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## Direct oxygen and hydrogen production by photo water splitting using a robust bioinspired manganese-oxo oligomer complex/tungsten oxide catalytic system

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### ARTICLE INFO

#### Article history:

Received 15 October 2011

Received in revised form

6 February 2012

Accepted 14 February 2012

Available online 16 March 2012

#### Keywords:

Manganese

Tungsten oxide

Water splitting

PS II

Catalysis

Hydrogen production

### ABSTRACT

The n-type semiconductor tungsten oxide is readily dissolved in aqueous solution at pH > 4 and may be problematic in water splitting catalysis. We have reported that a tungsten oxide photoanode prepared by atomic layer deposition can be stabilized with a Mn-oxo compound for efficient photo water splitting at pH 4 and pH 7. However the molecular mechanism of water oxidation reaction in this robust catalytic system is not known. In this work, the mechanism for oxygen and hydrogen production by photo water splitting using Mn-oxo complex/tungsten oxide heteronanostructures was examined under different experimental conditions by X-ray photoelectron spectroscopy as well as gas chromatographic analysis, O-18 isotope measurements, and pH dependence of photocurrent. We found that the Mn(II) species plays an important role in the catalytic cycle of water oxidation in the Mn-oxo oligomer complex/tungsten oxide system and propose a working model of the Mn-oxo oligomer complex/tungsten oxide catalytic system in photo water splitting.

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**Abbreviations:** ALD, Atomic layer deposition; EDS, Energy-dispersive X-ray spectroscopy; EPR, Electron paramagnetic resonance spectroscopy; FTIR, Fourier transform infrared spectroscopy; GC, Gas chromatography; GC/MS, Gas chromatography/mass spectrometry; Mn(III/IV)-oxo dimer,  $[\text{Mn(III)(O)}_2\text{Mn(IV)(H}_2\text{O)}_2(\text{Terpy})_2(\text{NO}_3)_3]$ ; OEC, Oxygen Evolving Complex; Oxone, Potassium Peroxy-monosulfate,  $\text{KHSO}_5$ ; PS II, Photosystem II; TEM, Transmission electron microscopy; Terpy, 2,2':6',2''-terpyridine; TW,  $10^{12}$  W;  $\text{WO}_3$ , Tungsten oxide; XPS, X-ray Photoelectron Spectroscopy.

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doi:10.1016/j.ijhydene.2012.02.074

## 1. Introduction

The use of fossil fuels produces carbon dioxide, creating a significant negative impact on the environment and causing global warming. To address these issues, novel renewable carbon-free or carbon-neutral energy sources must be identified and generated in next 10–50 years. Compared with all other energy options, solar energy is the most promising and the only source of truly renewable energy [1]. Earth receives solar energy at the rate of approximately 120,000 TW (1 TW =  $10^{12}$  W), which exceeds the current annual worldwide energy consumption rate of approximately 15 TW [1,2]. Photosynthesis provides an excellent example of utilization of solar energy on the large scale [3–6]. Solar energy conversion via water splitting occurs in the reaction center of photosystem II (PSII) in cyanobacteria, algae, and green plants. The three-dimensional structures of PSII with oxygen evolving activity were determined at the atomic and molecular level [7–9]. These advances in understanding the natural photosynthetic water splitting chemistry provide a solid basis for unraveling the mechanisms of water splitting and O-O band formation.

The synthetic biology using genetic engineering techniques might be used to enhance natural photosynthesis for improved solar energy conversion efficiency [2]. For example, some species of cyanobacteria possess chlorophyll d and chlorophyll f that use the sunlight energy in the near-IR (700 and 750 nm wavelength range) with the similar or higher energy storage efficiency similar to the chlorophyll a species [10–12]. The techniques of synthetic biology may offer a radical design of the photosynthetic apparatus for bioenergy application.

By mimicking the photoinduced charge separation and water oxidation in natural photosynthesis, molecular and supramolecular model systems based on transition metal elements can be developed for potentially practical solar fuel production [13–29]. The design of functional oxygen evolving catalysts was successfully achieved in synthesizing Mn-containing compounds [30]. One such example is a Mn-oxo tetramer compound,  $[\text{Mn}_4\text{O}_4(\text{dpp})_6]$ , developed by Dismukes and co-workers [31]. The key feature of the compound is its cubical  $[\text{Mn}_4\text{O}_4]^{n+}$  core surrounded by six bridging bidentate chelates to the manganese ions. Due to the insolubility of cubium in water and organic solvents, the Mn-oxo tetramer/Nafion system is developed by depositing the cubium into the thin Nafion membrane. The resulting Mn-oxo tetramer/Nafion system is able to efficiently photoelectrooxidize water to oxygen gas [22].

Another excellent example is Brudvig Mn-oxo dimer,  $([\text{OH}_2(\text{terpy})\text{Mn}(\text{O})_2\text{Mn}(\text{terpy})\text{OH}_2](\text{NO}_3)_3 \cdot 6\text{H}_2\text{O})$  [32]. The Mn-oxo dimer is able to evolve oxygen in the presence of chemical oxidants such as oxone or  $\text{Ce}^{4+}$  ion. The discovery provides significant insights into the mechanisms of water oxidation in PSII oxygen evolving complex (OEC) [32–37]. It is generally established that the active catalytic species is  $\text{Mn}(\text{V}) = \text{O}$  or  $\text{Mn}(\text{V})$ -oxo radical, which is capable of releasing oxygen and closes the S-state cycle. The Mn-oxo dimer compound can be directly deposited on the  $\text{TiO}_2$  nanoparticles [4,38,39]. Mn-oxo dimer on the  $\text{TiO}_2$  is dimerized and forms Mn-oxo tetramer. In the presence of chemical oxidant  $\text{Ce}^{4+}$ ,

the Mn-oxo tetramer attached to the  $\text{TiO}_2$  is able to oxidize water to oxygen.

However the Mn-oxo dimer is unstable under elevated temperature. We have observed the dissociation reaction of Mn(III/IV) dimer compound at 60–80 °C [40]. Unexpectedly, the oxygen evolution measurements showed an activity increase after the decomposition reaction was completed. We concluded that one water splitting catalyst with higher activity was formed in the solution. Several lines of evidence using Fourier transform infrared (FTIR), electron paramagnetic resonance (EPR), and elemental analysis demonstrated that the solid Mn-oxo catalytic material is neither Mn-oxo dimer nor  $\text{MnO}_2$  species. We assigned the solid unknown Mn-oxo catalyst to a Mn-oxo oligomer complex, which is thermal stable and may be a unique option for constructing catalytic system in solar energy storage via water splitting reaction.

Using the atomic layer deposition (ALD) method, we have previously synthesized tungsten oxide heterostructures for efficient photo water splitting [21]. The experimental data showed the ALD growth of tungsten oxide without production of corrosive byproducts. However, the tungsten oxide is readily dissolved in aqueous solution with  $\text{pH} > 4$  [21,41,42]. To solve this problem, a thin layer of Mn-oxo oligomer complex was coated on the tungsten oxide ( $\text{WO}_3$ ) surface. The resulting Mn-oxo oligomer complex/ $\text{WO}_3$  system is a robust photo water splitting catalyst to generate oxygen and hydrogen gas at pH 4 and pH 7 [21]. Multiple techniques including gas chromatography (GC) analysis, O-18 isotope measurements, and photoelectrochemical experiments demonstrated that the detected oxygen gas is the direct product of water splitting. However, the mechanism of the water splitting reaction in the Mn-oxo oligomer complex/ $\text{WO}_3$  system is unknown. In this work, we investigated the water splitting reaction under different conditions using XPS technique as well as GC, gas chromatography/mass spectrometry (GC/MS) and pH dependence of photocurrent and proposed a possible working model of the robust Mn-oxo Mn-oxo oligomer complex/ $\text{WO}_3$  catalytic system for direct oxygen and hydrogen production by photo water splitting.

## 2. Experimental

### 2.1. Synthesis of Mn(III/IV)-oxo dimer

The Mn(III/IV)-oxo mix valent dimer compound,  $[\text{Mn}(\text{III})(\text{O})_2\text{Mn}(\text{IV})(\text{H}_2\text{O})_2(\text{Terpy})_2](\text{NO}_3)_3$ , was synthesized according to the procedures reported previously [35]. In brief,  $\text{Mn}(\text{OAc})_2$  and 2,2':6,2''-terpyridine were dissolved in water, and then  $\text{KHSO}_5$  was added dropwise with stirring. The yellow solution turned dark green and was cooled resulting in a green precipitate. The product was confirmed by the microelemental analysis. All solutions were prepared using doubly deionized water.

### 2.2. Synthesis of the Mn-oxo oligomer complex/ $\text{WO}_3$ heterostructures

Tungsten oxide film was synthesized according to the published procedures [21]. In brief,  $\text{WO}_3$  was synthesized in

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