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A dinuclear copper(II) electrocatalyst both water reduction and oxidation

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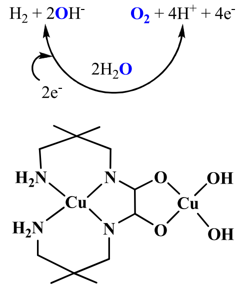
HIGHLIGHTS

- $Cu(Me_2oxpn)Cu(OH)_2]$ **1** can catalyze both water oxidation and reduction to provide O_2 and H_2, respectively.
- **1** can catalyze water reduction to generate H_2, with a TOF of 654 (pH 7.0) moles h^{-1} at an overpotential of 789 mV *vs* SHE.
- **1** can also catalyze water oxidation at an overpotential of 636 mV *vs* SHE to give O_2 with a TOF of ~2.14 s^{-1} (pH 10.4).
- Sustained water reduction catalysis to give H_2 over a 32 h electrolysis period with 95% Faradaic yield.

GRAPHICAL ABSTRACT



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ABSTRACT

Splitting water is a key challenge in the production of chemical fuels from electricity. Although several catalysts have been developed for these reactions, substantial challenges remain towards the ultimate goal of an efficient, inexpensive and robust electrocatalyst. Until now, there is as yet no report on both water oxidation and reduction by identical catalyst. Reported here is the first soluble copper-based catalyst, $Cu(Me_2oxpn)Cu(OH)_2]$ **1** (Me_2oxpn: N,N′-bis(2,2′-dimethyl-3-aminopropyl)oxamido) for both electrolytic water oxidation and reduction. Water oxidation occurs at an overpotential of 636 mV *vs* SHE to give O_2 with a turnover frequency (TOF) of ~2.14 s^{-1}. Electrochemical studies also indicate that **1** is a soluble molecular species, that is among the most rapid homogeneous water reduction catalysts, with a TOF of 654 mol of hydrogen per mole of catalyst per hour at an overpotential of 789 mV *vs* SHE (pH 7.0). Sustained water reduction catalysis occurs at glassy carbon (GC) to give H_2 over a 32 h electrolysis period with 95% Faradaic yield and no observable decomposition of the catalyst.

1. Introduction

Splitting water into hydrogen and oxygen is one of the most attractive scenarios for solar energy harvesting and sustainable energy production [1–5]. This endergonic electrochemical conversion stores 1.23 V and consists of the four electrons, four proton oxidation of water to oxygen and the reduction of the produced protons to hydrogen. One of the key challenges to water splitting is the development of efficient catalysts. These considerations have led to the development of molecular catalysts employing the more transition abundant metals, and several complexes based on nickel [6–11], cobalt [12–16] and molybdenum [17,18] have been developed as electrocatalysts for the reduction of water to form H_2. However, the search for robust and

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highly active catalysts for hydrogen evolution that can operate in purely aqueous solution by electrochemical approaches still remains a great challenge. Another notable progress has been made in homogeneous water oxidation catalysis with transition metal complexes, including manganese [18–20], cobalt [21–23], copper [24,25] and iron [26–31]. Despite much progress in water oxidation and reduction catalysis, major improvements in several areas, including lowering overpotentials, increasing catalyst durability, and using earth abundant elements, are needed before efficient electrocatalytic water splitting can be realized. In designing a model featuring both water oxidation and reduction functionality, we sought a synthetic cofactor with the following inspired properties: (1) The metal center coordination geometry is planar; (2) Mild redox couple closer to the H_2/H^+ couple and O_2/H_2O couple, in the range −0.75 to −1.45 V and 0.40–1.23 V versus SHE, respectively; (3) Chemical inertness, so that reactions would be localized at the metal centers. Until now, there is as yet no report on both water oxidation and reduction by identical catalyst. Reported here is a water soluble dinuclear copper electrocatalyst, $[Cu(Me_2oxpn)Cu(OH)_2]$ **1** that can catalyze both water oxidation and reduction.

2. Experimental

2.1. Materials and physical measurements

All commercially available reagents were used as received without further purification. Cyclic voltammograms were obtained on a CHI-660E electrochemical analyzer under oxygen-free conditions using a three-electrode cell in which a glassy carbon electrode was the working electrode, a saturated Ag/AgCl electrode was the reference electrode, and platinum wire was the auxiliary electrode. Controlled-potential electrolysis (CPE) in aqueous media was conducted using an air-tight glass double-compartment cell separated by a glass frit. The working compartment was fitted with a glassy carbon plate or an ITO plate and an Ag/AgCl reference electrode. The auxiliary compartment was fitted with a Pt gauze electrode. The working compartment was filled with 50 mL of 0.25 M phosphate buffer solution at different pH values, while the auxiliary compartment was filled with 35 mL phosphate buffer solution. Complex **1** was then added and cyclic voltammograms were recorded. After electrolysis, a 0.5 mL aliquot of the headspace was removed and replaced with 0.5 mL of CH_4. A sample of the headspace was injected into the gas chromatograph (GC). GC experiments were carried out with an Agilent Technologies 7890A gas chromatography instrument. UV–vis spectra were recorded on a U-3900H spectrophotometer. ICP of a glassy carbon electrode after 2 h electrolysis was recorded on a PHILIPS XL-30ESEM spectrometer.

2.2. Syntheses of $[Cu(Me_2oxpn)Cu(OH)_2]$ 1

1 was prepared by modification of the literature procedures [32,33]. To a solution of 0.04 mol of 2,2′-dimethyl-1,3-propylenediamine (4.08 g) in 15 mL of ethanol cooled by an ice bath was added dropwise a solution of 0.02 mol of diethyl oxalate (2.93 g) in 20 mL of ethanol. The mixture was heated at reflux for 2 h and then cooled down. A 0.044 mol sample of copper(II) hydroxide (prepared from the reaction of $CuSO_4 \cdot 5H_2O$ (10.99 g, 0.044 mol) with NaOH (3.52 g, 0.088 mol)) in suspension in 250 mL of water was added, which led to a deep blue solution. The mixture was filtered. The solid residue was washed with water in order to extract the expected compound. The solution was allowed to evaporate, affording deep blue small crystals, which were collected and dried in *vacuo* (6.84 g, 74.51% based on $CuSO_4 \cdot 5H_2O$). Calcd for $C_{12}H_{26}N_4Cu_2O_4$: C, 34.52; H, 6.23; N, 13.43. Found: C, 34.94; H, 6.32; N, 13.38. [H_2O, λ_{max}/nm (ε/L mol^{-1} cm^{-1})]: 234 (1.814×10^4), 599 (130).

3. Results and discussion

3.1. General characterization for complex 1

$[Cu(Me_2oxpn)Cu(OH)_2]$ is very soluble in water and insoluble in organic solvents, such as methanol and ethanol. The UV–vis spectrum was recorded in aqueous solution, with main features at 234 nm ($\varepsilon = 18{,}140$) and 599 nm ($\varepsilon = 130$) (Fig. S1). The shoulder observed at 234 nm corresponds to a LMCT transition between the ligands and copper ions; The band observed at 599 nm is characteristic of Cu(II) d–d transitions. Similar UV–visible features have been observed for several similar dicopper(II) complexes [34]. And the UV–vis spectra of **1** in buffered aqueous solutions in pH 5.2 to 11.2 exhibit similar peaks to those in water. When pH = 12.0, the absorption band at 234 nm disappeared, suggesting that complex **1** decomposes to a new component under these conditions (Fig. S2). Therefore, we will explore its electrochemical properties in pH 5.2 to 11.2.

3.2. Cyclic voltammetry studies

The cyclic voltammogram (CV) of an aqueous solution of **1** (Fig. 1) shows a quasi-reversible wave at $E_{1/2} = -0.35$ V (all potentials *vs* Ag/AgCl), which can be assigned to $Cu^{II}Cu^{II}/Cu^{II}Cu^{I}$ couple. Sweeping toward the anode shows two irreversible wave at 0.87 and 1.25 V, which are assigned to $Cu^{III}Cu^{II}/Cu^{II}Cu^{II}$ and $Cu^{III}Cu^{III}/Cu^{III}Cu^{II}$ couples, respectively.

We further explored the electrochemical behavior of **1** in buffered aqueous solution where pH = 5.7–11.2 which is the range associated with catalytic water reduction and oxidation. In pH 7.0 phosphate buffer, the reversible $Cu^{II}Cu^{II}/Cu^{II}Cu^{I}$ wave at −0.35 V was also observed for **1** (Fig. S3). The $Cu^{II}Cu^{II}/Cu^{II}Cu^{I}$ couple displays a pH-dependent redox potential change, with a slope of −55 mV pH^{-1} in the range from pH 7.9 to 10.1 (Fig. 2), suggesting a proton-coupled electron transfer process. CVs were also recorded at different scan rates in order to obtain kinetic information of this complex. The current response of the redox event at about −0.35 V shows a linear dependence on the square root of the scan rate (Fig. S4), which is an indicative of a diffusion-controlled process, with the electrochemically active species freely diffusing in the solution. Correspondingly, sweeping toward the cathode reveals two irreversible redox waves at about −0.51 and −1.10 V, which are assigned to $Cu^{II}Cu^{I}/Cu^{I}Cu^{I}$ and $Cu^{I}Cu^{I}/Cu^{I}Cu^{0}$ couples, respectively (Fig. S3). The current response of the redox events at −1.10 V also

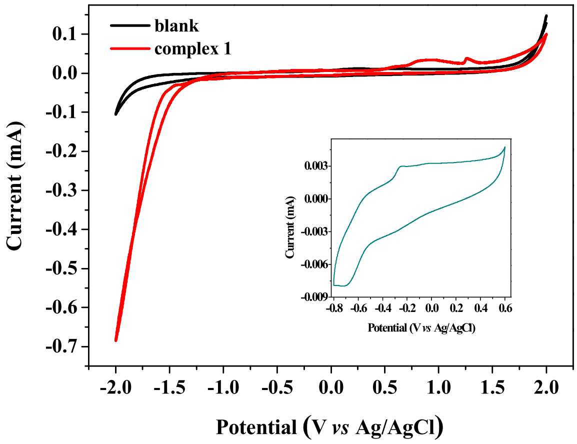

Fig. 1. Cyclic voltammograms of 0.10 M KNO_3 aqueous solution without and with 1.196 mM complex **1** at a glassy carbon electrode and a scan rate of 100 mV s^{-1}. The inset shows a magnified view of the $Cu^{II}Cu^{II}/Cu^{II}Cu^{I}$ couple.