Towards efficient and robust anodes for water splitting: Immobilization of Ru catalysts on carbon electrode and hematite by *in situ* polymerization

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ABSTRACT

Ru-bda based molecular water oxidation catalysts **1** and **2** (H$_2$bda = 2,2′–bipyridine–6,6′–dicarboxylic acid) containing a thiophene group are attached to the surfaces of electrodes by the method of electropolymerization. The Ru-bda molecular catalyst functionalized graphite carbon electrode can catalyze water oxidation efficiently under a overpotential of ca 500 mV to obtain current density of 5 mA cm^{-2}; and the similarly functionalized photoelectrode based on α-Fe$_2$O$_3$ (hematite) film can work as an photoanode for light driven water splitting.

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1. Introduction

The pursuing of cost effective and robust catalysts for water oxidation with low overpotentials is one of the most important challenges for solar energy conversion into fuels [1,2]. Intensive efforts have been paid to this question since decades ago. Many molecular catalysts such as Ru- [3–7], Ir- [8,9], Co- [10,11], Fe- [12,13] and Cu-based [14,15] complexes have been developed. Ru complexes have attracted tremendous attention due to their high stability, activity and suitability for the studying of mechanisms in details [16,17]. Our group also contributed a family of water oxidation catalysts based on Ru-bda complexes (H$_2$bda = 2,2′–bipyridine–6,6′–dicarboxylic acid) [4,18–20]. This series of catalysts show impressive activities of water oxidation in homogenous system with high turnover numbers (TONs) and turnover frequencies (TOFs).

After long term development of molecular catalysts, an inevitable challenge we are facing now is to construct stable and efficient water splitting devices using the molecular catalysts that we have developed [21]. To design a water splitting device, several issues are frequently encountered: (1) the choice of photoactive semiconductor or dye-sensitized semiconductor; (2) the effective method for catalyst loading; (3) and the search for cheap and effective photosensitizer which can lead to a high energy conversion efficiency. Aiming to the first two issues, in this work, we present two functionalized electrodes for electro-catalytic and photoelectro-catalytic water oxidation respectively by *in situ* polymerizing our Ru-bda catalyst onto the surface of the electrodes. For the electro-catalytic water oxidation electrode, we choose graphite carbon based electrode due to its high stability and good conductivity. For the photoelectro-catalytic electrode, an earth abundant material α-Fe$_2$O$_3$ (hematite) is employed herein to work as a photoanode. Hematite has been investigated extensively as a water splitting anode due to its suitable band gap (~2.1 eV) which can harvest visible light, and its low enough valence band which provides sufficient overpotential for oxidizing water [22,23]. However, due to the low conduction band, an external bias is still needed to
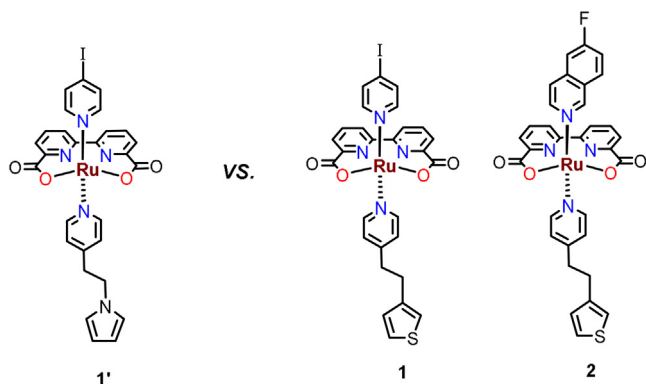
Fig. 1. Structures of catalysts **1**, **2** and **1**′.

Fig. 2. CV curves based on different electrodes: **1**@GE (blue), **2**@GE (red) and pristine GE (black dash line). Conditions: pH 7.2 phosphate buffer (0.1 M), scan rate: 0.1 V s^{-1}. The inset shows the first reversible redox waves of **2**@GE (Ru$^{III/II}$). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
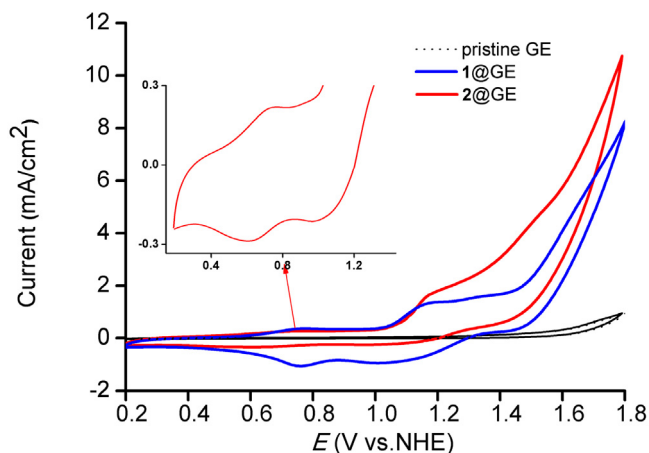
drive the proton reduction reaction which happens on the counter electrode.

Several strategies have been reported for immobilizing molecular catalysts onto electrodes surfaces in order to construct water splitting anode [24–34]. We immobilized water oxidation catalysts on carbon surface in our earlier study, in which we found that the catalytic current density for water oxidation was improved dramatically by using the strategy of *in situ* polymerizing of the Ru-bda catalysts onto the surface of the electrode [35]. This current enhancement is most likely due to the suitable catalyst loading method which allows the catalysts close to each other in space and further benefit the bimolecular O—O bond formation mechanism. Although the current density of the device was good, the challenge still remains on the stability of the device. The unsatisfactory durability of the functionalized electrode for water oxidation is due to the serious dissociation of the embedded catalysts from the electrode surface. The main reason of the catalyst desorption is that the polypyrrole cannot tolerate the relatively high oxidizing potential for oxidizing water. Therefore, a new anchoring group which can remain stable under high oxidation potential is needed in order to develop a more stable functionalized electrode. Polythiophene is a good candidate since it exhibits a good conductivity and meanwhile can resist the high oxidation potential during the water oxidation catalysis [36,37]. On the basis of the above considerations, we prepared a Ru-bda catalyst (**1** in Fig. 1) bearing a thiophene unit as appended-bridge ligand instead of pyrrole (**1**′). In an attempt to evaluate the hydrophobic effect of the axial ligand, catalyst **2** was also prepared using the same method. In comparison to **1**, a hydrophobic ligand 6-fluoroisoquinoline is used instead of 4-iodpyridine in **2** (Fig. 1).

2. Results and discussion

Both catalysts **1** and **2** were synthesized based on the previous reported method, and fully characterized by NMR, MS and elemental analysis (see Supporting information). Taking catalyst **1** as an example (Fig. S1), three ^{1}H NMR peaks at 8.65 (d, J = 10.0 Hz, 2H), 8.15 (d, J = 10.0 Hz, 2H) and 7. 98 (t, J = 10.0 Hz, 2H) ppm represent the proton resonances of bda^{2-}; two signals at 8.73 (s, 1H) and 7.59 (s, 1H) ppm belong to the aromatic protons of the 4−iodopyridine ligand; and the thiophene moiety shows the identical characteristic peaks that of 7.33 (m, 1H), 6.97 (s, 1H) and 6. 94 (d, J = 10.0 Hz, 1H) ppm after coordination, showing a symmetric structure with both carboxylates coordinated to the Ru center.

Followed by the characterization of these two ruthenium catalysts, homogeneous water oxidation catalysis was carried out in pH 1 aqueous solutions by using Ce(NH$_4$)$_2$(NO$_3$)$_6$ as chemical oxidant to evaluate the activities of both catalysts. A turnover number (TON) and initial turnover frequency (TOF) of 2400 and 14 s^{-1} were

obtained by catalyst **1**. Under the same condition, 6500 and 46 s^{-1} were found for catalyst **2** (Fig. S2). The higher efficiency of catalyst **2** compared to **1** is likely due to the π−π interaction between isoquinoline ligands which can promote the rate limiting step of O—O bond formation.

Electropolymerization was conducted using a typical three-electrode electrochemistry cell. A basal plane pyrolytic graphite electrode (GE, Ø = 3.0 mm) was used as the working electrode, and it was cycled from 0 to 1.6 V (vs Ag/AgNO$_3$) in acetonitrile solution of the Ru complex (10 mM complex, 0.1 M TBAPF$_6$) at the scan rate of 100 mV s^{-1}. After modification of the working electrodes, two cyclic voltammograms (CVs) of **1**-modified (**1**@GE) and **2**-modified GE (**2**@GE) were carried out in aqueous solution (pH 7 phosphate buffer, 50 mM) as shown in Fig. 2. Taking **2**@GE as an example, a reversible redox wave appeared at E$_{1/2}$ = 0.73 V *vs*. NHE followed by the catalytic onset potential of water oxidation at ∼1.2 V *vs*. NHE in an anodic scan (Fig. 2). In addition, the X-ray photoelectron spectroscopy (XPS, Fig. S4) indicates that Ru catalyst does not become Ru(IV) oxide on the surface. By running the CVs for the redox waves Ru$^{III/II}$ at differential scan rates (Fig. S5), the surface coverage of catalyst for **2**@GE was estimated to be 9.6 × 10^{-10} mol cm^{-2} according to the literature method [25].

Since **2**@GE exhibits more promising performance, the following electrochemical measurements were carried out mainly by using **2**@GE as working electrode for catalytic water oxidation. First, the chronoamperometric current density of **2**@GE was measured in pH 7 phosphate buffer, and then the TOF of the embedded catalyst were estimated according to a reported method [25]. With the overpotential ranging from 300 to 700 mV, the obtained TOF values increase from 3 s^{-1} to 15 s^{-1} and it follows the Tafel behaviour with a slope of 153 mV per decade, as shown in Fig. 3 upper. This slope is slightly bigger than that of the common inorganic water oxidation catalysts (< 100 mV) [38,39]; however, it is rather small compared to the values of other immobilized molecular catalysts [24,40,41], indicating a very efficient electron transfer process at the interface. Based on these observations, bulk electrolysis were carried out by using both **1**@GE and **2**@GE as working electrode under 1.3 V *vs*. NHE bias and oxygen production have been confirmed (Fig. 3, below). Taking **2**@GE as an example, the evolved oxygen gas was quantified by gas chromatography (GC) which gave ∼5 μmol O$_2$ after 7 h of electrolysis, and the TON of ∼72000 was determined with a Faradic efficiency over 90% (Fig. 3, Fig. S6). The current density was dropped slowly during the electrolysis which is probably