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Water oxidation catalytic ability of polypyridine complex containing a μ -OH, μ -O₂ dicobalt(III) core

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ABSTRACT

Two polypyridine complexes containing μ -OH, μ -O₂ dicobalt(III) cores, [(TPA)Co^{III}(μ -OH)(μ -O₂)Co^{III}(TPA)](ClO₄)₃ and [(BPMEN)Co^{III}(μ -OH)(μ -O₂)Co^{III}(BPMEN)](ClO₄)₃ (TPA = tris(2-pyridylmethyl)amine, BPMEN = *N,N'*-dimethyl-*N,N'*-bis(pyridin-2-ylmethyl)ethane-1,2-diamine), have previously been reported as inactive in the light-driven water oxidation reaction (*ACS Catal.*, **2016**, 6, 5062–5068). Herein, another dicobalt(III) compound, μ -OH, μ -O₂-[{(enN4)₂Co₂}](ClO₄)₃ (enN4 = 1,6-bis(2-pyridyl-2,5-diazaocta-2,6-diene), with a similar core structure was synthesized, characterized, and applied to the light-driven water oxidation reaction. Collective experiments showed that the complex itself was also inactive in the light-driven water oxidation, and that the activity observed originated from Co(II) impurities. This research establishes that complexes possessing a μ -OH, μ -O₂ dicobalt(III) core structure are not appropriate choices for true molecular catalysts of water oxidation.

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1. Introduction

The large-scale use of fossil fuels has resulted in various environmental problems. Accordingly, the development and utilization of renewable and environmentally friendly energy are needed [1–3]. Hydrogen is a promising alternative to traditional fossil fuels because it is a clean energy source with a high heat value [4,5]. Water splitting inspired by photosynthesis is considered an ideal pathway for the conversion of solar energy and water into hydrogen energy [6–8]. The overall water splitting process comprises two half reactions, namely water oxidation ($2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$) and proton reduction ($4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2$). The water oxidation step has a high activation energy

and is regarded as the limiting step of water splitting [9–11]. To improve the efficiency of water oxidation, much research has been focused on exploring water oxidation catalysts (WOCs) [3, 12,13]. However, the development of efficient WOCs remains challenging. Owing to their low cost and abundance, much recent research effort has focused on WOCs based on first row transitional metals [14–25]. Compared with heterogeneous WOCs, homogeneous WOCs, especially molecular organic complexes, have advantages in structure modification and mechanism research [26]. There are two main categories of homogeneous WOCs, namely inorganic polyoxometallates and organic ligand-based complexes.

Among the homogeneous WOCs, organic complexes con-

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taining Co have been widely investigated because they usually show good catalytic activity in light-driven water oxidation. Polycore complexes, such as cubane-like complexes with M_4O_4 (M = transition metal) frames, are attractive because of their biomimetic structures [27–31], which are similar to that of the oxygen-evolving Mn_4CaO_5 cluster in natural photosynthesis system II (PSII). For example, a $Co_4O_4(AC)_4(py)_4$ cluster and related derivatives were initially regarded as homogeneous WOCs [27,32]. However, a follow-up study by Nocera *et al.* [33] suggested that pure $Co_4O_4(AC)_4(py)_4$ cluster was inactive. Photochemical and electrochemical experiments confirmed that Co(II) impurities were responsible for the apparent catalytic ability [33]. A recent study by Lu *et al.* [34] showed that two dinuclear cobalt polypyridine complexes containing μ -OH and μ -O₂ core were unable to catalyze water oxidation. Chelating experiments and controlled potential electrolysis measurements attributed the observed catalytic activity of these synthesized samples to Co(II) impurities introduced during synthesis.

Sufficient experiments should be carried out to identify true WOCs, especially for Co-based molecular catalysts. Co(II) impurities can transform into CoO_x species, which are true WOCs. Therefore, the possibility that the catalytic activity originates from impurities should be ruled out before identifying substrates as true homogeneous WOCs.

Herein, binuclear complex μ -OH, μ -O₂-[$\{(enN4)_2Co_2\}(ClO_4)_3$] ($1(ClO_4)_3$, $enN4$ = 1,6-bis(2-pyridyl)-2,5-diazahex-1,5-diene) (Fig. 1) was synthesized and used to catalyze water oxidation. Its catalytic ability was investigated using a series of methods, which showed that **1** was inactive as a catalyst for light-driven water oxidation. The apparent activity of the as-synthesized catalyst originated from Co impurities introduced during synthesis. This finding supplements previous reported results and establishes that complexes containing a μ -OH, μ -O₂ dicobalt(III) core might be unsuitable as WOCs for light-driven water oxidation. This rule provides guidelines for the future exploration of efficient WOCs.

2. Experimental

2.1. Synthesis of $1(ClO_4)_3$

Purified water (18.2 M Ω ·cm) for the preparation of buffer solutions was obtained from a Molecular Lab Water Purifier. All chemical agents were commercially available and used without further purification.

The enN4 ligand was synthesized according to a literature

procedure [35]. 2-Pyridinecarboxaldehyde (3.2 g, 30 mmol) and ethylenediamine (0.9 g, 15 mmol) were dissolved in methanol (25 mL). The solution was refluxed for about 7 h, cooled to room temperature, and concentrated by rotary evaporation to obtain a yellow solid. A pure ligand sample was obtained by recrystallization from *n*-hexane followed by drying in a vacuum oven.

Compound **1** was synthesized according to a literature procedure [36] in the form of $1(ClO_4)_3 \cdot 2MeCN \cdot H_2O$ accompanied by one molecule of $py \cdot HClO_4$. This microcrystalline solid was obtained by adding $Co(ClO_4)_2 \cdot 6H_2O$ to an acetonitrile solution of 1,6-bis(2-pyridyl)-2,5-diazahex-1,5-diene and a small quantity of pyridine. The solution became red-brown within minutes, and then changed to dark brown. After stirring for 16 h under air to complete the metal oxidation, black microcrystals were formed. These crystals were collected by filtration and washed with Et₂O several times. Crystals suitable for X-ray diffraction analysis were obtained by slowly evaporating a saturated solution of the black microcrystals in acetonitrile/toluene (3:1, v/v). The addition of a few drops of pyridine aided crystal formation. Elemental analysis of $C_{37}H_{43}Cl_4Co_2N_{11}O_{20}$ gave the following results: calcd, C 36.38%, H 3.55%, N 12.61%; found, C 35.82%, H 3.45%, N 12.70%.

2.2. Electrochemical measurements

Cyclic voltammetry (CV) was recorded on a CHI660D electrochemical analyzer. Glassy carbon (GC; 0.071 cm²), Ag/AgCl (3.5 mol/L KCl), and Pt wire were used as the working, reference, and auxiliary electrodes, respectively. CV tests were carried out in buffer solutions at pH = 9.0 and room temperature using a scan rate of 100 mV/s. For controlled potential electrolysis experiments, indium-tin oxide (ITO) glass slides (2.0 cm × 1.0 cm, 1.0 cm² immersed in electrolyte), Ag/AgCl, and Pt wire were used as the working, reference, and auxiliary electrodes, respectively. ITO glass slides were cleaned by sonication in acetone, ethanol, and ultrapure water for 30 min, successively.

2.3. Photocatalytic water oxidation

Photocatalytic water oxidation was performed as follows. Catalyst was added to the reaction solution (80 mmol/L borate buffer solution) containing $[Ru(bpy)_3]Cl_2$ (bpy = 2,2'-bipyridine) (1 mmol/L) and $Na_2S_2O_8$ (10 mmol/L). The above solution was deaerated by purging with Ar gas for 10 min in a flask (total volume = 28 mL) and then sealed with a rubber septum (reaction solution volume = 15 mL). The reaction was initiated by irradiating the solution using light-emitting diodes (LEDs) as the light source (light intensity = 15.8 mW, beam diameter = 2 cm) through a transmitting glass filter ($\lambda \geq 420$ nm) at ambient temperature. After each irradiation period, Ar gas (150 μ L) was injected into the flask and the same volume of gas was withdrawn from the flask headspace using an SGE gas-tight syringe and analyzed by gas chromatography. The oxygen in the sampled gas was separated by passing through a packed molecular sieve 5A column (2 m ×

Fig. 1. Chemical structure of complex **1**.

Fig. 2. Crystal structure of **1**(ClO₄)₃ (Co, pink; C, black; O, red; N, blue; Cl, green; H, gray; H atoms on ligand were omitted for clarity).

3 mm) using Ar as the carrier gas and quantified using a thermal conductivity detector (TCD, Shimadzu GC-9A). The total amount of evolved oxygen was calculated from the oxygen concentration in the headspace. Contamination of the headspace with air was corrected by measuring the nitrogen present in the headspace from the nitrogen peak area in the gas chromatography traces.

2.4. Characterization technique

Single-crystal X-ray diffraction analysis was performed in a cooled nitrogen gas stream at 100 K on an Agilent Technologies supernova diffractometer equipped with a charge-coupled device bidimensional detector. UV-Vis absorption spectra were recorded on a TU-1810 spectrophotometer (Beijing Purkinje General Instrument Co., Ltd.) equipped with a photomultiplier tube detector.

3. Results and discussion

3.1. Characterization of **1**(ClO₄)₃

Fig. 2 and Fig. 3 show the X-ray single crystal structure of **1**. The two Co^{III} ions were linked by coordination to two

Fig. 3. ORTEP diagram of **1**³⁺; Hydrogen atoms on enN4 ligands are not shown for clarity.

Table 1

Crystal data and structure refinement for **1**(ClO₄)₃.

Empirical formula	C ₃₂ H ₃₇ Cl ₃ Co ₂ N ₁₀ O ₁₆
Formula mass	1041.93
Temperature (K)	298.84(10)
Crystal system	triclinic
Space group	P-1
<i>a</i> /Å (1 Å = 0.1 nm)	10.4773(12)
<i>b</i> /Å (1 Å = 0.1 nm)	13.5820(16)
<i>c</i> /Å (1 Å = 0.1 nm)	16.704(2)
α /°	76.044(10)
β /°	72.949(10)
γ /°	68.667(11)
Volume (Å ³) (1 Å = 0.1 nm)	2092.6(4)
<i>Z</i>	2
ρ_{calc} /(g/cm ³)	1.654
μ /mm ⁻¹	1.067
<i>F</i> (000)	1064.0
Crystal size (mm ³)	0.23 × 0.15 × 0.14
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/°	6.5–52.04
Index ranges	−12 ≤ <i>h</i> ≤ 12, −16 ≤ <i>k</i> ≤ 16, −20 ≤ <i>l</i> ≤ 19
Reflections collected	14270
Independent reflections	8212 [<i>R</i> _{int} = 0.0373, <i>R</i> _{sigma} = 0.0693]
Data/restraints/parameters	8212/0/577
Goodness-of-fit on <i>F</i> ²	1.047
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0487, <i>wR</i> ₂ = 0.1075
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0721, <i>wR</i> ₂ = 0.1248
Largest diff. peak/hole (e/Å ³)	1.13/−0.94

^a *R*₁ = $\Sigma||F_o| - |F_c|| / \Sigma|F_o|$; ^b *wR*₂ = $\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]^{1/2}$.

1,6-bis(2-pyridyl)-2,5-diazaocta-2,6-diene ligands, one μ -OH ligand, and one μ -O₂ ligand (Table 1–3). Complex **1**(ClO₄)₃ was further characterized by Fourier transform infrared (FTIR) spectroscopy. Notable IR bands were observed at 883, 772, and 651 cm⁻¹ in the lower energy region (Fig. 4). The bands at 883 cm⁻¹ were assigned to ν (O–O) [36].

3.2. Light-driven water oxidation

Together, the as-synthesized catalyst, sacrificial electron acceptor Na₂S₂O₈, and photosensitizer [Ru(bpy)₃]Cl₂ constituted the artificial photosynthesis oxygen evolution system. When 10 mmol/L Na₂S₂O₈ and 1 mmol/L [Ru(bpy)₃]Cl₂ were used, an optimal oxygen yield of 46.7% was achieved (Fig. 5(a)). To investigate the true catalytic ability of **1**, the light-driven water oxidation reaction was repeated under similar conditions except with bpy (0.2 or 0.5 equiv.) added as a chelating agent. When 2 μ mol/L bpy was added to chelate the as-synthesized catalyst (10 μ mol/L), the oxygen yield was reduced to 9.6%. A

Table 2

Selected bond lengths of **1**³⁺.

Atom	Atom	Length (Å)	Atom	Atom	Length (Å)
Co1	O2	1.844(2)	Co2	O3	1.894(2)
Co1	O3	1.886(3)	Co2	N1	1.929(3)
Co1	N3	1.913(3)	Co2	N2	1.942(3)
Co1	N4	2.004(3)	Co2	N5	1.998(3)
Co1	N7	1.926(3)	Co2	N6	1.918(3)
Co1	N8	1.933(3)	O1	O2	1.389(3)
Co2	O1	1.845(2)			

Table 3Bond angles of $1(\text{ClO}_4)_3 \cdot 2\text{MeCN} \cdot \text{H}_2\text{O}$.

Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
O2	Co1	O3	89.02(10)	N1	C1	C2	121.7(4)
O2	Co1	N3	89.56(12)	C3	C2	C1	119.1(4)
O2	Co1	N4	170.76(12)	C2	C3	C4	120.1(3)
O2	Co1	N7	92.33(12)	C5	C4	C3	117.5(4)
O2	Co1	N8	86.24(11)	N1	C5	C4	122.7(3)
O3	Co1	N3	89.14(12)	N1	C5	C6	113.1(3)
O3	Co1	N4	94.45(11)	C4	C5	C6	124.2(4)
O3	Co1	N7	90.62(12)	N2	C6	C5	116.9(3)
O3	Co1	N8	172.34(12)	N2	C7	C8	117.3(3)
N3	Co1	N4	81.95(13)	N3	C8	C7	114.0(3)
N3	Co1	N7	178.09(12)	N3	C9	C10	116.8(4)
N3	Co1	N8	96.82(13)	N4	C10	C9	112.6(3)
N7	Co1	N4	96.18(12)	N4	C10	C11	122.7(4)
N7	Co1	N8	83.58(13)	C11	C10	C9	124.7(4)
N8	Co1	N4	91.15(11)	C10	C11	C12	118.9(4)
O1	Co2	O3	88.12(11)	C13	C12	C11	118.7(3)
O1	Co2	N1	87.16(11)	C12	C13	C14	119.7(4)
O1	Co2	N2	91.29(12)	N4	C14	C13	121.9(4)
O1	Co2	N5	171.08(12)	N5	C15	C16	121.7(4)
O1	Co2	N6	89.43(12)	C17	C16	C15	120.1(4)
O3	Co2	N1	174.97(12)	C18	C17	C16	118.6(4)
O3	Co2	N2	94.82(12)	C17	C18	C19	119.1(4)
O3	Co2	N5	94.76(11)	N5	C19	C18	122.2(4)
O3	Co2	N6	84.34(11)	N5	C19	C20	113.2(3)
N1	Co2	N2	83.52(12)	C18	C19	C20	124.6(4)
N1	Co2	N5	90.16(11)	N6	C20	C19	116.9(3)
N2	Co2	N5	96.86(13)	N6	C21	C22	113.3(3)
N6	Co2	N1	97.37(12)	N7	C22	C21	116.9(3)
N6	Co2	N2	178.88(13)	N7	C23	C24	117.0(4)
N6	Co2	N5	82.47(13)	N8	C24	C23	112.8(3)
O2	O1	Co2	109.79(18)	N8	C24	C25	123.1(4)
O1	O2	Co1	110.10(16)	C25	C24	C23	124.1(4)
Co1	O3	Co2	114.58(14)	C26	C25	C24	117.9(4)
C1	N1	Co2	128.0(3)	C27	C26	C25	119.6(4)
C1	N1	C5	118.9(3)	C26	C27	C28	119.9(4)
C5	N1	Co2	113.1(2)	N8	C28	C27	121.3(4)
C6	N2	Co2	113.3(3)	N9	C29	C30	179.3(7)
C6	N2	C7	117.6(3)	N10	C32	C31	178.8(7)
C7	N2	Co2	129.1(2)	O12	Cl3	O13	109.6(3)
C8	N3	Co1	123.4(2)	O12	Cl3	O14	108.3(3)
C9	N3	Co1	115.8(3)	O13	Cl3	O14	109.4(3)
C9	N3	C8	120.1(3)	O15	Cl3	O12	112.4(3)
C10	N4	Co1	112.4(2)	O15	Cl3	O13	109.7(3)
C14	N4	Co1	129.2(3)	O15	Cl3	O14	107.4(3)
C14	N4	C10	118.0(3)	O8	Cl2	O9	109.0(2)
C15	N5	Co2	129.6(3)	O8	Cl2	O10	109.0(2)
C15	N5	C19	118.2(3)	O8	Cl2	O11	109.3(2)
C19	N5	Co2	111.8(3)	O9	Cl2	O10	108.86(18)
C20	N6	Co2	115.2(3)	O11	Cl2	O9	109.86(19)
C20	N6	C21	118.6(3)	O11	Cl2	O10	110.8(2)
C21	N6	Co2	125.1(2)	O4	Cl1	O5	108.1(2)
C22	N7	Co1	128.3(3)	O4	Cl1	O6	110.6(2)
C23	N7	Co1	113.6(2)	O4	Cl1	O7	109.7(2)
C23	N7	C22	118.0(3)	O5	Cl1	O7	109.2(2)
C24	N8	Co1	112.9(2)	O6	Cl1	O5	108.8(2)
C28	N8	Co1	128.8(3)	O6	Cl1	O7	110.3(2)
C28	N8	C24	118.1(3)				

further increase in the bpy concentration to 10 $\mu\text{mol/L}$ led to complete deactivation of the catalytic system (Fig. 5(b)). Previous studies by Nocera et al. [33] and Lu et al. [34] showed that this phenomenon was due to Co(II) impurities residing in the as-synthesized catalyst. Co(II) impurities in the

Fig. 4. FTIR spectrum of $1(\text{ClO}_4)_3$ in KBr (1%). The bands at 883 cm^{-1} were assigned as $\nu(\text{O}-\text{O})$.

as-synthesized catalyst can transform into CoO_x , which is a true WOC. The added bpy chelates Co impurities to produce the catalytically inactive Co-bipyridine complex. However, the addition of chelating agent does not affect the oxygen evolution system catalyzed by genuine homogeneous catalysts [31].

Fig. 5. (a) Light-driven water oxidation catalyzed by the as-synthesized catalyst at different concentrations. (b) Light-driven oxygen evolution catalyzed by the as-synthesized catalyst (10 $\mu\text{mol/L}$) with addition of 0 (1), 2 (2), and 5 $\mu\text{mol/L}$ bpy (3). Reaction conditions: LED lamp ($\lambda \geq 420\text{ nm}$) at 15.8 mW; 1 mmol/L $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$, 10 mmol/L $\text{Na}_2\text{S}_2\text{O}_8$, 80 mM sodium borate buffer, initial pH = 9.0, total reaction volume = 15 mL, overall volume = 28 mL, under vigorous agitation using a magnetic stirrer.

Fig. 6. (a) UV-Vis absorption spectra of as-synthesized catalyst (10 $\mu\text{mol/L}$) in 80 mmol/L borate buffer solution at pH = 9.0 with or without addition of bpy (0.5 equiv.); (b) UV-Vis absorption spectra of as-synthesized catalyst (10 $\mu\text{mol/L}$) in 80 mmol/L borate buffer solution at pH = 9.0 with or without addition of $\text{Na}_2\text{S}_2\text{O}_8$.

Fig. 7. Repeated CV scanning (10 cycles) of (a) the as-synthesized catalyst (0.5 mmol/L) and (b) $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol/L) in pH = 9.0 borate buffer solution (80 mmol/L) at a scan rate of 100 mV/s. GC (active area = 0.071 cm^2), Ag/AgCl (3.5 mol/L KCl), and Pt wire were used as the working, reference, and auxiliary electrodes, respectively.

Fig. 6(a) shows UV-Vis absorption spectra of the as-synthesized catalyst in pH = 9.0 borate buffer solution with and without bpy, which are identical, indicating that bpy did not destroy the structure of **1**. The UV-Vis absorption spectrum of the as-synthesized catalyst retained its characteristic peaks before and after the addition of $\text{Na}_2\text{S}_2\text{O}_8$, indicating that $\text{Na}_2\text{S}_2\text{O}_8$ did not destroy the structure of **1** without irradiation.

3.3. Electrochemical measurements

The catalytic ability of **1** was further investigated using electrochemical experiments. First, CV measurements of the as-synthesized catalyst were performed in pH = 9.0 borate buffer solution. As shown in Fig. 7(a), the borate buffer solution produced a negligible catalytic current. However, an increased catalytic current was observed during repeated CV scanning of the as-synthesized catalyst, which is a typical characteristic of the electrodeposition of heterogeneous active species as true WOCs on the surface of a GC electrode. The electrochemical behavior of the as-synthesized catalyst was similar to that of

free Co^{2+} ions (Fig. 7(b)). After ten cyclic scans, the used GC

Fig. 8. Tenth CV of the as-synthesized catalyst (0.5 mmol/L) and CV of the used GC electrode in 80 mmol/L borate buffer solution (pH = 9.0) at a scan rate of 100 mV/s.

Fig. 9. CV scanning of as-synthesized catalyst (0.5 mmol/L) in pH = 9.0 borate buffer solution (80 mmol/L) containing different bpy concentrations at a scan rate of 100 mV/s. The solution containing bpy was sonicated before CV measurements.

electrode was rinsed with ultrapure water, but not polished, and retested by CV in fresh pH = 9.0 borate buffer solution without addition of the as-synthesized catalyst. As expected, a significant catalytic current was produced (Fig. 8), demonstrating the presence of an active heterogeneous Co species on the surface of the GC electrode.

Co element in the active species may originate from impurities, or may have been released from $\mu\text{-OH}$, $\mu\text{-O}_2\text{-}[(\text{enN}_4)_2\text{Co}_2](\text{ClO}_4)_3$ during the CV test. To identify the source of Co element, CV experiments of the as-synthesized catalyst were conducted in the presence of bpy. Fig. 9 illustrates the catalytic current of as-synthesized catalyst (0.5 mmol/L) in borate buffer solution containing different concentrations of bpy. The catalytic currents at 1.51 V vs. NHE decreased with increasing bpy concentration. The Co-bipyridine complex was inactive for electrochemical water oxidation. CV tests of borate buffer solution containing as-synthesized catalyst sample (0.5 mmol/L) and bpy (0.25 mmol/L or 0.5 mmol/L) gave a negligible catalytic current compared with the

Fig. 10. CPE experiments carried out in 80 mmol/L borate buffer solution at pH = 9.0 with an ITO electrode. CPE experiments of as-synthesized catalyst (0.5 mmol/L) in borate buffer solution (black) and of the as used ITO electrode in catalyst-free buffer solution.

Fig. 11. I - t curves obtained by CPE experiments at 1.31 V vs. NHE carried out in 80 mmol/L borate buffer solution containing as-synthesized catalyst (0.5 mmol/L) and bpy (0.25 mmol/L) at pH = 9.0 with an ITO electrode.

background. UV-Vis absorption spectra verified that bpy did not destroy the chemical structure of **1** and that it only chelated Co impurities and not **1**. Therefore, **1** was inactive as a catalyst for electrocatalytic water oxidation.

Controlled potential electrolysis (CPE) experiments were used to examine the catalytic ability of **1**. As mentioned above, ITO was used as the working electrode instead of GC in all CPE tests. During CPE of the as-synthesized catalyst (0.5 mmol/L) in borate buffer at pH = 9.0, the catalytic current increased after the start of CPE, and then reached a maximum of 0.55 mA/cm² after 4 h (Fig. 10). ITO used for the above CPE experiment (ITO-1) was washed with ultrapure water and retested in CPE using fresh borate buffer solution. As expected, the used ITO electrode exhibited a high catalytic current compared with the background in fresh borate buffer at pH = 9.0. According to previous reports [34,37], the catalytic activity of used ITO is due to residual active species on the electrode surface.

The CPE experiment of as-synthesized catalyst (0.5 mM) in borate buffer solution containing 0.25 mmol/L bpy at 1.31 V vs. NHE is shown in Fig. 11. ITO used in this experiment is denoted as ITO-2. In the presence of bpy, a completely different catalytic current was produced. The catalytic current of borate buffer solution containing as-synthesized catalyst (0.5 mmol/L) and

Fig. 12. Image of ITOs used for CPE experiments. (a) ITO-1, (b) ITO-2.

Fig. 13. SEM photographs of (a) ITO-1, (b) ITO-2, and (c) clean ITO.

bpy (0.25 mmol/L) was negligible compared with that of the borate buffer solution without bpy addition. As the impurities were chelated by bpy, the negligible catalytic current (compared with the catalytic current of the as-synthesized catalyst sample, black line in Fig. 11) was attributed to **1** alone.

A yellow residue was present on the surface of ITO-1 (Fig. 12). This residue was also observed in the scanning electron microscopy (SEM) image of ITO-1 (Fig. 13(a)). However, the SEM image of ITO-2 (Fig. 13(b)) was no different from that of the clean ITO electrode (Fig. 13(c)). Furthermore, energy dispersive spectroscopy (EDS) analysis of the ITO electrodes was in good agreement with the SEM results. Co element was only detected on the surface of ITO-1 (Fig. 14(a)), while no Co was present on the surface of ITO-2 (Fig. 14(b)), which was similar

to the clean ITO electrode (Fig. 14(c)). Therefore, pure **1** was stable during the CPE test and did not decompose into heterogeneous Co species. The Co species responsible for water oxidation came from Co impurities. The above CPE experiments demonstrated the following: First, the observed catalytic capability of the as-synthesized catalyst was derived from Co impurities; second, bpy stabilized the Co impurities by generating a stable species that was inactive for water oxidation; and third, the synthesized sample lost activity when the Co impurities were chelated by bpy. Therefore, pure **1** was unable to catalyze water oxidation.

The process of catalyst deposition onto the ITO surface was further investigated by XPS. Fig. 15(a) shows XPS analysis of Co element on the ITO electrode obtained from the CPE of borate buffer solution (pH = 9.0) containing 0.5 mmol/L $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (ITO-3), which generated active Co species for water oxidation [34]. Two peaks with binding energies of 780.5 and 795.9 eV were assigned to $\text{Co } 2p_{3/2}$ and $\text{Co } 2p_{1/2}$, respectively. XPS analysis of Co element on ITO-1 showed two peaks at 780.6 and 796.0 eV (Fig. 15(b)), which was very similar to that of ITO-3 (Fig. 15(c)), indicating that Co impurities and free Co^{2+} had the same deposition behavior. Therefore, the Co impurities present in the as-synthesized catalyst had a valency of +2.

4. Conclusions

Herein, we investigated the catalytic ability of a dinuclear cobalt polypyridine complex containing $\mu\text{-OH}$ and $\mu\text{-O}_2$ ligands in the core structure. This complex was confirmed as inactive for water oxidation using photochemical and electrochemical measurements. In combination with previous reports by oth-

Fig. 14. EDS analysis of the surfaces of (a) ITO-1, (b) ITO-2, and (c) clean ITO electrodes.

Fig. 15. XPS analysis of cobalt element on (a) ITO-3 and (b) ITO-1, and (c) their comparison.

ers, this work establishes that dinuclear cobalt polypyridine complexes containing μ -OH and μ -O₂ structure do not catalyze water oxidation, with true WOCs requiring another specific chemical structure. This work provides new insight toward the exploration of new catalysts for water oxidation.

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Graphical Abstract

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Water oxidation catalytic ability of polypyridine complex containing a μ -OH, μ -O₂ dicobalt(III) core

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Complex μ -OH, μ -O₂-[$\{(\text{enN}4)_2\text{Co}_2\}(\text{ClO}_4)_3$] was found to be inactive for photocatalytic water oxidation. Insight was gained into homogeneous water oxidation catalysts based on dinuclear cobalt complexes.

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具有 μ -OH, μ -O₂双钴核结构的基于多吡啶配体的配合物催化水氧化反应的能力

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摘要: 化石燃料的大量使用已经带来了一系列的环境问题, 开发和使用可再生的清洁能源十分有必要. 氢能可以作为传统化石燃料的理想替代品, 因为它不但清洁而且热值高. 受光合作用启发的水裂解反应被认为是一种将太阳能转化为氢能的理想途径. 水裂解包括两个半反应, 即水的氧化($2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$)和质子的还原($4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2$). 水氧化反应需要高的活化能, 因此它也被认为是水裂解反应的瓶颈步骤. 为了提高水氧化反应的效率, 已经有很多关于水氧化催化剂的研究工作被开展. 然而, 迄今为止, 寻找高效的水氧化催化剂仍然是巨大挑战. 考虑到成本以及丰度的因素, 基于第一过渡系金属的水氧化催化剂日益受人关注. 相比于多相水氧化催化剂, 均相的水氧化催化剂, 特别是基于有机配合物的均相催化剂, 在结构调变, 机理研究方面更具有优势. 均相的水氧化催化剂主要分两类: 无机的多金属氧酸盐和基于有机配体的配合物.

在所有的均相的水氧化催化剂中, 含钴的配合物被广泛研究, 因为在光驱动水氧化反应中它们通常能表现出来较好的活性. 很多研究工作都集中于研究多核的含钴的均相催化剂, 特别是具有Co₄O₄框架立方烷结构的配合物, 因为它们具有类似于自然界光合作用光系统II活性中心Mn₄CaO₅簇的结构. 例如, Co₄O₄(Ac)₄(py)₄簇以及相关衍生物曾被报道过用于水氧化反应, 然而Nocera等人发现该化合物本身没有活性(*J. Am. Chem. Soc.*, **2014**, 136, 17681–17688), 表现的活性来源于催化剂合成过程中引入的二价钴离子. 2014年, 一个具有双核钴核心结构的多吡啶配合物[(TPA)Co^{III}(μ -OH)(μ -O₂)Co^{III}(TPA)](ClO₄)₃被报道具有催化光驱动水氧化反应的能力. 然而随后的研究工作(*ACS Catal.*, **2016**, 6, 5062–5068)表明其表现活性也是来自于自由钴离子杂质, 纯的化合物是没有活性的.

在检查一个均相分子水氧化催化剂的时候, 应当进行充分的实验, 特别是对于钴基的水氧化催化剂. 因为在合成含钴配合物的过程中可能引入杂质钴离子, 杂质钴离子在反应过程中会转化为CoO_x, 它本身就是很常见的高效的水氧化催化剂. 在定性一个真正的均相的钴基水氧化催化剂之前, 这一可能性必须要被排除. 在这里我们报道了另外一个同样以双三价钴离子为核心的, 具有 μ -OH, μ -O₂结构的基于多吡啶配体的均相配合物. 我们通过一系列的实验验证了它催化光驱动水氧化反应的能力. 实验证明, 该化合物没有催化活性, 表现活性依然是来自于合成过程中引入的杂质钴离子. 这一结果与之前的报道相比, 既是进一步的探索, 也是一个很好的补充. 结合前人的工作, 我们发现并总结了一个规律: 以双核三价钴为核心的, 拥有 μ -OH, μ -O₂核心结构的基于多吡啶配体的配合物不适合被选用于催化光驱动水氧化反应. 这一发现能为高效水氧化催化剂的开发设计提供见解与指导.

关键词: 水氧化; 光催化; 催化能力; 钴氧化物; 配合物

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