

Electronic Supporting Information for

Chemical etching of a cobalt-based metal-organic framework for enhancing the electrocatalytic oxygen evolution reaction

Ai-Xin Zhu, Ai-Na Dou, Xiao-Dan Fang, Li-Bo Yang and Quan-Qing Xu**

Faculty of Chemistry and Chemical Engineering, Yunnan Normal University, Kunming 650050, China.

E-mail: zax@ynnu.edu.cn (A.-X. Zhu); qqxu@ynnu.edu.cn

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Experimental details.

Materials and General Methods. Reagents and solvents were commercially available and were used without further purification. Elemental analyses (C, H, N) were performed with a Vario EL elemental analyzer. Thermogravimetric analyses were performed under N₂ with temperature increased with 10 °C min⁻¹ using a TA-Q500 system. N₂ sorption isotherms were measured at 77 K using an automatic volumetric sorption apparatus (BEL-MAX). The sample (weight of about 200 mg) was placed in the sample tube and dried for 12 h at 150 °C, to remove solvent molecules prior to measurements. Ultra-high-purity (99.999%) N₂ was used for all measurements. PXRD patterns for phase analysis were collected (0.02 °/step, 0.06 seconds/step) on a Bruker D8 Advance diffractometer (Cu K α) at room temperature.

Synthesis of 2,3-dioxido-1,4-benzenedicarboxylate (*o*-H₄dobdc). The compounds *o*-phenylenediamine (1.16 g, 6.24 mmol), KHCO₃ (2.00 g, 20.0 mmol), dry ice (4 g), and 1,2,4-trichlorobenzene (3 mL) were added to a PTFE insert within a steel acid digestion bomb (23 mL) and heated at 200 °C for 17 h. After cooling to room temperature, the mixture was collected via vacuum filtration and washed with diethyl ether. The solid was suspended in 300 mL of distilled water and filtered again. To the filtrate, neat HCl was slowly added until a pH between 1 and 2 was reached. The resulting crude product was collected via filtration. Recrystallization using 50 mL of acetone and 50 mL of water per gram of crude material afforded 0.68 g (40%) of pure product as a white powder.

Synthesis of (H₃O)₂[Co₆O(dobdc)₂(H₂dobdc)₂(EtOH)₄]. To a 2-mL Pyrex tube, *o*-H₄dobdc (0.015 mmol), CoCl₂·6H₂O (0.034 mmol), and 0.5 mL of mixed solvent (1:1 H₂O:EtOH; EtOH = Ethanol) were added. The tube was sealed and placed in a pre-heated oven at 100 °C. After 72 h, needle-shaped, colorless crystals had formed. The crystals were isolated by filtration and washed with hot EtOH to afford 3.7 mg (45%) of product. Anal. Calcd for (H₃O)₂[Co₆O(C₈O₆)₂(H₂C₈O₆)(C₂H₆O)] (C₃₄H₁₆Co₆O₂₈): C, 33.31; H, 1.32. Found: C, 33.52; H, 1.35.

Synthesis of [Co₆O(dobdc)₂(OH)₂(H₂O)₆]. After immersing the compound **1** in the solution of 1.0 M KOH for 24 h in presence of ultrasonic oscillation, the sheet sample were isolated by filtration and washed with EtOH. Anal. Calcd for [Co₆O(C₈O₆)₂(HO)₂(H₂O)₆] (C₁₆H₁₄Co₆O₂₁): C, 21.45; H, 1.58. Found: C, 21.36; H, 1.47.

Single-crystal X-ray diffraction studies. Diffraction intensities were collected on a Bruker Apex CCD diffractometer with graphite-monochromated Mo K α radiation. Absorption corrections were applied by using the multiscan program SADABS. The structures were solved with direct methods and refined with a full-matrix least-squares technique with the SHELXTL program package. Anisotropic thermal

parameters were applied to all non-hydrogen atoms of the host framework and, if possible, to some non-hydrogen atoms of the guest molecules. Hydrogen atoms on organic ligands were generated geometrically (C-H 0.95 Å). Hydrogen atoms on water molecules were located from difference maps. Crystal data for the complexes were summarized in Table S1. The X-ray crystallographic coordinates for structures reported in this Article have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number CCDC 1527297. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Because single-crystal specimen cannot be obtained for compound **2** so far, its crystal structure was solved by the Rietveld refinement of their powder X-ray diffraction data. The PXRD patterns were collected (0.02 °/step, 10 seconds/step) on a Bruker D8 Advance diffractometer (Cu K α) at room temperature. Pawley and Rietveld refinements were performed by the Reflex plus module of Material Studio 5.0. Pawley refinements were performed in the 2θ range of 5–70° on unit-cell parameters, zero point and background terms with the Pseudo-Voigt profile function and Berar-Baldinozzi asymmetry correction function under the $I-42m$ space group.

Preparation of working electrodes: The catalyst suspension was prepared by dispersing 20 mg of catalyst in 4 ml of solution containing 3.9 ml of ethanol and 10 μ l of 0.5 wt% Nafion solution followed by ultrasonication for 60 min. Then 8 μ L catalyst suspension was pipetted using a micropipettor on the glassy carbon electrode (GCE, 5 mm in diameter) surface (loading \sim 0.2 mg cm $^{-2}$). The working electrode was dried at ambient temperature before electrochemical measurements.

Electrochemical Measurements: To achieve fair comparison among all samples and well control the geometric area/impedance loss, all measurements were performed at room temperature. Electrochemical experiments were performed in a typical three-electrode system controlled using a CHI 760E. Linear sweep voltammetry was performed at a scan rate of 5 mV s $^{-1}$. All potentials were referenced to an SCE reference electrode, and carbon rod was used as the counter electrode in all measurements, in which the electrolyte was a 0.1 M KOH (pH=13) solution. All potentials were adjusted to compensate for the ohmic potential drop losses (R_u) that arose from the solution resistance and calibrated with respect to RHE. $E_{vs,RHE} = E_{vs,SCE} + 0.2412 + 0.05916\text{pH} - iR_u$.³⁵⁻³⁷ Tafel plots of the overpotential vs. log (current density) are recorded with the linear portions at low overpotential fitted to the Tafel equation ($\eta = a + b \log j$, where η is the overpotential, j is the cathodic current density, and b is the Tafel slope).

Measurement of the Faraday efficiency. A piece of GCE (surface area = 1.0 cm 2) attached with microcrystalline compound **2**, was used as the working electrode. Before measurement, the cell was

purged by He gas for about 60 min to reduce the O₂ background. The oxygen concentrations were measured using gas chromatography (Agilent 7920A) equipped with Molecular sieve 5 Å capillary column and thermal conductivity detector (**Figure S11**).

Table S1. Crystal Data and Structure Refinement results.

Compound	1
Formula	C ₃₄ H ₁₈ Co ₆ O ₂₇
Temperature (K)	150(2)
Crystal system	Tetragonal
Space group	<i>I</i> -42 <i>m</i>
<i>a</i> (Å)	15.79
<i>c</i> (Å)	22.81
<i>V</i> (Å ³)	5688
<i>Z</i>	4
reflns coll.	11485
unique reflns	3425
<i>D</i> _c (g cm ⁻³)	1.644
μ (mm ⁻¹)	2.188
GOF	1.085
<i>R</i> _{int}	0.035
<i>R</i> ₁	0.076
<i>wR</i> ₂	0.201

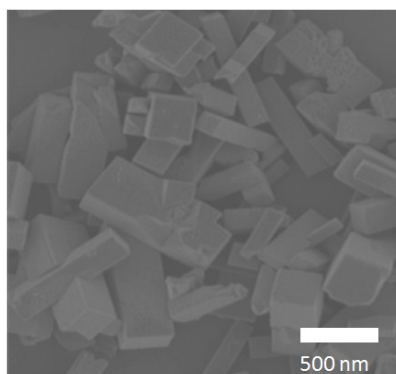


Fig. S1. SEM image of **1**.

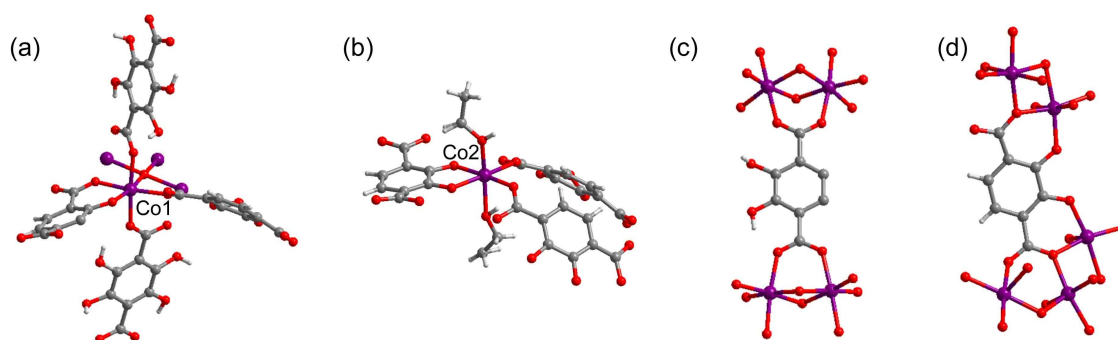


Fig. S2. The coordination environment of the Co(II) ions (a-b) and the organic ligand (c-d) in compound **1**.

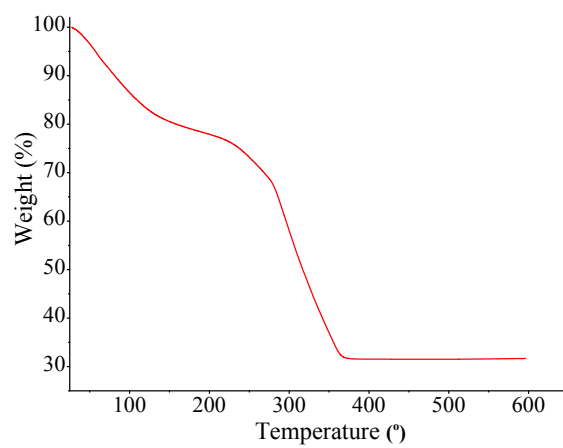


Fig. S3. Thermogravimetry curve of **1**.

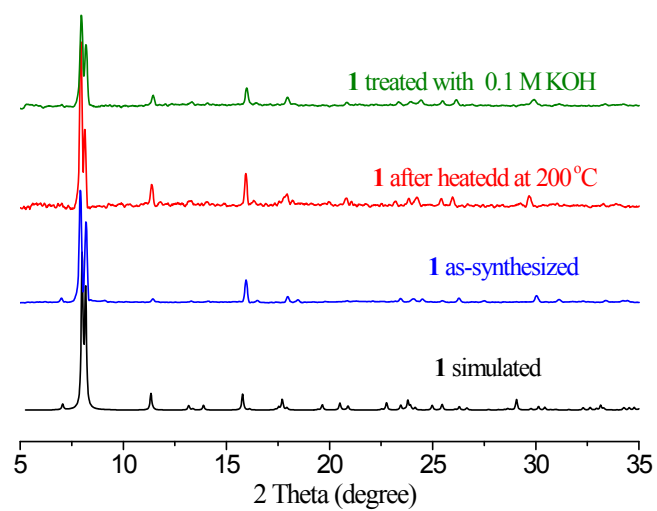


Fig. S4. PXRD patterns of compound 1.

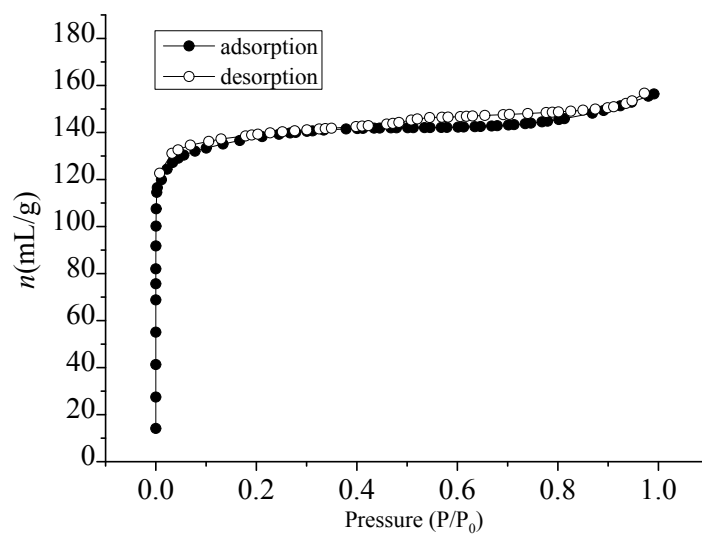


Fig. S5. N_2 sorption isotherms of compound 1 measured at 77 K.

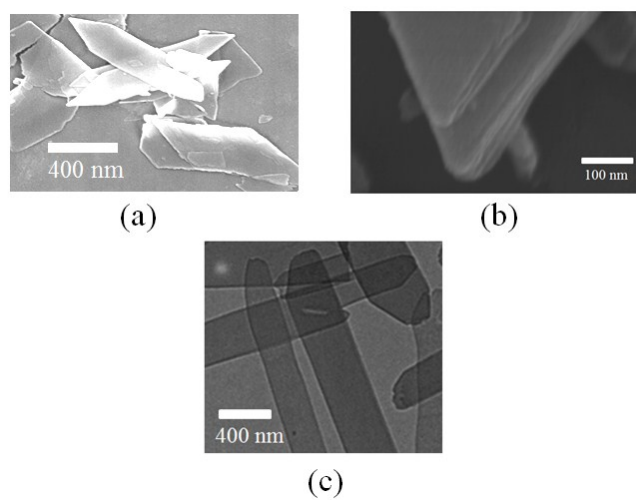


Fig. S6. (a-b) SEM and (c) TEM images of **2**.

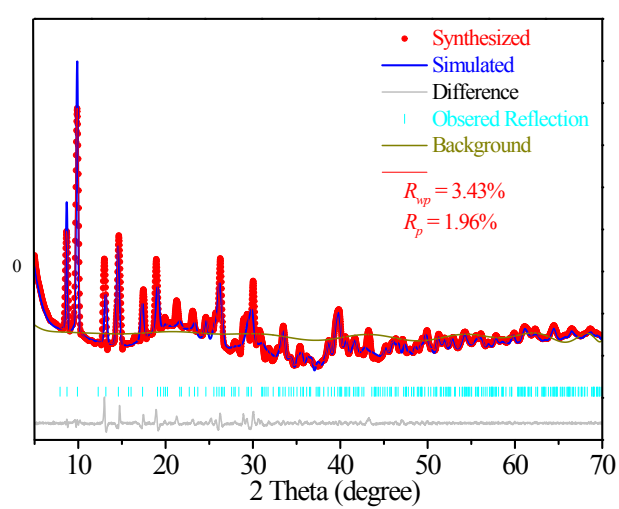


Fig. S7. Rietveld refinement plots of compound **2**.

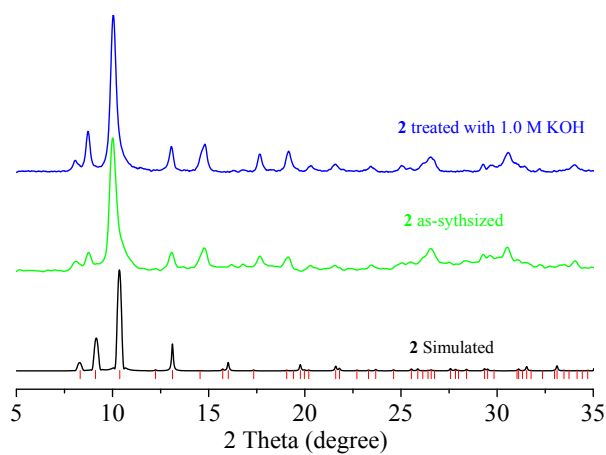


Fig. S8. PXRD patterns of compound 2.

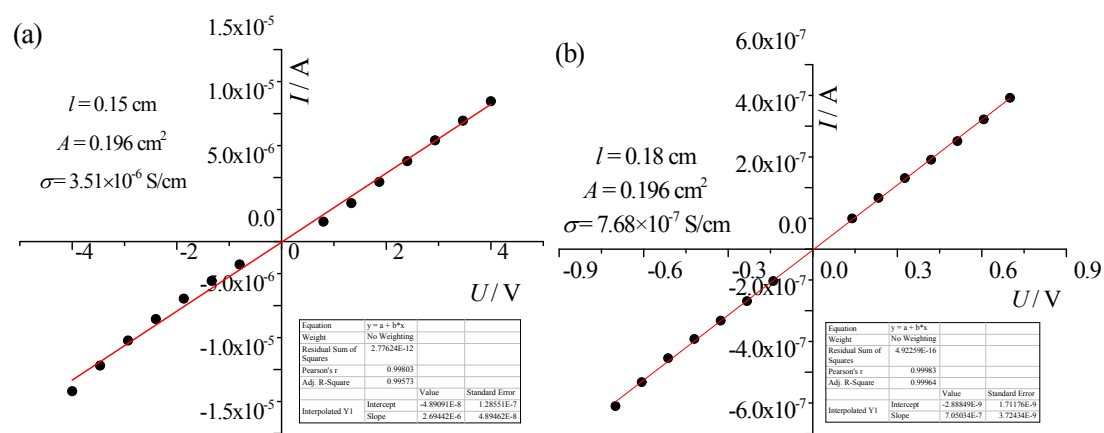


Fig. S9. Electrical conductivity measurements of (a) compound 2 and (b) compound 1.

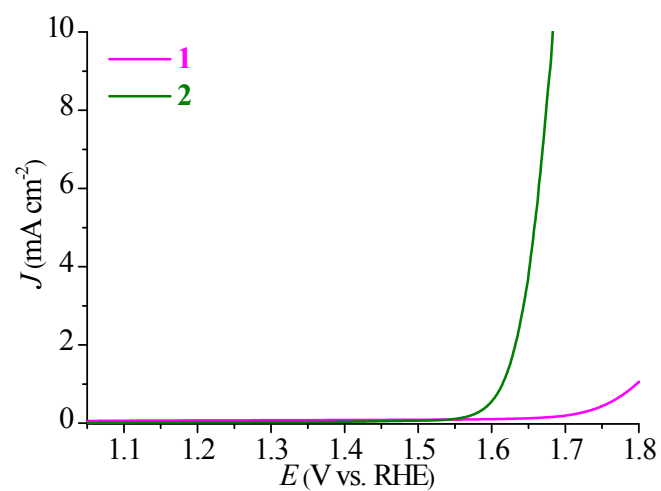


Fig. S10. LSV curves of compound 1 and 2 at pH = 7.

Table S2. Comparison of the OER activities of **2**, the relevant MOFs and recently reported highly active inorganic catalysts in 0.1 M KOH, The parameters better than that of **2** were highlighted in bold face. (Substrate is GCE Mass loading is mg cm⁻²)

Catalyst	Onset potential (V vs. RHE)	Overpotential at 10 mA cm ⁻² (mV vs. RHE)	Tafel slope (mV dec ⁻¹)	Molecular weight (g mol ⁻¹)	TOF (10 ⁻² s ⁻¹)	Ref
2	1.398	293	71	895.87 ^a 149.31 ^b	17.3^a 2.88 ^b	This work
1	1.503	441	82	1226.1 ^a 204.35 ^b	0.68 ^a 0.11 ^b	This work
IrO₂	1.508	377	61	224.2	0.25	This work
Fe₃-Co₂	1.463	283	43	295.4 ^b	27^a 9.0 ^b	<i>J. Am. Chem. Soc.</i> , 2017, 139 , 1778
Fe₂Co	1.515	453	63	873.9 ^a 303.0 ^b	0.088 ^a 0.031 ^b	<i>J. Am. Chem. Soc.</i> , 2017, 139 , 1778
Fe₃-Fe	1.633	460 at 1 mA cm ⁻²	137	292.2 ^a 1461.1 ^b	0.026 ^a 0.0052 ^b	<i>J. Am. Chem. Soc.</i> , 2017, 139 , 1778
Fe₃	1.593	482 at 1 mA cm ⁻²	112	301.9	0.035	<i>J. Am. Chem. Soc.</i> , 2017, 139 , 1778
MAF-X27-OH	1.55	461	66	173.0	0.00058	<i>J. Am. Chem. Soc.</i> , 2016 , <i>138</i> , 8336.
Co-WOC-1	1.62	390 at 1 mA cm ⁻²	128	2807 ^a 401.0 ^b	0.99 ^a 0.14 ^b	<i>Angew. Chem. Int. Ed.</i> 2016 , <i>55</i> , 2425.
IrO ₂ /C (20 wt%)	1.52	370	NA	224.2	4.4	<i>Nat. Commun.</i> 2013 , <i>4</i> , 2390
Co ₃ O ₄ /C nanowires array	NA	395	NA	82.27	NA	<i>J. Am. Chem. Soc.</i> 2014 , <i>136</i> , 13925.
NiFeLDH/CNT	NA	308	35	NA	NA	<i>J. Am. Chem. Soc.</i> , 2013 , <i>135</i> , 8452.

TOF (10⁻² s⁻¹) is calculated by the current density when the overpotential of 300 mV. Based on the LSV, TOF = $j/(4 \times F \times m/M)$, where j is the current density (mA cm⁻²) at a given overpotential, F is the faraday constant (96485 C mol⁻¹), m are the mass loading of the catalyst (mg cm⁻²), and M is the molecular weight of the catalyst unified with one active center per formula unit, respectively. All the catalytically related metal atoms were assumed to be accessible for catalysis the OER. ^a based on active metal; ^b based on all metal;

Table S3. The obtained GC peak areas of O₂/N₂ in the electrolytic cell before and after electrolysis.

	O ₂	N ₂	O ₂ /N ₂ Ratio
Air	1038.6	3185.6	0.326
After 0 s	13.22	41.32	0.320
After 1200 s	122.20	43.92	5.44

The GC peak area (denoted as A), A (oxygen produced) = A (oxygen 1200 s) – A (oxygen 0 s) – A (oxygen leak from air) = 122.20 – 13.22 – 0.848 = 108.13. Giving n_{O_2} (experimental) = O₂ concentration (%) × head space volume / (22.4 × 298/273) = (108.13+1.322)/6815.9 × 47.0 / 1000 / 24.45 = 30.87 μmol. The ideal product amount is n_{O_2} (theoretical) = $It/4F$ = 0.010 × 1 × 1200/96485/4 = 31.09 μmol, where t is the reaction time (s) under constant oxidation current I (A), F is the faraday constant (96485 C mol⁻¹). The Faraday efficiency is n_{O_2} (experimental)/ n_{O_2} (theoretical) × 100% = 30.87/31.09 × 100% = 99.3%.

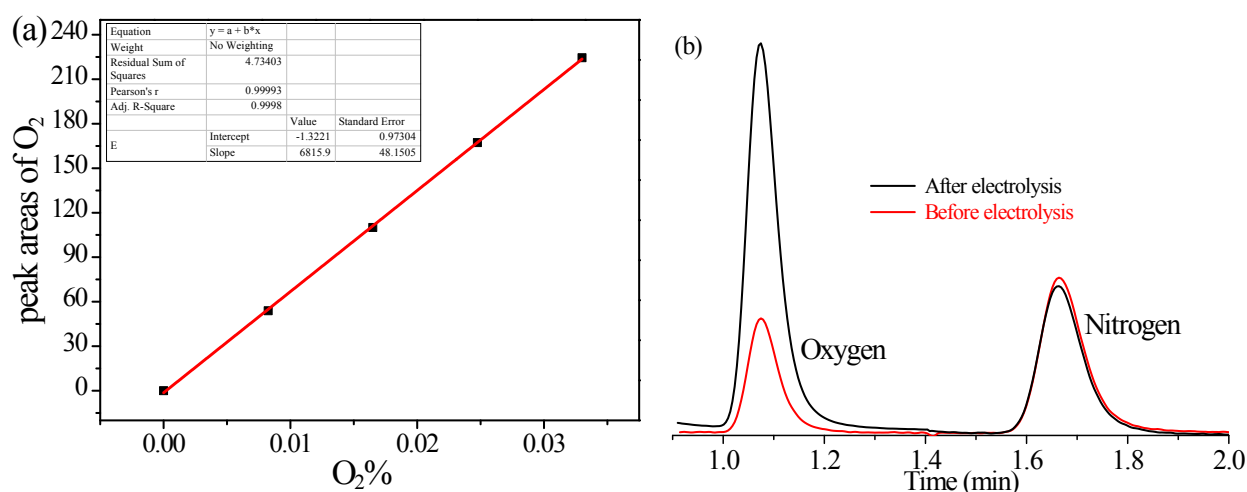


Fig. S11. (a) The linear relationship between O₂ concentration and its GC peak area. (b) The GC profiles of nitrogen and oxygen for **2** before and after electrolysis at the current density of 10 mA cm⁻² at pH = 13.

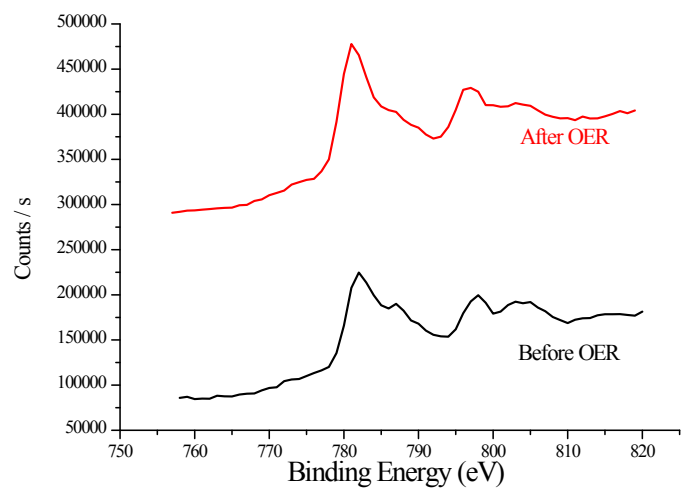


Fig. S12. The XPS spectra of 2 before and after OER.