



A nickel (II) PY5 complex as an electrocatalyst for water oxidation



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ABSTRACT

A Ni-PY5 [PY5 = 2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine] complex has been found to act as an electrocatalyst for oxidizing water to dioxygen in aqueous phosphate buffer solutions. The rate of water oxidation catalyzed by the Ni-PY5 is remarkably enhanced by the proton acceptor base HPO_4^{2-} , with rate constant of $1820 \text{ M}^{-1} \text{ s}^{-1}$. Controlled potential bulk electrolysis with Ni-PY5 at pH 10.8 under an applied potential of 1.5 V vs. normal hydrogen electrode (NHE) resulted in dioxygen formation with a high faradaic efficiency over 90%. A detailed mechanistic study identifies the water nucleophilic attack pathway for water oxidation catalysis.

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1. Introduction

Tremendous efforts have been devoted by scientists worldwide to replace fossil fuels with sustainable energy sources, such as hydrogen generated by water splitting based on the concept of artificial photosynthesis [1–3]. The process of water splitting consists of two half reactions, oxygen and hydrogen evolution shown as in Eqs. (1) and (2) respectively.



Water oxidation (Eq. (1)) is identified as the bottleneck of water splitting as it is a multi-electron and multi-proton stepwise reaction which is highly energy demanding. As a result, major research efforts are made to the development of efficient water oxidation catalysts including molecular systems and materials [4–6]. The advantages of homogenous water oxidation catalysis compared to those of heterogeneous are the comprehensive mechanistic studies and tunable chemical structures and properties [4]. Notable progress has been made in molecular water

oxidation catalysts (WOCs) which mainly include second row transition metal complexes, including ruthenium [7–30] and iridium [31–34]. In a pursuit of economically viable WOCs, first row transition metal complexes such as cobalt [35–42], iron [43–46], copper [47,48], and manganese [49–54] have attracted tremendous attentions. On the other hand, as an earth abundant metal, nickel is biologically important, however seldom investigated in the context of water oxidation catalysis. Recently, two nickel complexes have been proved to function as water oxidation catalysts: a Ni(II) amine complex and a Ni-porphyrin complex [55,56]. In the earlier case, one of the key conclusions is that the *cis*-isomer (converted from the *trans*-isomer, causing a long induction time) of the reported Ni-complex is crucial for the catalytic activity. The oxidatively stable PY5 types of ligands are good candidates for tolerating the harsh conditions which are necessary for water oxidation [12,39]. In addition PY5 based complexes can avoid the structure transformation and readily for the catalytic reaction. Based on the above understanding, we wanted to investigate the PY5 ligand in combination with nickel aiming for a water oxidation catalyst. In this work, we report the synthesis, characterization and catalytic water oxidation activity of a Ni-PY5 complex (Fig. 1). The designed Ni complex acts indeed as an efficient and robust electrocatalyst for water oxidation under basic conditions. Based on the first order kinetics studies, water nucleophilic attack mechanism for the O–O bond formation is proposed.

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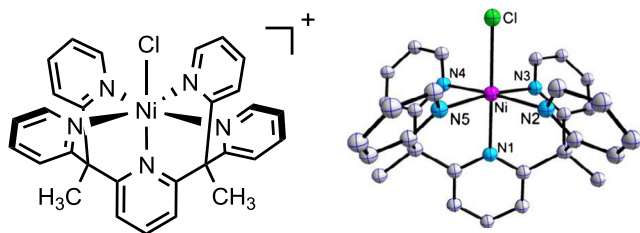


Fig. 1. The structure of the Ni-PY5 [PY5 = 2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine] complex and its corresponding X-ray crystal structure.

2. Experimental—synthesis and structure

The synthesis of the PY5 ligand and its coordination to Ni²⁺ have been investigated and reported previously [57]. The ligand PY₅Me₂ was prepared according to the method found in the literature. Refluxing an equivalent molar amount of PY₅Me₂ and NiCl₂·4H₂O in MeOH under N₂, followed by layering with diethyl-ether on the resulted solution induced the crystallization of the final product Ni-PY5 as purple single crystals which were suitable for X-ray analysis. As shown in Fig. 1, the X-ray single-crystal structure of the Ni-PY5 complex reveals that the divalent nickel ion is ligated by the five pyridine subunits and a chloride resulting in a nearly ideal octahedron geometry. Crystal data and structure refinement for complex Ni-PY5 are shown in Table S1. The N–Ni–N bond angle and the Ni–N bond distances are almost identical with those of the previously reported corresponding complex [57]. The UV–vis absorption spectrum of Ni-PY5 shows a metal-to-ligand charge transfer (MLCT) absorption band at 310 nm with a molar absorptivity of $\epsilon_{\text{max}} \approx 900 \text{ M}^{-1} \text{ cm}^{-1}$ in an aqueous solution (Fig. S1).

3. Results and discussions

3.1. Electrochemistry

The redox properties of Ni-PY5 were investigated in a phosphate buffer by cyclic voltammetry (CV). In aqueous solution, the potentials are reported vs. normal hydrogen electrode (NHE) by adding 0.197 V (Ag/AgCl as reference electrode, and [Ru(bpy)₃]Cl₂ as an internal reference) to the measured potentials. In organic solution, the potentials are reported vs. ferrocenium/ferrocene (Fc/Fc⁺) using Ag/AgNO₃ as the reference electrode. The CV of Ni-PY5 in a pH 7 phosphate buffer is depicted in Fig. 2a and it shows a single reversible metal based redox process (Ni^{III/II}) at +1.41 V vs. NHE. This is almost 0.2 V higher than the corresponding redox waves of the documented Ni oxide under the same pH conditions [58,59]. There is a sharp current rise following these reversible redox waves which is due to the oxidation of water (Fig. S2). Indeed, the catalytic current increased dramatically at pH 10.8 in comparison with that of pH 7.0. Additional CVs at variable pH of 7.0, 8.0, 8.8, 9.8 and 10.8 were obtained. With increasing pH the catalytic current increased dramatically and the potential of the redox couple Ni^{III/II} dropped by ~59 mV per pH unit (Fig. 2b) revealing a proton coupled electron transfer (PCET) process. The shape of CV remains unchanged suggesting that Ni-PY5 remains stable over the pH range of 7–11.

As shown in Fig. 3, the CV of the ligand PY5 is silent in the same potential window with that of Ni-PY5 in CH₃CN; therefore, the three different redox processes in the CV of Ni-PY5 can be tentatively assigned as Ni^{III/II}, Ni^{IV/III}(Ni-PY5-Cl), and Ni^{IV/III}(Ni-PY5-CH₃CN) respectively (see the discussion in Fig. S3). The huge peak separation of the quasi reversible Ni^{III/II} at 0.3 V is most likely due to the axial ligand exchange process from Cl to CH₃CN. When 5% of phosphate buffer (v:v) was added into the above organic solution, a

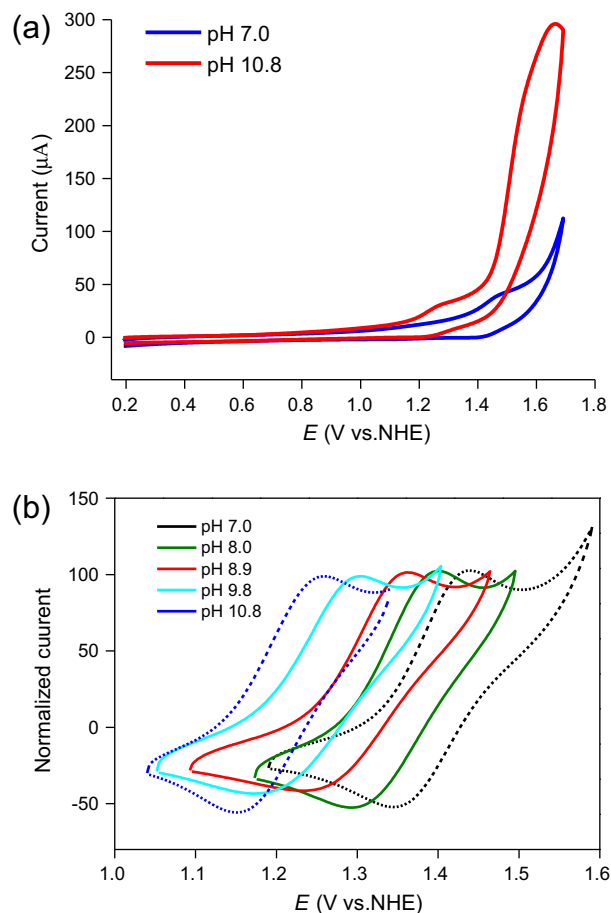


Fig. 2. (a) The CVs of 0.5 mM Ni-PY5 in solutions of 0.2 M phosphate buffer at pH 7 and pH 10.8. (b) Selective CVs (keep the potentials of the redox waves, and normalize the current of the oxidation peaks of the redox waves) for the reversible peak of complex Ni-PY5 at different pH buffers.

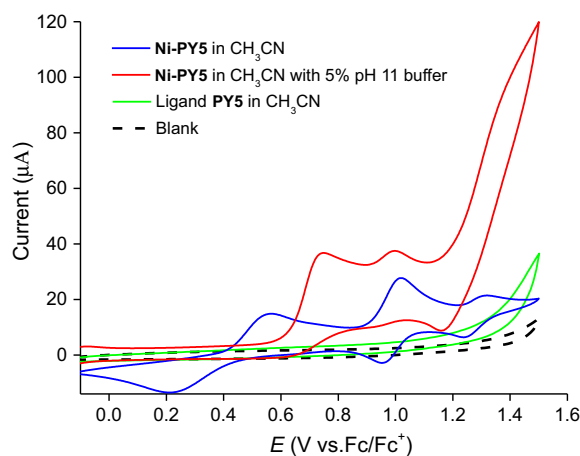


Fig. 3. CVs of 0.5 mM Ni-PY5 in pure CH₃CN solution (blue curve), (0.1 M Bu₄NPF₆) and CH₃CN with 5% pH 10.8 aqueous buffer (red curve), and CV of ligand PY5 as a control (green curve).

catalytic current rise was observed at the position of redox Ni^{IV/III}(Ni-PY5-CH₃CN) indicating that the Ni^{IV} species triggers the oxygen evolution. Meanwhile, the $E_{1/2}$ value of Ni^{III/II} was anodically shifted by 0.25 V; however, the $E_{1/2}$ value of Ni^{IV/III}(Ni-PY5-Cl) remains the same.

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