

Supporting information

Rational Design of Heterostructural Heterometallic Phosphonates as Highly Efficient Electrocatalysts for Overall Water Splitting Under Alkaline Condition

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Instruments and Methods

Powder X-ray diffraction measurements were performed on a Tongda TD-3700 using CuK α radiation. IR spectra were recorded in the range of 4000-500 cm⁻¹ on a Thermo Fisher Nicolet iS-10 FTIR Spectrometer with KBr pellets. Thermogravimetric analyses (TGA) of QAU-1-Ni-C and QAU-1-Co-C were performed using a TA SDT 650 unit at a heating rate of 10 °C/min in the range of 50-1100 °C under nitrogen atmosphere. The solid-state UV-Vis spectra of the metal phosphonates were recorded on HITACHI U-3900 spectrophotometer. Nitrogen adsorption desorption isotherms were analyzed using a Micromeritics ASAP 2020 PLUS HD88 at 77 K after degassing the samples at 80 °C for 8 h. Inductively coupled plasma-Optical emission spectrometer (ICP-OES) measurements were carried out on PE OPTMA8000DV. X-ray photoelectron spectroscopy (XPS) was recorded on a VG ESCALABMK II spectrometer using an Al K α (1486.6 eV) photon source. Scanning electron microscopy images were taken on a JEOL JSM-IT500. Transmission electron microscopy images were obtained on a FEI Tecnai G2 F20 at a voltage of 220 kV. Elemental mapping images were obtained on EDAX GENESIS.

Single-Crystal Structure Determination.

The diffraction intensity data were collected on a Bruker SMART APEX II CCD diffractometer (Mo K α radiation, λ = 0.71073 Å) at room temperature. SAINT was

used for integration of intensity of reflections and scaling^{S1}. Absorption corrections were carried out with the program SADABS^{S2}. Crystal structures were solved by direct methods using SHELXS^{S3}. Subsequent difference Fourier analyses and least squares refinement with SHELXL-2013^{S4} allowed for the location of the atom positions. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms on the water molecules were located from the difference Fourier map. All hydrogen atoms were refined using a riding model. The crystallographic details are summarized in Table S2. The data have been deposited in the Cambridge Crystallographic Data Centre (CCDC), deposition numbers CCDC 2166568-2166569 for compounds QAU-2 and QAU-3, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223336033.

Electrochemical measurements

Preparation of the working electrode. The catalyst ink was first prepared by dispersing 10 mg of the as prepared catalysts and 2 mg of acetylene black (AB) in a mixed solvent of isopropanol (900 μL), DI water (90 μL) and Nafion solution (10 μL , 5 wt%), and ultrasonication for 30 min. The working electrode was then prepared by drop coating of the catalyst ink (200 μL) on Ni foam (NF) (1 cm $\times$ 1 cm) and drying at 60 $^{\circ}\text{C}$ in a vacuum oven for 12 hours.

The electrochemical experiments were carried out on a CHI760E electrochemical workstation with the catalyst loaded on NF, Hg/HgO and a graphite rod as the working, reference and counter electrodes, respectively. Linear sweep voltammetry (LSV) polarization curves were recorded at a scan rate of 5 mV s^{-1} with 75% iR-compensation. Electrochemical impedance spectroscopy (EIS) was measured in the frequency range of 100000 Hz - 0.01 Hz with an amplitude of 5 mV (OER: 0.6 V vs Hg/HgO, HER: -1.2 V vs Hg/HgO). The long-term stability was evaluated by 2000 cycles of CV scanning at 100 mV s^{-1} and chronoamperometry measurements for 20 h. All the potentials were referenced to a reversible hydrogen electrode (RHE):

$$E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.059 \times \text{pH} + 0.098 \text{ V}$$

The turnover frequency (TOF) value was calculated based on the experimental metal contents from ICP-OES test (Table S1) using the equation below:

$$TOF = \frac{J \times A}{a \times F \times n}$$

where J is the current density at an overpotential of 300 mV, A is the area of the working electrode ($1 \times 1 \text{ cm}^2$), a is the number of transferred electrons. In the process of generating a molecule of products ($a = 4$ for OER, $a = 2$ for HER), F is the Faraday constant (96485 C mol^{-1}), and n is the total mole number of the exposed active sites.

$$n = \frac{m \times A \times \omega}{M}$$

where m is the loading weight of the catalyst, A is the area of the working electrode, ω is the theoretical weight ratio of metal elements of the catalyst from ICP-OES, and M is the atomic weight of metal elements.

Mass activity equals that the measured current density J at $\eta = 300 \text{ mV}$ divided by the catalyst loading amount m .

$$\text{Mass activity} = \frac{J}{m}$$

The efficient electrochemical surface area (ECSA) was determined from the double layer capacitance (C_{dl}). The C_{dl} was evaluated by CV measurements with scan rates varying from 60 to 100 mV s^{-1} in the non-faradaic potential region. By plotting the capacitive currents against the scan rates, the C_{dl} of the electrocatalysts could be obtained from the slopes.

Overall water splitting was conducted in a two-electrode system with QAU-4/QAU-2 as anode and QAU-3/QAU-2 as cathode (QAU-3/QAU-2||QAU-4/QAU-2). Linear sweep voltammetry (LSV) polarization curves were acquired from 1 to 2 V at a scan rate of 5 mV s^{-1} . Chronoamperometry measurements were used to test the long-term stability.

Table S1. Elemental analysis results of the phosphonates by ICP-OES.

Samples	P (wt%)	Ni (wt%)	Co (wt%)	Fe (wt%)
QAU-2-C	12.88	21.44	--	--
QAU-3-C	16.43	--	23.20	--
QAU-2	14.70	21.51	--	--
QAU-3	16.06	--	24.35	--
QAU-4	12.64	--	--	15.68
QAU-3/QAU-2	14.36	8.75	11.11	--
QAU-4/QAU-2	13.25	7.86	--	11.45

Table S2. Crystal parameters of compounds QAU-2 and QAU-3.^{a,b}

compound	QAU-2	QAU-3
CCDC Nr.	2166568	2166569
formula	C ₈ H ₄₀ Ni ₃ O ₃₀ P ₄	C ₈ H ₂₂ Co ₂ O ₂₀ P ₄
fw	916.41	679.99
space group	<i>P2₁/c</i>	<i>P2₁/n</i>
<i>a</i> (Å)	10.6044(4)	6.8699(3)
<i>b</i> (Å)	10.3561(4)	19.1850(9)
<i>c</i> (Å)	13.9206(6)	8.3920(4)
<i>α</i> (deg)	90	90
<i>β</i> (deg)	97.3230(10)	105.318(2)

γ (deg)	90	90
V (Å ³)	1516.29(10)	1066.76(9)
Z	2	2
$D_{\text{calcd}}/\text{g cm}^{-3}$	2.007	2.117
abs coeff /mm ⁻¹	2.169	1.953
F(000)	944	688
theta range	3.244-25.000	3.293-24.990
completeness /%	96.8	96.7
reflns collected	20068	14276
independent reflns/ R_{int}	2664/0.0460	1863/0.0644
GOF on F^2	1.069	1.050
final R indices [$I > 2\sigma(I)$]: R_1 , wR_2	0.0399, 0.0946	0.0358, 0.0792
R indices (all data): R_1 , wR_2	0.0528, 0.1015	0.0527, 0.0854

$$^a R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|. \quad ^b wR_2 = \{\Sigma[\omega(F_o^2 - F_c^2)^2] / \Sigma\omega(F_o^2)\}^{1/2}$$

Table S3. Selected bonds (Å) in compounds QAU-2 and QAU-3.

QAU-2			
Ni(1)-O(2W)	2.022(3)	Ni(2)-O(4)	2.048(3)
Ni(1)-O(3W)	2.047(3)	Ni(2)-O(4)#1	2.048(3)
Ni(1)-O(2)	2.048(3)	Ni(2)-O(1)	2.072(3)
Ni(1)-O(1W)	2.051(3)	Ni(2)-O(1)#1	2.072(3)
Ni(1)-O(5)	2.056(3)	Ni(2)-O(4W)	2.088(3)
Ni(1)-O(7)	2.163(3)	Ni(2)-O(4W)#1	2.088(3)
QAU-3			
Co(1)-O(2)#1	2.046(3)	Co(1)-O(1W)	2.104(3)
Co(1)-O(7)	2.077(3)	Co(1)-O(4)	2.114(3)
Co(1)-O(5)#1	2.080(3)	Co(1)-O(1)	2.240(3)

Symmetry transformations used to generate equivalent atoms: QAU-2: #1 -x, -y+1, -

z+1; QAU-3: #1 x-1/2, -y+1/2, z-1/2.

Table S4. Selected angles (°) in compounds QAU-2 and QAU-3.

QAU-2			
O(2W)-Ni(1)-O(3W)	96.94(16)	O(4)-Ni(2)-O(4)#1	180.0
O(2W)-Ni(1)-O(2)	88.99(13)	O(4)-Ni(2)-O(1)	91.06(11)
O(3W)-Ni(1)-O(2)	91.78(13)	O(4)#1-Ni(2)-O(1)	88.94(11)
O(2W)-Ni(1)-O(1W)	86.52(15)	O(4)-Ni(2)-O(1)#1	88.94(11)
O(3W)-Ni(1)-O(1W)	92.25(15)	O(4)#1-Ni(2)-O(1)#1	91.06(11)
O(2)-Ni(1)-O(1W)	174.29(14)	O(1)-Ni(2)-O(1)#1	180.0
O(2W)-Ni(1)-O(5)	175.24(14)	O(4)-Ni(2)-O(4W)	88.73(12)
O(3W)-Ni(1)-O(5)	87.76(13)	O(4)#1-Ni(2)-O(4W)	91.27(12)
O(2)-Ni(1)-O(5)	90.15(12)	O(1)-Ni(2)-O(4W)	91.29(12)
O(1W)-Ni(1)-O(5)	94.05(13)	O(1)#1-Ni(2)-O(4W)	88.71(12)
O(2W)-Ni(1)-O(7)	93.15(13)	O(4)-Ni(2)-O(4W)#1	91.27(12)
O(3W)-Ni(1)-O(7)	168.55(14)	O(4)#1-Ni(2)-O(4W)#1	88.73(12)
O(2)-Ni(1)-O(7)	82.99(11)	O(1)-Ni(2)-O(4W)#1	88.71(12)
O(1W)-Ni(1)-O(7)	93.75(13)	O(1)#1-Ni(2)-O(4W)#1	91.29(12)
O(5)-Ni(1)-O(7)	82.10(11)	O(4W)-Ni(2)-O(4W)#1	180.0
QAU-3			
O(2)#1-Co(1)-O(7)	176.11(11)	O(5)#1-Co(1)-O(4)	169.86(10)
O(2)#1-Co(1)-O(5)#1	88.64(10)	O(1W)-Co(1)-O(4)	97.94(11)
O(7)-Co(1)-O(5)#1	88.14(10)	O(2)#1-Co(1)-O(1)	102.07(10)
O(2)#1-Co(1)-O(1W)	91.22(11)	O(7)-Co(1)-O(1)	80.26(10)
O(7)-Co(1)-O(1W)	86.71(11)	O(5)#1-Co(1)-O(1)	92.32(10)
O(5)#1-Co(1)-O(1W)	92.19(11)	O(1W)-Co(1)-O(1)	166.06(11)
O(2)#1-Co(1)-O(4)	91.62(11)	O(4)-Co(1)-O(1)	77.71(9)
O(7)-Co(1)-O(4)	91.93(11)		

Symmetry transformations used to generate equivalent atoms: QAU-2: #1 -x, -y+1, -

z+1; QAU-3: #1 x-1/2, -y+1/2, z-1/2.

Table S5. Hydrogen bonds in compounds QAU-2 and QAU-3.

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
QAU-2				
O(1W)-H(1W)···O(6W)#1	0.85	2.10	2.8157	142
O(1W)-H(1W)···O(4W)#2	0.85	2.56	3.1902	132
O(1W)-H(2W)···O(8W)#3	0.85	2.19	2.9688	152
O(2W)-H(3W)···O(6W)#1	0.85	2.47	3.2132	146
O(2W)-H(3W)···O(7W)#3	0.85	2.35	2.8238	116
O(2W)-H(4W)···O(2)	0.85	2.50	2.8520	106
O(2W)-H(4W)···O(4)#4	0.85	1.96	2.6751	141
O(3W)-H(5W)···O(5)#2	0.85	1.88	2.7194	171
O(6)-H(6A)···O(3)#5	0.82	1.78	2.5848	165
O(3W)-H(6W)···O(3)#6	0.85	2.26	3.0028	145
O(4W) --H(7W)···O(5)	0.85	2.05	2.8447	155
O(4W)-H(8W)···O(7W)#7	0.85	2.38	2.7859	110
O(5W)-H(10W)···O(8W)#3	0.85	2.19	2.8549	135
O(6W)-H(11W)···O(7W)#8	0.85	2.01	2.6467	131
O(7W)-H(14W)···O(2W)#8	0.85	2.53	2.8238	101
C(2)-H(2A)···O(7)	0.93	2.48	2.8354	103
C(4)-H(4A)···O(1)	0.93	2.56	3.2192	128
C(4)-H(4A)···O(4W)#9	0.93	2.50	3.3827	160
QAU-3				
O1-H1A···O2W#1	0.90	2.25	2.7985(1)	119
O1W-H1W···O3W#2	0.85	2.05	2.8887(1)	168
O1W-H2W···O2W#2	0.85	2.12	2.8773(1)	148
O3-H3B···O5#1	0.82	1.73	2.5278(1)	165
O2W-H3W···O1W#3	0.85	2.57	2.8773(1)	103

O2W-H4W···O6#4	0.85	2.55	3.3503(2)	157
O6-H6A···O4#5	0.82	1.74	2.5585(1)	174
C3-H3A···O5	0.93	2.48	3.1952(2)	133
C4-H4A···O1	0.93	2.46	2.8052(1)	102

Translation of ARU-Code to CIF and Equivalent Position Code:

QAU-2: #1: x, -1+y, z; #2: -x, -y, 1-z; #3: 1-x, -1/2+y, 1/2-z; #4: x, 1/2-y, -1/2+z; #5: x, 1/2-y, 1/2+z; #6: -x, -1/2+y, 1/2-z; #7: -1+x, y, z; #8: 1-x, 1/2+y, 1/2-z; #9: -x, 1-y, 1-z.

QAU-3: #1: #1: -1+x, y, z; #2: x, y, 1+z; #3: x, y, -1+z; #4: 1+x, y, z; #5: 1/2+x, 1/2-y, -1/2+z.

Table S6. Summary of the electrocatalytic performances of various as-prepared phosphonates catalysts for OER.

Catalyst	η_{10} (mV)	Tafel slope (mV dec ⁻¹)	R_2 (Ω)	C_{dl} (mF cm ⁻²)	TOF (s ⁻¹)	Mass activity (A g ⁻¹)
QAU-2	280	178	35.44	5.35	0.0424	6.0
QAU-3	329	84	51.71	3.63	0.0177	2.8
QAU-4	278	52	2.84	6.73	0.1310	14.2
QAU-3/QAU-2	303	408	22.56	5.02	0.0367	4.8
QAU-4/QAU-2	228	41	1.58	7.84	0.3461	40.3
IrO ₂	292	75	4.58	--	--	--
NF	367	--	--	--	--	--

Table S7. Summary of the electrocatalytic performances of various as-prepared phosphonates catalysts for HER.

Catalyst	η_{10} (mV)	Tafel slope (mV dec ⁻¹)	R_2 (Ω)
QAU-2	169	89	2.00
QAU-3	169	83	1.86
QAU-4	185	111	2.95
QAU-3/QAU-2	123	81	1.45
QAU-4/QAU-2	186	118	3.12
NF	284	--	--

Table S8. Comparison of the OER activity of recently reported phosphonate materials.

Catalysts	Electrolyte	Overpotential (mV)	Tafel slope (mA dec ⁻¹)	Ref.
[H ₂ TETA][Co(H ₂ hedp) ₂].2H ₂ O	1.0 M KOH	341	71	S5
QAU-1-FeNi(1:2)	1.0 M KOH	230	47	S6
FeCoNTMP	1.0 M KOH	289	59.3	S7
CoNTO-1-3	1.0 M KOH	312	61.1	S8
NiFe16-phenylphosphonate	1.0 M KOH	240	40	S9
CoPIM	1.0 M KOH	334	58.6	S10
NiPPA	1.0 M KOH	434	116.7	S11
CoPi-1	1.0 M KOH	380	58.7	S12
CoNiPP-600	1.0 M KOH	264	60	S13
H ₃ LCoCN800	1.0 M KOH	260	64	S14
Co ₃ (O ₃ PCH ₂ -NC ₄ H ₇ -CO ₂) ₂ .4H ₂ O	0.1 PBS	484	83	S15

		(1 mA cm ⁻²)		
CoPn	1.0 M KOH	240	--	S16
QAU-4/QAU-2	1.0 M KOH	228	41	This work

Table S9. Comparison of the HER activity of recently reported phosphonates materials.

Catalysts	Electrolyte	Overpotential (mV)	Tafel slope (mA dec ⁻¹)	Ref.
[H ₂ TETA][Co(H ₂ hedp) ₂].2H ₂ O	0.5 M H ₂ SO ₄	276	111	S5
NiCoDPA	1.0 M KOH	112	78	S17
H ₈ L-Co-crystal	0.5 M H ₂ SO ₄	243	102	S18
CoPn	1.0 M KOH	144	--	S16
1Co-ns	Tris-HNO ₃ (pH=7.4)	84	48	S19
QAU-3/QAU-2	1.0 M KOH	123	81	This work

Table S10. Comparison the voltages of overall water splitting at current density of 10 mA cm⁻² of some newly reported electrolyzers.

Water electrolysis system	Voltage (V)	Ref.
Ni _{0.5} Fe _{0.5} -HP Ni-HP	1.57	S20
CoFe/NF	1.64	S21
NiFeP/NF ₃₀	1.63	S22
Fe7.4%-NiSe/NF ₃₀	1.585	S23
Co _{1-x} Fe _x -LDH Ni _{1-x} Fe _x -LDH	1.59	S24
Ni ₃ S ₂ /NF	1.61	S25
Ni ₁₁ (HPO ₃) ₈ (OH) ₆ Ni ₁₁ (HPO ₃) ₈ (OH) ₆	1.6	S26
Al, Fe-codoped CoP/RGO	1.66	S27

BrHT@CoNC BrHT@CoNC	1.55	S28
Co-NCNTFs//NF Co-NCNTFs//NF	1.62	S29
FeCoMnNi-MOF-74/NF	1.62	S30
NiFe-MOF-5	1.57	S31
CoP/GO-400	1.7	S32
QAU-4/QAU-2 QAU-3/QAU-2	1.59	This work

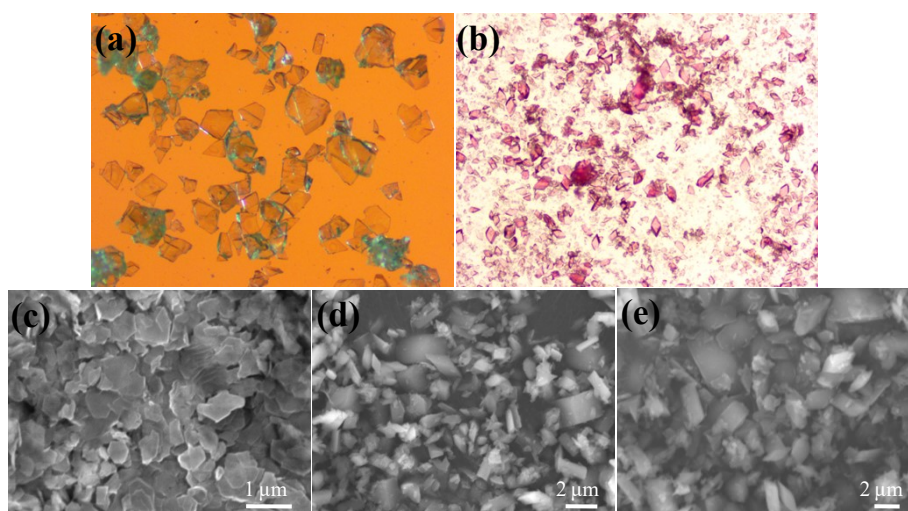


Fig. S1 The optical microscope photographs of QAU-2 (a) and QAU-3 (b);
The SEM pictures of QAU-2 (c), QAU-3 (d) and QAU-4 (e).

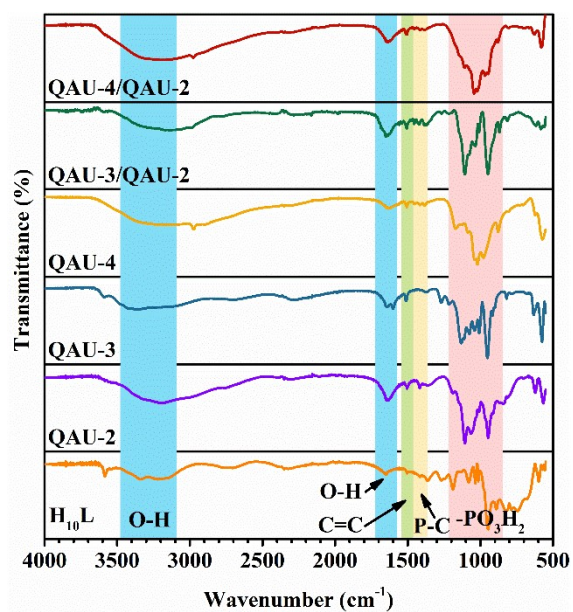


Fig. S2 FT-IR spectra of ligand $H_{10}L$, QAU-2, QAU-3, QAU-4, QAU-3/QAU-2 and QAU-4/QAU-2.

Fourier transform infrared spectroscopy (FTIR) and UV-visible absorption spectra

Fourier transform infrared (FT-IR) spectra of the tetraphosphonic acid ligand and as-prepared phosphonate materials were recorded and presented in Fig. S2. In the FT-IR spectrum of QAU-2, the broad peak at approximately 3193 cm^{-1} and the sharp peak at 1634 cm^{-1} are related to the O-H stretching vibration of lattice water and organic ligand. The peak at 1505 cm^{-1} can be assigned to the vibration of the C=C in the benzene skeleton. The weak peaks centered at 1417 cm^{-1} are attributed to the P-C stretching vibration. The intense peaks at 1198 , 1106 and 946 cm^{-1} are characteristic absorption peaks of P=O and P-OH bonds, and there are red shifts relative to the free ligand H_{10}L (1188 , 1080 , 946 cm^{-1}), indicating the existence of phosphonate groups and the coordination of the phosphonate groups with the metal ions. In addition, the peak at 1065 cm^{-1} is ascribed to the P-O-Ni vibrations, clearly demonstrating the coordination of inorganic and organic species in the phosphonate hybrid again. For QAU-4 and QAU-4/QAU-2, the peak at 1036 cm^{-1} attributed to P-O-Fe is even stronger, suggesting the strong interaction between Fe^{3+} and phosphonate oxygen atoms^{S20,S34}.

Thermal stability

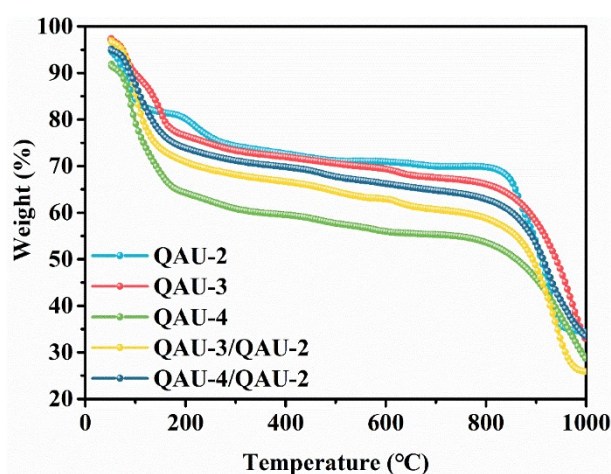


Fig. S3 TGA curves of as-prepared metal phosphonate samples.

The thermal stability of the materials was analyzed by the thermogravimetric

analysis (TGA) experiments in the temperature range of 50 to 1000 °C under N₂ atmosphere. As shown in Fig. S3, these samples experienced analogously two main weight loss steps before 1000 °C. On the TGA curve of QAU-2, a weight loss of 14.5% can be observed before 160 °C and can be attributed to the loss of lattice water molecules (theoretical weight loss: 15%). When the temperature is risen to 790 °C, the sample start to lose weight dramatically, suggesting the decompose of the sample. For QAU-3, the removal of the lattice water molecules (17%) occurs in the temperature range of 25-165 °C and matches well with the theoretical value (15.9%). Upon the temperature is risen to 670 °C, the sample starts to decompose. Similarly, QAU-4 loses its aqua ligands and lattice water molecules (29%) in the range of 50-179 °C and decomposes above 700 °C.

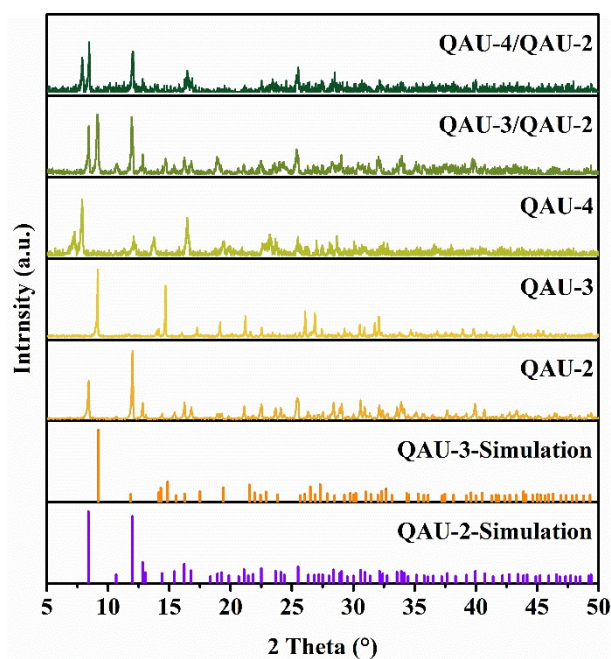


Fig. S4 Powder XRD patterns of as-prepared samples.

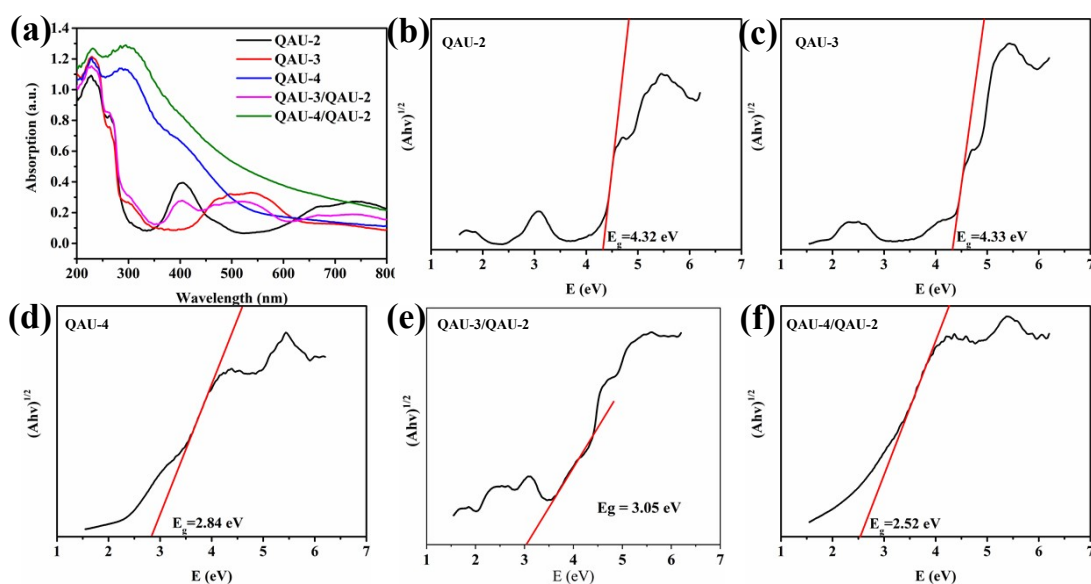


Fig. S5 (a) UV-vis absorption spectra and the corresponding E_g values of (b) QAU-2, (c) QAU-3, (d) QAU-4, (e) QAU-3/QAU-2 and (f) QAU-4/QAU-2.

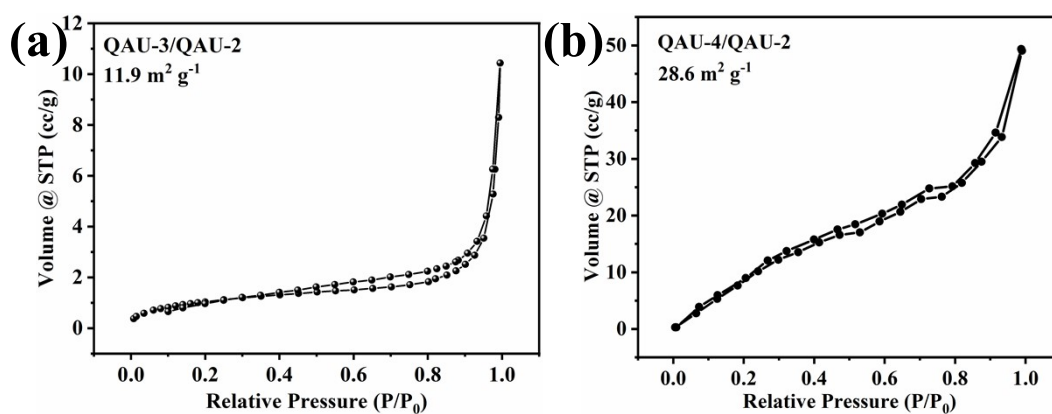


Fig. S6 N_2 adsorption-desorption isotherms of (a) QAU-3/QAU-2 and (b) QAU-4/QAU-2.

As shown in the Fig. S6, the N_2 adsorption-desorption isotherms show that the Brunauer-Emment-Teller (BET) specific surface areas of QAU-3/QAU-2 and QAU-4/QAU-2 are about $11.9 \text{ m}^2 \text{ g}^{-1}$ and $28.6 \text{ m}^2 \text{ g}^{-1}$ respectively, suggesting porous structural characters of these composite MOF materials which are conducive to promote the charge transfer efficiency and kinetics during the electrocatalytic energy conversion process^{S33}.

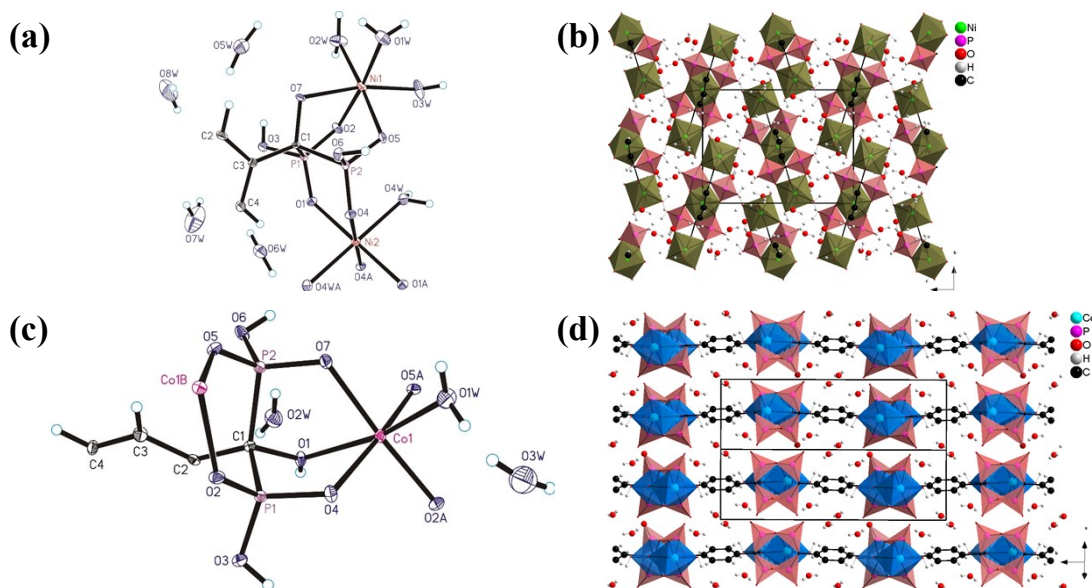


Fig. S7 (a) Coordination environment of the phosphonate ligand and the nickel ion, (b) three-dimensional packing diagram view along a -direction of QAU-2; (c) (a) Coordination environment of the phosphonate ligand and the cobalt ion, (d) three-dimensional packing diagram viewing along 101-direction of QAU-3.

Structural analyses of QAU-2 and QAU-3. QAU-2 displays a one-dimensional chain crystal structure. It crystallizes in monoclinic $P2_1/n$ space group (Table S2). In the asymmetric unit, there are half phosphonate ligand (H_4L^{6-}), two crystallographic independent Ni ions (Ni1 and Ni2), four aqua ligands and four lattice water molecules (see Fig. S7(a)), indicating a formula of $[Ni_{1.5}(H_4L)_{0.5}(H_2O)_4] \cdot 4H_2O$. Ni1 is octahedrally coordinated by three phosphonate oxygen atoms and three water molecules. Ni2 lies at a special position (0, 0.5, 0.5), it is octahedrally coordinated by four symmetry-related phosphonate oxygen atoms and two water molecules. The Ni-O bond lengths of Ni1 and Ni2 are observed in the ranges of 2.022(3)-2.163(3) Å and 2.048(3)-2.088(3) Å, respectively. The nearest Ni $\cdots$ Ni distance between neighboring nickel ions is about 4.912 Å. The O-Ni-O bond angles around Ni1 and Ni2 are in the ranges of 82.10(11)-96.94(16)° and 88.71(12)-91.29(12)° (Table S3 and S4), respectively, indicating higher symmetry of Ni2 octahedron. The phosphonate ligand is six-deprotonated and bind with four nickel ions using its five oxygen atoms in chelate-bridging coordination mode. These nickel ions are chelated and bridged into a zigzag chain along a -direction (Fig. 2(a)) and are further assembled into three-

dimensional supramolecular structure (Fig. 2(b) and Fig. S7(b)) via plenty of hydrogen bonds between water molecules and phosphonate oxygen atoms (Table S5).

Different from QAU-2, QAU-3 crystallizes in $P2_1/c$ and shows a two-dimensional layer crystal structure. In the asymmetric unit, there are half phosphonate ligand, one crystallographic independent cobalt ion, one aqua ligand and two lattice water molecules (Fig. S7(c)), indicating a formula of $[\text{Co}(\text{H}_4\text{L})_{0.5}(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$. The Co-O bond lengths and nearest $\text{Co} \cdots \text{Co}$ distances are observed in the range of 2.046(3)-2.240(3) Å and about 4.991 Å, respectively. The cobalt ion is octahedrally coordinated by five phosphonate oxygen atoms from two neighboring tetrakisphosphonate ligands and one aqua ligand. The tetrakisphosphonate ligand is double deprotonated and bind four cobalt ions with its ten oxygen atoms (Fig. S7(c)). Neighboring cobalt ions are interconnected by these tetrakisphosphonate ligands into a two-dimensional layer in bc -plane (Fig. 2(c)) which are further assembled into a three-dimensional supramolecular structure (Fig. 2(d) and Fig. S7(d)) via $\text{O}-\text{H} \cdots \text{O}$ and $\text{C}-\text{H} \cdots \text{O}$ interactions (Table S5).

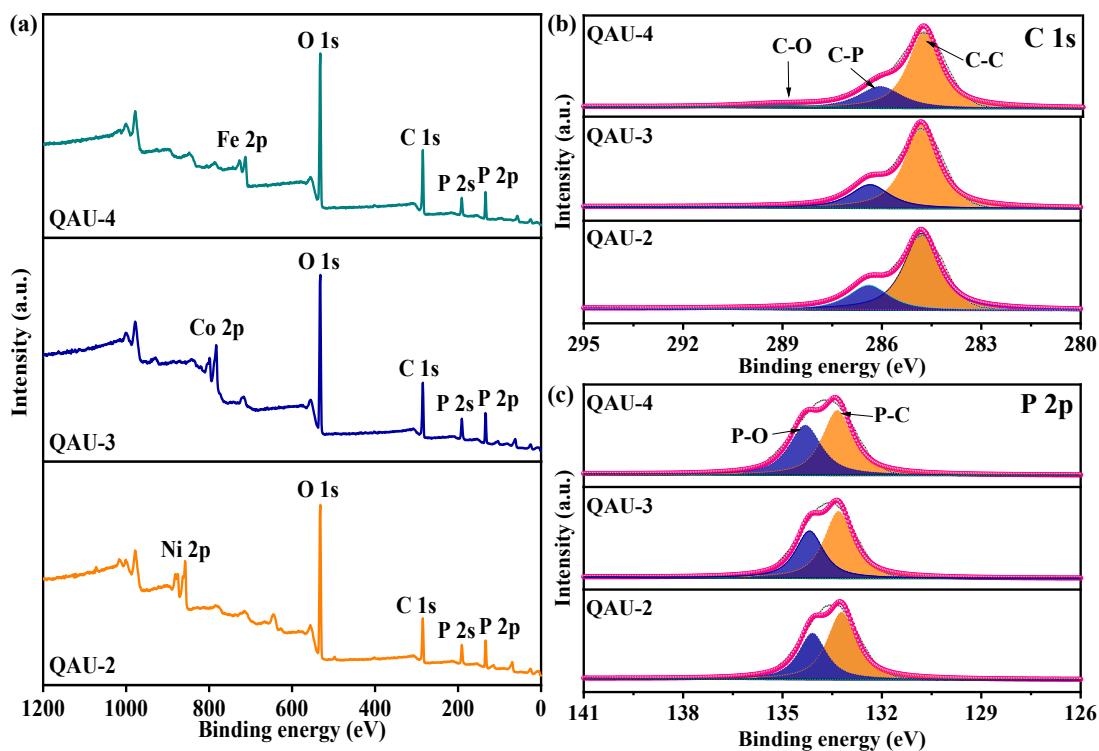


Fig. S8 XPS survey spectra (a), high-resolution C 1s (b) and P 2p (c) spectra of QAU-

2, QAU-3 and QAU-4.

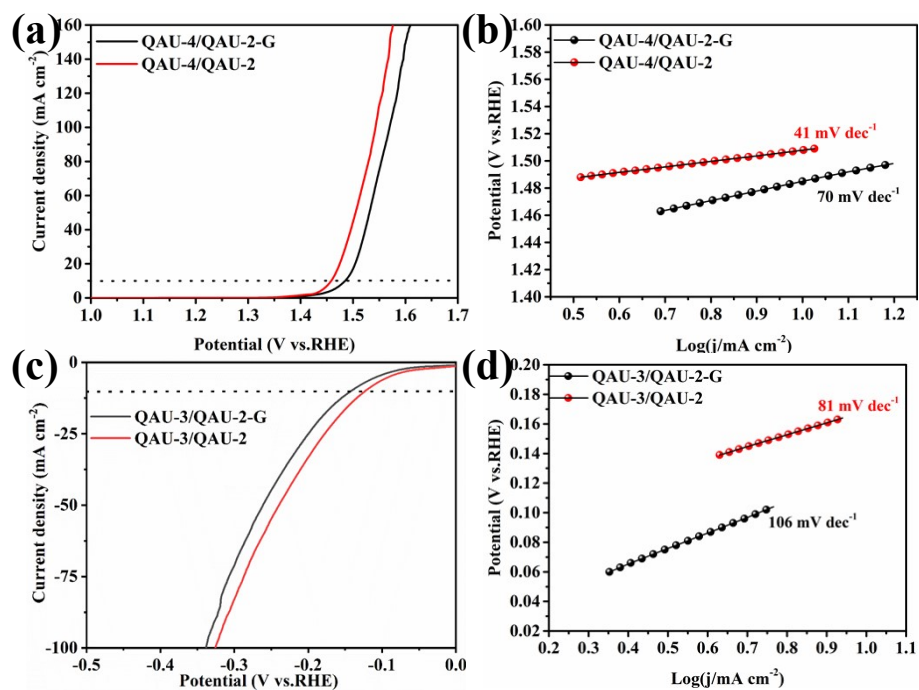


Fig. S9 (a) OER LSV polarization curves, (b) the corresponding Tafel slopes of QAU-4/QAU-2-G and QAU-4/QAU-2; (c) HER LSV polarization curves, (d) the corresponding Tafel slopes of QAU-3/QAU-2-G and QAU-3/QAU-2

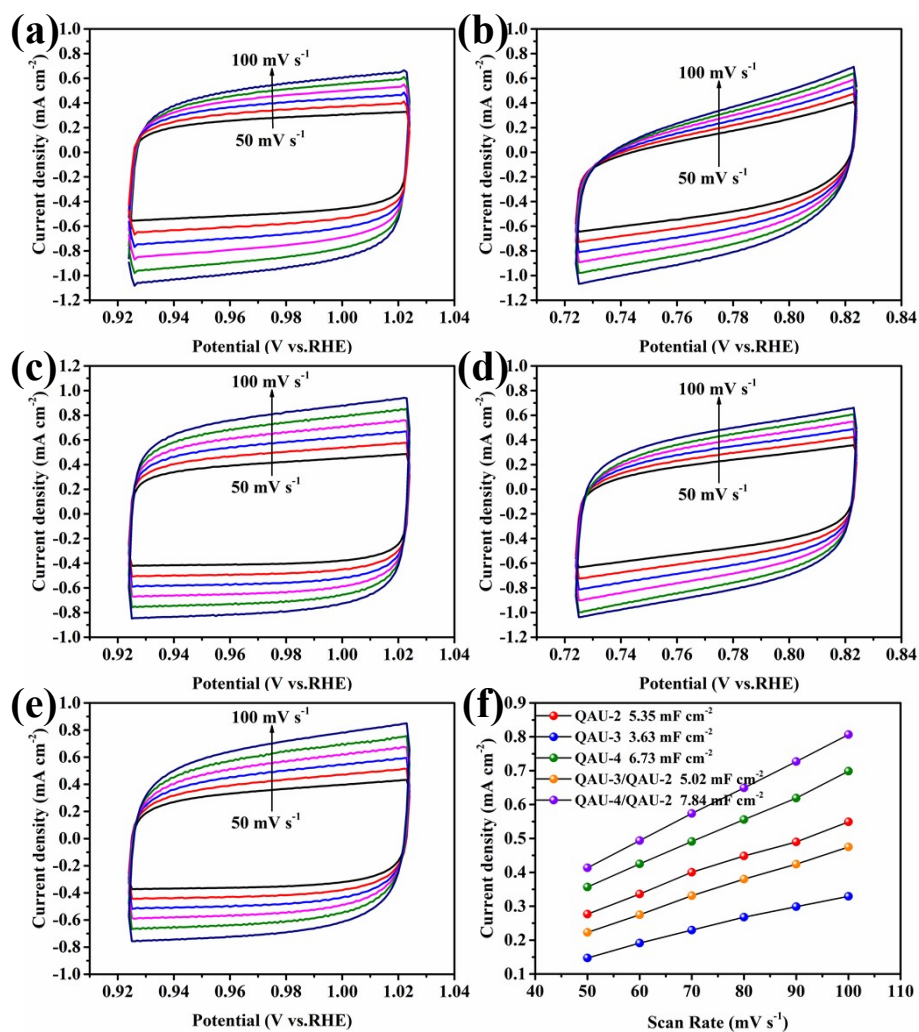


Fig. S10 Cyclic voltammetry curves of as-prepared phosphonate samples at 50, 60, 70, 80, 90, and 100 mV s^{-1} .

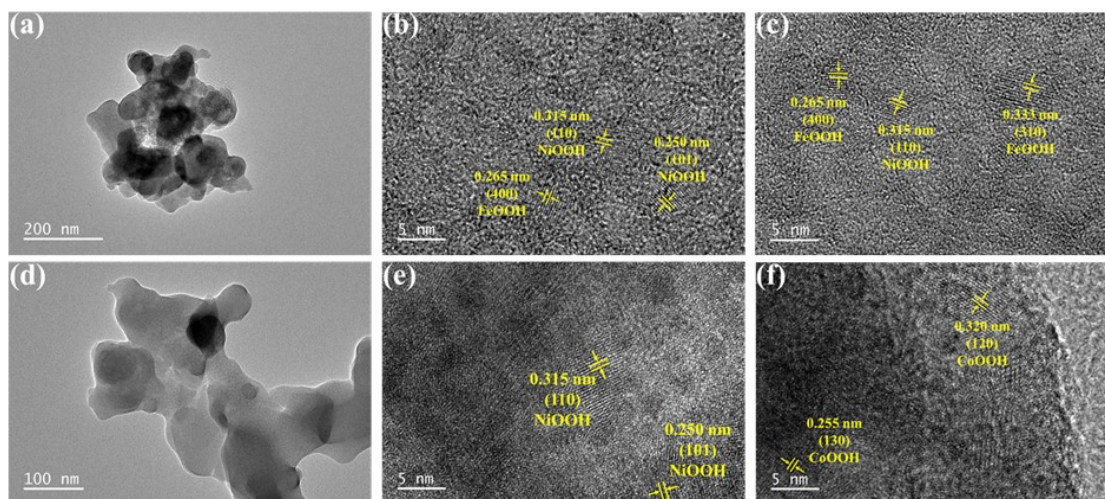


Fig. S11 TEM (a) and HRTEM (b-c) images of QAU-4/QAU-2 after OER measurements; TEM (d) and HRTEM (e-f) images of QAU-3/QAU-2 after HER measurements.

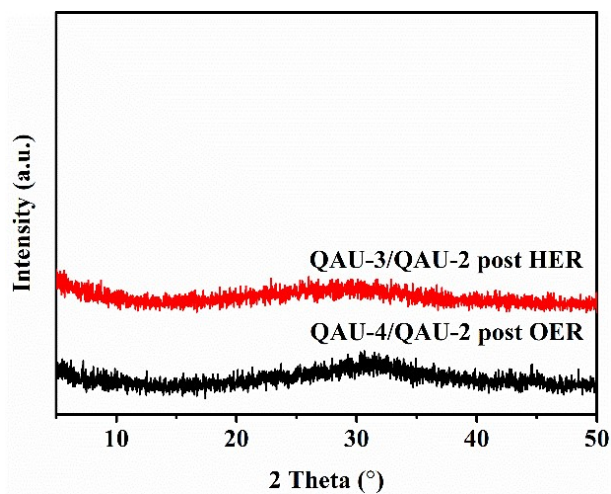


Fig. S12 The XRD patterns of QAU-4/QAU-2 after OER and QAU-3/QAU-2 after HER.

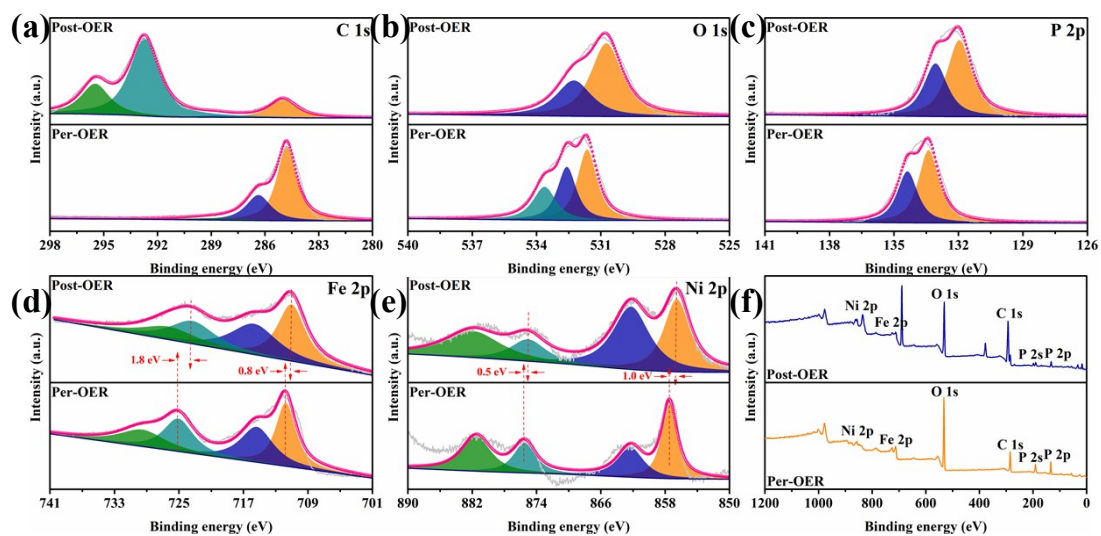


Fig. S13 XPS survey spectra of QAU-4/QAU-2 post- and per-OER.

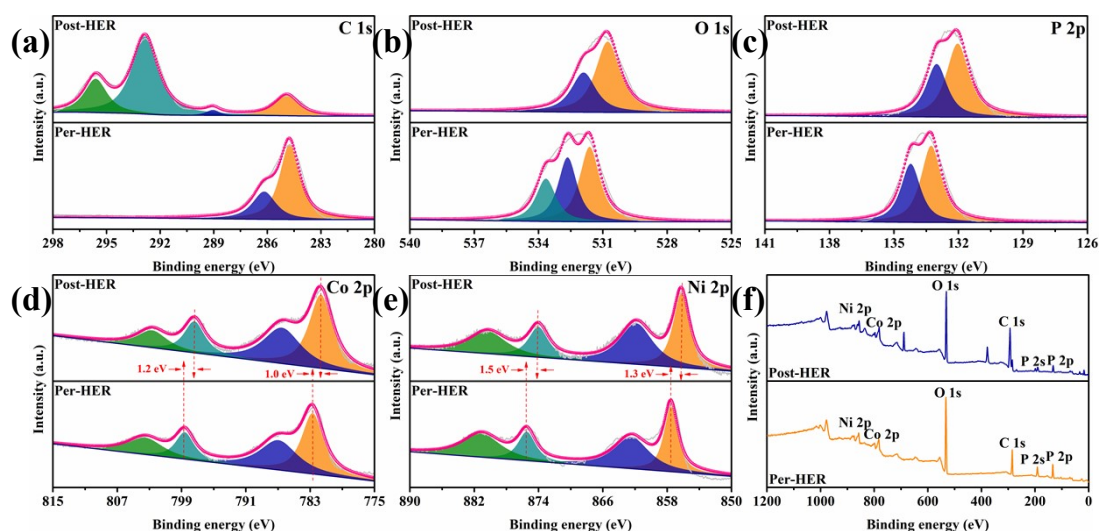


Fig. S14 XPS survey spectra of QAU-3/QAU-2 post- and per-HER.

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