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IMMOBILIZATION AND CHARACTERIZATION OF WATER-INSOLUBLE FE COMPLEXES AS MOLECULAR CATALYSTS FOR WATER OXIDATION

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Abstract: *The apparent difference between the expanding consumption of fossil fuels and chemicals and the limited amount of resources has motivated many researchers to seek solutions for maintaining the sustainability of our community. Artificial photosynthesis (AP), which utilizes sunlight to produce high-value chemicals, including H_2 from abundant resources, is regarded as the most encouraging and viable method. Modern AP systems necessitate in the first place to develop inexpensive, highly active, and stable catalysts for hydrogen production (Hydrogen Evolving Reaction, HER) and water oxidation (Oxygen Evolving Reaction, OER), both are a crucial challenge. However, prior to implementing any artificial systems on water-splitting catalysts that generate oxygen from water without extreme driving potentials are demanded. Many recent studies concentrate on molecular systems based on the highly abundant first-row transition metals (TMs) proper as water oxidation catalysts (WOCs) due to their structural versatility, transparent catalytic mechanisms, and ultimate atomic efficiency concerning catalytic centers. Herein, we report Fe-based compounds among these TMs as efficient electrocatalysts for OER. In this context, we studied the electrochemical behaviour of water-insoluble Fe complexes in homogeneous water/organic mixtures to reveal their intrinsic molecular properties. The water-insolubility of the selected Fe complexes allowed for simple immobilization methods (dip-coating and drop-casting) on model semiconductors. Ultimately, electrodeposition has been explored to reduce to a minimum amount of the complex required for long-term operando stability. The consequence of these studies is that water-insolubility presents a viable strategy for designing new molecular catalyst/(photo)anode hybrids.*

Keywords: *Artificial photosynthesis; water oxidation; molecular precursor; iron complex; immobilization; Electrodeposition*

INTRODUCTION

Fossil fuels are essential to match our daily energy consumption demands due to their ready availability, suitable energy density, and ease of handling, storage, and distribution [1]. The combustion of fossil fuels has fundamental adverse effects on the global climate, which is acknowledged as the primary contributor to global warming. Increasing carbon dioxide (CO_2) emissions to the atmosphere from various fuel types and immoderate emissions of exhaust gases have constituted a severe problem in many countries, affecting human health [2], [3]. Therefore, a clean, abundant, sustainable, and safe energy source is the real challenge for establishing an economy in continuous development. Artificial photosynthesis (AP),

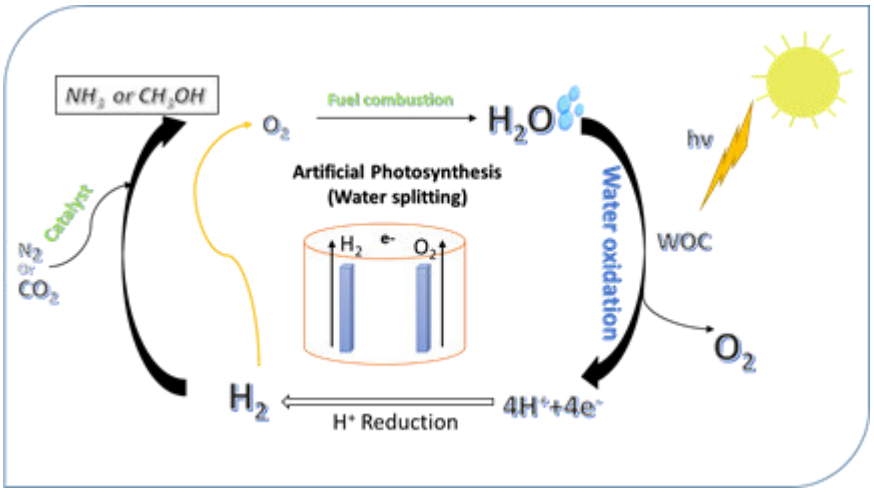
aiming to catch the sunlight, has the potential of producing clean, sustainable, and large-scale energy resources through water splitting and generating hydrogen gas as a renewable chemical fuel [4]. Water splitting by using AP attracted distinguished attention from researchers, and it is considered the most encouraging method for producing hydrogen (H_2) as fuel and oxygen (O_2) as a side-product [5]. Hydrogen gas is a potential fuel for the future because of its suitable energy density, carbon-free combustion (or use in fuel cells) that is important to protect our community.

Considering the model below (Scheme 1, Eqs. 1-3), splitting two water molecules to produce H_2 as a clean energy carrier (Eq. 1) results from two coupled half-reactions. The first half-reaction, the Oxygen Evolving Reaction (OER) (Eq. 2), is generally considered the overall system's bottleneck due to its sluggish kinetics that results from the complicated transfer of four electrons and four protons. The second half-reaction that demands much lower kinetic overpotential is the reduction of the protons to molecularH_2 using the released electrons (Eq. 3) [6].

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 2H_{2(g)} \quad (1)$$

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4e^- + 4H^+_{(aq)};\ E^o = +1.23\ V\ vs\ NHE \quad (2)$$

$$2H^+_{(aq)} + 4e^- \rightarrow H_{2(g)};\ E^o = 0\ V\ vs\ NHE \quad (3)$$



Scheme 1. The general concept of artificial photosynthesis

Water oxidation catalysts (WOC) are intended to improve the OER's efficiency, thus aiding solar-to-chemical energy conversion as in the artificial photosynthesis concept [7]. The fundamental challenge is the rational design and development of catalysts for each reaction and creating a device proficient at completing the whole water splitting process. Efforts have resulted in promising findings by applying different first-row transition metal-based electrocatalysts that can help develop catalysts suitable forindustrial and practical applications to replace noble metal-based materials.

Recently, extensive efforts have been made to develop efficient WOCs composed of more abundant metals, such as manganese [7], [8], iron [9],[11], cobalt [12], [13], nickel [14], [15], and copper [16], [17] that have received significant attention. Iron earned distinguished attention among these metals since thisis the 4th most abundant element on Earth and an environmentally friendly metal. Molecular catalysts are promising compounds for water oxidation due to their well-defined active site structures and ease of mechanistic investigation [18]. As a recent example, mono- and binuclear iron corroles successfully immobilized in Nafion films were published to act as efficient electrochemical WOCs [19]. Fe^{III}-TAML (TAML = tetraamido macrocyclic ligands) complexes immobilized on carbon black/Nafion carbon-based

electrodes have been published as effective electrocatalysts; their performance strongly depends on the ligand structure [20]. However, simple immobilization of molecular catalysts on the surface of electrodes is still a great challenge for many compounds. Consequently, we concentrated on molecular complexes that seemed suitable for simple grafting, and the selected Fe-based compounds have been tested as immobilized electrocatalysts for OER. In this perspective, we summarize our results on the electrochemical characterization of water-insoluble Fe complexes with (**a**) non-symmetric, readily available bidentate ligands, i.e., 2-(2'- pyridyl)benzimidazole (PBI) in $[Fe(PBI)_3](OTf)_2$ (**1**, OTf- = trifluoromethyl sulfonate anion), 2-(2'- pyridyl)benzoxazole (PBO) in [Fe(PBO)2(OTf)2] (**2**) [21],and (**b**) pincer ligands like in the $[Fe^{III}Cl_2$(tia-BAI)] complex (**3**, where tia-BAI^- = 1,3-*bis*(2'-thiazolylimino)isoindolinate(−)) [22](Fig. 1). Importantly, we discuss some simple immobilization methods (dip-coating and drop-casting, Fig. 2, method A-C) on model semiconductors.

We demonstrated with the $[Fe^{III}Cl_2$(btia-BAI)] complex (**4**, btia-BAI− = 1,3-bis(2'-benzothiazolylimino)isoindolinate (−)) [23] the effectiveness of electrodeposition (ED) (Fig. 2 , method D) to fabricate catalytically active layers helped by the controlled solubility of complex 4 in the obligate solvent mixtures. Ultimately, electrodeposition proved to be suitable for reducing the complex's amount to a minimum needed for the long-term stability of the produced catalytic layer. The critical result of these comparisons is that water-insolubility offers a viable strategy for designing new molecular catalyst/(photo)anode hybrids.

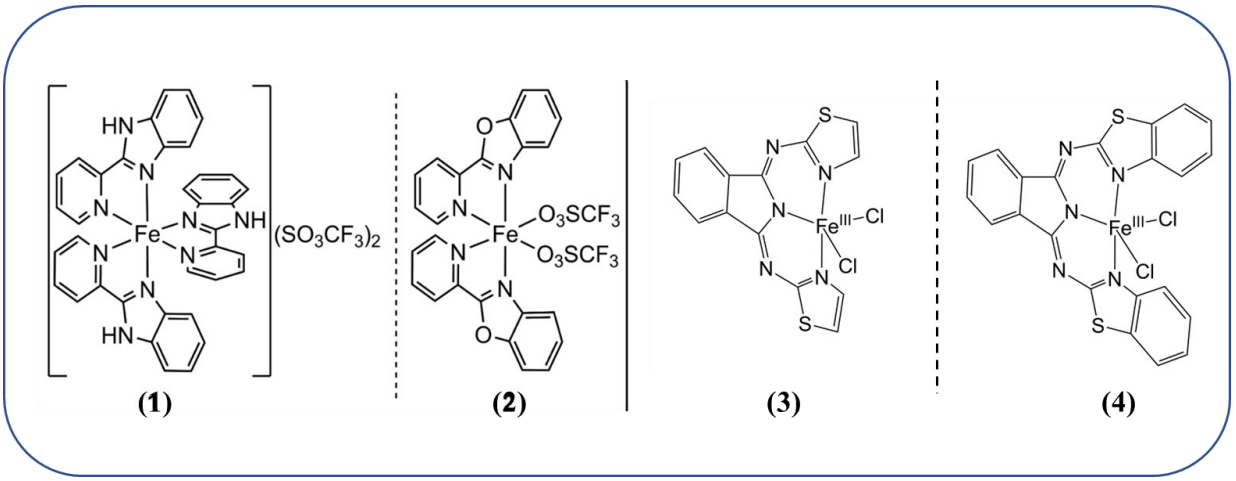


Figure 1. Molecular structure of the precursor Fe complexes 1-4 utilized in OER electrocatalysis

MATERIALS AND METHODS

The used solvents: methanol, ethanol, acetone, and dichloromethane (DCM) were HPLC grade, purchased from commercial sources, and used without further purification. These solvents were used in synthesis or electrolytes for nonaqueous electrochemical experiments. Tetrabutylammonium perchlorate (TBAP) was purchased from commercial sources and used without further purification. For complex synthesis, the $FeCl_3 \cdot 6H_2O$ and $Fe(CF_3SO_3)_2$ were purchased from Sigma-Aldrich and Strem Chemicals, respectively. Nafion polymer (a commonly used support for molecular electrocatalysts) was purchased from Sigma-Aldrich as a methanolic solution.

Ligands and complexes

The ligand 2-(2′-pyridyl)benzimidazole (PBI) was purchased from Sigma-Aldrich, while 2-(2′-pyridyl)benzoxazole (PBO) was synthesized following literature procedure [21]. The ligands 1,3–*bis*(2′–thiazolyl), iminoisoindoline (tia-BAIH), and 1,3-*bis*(2'-benzothiazolylimino)isoindoline (btia-BAIH) were synthesized according to known procedures [22]. The complexes 1-4 were synthesized and re-crystallized according to published procedures [21], [22].

Electrodes and semiconductor substrates
For heterogeneous electrochemistry and catalysis (using the immobilized complexes), indium tin oxide-coated glass slides (ITO, ~100 nm thickness) were purchased from PGO GmbH, Germany, or Ossila Ltd., Great Britain. Fluorine-doped tin oxide (FTO), which can be applied for long periods of OER electrocatalysts, was purchased from Ossila Ltd. Platinum coil (Pt) was used as an auxiliary electrode. The reference electrode was Ag/AgCl (3 M KCl) for aqueous experiments.

Electrocatalytic investigations/ Heterogeneous electrocatalysis
Standard electrochemical techniques were applied to characterize the immobilized complexes, including LSV, EIS, and CA. Low surface roughness FTO (20×15 mm, 600 nm thickness, 6-9 Wð$^{-1}$, 34.8 nm RMS) and ITO (20×15 mm, 100 nm thickness, 20 Wð$^{-1}$, 1.8 nm RMS) coated glass slides of uniform size were used as standard model electrodes, which were modified with thin films of the complexes as described in the followings. These modified electrodes were set as a working electrode in a three-electrode setup (Pt aux. and Ag/AgCl ref.) in a small cell, and the electrochemical behavior was compared to that of the unmodified ITO or FTO under the same conditions. ITO or FTO coated glass slides were cleaned with ethanol in an ultrasonic bath for 20 min, then rinsed with deionized water and dried with dry N_2 gas. All experiments were conducted in 0.2 M borate buffer at pH 8.2(1) for better comparison.

Deposition of the complexes on semiconductor (ITO, or FTO)
Different procedures (dip-coating, drop-casting, and electrodeposition) were applied to immobilize the complexes on a semiconductor surface. These were used to fabricate active catalytic layers of the complexes on the surface of ITO, or FTO [23]–[25]. Herein, we list all methods used, as shown in Fig. 2 (methods A-D). Methods (A-C) include drop-casting (DC) and dip-coating (DIP) with/no Nafion, whereasmethod D shows the electrodeposition (ED) method.

METHODS

Drop-casting (DC): the same procedure in the method (A) was used for complexes **1** and **2** dissolved in methanol in 6 mM concentration. As shown in Fig. 1, small portions of the solutions (50–150 μL) were evenly layered onto ITO using a micro-syringe. For these two complexes, methanol was evaporated at room temperature and, after that, dried for 30 min using an infrared lamp to provide evenly distributed catalyst films (Figure 3) [23].
The same procedure was repeated with Nafion and complex 1 in methanol to prepare complex/Nafion/ITO composite films, but no significant difference was observed compared to the complex/ITO sample [23]. Method (C) was followed to produce Nafion/substrate electrode for reference [25].
This procedure was used for complex 3, dissolved in methanol in 3 mM concentration. Small aliquots (50–200 μL) were evenly layered onto ITO using a micro-syringe. The solvent was evaporated, and the solid was dried by infrared heating for 30 min (Figure 3) [24].

Dip-coating (DIP): method (B) was used for complex 1 was dissolved in methanol with or without adding Nafion (5 wt% in water/methanol) to reach a final concentration of 0 or 0.4 wt% for Nafion and 0.4–6.0 mM for the complex. With complex **2** (0.4–10.0 mM), the concentration of Nafion was varied between 0 and 0.8 wt% to obtain different composite films. The ITO pieces were dipped into the coating solutions for 1 min, then kept at room temperature for 30 min, finally heated for 30 min at 90–110°C [23]. A similar procedure could be applied for complex **3** [25].

Electrodeposition (ED): We developed method (D) due to the poor solubility of **4** in methanol. The deposition was performed using a three-electrode configuration, containing FTO or ITO, Pt, and Ag^+/Ag (0.01 M $AgNO_3$, 0.1 M TBAP/MeCN), as working, counter and reference electrodes, respectively. The solution consisted of 0.8 mM of complex **3**, or **4** in DCM, and a mixture of 500 μL acetone and 54 μL MilliQ water. ED was conducted by CV at 100 mV/s, turning potentials of −0.4 V and 1.7 V *vs* Fc^+/Fc, for

a total of 20 cycles. The surface concentration of the deposited complex was determined from the current peak integral after the final cycle by presuming a $1e^-$ Fe(III)/Fe(II) transition (z = Q/F). The electrodes could be dried at room temperature after rinse [25].
All electrolysis experiments were carried out in 0.2 M borate buffer (pH ~ 8.3) for control potential electrolysis by (CPE) using a three-electrode configuration, containing ITO, or FTO, Pt, and Ag/AgCl as working electrode, counter, and reference electrodes, respectively.

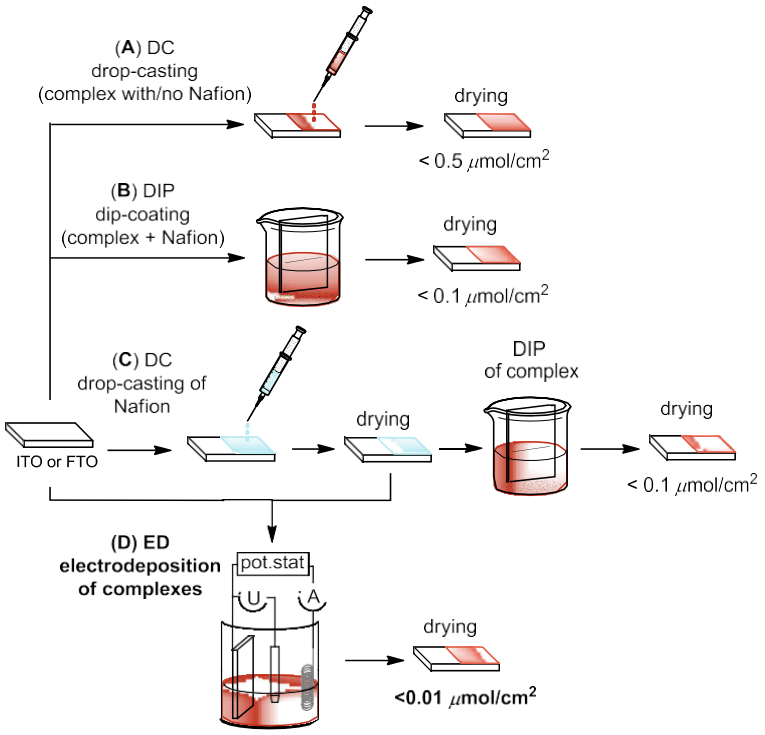


Figure 2. Schematic presentation of the different deposition methods [25]

Figure 3. Typical drop-casted samples of complexes **1**, **2,** and **3** on the ITO slides, applied in improved electrocatalysis to generate O_2 [23], [24].

RESULTS AND DISCUSSION

The simplest way of immobilizing molecular catalysts is to drop-cast the compounds onto electrode surfaces and dry the so formed thin films. These compounds are all water-insoluble due to the chosen ancillary ligands. However, suppose no further supporting additive is applied. In that case, the necessary but sufficient requirement is the water-insolubility and hydrophobic binding of the molecules to the surface, as proven by the successful deposition of the active molecular catalysts **1**, **2**, and **3** (see Fig. 3). We hypothesized that hydrophobic interactions would keep the surface-deposited complexes on the ITO electrode in an aqueous buffer during electrolysis.

As deposited onto the ITO working electrode, the catalyst layers were allowed to oxidize water to oxygen electrochemically under an applied potential of 1.4 V (vs. Ag/AgCl, pH 8.3). Following 2 hours of reaction time, we found that simple atomic level modification in the heterocyclic ancillary ligands causes drastic changes in the catalytic behavior. While catalyst **1** displayed long-term electrocatalysis to produce O_2 without remarkable decomposition of the catalysts layer on the ITO electrode, complex **2** underwent rapid in situ decomposition. The procedure was also applied to complex **3** (Fig. 3), which showed a 94% Faradaic efficiency after 4 hours of electrolysis in borate buffer at 8.3 pH comparable to that found for complex **1**. Note that complex **3** displayed Fe ion loss from the surface, causing its deactivation, while the surface modified with complex **1** showed enrichment in Fe that can be associated with a change in metal- to-PBI ligand ratio.

Method (B) created a thin layer of the complexes through simultaneous drying and heating to 120°C. Dip-coated ITO slides were possible to fabricate with complexes **1-3**, with and without the addition of Nafion (as support to see if long-term stability of the film in electrolysis is affected or not by this commonly used carrier additive). The modified electrodes were compared to plain ITO in borate buffer at pH 8.3. We found that Nafion had no detectable effect on the catalytic performance; thus, we could conclude that the hydrophobic interactions supplied by the ancillary ligands are indeed sufficient to warrant long-term stability for the system. In this respect, the choice of the ligand is the determinant factor.

The question remained, how can the surface-adsorbed complexes become active as a catalyst at the molecular level, despite their coordination sites being occupied by organic donor groups. It has been known for a long that water oxidation requires the binding of a minimum of one H_2O molecule to the catalytic center, which is the metal ion in the complex in our case. We presumed that ligand exchange reaction as experimentally observed in water/organic mixtures would also occur at the solid-liquid interface upon contact of the film-coated ITO with the aqueous phase, enabling the molecular systems to show catalytic activity [23], [24]. Indeed, surface composition analysis supported this hypothesis since thetotal absence of chloride could be concluded in the case of complex **3** during our detailed investigations. This means that chloride ligands exchange with water molecules upon contact with aqueous buffer, thus allowing for efficient catalysis, but the ancillary ligands, as shown in Fig. 1, remain coordinated and tune the catalytic capabilities.

In method (C) (see Fig. 2), the drop-casting was carried out using Nafion as support, and after that, the ITO pieces were immersed in a solution containing the complexes. However, adding Nafion did not result any notable effectiveness in OER.

Methods (A-C) were unsuited to fabricate catalytically active layers of complex **4**; as mentioned before, it has poor solubility in the obligate solvent. On the other hand, electrodeposition (see Fig. 2) was the proper selection to afford layers with better charge transfer properties and stability. This method was applied for complexes **3** and **4** that clearly showed a more satisfying performance. Table 1 summarizes all electrolysis performance data for complexes **1-4**. When applicable, ED is the most atom-efficient method that yields complex ad-layers with the highest activity in OER catalysis; therefore, further investigation is justified.

Table 1. Summary of the data of three immobilization methods onto ITO and FTO electrodes.*

complex¤	Electrode¤	method¤	j·(μAcm^{-2})¤	E·*vs*·(Ag/Ag$^+$)¤	TON¤	TOF·(s^{-1})¤	Faraday·eff.·(%)¤
1¤	ITO¤	DIP¤	107¤	1.4¤	n.d.¤	n.d.¤	n.d.¤
2**¤		DIP¤	36¤	1.4¤	n.d.¤	n.d.¤	n.d.¤
1¤	ITO¤	DC¤	533¤	1.4¤	73¤	0.012¤	98¤
2**¤		DC¤	800¤	1.4¤	n.d.¤	n.d.¤	n.d.¤
3¤	¤	DC¤	612¤	1.4¤	228¤	0.014¤	94¤
3¤	FTO¤	ED¤	900¤	1.5¤	n.d.¤	n.d.¤	n.d.¤
4¤		ED¤	1200¤	1.5¤	5000¤	0.4¤	83¤

*not·determined·due·to·low·or·declining·activity·on·the·timescale·of·the·experiment¶
**Complex·2·decomposes·during·electrolysis·(it·is·not·a·molecular·catalyst)¶

CONCLUSIONS AND RECOMMENDATIONS

Water splitting is a promising strategy to produce H_2 as a green fuel. In the overall process, the water oxidation reaction to produce O_2 at the anode (OER) is the most challenging task. This reaction produces electrons and protons for the reduction reaction generating H_2 at the cathode (HER). Efficient water splitting operated by solar energy can be accomplished by immobilizing a catalyst onto an electrode to achieve an efficiently catalyzed OER. Substantial variations of the ligand can adjust the catalytic activity of molecular complexes, but these ligands can influence the surface affinity, too, and allow scalable and straightforward immobilization of the catalysts on model semiconductors. The activity of the immobilized electrocatalysts based on essential parameters such as overpotential, stability, Faradic efficiency, and turnover frequency can be related to the molecular properties. Herein, we summarized and compared three scalable and straightforward methods (drop-casting, dip-coating, and electrodeposition) to immobilize the complexes onto ITO, FTO and investigated the activity and stability by extended electrolysis tests. The results showed that all three methods could be suitable for fabricating modified (and activated) electrodes for OER, but electrodeposition is the most atom efficient among those, easily yielding the most active ad- layers. The long-term stability of the **4**/FTO modified electrode is remarkable and, to our knowledge, barely matched by any other known Fe complex catalyst; therefore, this research direction is very promising in the utilization of first-row transition metal complexes for better OER performance.

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