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Sakai, Ken
Department of Chemistry, Faculty of Science, Kyushu University | International Institute for Carbon-Neutral Energy Research (WPI-I2CNER) | Center for Molecular Systems (CMS)

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Water Oxidation and CO$_2$ Reduction Catalyzed by Co-, Cu- and Ru-Centered Catalysts including Cobalt Porphyrins

Ken Sakai[a,b,c]

[a]*Department of Chemistry, Faculty of Science, Kyushu University*
[b]*International Institute for Carbon-Neutral Energy Research (**WPI-I2CNER**), Kyushu University*
[c]*Center for Molecular Systems (**CMS**), Kyushu University*

The tetramanganese cluster having a Mn$_4$CaO$_5$ core was successfully invented by Nature so that the photosynthetic centers can extract protons and electrons from water at an extremely high turnover frequency (TOF = 100-500 s^{-1}), even though such fast rates are not only limited by the water oxidation (WO) rate but also by all other photochemical events as well as the relevant electron transport events around the lipid bilayers. One of our initial approaches in the area of water oxidation catalysis was given by finding the fact that a mononuclear aquaruthenium center in [Ru(terpy)(bpy)(H$_2$O)]$^{2+}$ can serve as an effective water oxidation catalyst (WOC), in which a Ru(V)=O species was proven to be the active intermediate involved in the rate-limiting O-O bond forming step.[1] We also pointed out that the Ce(IV)(OH) species is also involved in this O-O bond forming step.[1] In relation to the finding in the high WO activity by heterogeneous cobalt(II) phosphates (Kanan & Nocera, *Science* **2008**, *321*, 1072) , we started to pay attention to the cobalt-centered WOCs with our special focus put on the utilization of single-metal-centered WOCs. Actually, we evidenced that mono-cobalt- and di-cobalt-centered POMs (polymolybdates) are highly active for WO.[2] We were even aware of the fact that such simpler WOCs are even higher in activity, for example, when compared with the tetra-cobalt-centered POM reported by Hill *et al.* (*Science* **2010**, *328*, 342). Thus, our recent study is still focused on the clarification of reaction kinetics of WO by the mono-cobalt POM, the part of which may be discussed in this presentation. On the other hand, we also unveiled the fact that simple water-soluble cobalt porphyrins are sufficiently active as WOCs in photochemical WO system consisting of [Ru(bpy)$_3$]$^{2+}$ (photosensitizer) and persulfate (electron donor).[3-5] During these studies, we also clarified that cobalt porphyrin WOCs are gradually degrading into non-heterogeneous (i.e., homogeneous) ligand-oxidized species which are much less active for WO due to attack by singlet oxygen which is generating during the photochemical WO catalysis.[3] We succeeded in improving the resistance of porphyrins to the attack by singlet oxygen by introducing fluorine or chlorine atoms at the 2,6-positions of arryl groups in TPPs (tetraphenylporphyrins).[4,5] Our recent studies also involve the WO activity of a water-soluble copper phthalocyanine together with that of a triruthenium WOC having a Ru-O-Ru-O-Ru backbone.[6-8] Part of these studies may also be discussed in this presentation. If the time allows, our recent results on the CO$_2$ reduction catalysed by water-soluble cobalt porphyrins may also be discussed.

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