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Article

A novel dicobalt-substituted tungstoantimonate polyoxometalate: Synthesis, characterization, and photocatalytic water oxidation properties

Qing Han ^a, Di Sun ^c, Junwei Zhao ^d, Xiangming Liang ^a, Yong Ding ^{a,b,*}^a State Key Laboratory of Applied Organic Chemistry, Key Laboratory of Nonferrous Metals Chemistry and Resources Utilization of Gansu Province, and College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, Gansu, China^b State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, Gansu, China^c Key Laboratory of Colloid and Interface Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, Shandong, China^d Henan Key Laboratory of Polyoxometalate Chemistry, Institute of Molecule and Crystal Engineering, College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, Henan, China

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ABSTRACT

The one-pot assembly reaction of a trilacunary, lone-pair-containing $[B-\alpha-SbW_9O_{33}]^{9-}$ precursor with Co^{2+} ions in an aqueous medium led to the isolation of a novel $\{SbO_3(H_2O)_3\}$ bridging, dicobalt-substituted, sandwich-type tungstoantimonate $\{Co_2Sb_2(H_2O)_{10}[B-\beta-SbW_9O_{33}]_2\}^{4-}$ (**1a**). This compound was structurally characterized in the solid state by single-crystal X-ray diffraction, elemental analyses, thermogravimetric analysis, and IR spectroscopy. The most remarkable feature was that **1a** comprises two trilacunary $[B-\beta-SbW_9O_{33}]^{9-}$ fragments trapping a novel, centrally symmetric, rhomb-like $\{Co_2Sb_2\}$ belt with 10 terminal water molecules. When combined with the photosensitizer $[Ru(bpy)_3]^{2+}$ and the sacrificial electron acceptor $S_2O_8^{2-}$, **1a** exhibited efficient catalytic activity for water oxidation with a remarkable turnover number (TON) of 193, initial turnover frequency (TOF_{initial}) of $5.3\ s^{-1}$, O_2 yield of 30.8%, and quantum yield (Φ_{O_2}) of 36.2% under light-driven conditions.

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1. Introduction

Light-driven water splitting to hydrogen and oxygen, which is one of the most desirable and promising strategies to resolve the current energy and environmental crisis, has been receiving much attention [1–4]. Water oxidation (WO) ($2H_2O \rightarrow 4H^+ + 4e^- + O_2$) is considered the bottleneck in water splitting during the energy conversion scheme, in both natural and artificial

photosynthesis [5], which requires efficient and stable water oxidation catalysts (WOCs) [6,7]. In the last few decades, worldwide research efforts have contributed to the design of robust and highly active homogeneous and heterogeneous WOCs [8–12].

In the field of homogeneous WOCs, polyoxometalates (POMs) [13–15], an excellent class of molecular metal-oxygen clusters with highly oxidized early transition metals (TM), have

* Corresponding author. E-mail: dingyong1@lzu.edu.cn

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attracted widespread attention. This is because of their ability to undergo fast, reversible, and stepwise multielectron-transfer reactions without changing their structures due to their high oxidative, thermal, and hydrolytic stability [16–20]. In 2009, Hill and co-workers [21] reported the first use of a tetra-ruthenium polyoxometalate complex, $[\{\text{Ru}_4\text{O}_4(\text{OH})_2(\text{H}_2\text{O})_4\}(\text{SiW}_{10}\text{O}_{36})_2]^{10-}$, to catalyze WO in a totally homogeneous, visible light-driven, and artificial photosynthesis system at neutral pH. In 2011, they found that a cobalt-based POM, $[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$ (abbreviated as $\text{Co}_4\text{P}_2\text{W}_{18}$), was competent as an efficient molecular catalyst for the visible light-driven catalytic oxidation of water [22]. In 2014, Wang's group [23] reported on a series of high-nuclearity cobalt-based POM-WOCs such as $[\{\text{Co}_4(\text{OH})_3(\text{PO}_4)_4\}(\text{SiW}_9\text{O}_{34})_4]^{32-}$, $[\{\text{Co}_4(\text{OH})_3(\text{PO}_4)_4\}(\text{GeW}_9\text{O}_{34})_4]^{32-}$, $[\{\text{Co}_4(\text{OH})_3(\text{PO}_4)_4\}(\text{PW}_9\text{O}_{34})_4]^{28-}$, and $[\{\text{Co}_4(\text{OH})_3(\text{PO}_4)_4\}(\text{AsW}_9\text{O}_{34})_4]^{28-}$. This study not only provides a valuable molecular model structurally analogous to the $[\text{Mn}_3\text{O}_5\text{Ca}]$ core but also an unprecedented opportunity to construct polynuclear TM-based POM-WOCs for visible light-driven WO. Our group has worked extensively in this area and reported a highly stable and effective mixed-valence WOC $[\text{Co}^{\text{III}}\text{Co}^{\text{II}}(\text{H}_2\text{O})\text{W}_{11}\text{O}_{39}]^{7-}$ in 2013 and a mononuclear cobalt(II)-substituted silicotungstate WOC $[\text{Co}(\text{H}_2\text{O})_2(\gamma\text{-SiW}_{10}\text{O}_{35})_2]^{10-}$ in 2014 [24,25]. Recently, we had reported an oxidatively and hydrolytically stable bioinspired molecular WOC based on a polyoxometalate $[(\text{SiW}_9\text{O}_{34})_2\text{Co}_8(\text{OH})_6(\text{H}_2\text{O})_2(\text{CO}_3)_3]^{16-}$, which exhibited excellent WO activity with a very high turnover number (TON) of 1436 [26].

There are very few reports on TM-substituted tungstoantimonates that act as WOCs, because Sb^{3+} hydrolyzes in aqueous solutions, which to a great extent impedes combination with TM ions into POM clusters. A majority of the addressed TM-substituted tungstoantimonates were prepared through the assembly of the trivacant Keggin polyoxoanion $[\text{SbW}_9\text{O}_{33}]^{9-}$ with different types of TM ions [27–34]. This is of great interest to us, as it provides an excellent opportunity to further research on tungstoantimonate incorporating TM clusters. Thus, we adopted a one-pot self-assembly strategy that allowed us to effectively prepare a novel TMSP by integrating the well-defined secondary building blocks $[\text{SbW}_9\text{O}_{33}]^{9-}$ with Co^{2+} ions.

Herein, we first synthesized an octahedral, $[\text{SbO}_3(\text{H}_2\text{O})_3]$ bridging, dicobalt-substituted, sandwich-type tungstoantimonate $[\text{Na}_4\{\text{Co}_2\text{Sb}_2(\text{H}_2\text{O})_{10}(\text{B-}\beta\text{-SbW}_9\text{O}_{33})_2\} \cdot 39\text{H}_2\text{O}]$ (**1**) and found that it could be used as a homogeneous catalyst for the efficient production of O_2 under visible-light irradiation. Under the optimal photocatalytic conditions, i.e., photoirradiation at $\lambda = 460$ nm with $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ as a photosensitizer and $\text{Na}_2\text{S}_2\text{O}_8$ as an oxidant in borate buffer (pH = 8.5), the TON could reach a value as high as 193 with an O_2 yield of 30.8%. The initial quantum yield (Φ_{QY}) and initial turnover frequency ($\text{TOF}_{\text{initial}}$) in the first 20 s were 36.2% and 5.3 s^{-1} , respectively. Variables of the photocatalytic reaction, including catalyst concentration, buffer type and concentration, pH, dye concentrations, and oxidant concentration, were systemically studied.

2. Experimental

2.1. Synthesis of **1**

$[\text{Na}_9(\text{B-}\alpha\text{-SbW}_9\text{O}_{33})] \cdot 19.5\text{H}_2\text{O}$ was prepared as described in the literature and confirmed based on the IR spectra [35]. Other common laboratory chemicals were analytically pure, purchased from commercial sources, and used without further purification.

$\text{Na}_9[\text{B-}\alpha\text{-SbW}_9\text{O}_{33}] \cdot 19.5\text{H}_2\text{O}$ (2.004 g, 0.70 mmol), AgNO_3 (0.102 g, 0.60 mmol), and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.152 g, 0.52 mmol) were dissolved in 30 mL of deionized water with stirring, and the pH of the solution was carefully adjusted to 4.0 at room temperature by the addition of dilute HNO_3 solution (6 mol/L). The solution was stirred continuously for 1 h, heated at 80°C for 3 h, and then filtered upon cooling to room temperature. Slow evaporation of the filtrate for two weeks at room temperature led to the formation of purple cubic block crystals of **1**. Yield: ca. 28% (based on $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). Anal. Calcd (%) for $\text{H}_{98}\text{Co}_2\text{Na}_4\text{O}_{115}\text{Sb}_4\text{W}_{18}$: H 1.66, Na 1.54, Co 1.98, Sb 8.19; found: H 1.90, Na 2.42, Co 1.81, Sb 8.25. IR (KBr pellets, cm^{-1}): 3432 (vs), 1623 (s), 925 (m), 894 (m), 770 (w), 706 (w), 611 (w), 518 (w), 445 (m).

2.2. Photocatalytic WO experiments

The photocatalytic WO was performed as follows. In a typical experiment, 10 mL of 80 mmol/L sodium borate buffer (pH 8.0–9.4) containing $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (0–1.5 mmol/L), $\text{Na}_2\text{S}_2\text{O}_8$ (0–7.0 mmol/L), and **1** (4.0 $\mu\text{mol/L}$) were introduced in a glass reactor sealed with a rubber septum. The above solution was deaerated by purging it with Ar gas for 5 min in a flask (21 mL) sealed with a rubber septum. The reaction was initiated by irradiating the solution with an LED (light intensity 33.8 mW, beam diameter 2 cm) through a transmitting glass filter ($\lambda = 460$ nm) at room temperature. After each sampling time, 100 mL of Ar was injected into the flask, and the same volume of the gas sample in the headspace of the flask was withdrawn by an SGE gas-tight syringe and analyzed by gas chromatography (GC). O_2 in the sampled gas was separated by passing the gas through a $2 \text{ m} \times 3 \text{ mm}$ packed molecular sieve (5 Å) column with Ar as the carrier gas and quantified by a thermal conductivity detector (TCD). The total amount of O_2 evolved was calculated from the concentration of O_2 in the headspace gas. Air contamination in the headspace was corrected by measuring the N_2 concentration present in the headspace. The turnover number is defined as $\text{TON} = (\text{O}_2 \text{ yield at end of run}) / (\text{catalyst concentration}) = (\text{mol of O}_2)_t / (\text{mol of catalyst})$. The O_2 yield is defined as $\text{O}_2 \text{ yield} = 2 \times (\text{mol of O}_2)_t / (\text{mol of Na}_2\text{S}_2\text{O}_8)$. The initial TOF for oxygen evolution is defined as $\text{TOF}_{\text{initial}} = (\text{mol of O}_2) / (\text{mol of catalyst} \times 20 \text{ s})$, based on the amount of evolved O_2 after 20 s of visible-light irradiation.

2.3. Characterization technique

A single crystal of **1** with the appropriate dimensions was chosen, quickly coated with high-vacuum grease, and mounted

on a glass fiber. The intensity data were recorded on a Bruker Apex II diffractometer using graphite-monochromated Cu $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). IR spectra were obtained using a Bruker VERTEX 70v FT-IR spectrometer with 2–4 wt% sample in KBr pellets in the range of 4000–400 cm^{-1} . Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was performed with a TJA ICP-atomic emission spectrometer (IRIS Advantage ER/S). Thermogravimetric analysis (TGA) was carried out using a Linseis STA PT1600 in the temperature range 25–850 $^{\circ}\text{C}$, at a heating rate of 10 K min^{-1} , in N_2 atmosphere. UV-Vis absorption data were obtained using a TU-1810 spectrophotometer equipped with a photomultiplier tube detector. C, H, and N elemental analyses were performed using a Vario EL CHNS/O analyzer. Powder X-ray diffraction (PXRD) measurements were carried out on a Rigaku D/MAX 2400 diffractometer operated at 40 kV and 40 mA with Cu $K\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). Photon flux of the incident light was determined using a Ray virtual radiation actinometer (FU 100, silicon ray detector, light spectrum 400–700 nm, sensitivity 10–50 $\mu\text{W } \mu\text{mol}^{-1} \text{ m}^{-2} \text{ s}^{-1}$), which afforded a value of 1600 $\mu\text{W } \mu\text{mol}^{-1} \text{ m}^{-2} \text{ s}^{-1}$.

3. Results and discussion

3.1. Crystal structure

The crystallographic data and structural refinements are summarized in Table S1 (see the Supporting Information). The crystallographic data for **1** were deposited at the Cambridge Crystallographic Data Center with CCDC 1835378. Bond valence sum (BVS) (Tables S2 and S3) calculations revealed that the oxidation states of all the Co and W atoms were +2 and +6, respectively. The oxidation states of the Sb1 and Sb2 atoms were +3 and +5, respectively. The presence of Sb^{5+} ions in the final product suggested that some of the Sb^{3+} ions were oxidized by Ag^+ ions in the presence of O_2 for the formation of **1**.

The new dicobalt-substituted and sandwiched tungstoantimonate dimer $[\text{Na}_4\{\text{Co}_2\text{Sb}_2(\text{H}_2\text{O})_{10}[\text{B}-\beta\text{-SbW}_9\text{O}_{33}]_2\}]\cdot 39\text{H}_2\text{O}$ (**1**) was synthesized by the reaction of Co^{2+} ions with trilacunary POM precursor $[\text{B}-\alpha\text{-SbW}_9\text{O}_{33}]^{9-}$ in a weakly acidic aqueous medium, and it crystallized in the monoclinic space group $P2_1/c$. The molecular structure of **1** consists of one dimeric $\{\text{Co}_2\text{Sb}_2(\text{H}_2\text{O})_{10}[\text{B}-\beta\text{-SbW}_9\text{O}_{33}]_2\}^{4-}$ (**1a**) cluster (Fig. 1a and 1b), four sodium ions, and thirty-nine lattice water molecules. Compound **1a** is composed of two trivacant $[\text{B}-\beta\text{-SbW}_9\text{O}_{33}]^{9-}$ units (Fig. 1c) linked together by a $\{\text{Co}_2\text{Sb}_2\}$ belt (Fig. 1e), in which two inner Sb^{3+} ions (Sb1, Sb1A) and two outer Co^{2+} ions (Co1, Co1A) lie at the corners of a rhombus with two adjacent edges of 5.789 and 5.897 $\text{\AA}$, and all ions adopt the six-coordinate octahedral geometry (Fig. 1f and 1g).

The trivacant $[\text{B}-\beta\text{-SbW}_9\text{O}_{33}]^{9-}$ subunit is derived from the trilacunary $[\text{B}-\alpha\text{-SbW}_9\text{O}_{33}]^{9-}$ (Fig. 1d) anion by rotating one of the edge-shared $\{\text{W}_3\text{O}_{13}\}$ groups. Moreover, it is particularly interesting to note that the sandwich-type $\{\text{Co}_2\text{Sb}_2(\text{H}_2\text{O})_{10}[\text{B}-\beta\text{-SbW}_9\text{O}_{33}]_2\}^{4-}$ polyanion in **1** is the first reported example of a compound bearing the $\{\text{Co}_2\text{Sb}_2\}$ moiety. We believe that isomerization of the $[\text{B}-\alpha\text{-SbW}_9\text{O}_{33}]^{9-}$ precursor and degradation of the $[\text{SbW}_9\text{O}_{33}]^{9-}$ building block must have occurred dur-

Fig. 1. (a) Combined polyhedral/ball-and-stick representation of the molecular structure of **1a**. (b) A simplified view of the molecule structure of **1a**. (c) The trivacant Keggin unit $[\text{B}-\beta\text{-SbW}_9\text{O}_{33}]^{9-}$ and (d) $[\text{B}-\alpha\text{-SbW}_9\text{O}_{33}]^{9-}$ precursor in **1a**. (e) A $\{\text{Co}_2\text{Sb}_2\}$ moiety in the center belt of two $[\text{B}-\beta\text{-SbW}_9\text{O}_{33}]^{9-}$ units, with two different metal ions that constitute a rhombus. (f) The octahedral environment of Co^{2+} ion and (g) Sb^{3+} ion. Color code: Co (blue), Sb (yellow), $\{\text{WO}_6\}$ octahedra (red).

ing the formation of **1**. This observation provides not only the synthetic viewpoint for this compound but also some new ideas for the rational design and synthesis of TMSPs, such as the addition of oxidants (such as Ag^+ , $\text{S}_2\text{O}_8^{2-}$, and MnO_4^-) for the preparation of novel TMSPs. In addition, discrete $\{\text{Co}_2\text{Sb}_2(\text{H}_2\text{O})_{10}[\text{B}-\beta\text{-SbW}_9\text{O}_{33}]_2\}^{4-}$ polyoxoanions were regularly distributed in the $-\text{ABAB}-$ mode along the b and c axes (Fig. S1). The phase purity of **1** was corroborated by the PXRD patterns (Fig. S2a). IR and TG analyses were performed to determine the structure and elemental composition, respectively (Figs. S2b and S3).

3.2. Photocatalytic WO

WO was performed to evaluate the photocatalytic ability of **1** in the system, utilizing $[\text{Ru}(\text{bpy})_3]^{2+}$ (1 mmol/L) as the photosensitizer and $\text{Na}_2\text{S}_2\text{O}_8$ (5 mmol/L) as the sacrificial electron acceptor in sodium borate buffer (80 mmol/L, pH 8.5, 10 mL) under visible-light irradiation ($\lambda = 460 \text{ nm}$) for O_2 evolution.

The proposed catalytic mechanism of **1** for the light-driven WO is depicted in Fig. 2. Fig. 3 illustrates the amount of O_2 evolution over **1** under different pH conditions. Evidently, O_2 evolution was very quick, reaching a plateau in 120 s due to the consumption of the sacrificial electron acceptor, $\text{Na}_2\text{S}_2\text{O}_8$ [36,37].

A higher pH is thermodynamically favorable for WO; thus, the reaction at pH 8.0 with **1** showed poor activity. When the buffer pH was raised to 8.5, the amount of O_2 evolved reached 7.7 μmol with a higher O_2 yield of 30.8%, TON of 193, $\text{TOF}_{\text{initial}}$ of 5.3 s^{-1} , and Φ_{QY} of 36.2% (see details in SI). However, upon continuously increasing the pH to 9.0, the amount of O_2 evolved suddenly decreased from 7.7 to 5.9 μmol , and the corresponding O_2 yield, TON, and Φ_{QY} also decreased to 23.6%, 148, and

Fig. 2. Photocatalytic water oxidation catalyzed by **1**.

Fig. 3. Kinetics of O_2 evolution in the photocatalytic system under various pH conditions. Conditions: LED lamp ($\lambda = 460$ nm), 5.0 mmol/L $Na_2S_2O_8$, 1 mmol/L $[Ru(bpy)_3]^{2+}$, 4 μ mol/L **1**, 80 mmol/L sodium borate buffer, total reaction volume is 10 mL.

34.2%, respectively. The main reason for this phenomenon is the possible decomposition of the photosensitizer $[Ru(bpy)_3]^{2+}$ at high pH during the photocatalytic process.

Moreover, other factors influencing the photocatalytic reaction, including the concentration of photosensitizer and the sacrificial electron acceptor, were systematically studied when the concentration of **1** was 4.0 μ mol/L (Figs. S4 and S5). The O_2 yield first showed a rapid increase as the concentration of $[Ru(bpy)_3]Cl_2$ and $Na_2S_2O_8$ was increased up to 1.0 mmol/L and 5 mmol/L, respectively, and then presented an unapparent increasing trend upon a further increase in the concentrations of $[Ru(bpy)_3]Cl_2$ and $Na_2S_2O_8$. Furthermore, it could be seen from Fig. 4 that O_2 evolution was almost absent or negligibly small in the absence of light, $Na_2S_2O_8$, or catalyst **1**. Thus, light, catalyst, photosensitizer, and sacrificial electron acceptor are essential factors for this WO system. As is known, the hydrolytic stability of POMs may be influenced by various factors, in which the POMs may decompose into catalytically active oxide nanoparticles. We compared the photocatalytic kinetic behavior between **1** and a benchmark homogeneous WOC, $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$, under the same reaction conditions. The amount of oxygen evolution from **1** was higher than that from $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ (Fig. S6).

UV spectra of the aqueous solution and IR spectra were rec-

Fig. 4. Kinetics of O_2 formation in the photocatalytic system without (a) light (black), (b) **1** (red), and (c) $Na_2S_2O_8$ (cyan).

ordered to probe the catalyst stability. As shown in Figs. S7–S9, the UV spectra of **1** in the sodium borate buffer were monitored by varying the pH from 7.5 to 9 or aging for 120 min (pH 8.5), and no apparent changes were observed. There was no absorption band between 500 and 600 nm in the spectrum of **1** because of the rather weak absorbance corresponding to the Co-centered $d-d$ transitions, consistent with previous reports [38]. To further investigate the stability of **1** during photocatalytic WO, we carried out tetra-*n*-heptylammonium nitrate (THpANO₃)-toluene extraction, which is proved to be an effective method for extracting POMs from the reaction solutions [39].

As shown in Table S4, after extracting **1** from the solutions before and after the reaction, there was almost no cobalt ion present in the solution. We also measured the O_2 evolution dynamic curves at a low concentration of Co^{2+} (0.05 μ mol/L) under the optimal reaction conditions (Fig. S10). The blue and red curves represent the kinetics of O_2 formation with 4 μ mol/L **1** and 0.05 μ mol/L Co^{2+} , respectively, in the photocatalytic system. Second, capillary electrophoresis was applied to detect the stability of **1** in the WO system. In this method, chemical species in the interior of a small capillary filled with an electrolyte are separated according to their charge to size ratio. Therefore, this method was carried out to investigate the stability of **1** during photocatalytic water oxidation. Although the characteristic peaks of **1** before and after the photocatalytic reactions shifted slightly to the right, they basically remained unchanged (Fig. 5). The reason for this shift was the change in the electrolyte concentration before and after the WO reaction. No extra peaks due to Co were observed in the electropherogram after the WO experiment. The results of capillary electrophoresis demonstrated that the structure of **1** was unchanged after the WO reactions. Moreover, the IR spectrum of the recovered catalyst **1** after the first run was consistent with that of the unused **1**, which is a positive proof for the structural integrity of **1** (Fig. S11).

4. Conclusions

In summary, we synthesized a unique dicobalt-substituted sandwich-type tungstoantimonate **1** within a rare octahedral

Fig. 5. Electropherogram of **1**. Black line: 4 $\mu\text{mol/L}$ of **1** in 80 mmol/L sodium borate buffer solution (pH 8.5); red line: 4 $\mu\text{mol/L}$ of **1** in 80 mmol/L sodium borate buffer solution (pH 8.5) containing $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (1.0 mmol/L) and $\text{Na}_2\text{S}_2\text{O}_8$ (5.0 mmol/L) before illumination; blue line: 4 $\mu\text{mol/L}$ of **1** in 80 mmol/L sodium borate buffer solution (pH 8.5) containing $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (1.0 mmol/L) and $\text{Na}_2\text{S}_2\text{O}_8$ (5.0 mmol/L) after 2 min of illumination.

$\{\text{SbO}_3(\text{H}_2\text{O})_3\}$ bridge and systematically characterized the compound by multiple techniques. We found that **1** acts as an efficient and stable photocatalytic WO catalyst. Under the optimal photocatalytic conditions (photoirradiation at $\lambda = 460$ nm, $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ as the photosensitizer, $\text{Na}_2\text{S}_2\text{O}_8$ as the oxidant in a basic borate buffer), the TON and O_2 yield were as high as 193 and 30.8%, respectively. Φ_{QY} and $\text{TOF}_{\text{initial}}$ in the first 20 s of the reaction were 36.2% and 5.3 s^{-1} , respectively. This study presents the feasibility of the design and use of Co-containing inorganic clusters as effective WOCs, and the discovery of this novel Co-based catalyst enriches the photocatalytic WO catalyzed by polyoxometalates.

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Graphical Abstract

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A novel dicobalt-substituted tungstoantimonate polyoxometalate: Synthesis, characterization, and photocatalytic water oxidation properties

Qing Han, Di Sun, Junwei Zhao, Xiangming Liang, Yong Ding*
Lanzhou University; Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences; Shandong University; Henan University

The one-pot assembly reaction of a trilacunary $[\text{B}-\alpha\text{-SbW}_9\text{O}_{33}]^{9-}$ precursor with Co^{2+} and Ag^+ in an aqueous medium led to the isolation of a novel tungstoantimonate $\{\text{Co}_2\text{Sb}_2(\text{H}_2\text{O})_{10}[\text{B}-\beta\text{-SbW}_9\text{O}_{33}]_2\}^{4-}$ (**1a**), which showed efficient catalytic activity for water oxidation with a remarkable TON of 193, $\text{TOF}_{\text{initial}}$ of 5.3 s^{-1} , O_2 yield of 30.8%, and quantum yield (Φ_{QY}) of 36.2%.

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一例新型二钴取代铈钨酸盐：合成、表征及光催化水氧化性能

韩庆^a, 孙頔^c, 赵俊伟^d, 梁向明^a, 丁勇^{a,b,*}

^a兰州大学化学化工学院, 甘肃省有色金属重点实验室, 功能有机分子国家重点实验室, 甘肃兰州730000

^b中国科学院兰州化学物理研究所羰基合成与选择氧化国家重点实验室, 甘肃兰州730000

^c山东大学化学化工学院, 胶体与界面化学教育部重点实验室, 山东济南250100

^d河南大学化学化工学院, 河南省多酸化学重点实验室, 分子与晶体研究所, 河南开封475004

摘要: 太阳能分解水制氢作为解决当前能源危机和环境危机最理想和最有前途的策略之一正受到越来越多的关注。在人工模拟光合作用过程中, 水的氧化($2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$)是整个反应过程的瓶颈, 因此开发高效稳定水氧化催化剂是提高人工光合作用性能的关键。在过去的几十年里, 全世界科研工作者已经为设计合成高效稳定的均相和多相水氧化催化剂做了大量工作。在均相水氧化领域, 多金属氧酸盐(简称多酸)作为一类结构多样的多金属氧簇化合物, 由于其良好的氧化、热、水解稳定性, 能够在不改变结构的前提下进行快速、可逆、多电子转移反应, 因而受到广泛关注。2009年, Hill课题组首次将四钨多酸用于光驱动水氧化体系。随后, 他们报道了不含贵金属的四钴多酸($\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2$)¹⁰⁻催化水氧化的工作。王恩波团队和我们课题组在该领域也进行了一些深入研究。

值得注意的是, 由于 Sb^{3+} 易于在水溶液中水解, 这在很大程度上阻碍了铈钨酸盐前驱体与过渡金属离子结合形成多酸簇, 所以导致有关过渡金属取代铈钨酸盐的报道非常少。本文采用一锅自组装策略, 利用缺位多酸前驱体 $[\text{B}-\alpha\text{-SbW}_9\text{O}_{33}]^{9-}$ 与 Co^{2+} 在弱酸性条件下反应, 首次合成出一个结构新颖的夹心型铈钨酸盐 $\text{Na}_4[\text{Co}_2(\text{H}_2\text{O})_6\text{Sb}_2(\text{H}_2\text{O})_4(\text{B}-\beta\text{-SbW}_9\text{O}_{33})_2]\cdot 39\text{H}_2\text{O}$ (**1**)。在可见光照射下, 可有效催化水氧化反应, 在最佳反应条件($\text{Na}_2\text{S}_2\text{O}_8$ 为牺牲电子受体, $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ 为光敏剂, 缓冲溶液 $\text{pH} = 8.5$)下, 反应的转化数和氧气收率最高分别可达193和30.8%, 初始量子效率和初始转化频率分别为36.2%和 5.3 s^{-1} 。紫外-可见吸收光谱、反应前后催化剂的红外光谱、毛细管电泳及甲苯萃取等实验结果表明, 该铈钨酸盐**1**是一个稳定的光催化水氧化催化剂。

关键词: 光驱动水氧化; 铈钨酸盐; 自组装

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*通讯联系人. 电子信箱: dingyong1@lzu.edu.cn

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