, R. P. Thummel, *J. Am. Chem. Soc.* **2005**, *127*, 12802.

3 S. Masaoka, K. Sakai, Presented at the 88th Annual Meeting of the Chemical Society of Japan, Tokyo, March 26, **2008**, Paper No. 1E6-39.

4 S. Masaoka, K. Sakai, *Chem. Lett.* **2009**, *38*, 182.

5 a) H.-W. Tseng, R. Zong, J. T. Muckerman, R. Thummel, *Inorg. Chem.* **2008**, *47*, 11763. b) J. J. Concepcion, J. W. Jurss, J. L. Templeton, T. J. Meyer, *J. Am. Chem. Soc.* **2008**, *130*, 16462. c) L. Duan, A. Fischer, Y. Xu, L. Sun, *J. Am. Chem. Soc.* **2009**, *131*, 10397. d) M. Yagi, A. Syouji, S. Yamada, M. Komi, H. Yamazaki, S. Tajima, *Photochem. Photobiol. Sci.* **2009**, *8*, 139. e) J. J. Concepcion, M.-K. Tsai, J. T. Muckerman, T. J. Meyer, *J. Am. Chem. Soc.* **2010**, *132*, 1545. f) D. J. Wasylenko, C. Ganesamoorthy, B. D. Koivisto, M. A. Henderson, C. P. Berlinguette, *Inorg. Chem.* **2010**, *49*, 2202.

6 M. Yoshida, S. Masaoka, K. Sakai, *Chem. Lett.* **2009**, *38*, 702.

7 M. Yoshida, S. Masaoka, J. Abe, K. Sakai, *Chem. Asian J.*, in press.

8 A. Kimoto, K. Yamauchi, M. Yoshida, S. Masaoka, K. Sakai, submitted to *Chem. Lett.*

9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

10 a) K. Terada, K. Kobayashi, M. Haga, *Dalton Trans.* **2008**, 4846. b) Z. Chen, J. J. Concepcion, J. W. Jurss, T. J. Meyer, *J. Am. Chem. Soc.* **2009**, *131*, 15580.

11 a) J.-Y. Shim, J. P. Bowen, *J. Comput. Chem.* **1998**, *19*, 1370. b) N. L. Allinger, *J. Am. Chem. Soc.* **1977**, *99*, 8127. c) N. L. Allinger, Y. H. Yuh, J.-H. Lii, *J. Am. Chem. Soc.* **1989**, *111*, 8551.

12 H. Gotō, E. Ōsawa, *J. Chem. Soc., Perkin Trans. 2* **1993**, 187.

13 J. K. Hurst, J. L. Cape, A. E. Clark, S. Das, C. Qin, *Inorg. Chem.* **2008**, *47*, 1753.