Supporting Information for

In situ assembly of nickel-based ultrathin catalyst film for water oxidation

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1. Experimental Procedures

All reagents and solvents used in the present work were obtained commercially available without further purification. The single-crystal X-ray diffraction data was collected by Image Plate X-Ray Diffractometer RAPID-S at 180 K. Inductively coupled plasma (ICP) experiments were performed on a Varian 710-OES instrument. UV-vis absorption spectrum was determined on a Shimadzu UV-1601PC UV-visible spectrophotometer. HRMS of complex 1 was performed using an Agilent 6530 and a Q-Exactive mass spectrometer, using electron spray ionization source. All pH measurements were made with Model pHS-3C meter (Mettler Toledo FE20, China). Electrochemical experiments were performed on an electrochemical workstation (CHI 630E). All electrochemical experiments were performed in a 30 mL gas-tight single cell. All potentials were reported versus saturated Ag/AgCl. The X-ray photoelectron spectra (XPS) measurements were performed on an ESCALAB 250 spectrophotometer with Al-K α radiation. The binding energy scale was using the C 1s peak at 284.8 eV. Scanning electron microscopy (SEM) images were collected by field emission scanning electron microscope (HITACHI S4800). Transmission electron microscopy (TEM) images, selected area electron diffraction (SAED) pattern and energy dispersive X-ray spectroscopy (EDS) spectra were collected on a JEM-2100. Oxygen evolution of CPE at 1.4 V was performed on a Shimadzu Nexis GC-2030 gas chromatograph. X-Ray Diffraction (XRD) plot was performed on a Rigaku Ultima IV.

Solution preparation method with different pH is as follows.

1.907 g Na₂B₄O₇•10H₂O and 1.237 g H₃BO₃ were diluted to 100 mL for 0.05 M borax and borate aqueous solution, respectively. By varying the amount of the solutions, a range of different pH solutions can be prepared. The pH of each prepared solution was measured using a calibrated pH meter.

pН	0.05 M borax	0.2 M borate	рН	0.05 M borax	0.2 M borate
	solution (mL)	solution (mL)		solution (mL)	solution (mL)
7.4	1.0	9.0	8.2	3.5	6.5
7.6	1.5	8.5	8.4	4.5	5.5
7.8	2.0	8.0	8.7	6.0	4.0
8.0	3.0	7.0	9.0	8.0	2.0

2. Synthesis procedure of complex 1

The synthesis pathway of complex **1**.



Synthesis of Ligand: According to the literature.¹

Synthesis of complex 1: 1 mmol ligand and 1 mmol Ni(OAc)₂ was separately dissolved in 5 mL water. Then added Ni(OAc)₂ aqueous solution into the ligand aqueous solution and stirred overnight. The green precipitate was the rude product. After filtration, the precipitate was redissolved in water. Recrystallization of **1** from water gave green crystals.

3. Single-crystal X-ray structure of complex 1.

Table S1. Crystal data and structure refinement for

Empirical formula	C ₁₀ H ₁₉ NNiO ₉		
CCDC number	2264720		
Formula weight	355.97		
Temperature / K	180.00(10)		
Crystal system	Monoclinic		
Space group	P21/n		
a / Å	7.2401(3)		
b / Å	7.9797(3)		
c / Å	24.8846(9)		
α/°	90		
β/°	95.433(4)		
γ / °	90		
Volume / Å ³	1431.22(10)		
Ζ	4		
$\rho_{calc}g / cm^3$	1.652		
μ / mm ⁻¹	1.400		
F(000)	744.0		
Crystal size / mm ³	0.6 imes 0.1 imes 0.05		
Radiation	ΜοΚα (λ =0.71073)		
2Θ range for data collection /°	5.364 to 54.968		
Index ranges	$-9 \le h \le 9, -10 \le k \le 8, -31 \le 1 \le 32$		
Reflections collected	9069		
Independent reflections	$3275 [R_{int} = 0.0290, R_{sigma} = 0.0356]$		
Data/restraints/parameters	3275/15/221		
Goodness-of-fit on F2	1.050		
Final R indexes [I>= 2σ (I)]	$R_1 = 0.0295, wR_2 = 0.0790$		
Final R indexes [all data]	$R_1 = 0.0354, wR_2 = 0.0818$		
Largest diff. peak/hole / e Å ⁻³	0.32/-0.57		



Fig. S1 Single-crystal X-ray structure of **1** (Ni, green; N, blue; C, grey; O, red; thermal ellipsoids at 50% probability level. H atoms were omitted for clarity).

4. UV-vis absorption spectra



Fig. S2 UV-vis absorption spectra of 1 and ligand in water.



Fig. S3 UV-vis absorption spectra of 1 dissolved in BBS and mixed solution of ligand and Ni(OAc)₂.



Fig. S4 UV-vis absorption spectra of Ni-Schiff electrode and bare electrode.

5. HRMS experiments







Fig. S6 Complex 1 in 0.2 M BBS (pH = 9) by high-resolution ESI-MS.



Fig. S7 Complex **1** in 0.2 M BBS (pH = 7.4) by high-resolution ESI-MS.



Fig. S8 High-resolution ESI-MS spectrum. Condition: CPE at 1.4 V for 10 h using 1mM **1** in 0.2 M BBS.



Fig. S9 The magnification of the Fig. S8 at positive mode in the range of m/z = 50-300.

О ОН

Ligand



Demethylated products

 $C_9H_9NO_4$

[M+H]⁺: Calc: m/z = 210.0671 Found: m/z = 210.0760

C₁₀H₁₁NO₄

[M+H]⁺: Calc: m/z = 196.0604 Found: m/z = 196.0576 [M+Na]⁺: Calc: m/z = 218.0422 Found: m/z = 218.0422 Decarboxylated products



C₈H₇NO₃

[M+H]⁺: Calc: m/z = 166.0499 Found: m/z = 166.0474

Possible products after CPE at 1.4 V for 10 h based the results of Fig. S9.

6. Electrochemical experiments



Fig. S10 CVs of 1 in 0.2 M BBS at different pH values.



Fig. S11 DPVs using Ni-Schiff film as working electrode in BBS at different pH values.



Fig. S12 Multiple CVs using Ni-Schiff film as working electrode in a fresh BBS (pH = 9) without complex 1.



Fig. S13 CV using Ni-Schiff film as working electrode in a fresh BBS (pH = 9) without complex **1**.

The onset potential of water oxidation at different pH obeys the following equation:

$$E = 1.23 - 0.059 \times pH$$
 (V vs. NHE)

When pH at 9, the onset potential can be calculated as 0.699 V vs. NHE ($1.23 - 0.059 \times 9 = 0.699$). When the reference was changed to Ag/AgCl, the onset potential can be calculated as 0.502 V vs. Ag/AgCl (0.699 - 0.197 = 0.502). As shown in Figure S13, when the current density was 1 mA/cm², the potential was at 0.83 V vs. Ag/AgCl. The overpotential was the difference between the values of onset potential and the applying potential, which was calculated as ~330 mV (0.83 - 0.502 = 0.328).'



Fig. S14 XRD plot of complex 1.



Fig. S15 XRD plots of bare FTO electrode and Ni-Schiff electrode.

As shown in Fig. S15, Ni-Schiff electrode shows the same plot as the bare FTO electrode. First, the catalyst on the electrode is too thin to be detected by XRD, even GIXRD. Second, the catalyst is composed of polycrystalline and amorphous particles. Thus, the two electrodes exhibit the same plots.



Fig. S16 SEM spectra of a) bare FTO electrode, b) Ni-Schiff electrode and c) Ni-Aqua electrode.



Fig. S17 SEM spectra of Ni-Schiff electrode before (a) and after (b) 2 h CPE at 1.4 V.

After 2 h CPE at 1.4 V, SEM image of Ni-Schiff electrode shows particles similar to those before CPE experiments.



Fig. S18 XPS spectrum of Ni-Schiff Electrode.



Fig. S19 High-revolution XPS spectrum of Ni-Schiff electrode for Ni 2p.



Fig. S20 High-revolution XPS spectrum of Ni-Schiff electrode for O 1s.



Fig. S21 i-t spectrum. Condition: CPE at 1.4 V for 2 h using Ni-Schiff electrode as working electrode in 0.2 M BBS (pH = 9) with stirring.



Fig. S22 Oxygen monitored spectrum. Condition: CPE at 1.4 V for 2 h using Ni-Schiff electrode as working electrode in 0.2 M BBS (pH = 9) with stirring.

The formula to obtain FE were as follows.

$$FE(O_2) = \frac{Q_1}{Q} = \frac{4 \times 96485 \times n_1}{Q} \times 100\%$$
$$FE(H_2) = \frac{Q_2}{Q} = \frac{2 \times 96485 \times n_2}{Q} \times 100\%$$

where Q_1 and Q_2 are the amount of charge that actually consumed in oxygen and hydrogen evolution reactions, respectively; Q is the total amount of charge through external circuit; n_1 and n_2 are the mole number of produced oxygen and hydrogen, respectively.

When CPE was performed at 1.4 V for 2 h, 33.47 C electrons were transferred, 179.1 μ mol H₂ were detected by gas chromatography (GC). And FE was calculated as ~99 %.



Fig. S23 CVs with or without 1 mM 1 in BBS at pH = 7.4.



Fig. S24 Continuous CV scans spectrum of 1 mM 1 in BBS at pH = 7.4.



Fig. S25 Multiple CVs using Ni-Schiff film as working electrode in a fresh BBS (pH = 7.4) without complex 1.

Bare FTO	Ni-Schiff	Ni-Aqua	

Fig. S26 Image of bare FTO electrode, Ni-Schiff electrode and Ni-Aqua electrode.



Fig. S27 CPE at 1.4 V in BBS (pH = 7.4) using different anodic electrodes.

Reference

(1) Jiang, X.; Li, J.; Yang, B.; Wei, X. Z.; Dong, B. W.; Kao, Y.; Huang, M. Y.; Tung, C. H.; Wu, L. Z., A Bio-inspired Cu₄O₄ cubane: effective molecular catalysts for electrocatalytic water oxidation in aqueous solution. *Angew. Chem. Int. Ed.* **2018**, *57* (26), 7850-7854.