

論文名 : Development of efficient photoanodes and cluster catalysts for water oxidation toward an artificial photosynthetic device (Abstract)

人工光合成デバイスに向けた高効率光アノードおよび水の酸化触媒の開発 (要約)

新潟大学大学院自然科学研究科

氏名 張 曉紅

---

Artificial photosynthesis is expected as an innovative energy conversion device to generate high energy compounds such as hydrogen and carbohydrate using solar energy as driving force and water as an electron source. Water oxidation catalysts are required to extract electrons from water for artificial photosynthesis. Although water oxidation catalysts have been reported in recent years, construction of artificial photosynthesis has been hampered by a lack of efficient catalysts being made from earth-abundant elements. The photoanodes for water oxidation are needed in photoelectrochemical (PEC) cells as one of artificial photosynthesis models, following the pioneer work on a  $\text{TiO}_2$  photoanode for water splitting by Honda and Fujishima. Unfortunately a wide band gap of  $\text{TiO}_2$  (3.0-3.2 eV) causes to absorb only an ultraviolet fraction of a solar spectrum (accounts for just 4% of solar irradiation) and consequently responsible for low efficiency in utilization of solar light. Therefore, intensive researches have been focused on materials with a relatively narrower band gap than  $\text{TiO}_2$  to expand light absorption to a visible region.  $\text{WO}_3$  as an n-type semiconductor has attracted immense attention as a photoanode material for water oxidation in PEC cells because of its visible light response (band gap,  $E_g = 2.6\text{-}2.8$  eV), a valence band edge position possible for water oxidation (3 V versus the normal hydrogen electrode) and good photochemical stability under acidic conditions. The purpose of the present research for my doctoral dissertation is development of efficient photoanodes and cluster catalysts for water oxidation to

develop an artificial photosynthesis system.

We synthesized nanocluster catalysts for water oxidation by hybridization of mononuclear complexes and clay compounds using *trans*-[Co(NO<sub>2</sub>)<sub>2</sub>(en)<sub>2</sub>]<sup>+</sup> (**1**), *cis*-[Co(NO<sub>2</sub>)<sub>2</sub>(en)<sub>2</sub>]<sup>+</sup> (**2**), *cis*-[Co(NO<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]<sup>+</sup> (**3**), *trans*-[Co(NO<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]<sup>+</sup> complexes as precursors. Among these hybrid catalysts, (mica / Co)<sub>cal.400</sub> (Co = **1**, **2** or **3**) prepared by calcination at 400 °C, the maximum turnover frequency (k<sub>O<sub>2</sub></sub>) of **1**, **2** and **3** were 7.24 × 10<sup>-4</sup>, 0.70 × 10<sup>-4</sup> and 2.11 × 10<sup>-4</sup> s<sup>-1</sup> respectively. (mica / **1**)<sub>cal.400</sub> exhibited the highest activity for catalytic O<sub>2</sub> evolution, demonstrating that the geometric structure of the precursor complex is very important for the high catalytic activity of the Co nanocatalyst. This result further encouraged us to design a photochemical O<sub>2</sub> evolution system by using (mica / Co)<sub>cal.400</sub> together with a photosensitizer ([Ru(bpy)<sub>3</sub>]<sup>2+</sup>) (bpy = 2, 2'-bipyridine) and an electron acceptor (Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>). Mica is able to adsorb cationic **1** and [Ru(bpy)<sub>3</sub>]<sup>2+</sup> by cation exchange with Na<sup>+</sup>. **1** was adsorbed onto mica from an aqueous solution of **1** to yield a mica / **1** adsorbate. Then, mica / **1** adsorbate was calcined at 400°C for 3h in air, resulting in (mica / **1**)<sub>400</sub>. Next, It followed by similar adsorption of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> to yield a (mica / **1**)<sub>400</sub> / [Ru(bpy)<sub>3</sub>]<sup>2+</sup> adsorbate. The reaction of the (mica / **1**)<sub>400</sub> / [Ru(bpy)<sub>3</sub>]<sup>2+</sup> adsorbate in acetic acid buffer suspension containing Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> under visible light irradiation (λ = 420 nm) yielded O<sub>2</sub> evolution. The turnover frequency of the cobalt catalyst was 3.0 × 10<sup>-5</sup> s<sup>-1</sup>. In the absence of neither a component of **1**, [Ru(bpy)<sub>3</sub>]<sup>2+</sup> nor Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, was O<sub>2</sub> evolved, showing these three components are essential for the photoinduced O<sub>2</sub> evolution. The photocatalytic activities of these nanocluster catalysts were investigated.

Tungsten trioxide (WO<sub>3</sub>) films with nanoporous morphology were prepared by a facile and simple method utilizing commercially available WO<sub>3</sub> nanopowder with polyethylene glycol to guide porosity of a nanostructure, and the resulted photoanode

was working efficiently for visible-light-driven water oxidation. The SEM observation and XRD measurement revealed formation of interparticulate nanopores between the well-connected WO<sub>3</sub> crystalline particles of dimension ca. 100-200 nm. The nanoporous WO<sub>3</sub> electrode generated a significant photoanodic current density of 1.8 mA cm<sup>-2</sup> due to water oxidation at 1.0 V versus Ag/AgCl on visible light irradiation ( $\lambda > 390$  nm, 100 mW cm<sup>-2</sup>). The onset potential of the WO<sub>3</sub> electrode was 0.67 V versus a reversible hydrogen electrode (RHE), being lower by 0.56 V than the theoretical potential for water oxidation (1.23 V versus RHE). The incident photon to current conversion efficiency (IPCE) reached 45% at 400 nm of light wavelength and 1.04 V versus Ag/AgCl of an applied potential. The photoanodic current and photostability of the WO<sub>3</sub> electrode were improved by addition of Co<sup>2+</sup> ions in the electrolyte solution during photoelectrocatalysis.