Efficient Photochemical Water Oxidation by a Molecular Catalyst Immobilized onto Metal Oxides

Hidenobu Shiroishi, Mieko Nukaga, Satoshi Yamashita, and Masao Kaneko*
Faculty of Science, Ibaraki University, 2-1-1 Bunkyo, Mito, Ibaraki 310-8512

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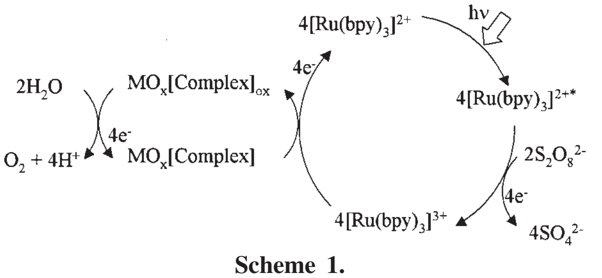
Photocatalytic water oxidation with a sacrifical electron acceptor has been studied using a ruthenium complexes adsorbed onto metal oxides as an active water oxidation catalyst. The amount of the O_2 evolved with the complex incorporated into RuO_2 was five to fourteen times as large as that with RuO_2.

Global warming caused by the increase in the consumption of fossil fuels is becoming more and more a serious problem. It is important to develop a permanent CO_2-free energy resource. The solar energy is one of the most promising energy resources for this purpose. Water splitting with visible light has been investigated during these two decades.[1–10] In order to achieve this, water molecules must be photochemically oxidized to provide electrons for the system to produce a reduction product (H_2).[11] However, it has been difficult to develop an active photochemical water oxidation catalyst because water oxidation is a four-electrons process that should be coupled with a one-electron process of a photoexcitation center. Photocatalytic water oxidation has been studied using sacrificial acceptor,[8–10] where metal oxides (i.e., IrO_2, Co_3O_4, RuO_2, $NiCo_2O_4$, Rh_2O_3, and Mn_2O_3) have been reported as water oxidation catalysts. In a photocatalytic water oxidation system, only few molecular catalysts have been reported as active water oxidation catalysts, although several water oxidation catalysts are active in dark such as $[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2]^{4+}$, Ru-red ($[(NH_3)_5RuO\text{-}Ru(NH_3)_4ORu(NH_3)_5]^{6+}$), *cis*-$[RuCl_2(NH_3)_4]^+$ and *trans*-$[RuCl_2(NH_3)_4]^+$ as reported by our group and others.[11–13] We have reported that the activity of molecular water oxidation catalysts in dark is remarkably enhanced and stabilized when incorporated into a polymer matrix.[11,13,14]

We have now found that these molecular catalysts are remarkably active for photochemical water oxidation when incorporated into RuO_2 particles, and will report the result.

Scheme 1 shows the photochemical water oxidation system used throughout this work. In the scheme, tris(2,2′-bipyridine) ruthenium(II) (abbreviated as $Ru(bpy)_3{}^{2+}$) absorbs visible light to form MLCT excited state of $Ru(bpy)_3{}^{2+*}$, which is then oxidized to $Ru(bpy)_3{}^{3+}$ by the persulfate ion ($S_2O_8{}^{2-}$), and water molecules are oxidized by this 3+ complex through a molecular catalyst incorporated into metal oxide (MO_x).



Scheme 1.

RuO_2, $[Ru(p\text{-cymene})Cl_2]_2$, $Et_4N[Ru(MeCN)_2Cl_4]$ and ($K_4[Ru(CN)_6]$) were purchased from Aldrich, and Ru-red and $K_2S_2O_8$ from Wako Pure Chemical Industries. $K_2S_2O_8$ was recrystallized twice before use.

The metal oxide was suspended in water at 298 K by sonication for 30 min after being ground with an agate mortar. Aqueous molecular catalyst was added to the metal oxide suspension and stirred for 9 h under dark. After centrifuging the suspension, the adsorption of the complex into the metal oxide was confirmed by the UV-Vis absorption spectrum of the supernatant.

The photoreaction was performed in a 5 cm^3 mixed solution of the water oxidation catalyst (MO_x[complex]), $K_2S_2O_8$ and $[Ru(bpy)_3]^{2+}$ in a reactor (12 cm^3). The pH of the solution was adjusted to 3 with phosphate buffer (H_3PO_4, 3.72×10^{-2} mol dm^{-3}; KH_2PO_4, 0.40 mol dm^{-3}). After the reactor was deaerated by argon gas for 30 min, it was irradiated with stirring using a tungsten-halogen lamp (140 mW cm^{-2}) through a cut-off filter of Toshiba L-42 for 1 h. Evolved dioxygen was analyzed by a Shimadzu GC-4A gas chromatograph using an Ar carrier gas.

Table 1 shows the results of the photochemical O_2 evolution using various complexes incorporated into RuO_2. Although RuO_2 works as a water oxidation catalyst solely,[8–10] the amount of the O_2 evolved with the complex incorporated into RuO_2 was five to fourteen times as large as that with RuO_2. Especially, $[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2]^{4+}$ incorporated into RuO_2 was the most active catalyst. After subtracting the catalysis by RuO_2, the turnover number of the complex attains 3284 h^{-1}.

It should be noted here that aqueous solution of these complexes is not active for the present photochemical water oxidation system probably because of their too much higher oxidation potential than that of the $Ru(bpy)_3{}^{2+/3+}$. Only when the complexes are incorporated into RuO_2, they worked as a photochemical water oxidation catalyst. This might be ascribed to a negative-shift of the redox potential of the adsorbed complex, which facilitates the oxidation by the $Ru(bpy)_3{}^{3+}$. Another reason could be much shorter distance between the adjacent complex molecules adsorbed onto RuO_2 than that in an aqueous solution, and such a condition would facilitate a bimolecular catalysis for the water oxidation.

Photochemical water oxidation was carried out using Ru-red incorporated into other metal oxides matrixes. The evolved O_2 increased when using IrO_2 as a matrix. When the metal oxide itself was inactive for water oxidation (MnO_2, CuO, Y_2O_3, and Ta_2O_5), the complex incorporated into the metal oxide did not function as a water oxidation catalyst, so that both the complex and the matrix might work cooperatively to oxidize water molecules.

Table 1. Activity of photochemical water oxidation catalysts immobilized onto RuO_2[a]

Complex[b]	Matrix[c]	$O_2/\mu l\,h^{-1}$	Turnover number of the complex[d]/h^{-1}	Quantum effeciency/%
—	RuO_2	52	—	0.05
$[Ru_2(p\text{-cymene})Cl_2]_2$	—	0	—	—
	RuO_2	322	1304	0.34
$Et_4N[Ru(MeCN)_2Cl_4]$	—	0	—	—
	RuO_2	285	1125	0.30
$[Ru(NH_3)_6]^{3+}$	—	0	—	—
	RuO_2	561	2458	0.59
$[(bpy)_2(H_2O)_2RuORu(H_2O)_2(bpy)_2]^{4+}$	—	39	—	0.04
	RuO_2	732	3284	0.77
$cis\text{-}[RuCl_2(NH_3)_4]^+$	—	10	—	0.01
	RuO_2	70	87	0.07
$[Ru(CN)_6]^{4-}$	—	0	—	—
	RuO_2	443	1888	0.47
$[Ru(terpy)_2]^{2+}$	—	0	—	—
	RuO_2	316	1275	0.33
Ru-red	—	4	—	—
	RuO_2	116	309	0.12

[a] $Ru(bpy)_3{}^{2+}$, 1 mmol dm^{-3}; pH, 3; Buffer, H_3PO_4/KH_2PO_4; $K_2S_2O_8$, 0.1 mol dm^{-3}; the amount of solution, 5 ml. [b] The concentration of the complexes is 1 mmol dm^{-3}. [c] The amount of RuO_2 is 6.65×10^{-4} g/5 ml which is corresponding to 1 mmol dm^{-3}. The amount of the complexes adsorbed onto RuO_2 is 1.26×10^{-5} mol/g. [d] Turnover number was estimated after subtraction of the catalysis by RuO_2.

It is known that hydrated state and structure of RuO_2 can change by treatment condition.[15] The activity of the RuO_2[complex] could also be affected by the pre-treatment conditions. Further investigation is in progress in this regard.

In summary, the ruthenium complexes incorporated into RuO_2 worked as highly efficient photochemical water oxidation catalysts. The present result is an important step for the water photolysis.

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