



Polyoxometalate-based manganese clusters as catalysts for efficient photocatalytic and electrochemical water oxidation



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ABSTRACT

A manganese containing polyoxometalate (POM) $[\text{Mn}_3(\text{H}_2\text{O})_3(\text{SbW}_9\text{O}_{33})_2]^{12-}$ (**1**) was synthesized and characterized in detail. The photocatalytic activity of **1** is definitely better than other manganese containing POM water oxidation catalysts reported so far according to oxygen yield, whereas the analogues $[\text{Mn}_3(\text{H}_2\text{O})_5(\text{PW}_9\text{O}_{34})_2]^{9-}$ (**2**) and $[\text{Mn}_3(\text{H}_2\text{O})_3(\text{AsW}_9\text{O}_{33})_2]^{12-}$ (**3**) show no to slight photocatalytic O_2 evolution amount. Meanwhile, the electrocatalytic activities of **1-3** were investigated in 80 mM pH 9.0 borate buffer, which follows the catalytic activity order of **1** > **2** > **3**. Multiple experiments including UV–vis absorption, catalysts aging experiments, tetra-*n*-heptylammonium nitrate (THpANO₃) toluene extraction, electrochemical experiments and capillary electrophoretic measurements results confirm that catalyst **1** is a homogeneous molecular catalyst. No Mn^{2+} (aq.) or manganese oxide under the reaction conditions of photocatalytic and electrochemical water oxidation was detected.

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1. Introduction

Energy is a universal human requirement and most energy is derived from fossil fuels. Some of which are rapidly exhausting, and their final product is CO_2 , a major source of anthropogenic global warming. To address those issues, we should exploit more renewable and carbon-neutral energy sources of sufficient scale [1–4]. Splitting water into H_2 and O_2 by sunlight is considered as one of the most promising ways to produce green and renewable energy, which is expected to meet the rising global energy demand in future. Photolysis of water consists of two half-reactions: the reduction of protons to H_2 and the oxidation of water to O_2 [5]. The oxidation of water can be viewed as a vital step of the energy-transfer process in both natural and artificial photosynthesis [6]. Therefore, the development of stable, efficient, and low-cost water oxidation catalysts (WOCs) has become especially important for the conversion of sunlight into green and accumulation chemical energy [7]. Just in the last few years, under photochemical or elec-

trochemical conditions, a lot of meaningful WOCs based on Cu [8,9], Ni [10,11], Fe [12,13], Co [14,15], and Mn [16,17] elements have been developed for water oxidation. Among the various transition-metal-based WOCs, manganese is a very abundant element in the Earth's crust and Mn-based compounds are already considered to be one of prominent WOCs due to their characteristic of non-toxic and excellent water oxidation ability. What is more, Mn-based compounds containing cubane unit can function as models for the catalytic Mn_4CaO_5 center in the oxygen evolving complex (OEC) of photosystem II (PSII) [18].

In the last couple of years, there were various kinds of WOCs have been developed for water oxidation. One of the most promising WOCs is polyoxometalates (POMs) because they can stand against fast, invertible, and stepwise multielectron-transfer reactions without changing their structures [19–22]. It should be noted that the introduction of transition metal into POMs can adjust the band gap structures and even broaden the absorption range from UV to visible light region of such molecular clusters [23,24]. Recently, a mass of POMs based on Cu [25], Ni [26–28], Fe [29], Co [30–37], Mn [16,38], and V [39] have been researched extensively as catalysts for water oxidation by different groups. However, in contrast to other transition metal-based WOCs, few manganese containing POM as WOCs have been achieved for water oxidation.

Herein, we first report manganese containing POM of $[\text{Mn}_3(\text{H}_2\text{O})_3(\text{SbW}_9\text{O}_{33})_2]^{12-}$ (**1**) as an efficient photocatalytic and

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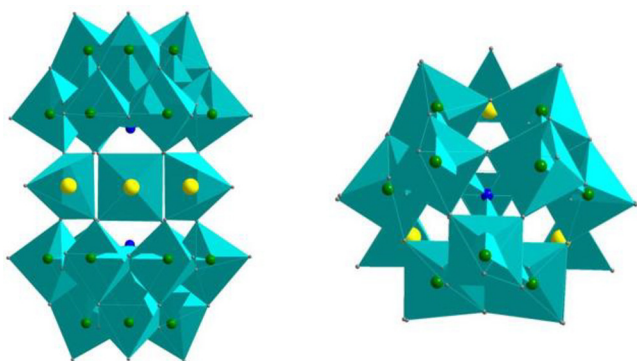
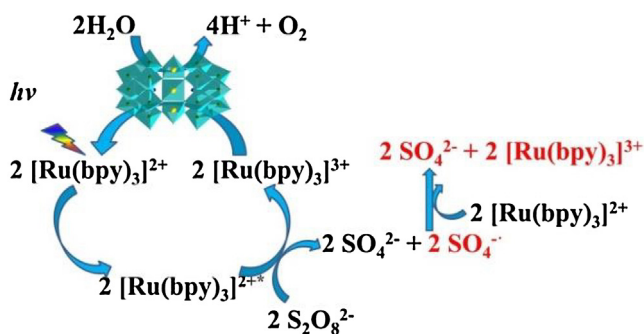


Fig. 1. Combined polyhedral representation of **1**. The color code is as follows: manganese, yellow; tungsten, green; antimony, blue; oxygen, gray.



Scheme 1. Principal processes of an O_2 evolution light-driven water oxidation system.

electrochemical water oxidation catalyst. This Mn-substituted POM **1** was first reported by Bernt Krebs and co-workers in 1998 [40]. The heteropolyanion **1** consists of two identical $\text{Na}_9[\text{SbW}_9\text{O}_{33}]$ Keggin portion, in which the arrangement of the WO_6 octahedron around the SbO_3 pyramid. The two Keggin portion are linked together by three manganese (II) ions, leading to a sandwich-type assembly (Fig. 1). **1** was made up of only earth-abundant elements (manganese, antimony, tungsten, and oxygen), which can catalyze water oxidation under photochemical and electrochemical conditions. The catalytic ability of **1** was compared with its analogues: $[\text{Mn}_3(\text{H}_2\text{O})_5(\text{PW}_9\text{O}_{34})_2]^{9-}$ (**2**) and $[\text{Mn}_3(\text{H}_2\text{O})_3(\text{AsW}_9\text{O}_{33})_2]^{12-}$ (**3**) and other POMs containing Mn with different structures. Furthermore, the corresponding simple manganese salt ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) was investigated as control comparison experiment for water oxidation. Under reaction conditions, a turn-over number (TON) of 103 and turn-over frequency ($\text{TOF}_{\text{initial}}$) of 0.4 s^{-1} over **1** were obtained for the photocatalytic water oxidation and the analogues **2** and **3** show no to slight activity. The same reactive activity sequence is further supported by electrocatalytic behavior. The reaction mechanism of the visible light-driven water oxidation catalyzed by **1** is depicted in Scheme 1.

2. Experiment section

2.1. Materials

All chemicals and salts (analytical grade) were used as received without any further purification. $\text{Na}_9[\text{SbW}_9\text{O}_{33}]$, $\text{Na}_9[\alpha\text{-PW}_9\text{O}_{34}]$ and $\text{Na}_9[\alpha\text{-AsW}_9\text{O}_{33}]$ were synthesized according to the literature [41,42]. Purified water ($18.2 \text{ M}\Omega \text{ cm}$) for the preparation of solutions was attained from a Molecular Lab Water Purifier.

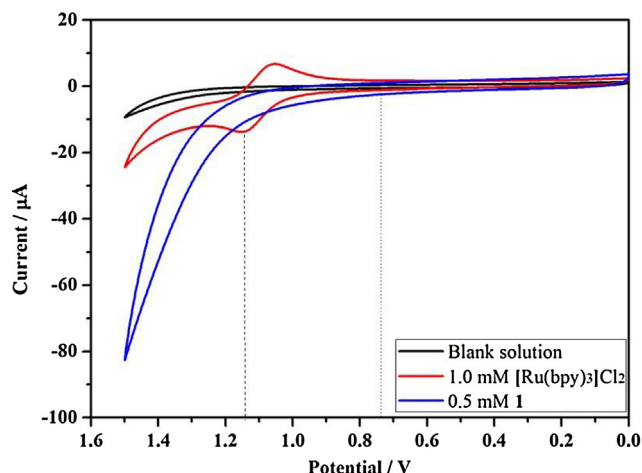


Fig. 2. CV of 0.5 mM **1** (blue curve) and 1.0 mM $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (red curve) in borate buffer solution (80 mM, pH 9.0). Black curve shows the CV curve of borate buffer (80 mM, pH 9.0) in the absence of **1** and $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$. Conditions: glassy carbon working electrode, Ag/AgCl (saturate KCl) reference electrode and Pt wire counter electrode; scan rate 100 mV/s. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.2. Catalyst preparation

$\text{Na}_{11}(\text{NH}_4)[(\text{Mn}(\text{H}_2\text{O}))_3(\text{SbW}_9\text{O}_{33})_2]$ ($\text{Na}_{11}(\text{NH}_4)$ -**1**). $\text{Na}_{11}(\text{NH}_4)$ -**1** was synthesized according to the report by Bernt Krebs [40]. 4 g of $\text{Na}_9[\text{SbW}_9\text{O}_{33}]$ was dissolved in 8 mL water with gentle heating. 0.414 g of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in 10 mL water was then added slowly to the above system with stirring and resulting in an orange solution with pH 6–7. This solution was refluxed for 1 h, and then 0.673 g of NH_4NO_3 was added, allowed to cool. Slow evaporation of the mixture at ambient temperature led to the formation of dark orange crystals of $\text{Na}_{11}(\text{NH}_4)$ -**1** within several days. Yield: 35 mg. FT-IR (cm^{-1}) for $\text{Na}_{11}(\text{NH}_4)$ -**1**: 938, 835, 770, 717. Elemental analysis calculated (%) for **1**: Mn, 2.78. Found: Mn, 2.89.

$\text{K}_6\text{Cs}[\text{C}(\text{NH}_2)_3]_2[\text{Mn}_3(\text{H}_2\text{O})_5(\text{PW}_9\text{O}_{34})_2]$ ($\text{K}_6\text{Cs}[\text{C}(\text{NH}_2)_3]_2$ -**2**). $\text{K}_6\text{Cs}[\text{C}(\text{NH}_2)_3]_2$ -**2** was synthesized according to a procedure reported by Ulrich Kortz [43]. Yield: 29 mg. FT-IR (cm^{-1}) for $\text{K}_6\text{Cs}[\text{C}(\text{NH}_2)_3]_2$ -**2**: 1085, 1027, 945, 900, 790, 596. Elemental analysis calculated (%) for **2**: Mn, 2.93. Found: Mn, 3.05.

$\text{K}_{11}\text{Na}_1[\text{Mn}_3(\text{H}_2\text{O})_3(\text{AsW}_9\text{O}_{33})_2]$ (K_{11}Na_1 -**3**). K_{11}Na_1 -**3** was synthesized according to a procedure reported by Pierre Mialane [44]. Yield: 58 mg. FT-IR (cm^{-1}) for K_{11}Na_1 -**3**: 1087, 1046, 1013, 933, 876, 829, 773, 598, 520. Elemental analysis calculated (%) for **3**: Mn, 2.90. Found: Mn, 3.08.

3. Results and discussion

3.1. Photocatalytic water oxidation performance

In order to investigate the ability of **1** catalyzing water oxidation, the cyclic voltammetry (CV) characterizations was performed with $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ and **1**. As shown in Fig. 2, a catalytic water oxidation wave of **1** is observed at onset potential at approximately 0.72 V (vs. Ag/AgCl). However, in the absence of **1**, no obvious catalytic current was detected in the same reaction conditions and operation procedure. So it is demonstrable that **1** has the ability to catalyze the water-oxidation reaction. In addition, the redox potential of $[\text{Ru}(\text{bpy})_3]^{3+}/[\text{Ru}(\text{bpy})_3]^{2+}$ in the same reaction system is much more positive (1.14 V vs Ag/AgCl) than the onset potential of the catalyst (Fig. 2 dash curve and dot curve). Considering the

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