Supporting Information

Electronic Supporting Information

Reconstruction and immobilization of polymolybdate induced by metal-organic coordination units for enhanced electrocatalytic hydrogen generation

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X-ray Crystallography

Crystallographic data for complexes **1-3** were collected on a Bruker SMART APEX II with Mo Kα (λ =0.71073 Å) by ω and θ scan mode. All structures were solved by direct methods and refined on F^2 by full-matrix least squares using the OLEX2 package. The command "ISOR" was used to refine atoms O42,in complex **4**. The command "SIUM" was used to refine atoms O42,in complex **4**.The command "DFIX" was used to refine atoms O49 O18_$1 and H9A O17 in complex **4**. The command "SADI" was used to refine atoms Ni1 H4Wa Ni1 H4Wb and Ni1 H3Wa Ni1 H3Wb in complex **1** and O18 O18_$1 O49 O49_$1 O18 O18_$1 O43 O43_$1 in complex **4**. The command "SFAC" was used to refine atoms C H Mo N Ni O, in complex **1**, C H Mo N O Zn,in complex **2** and C H Al Cu Mo N O, in complex 3. Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC Numbers 2375586、2381066、2375622 and 2375589. Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Materials and measurements

The ligand H_2dpyh was prepared according to a literature method.[1] All other chemicals and carbon cloth are of commercial origin and used directly without further purification. The FT-IR spectra were performed on a Varian 640-IR spectrometer (KBr pellets). X-ray diffraction (XRD) patterns of powdered samples were performed using an Ultima IV with D/teX Ultra diffractometer at 40 kV, 40 mA with Cu Kα radiation. The morphology of the samples were characterized by scanning electron microscopy (SEM, S-4800, HITACHI, Japan).The stability of the material was verified by testing the content of Mo contained in the solution after the testing using Inductively Coupled Plasma Optical Emission Spectrometer (ICPE-9820).

Preparation of complexes 1-4

Synthesis of $Ni_2(H_2O)_8(H_2dpyh)(Mo_8O_{26})$ (1) A mixture of $Ni(NO_3)_2 \cdot 6H_2O$ (0.10 g, 0.34 mmol), H_2dpyh (0.03 g, 0.0067 mmol), and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.124 g, 0.01 mmol) was stirred in 8 ml demonized water and the pH value was adjusted to about 1.95 by 0.5 M HNO_3 solution. Then the suspension was transferred to a Teflon-lined autoclave (25 mL) and kept at 120 °C for 4 days. Green block crystals of **1** were obtained (Yield 42 % based on Mo) after cooling to room temperature.

$Zn_2(H_2O)_2(H_2dpyh)_2(\beta\text{-}Mo_8O_{26})$ (2) A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.10 g, 0.34 mmol), H_2dpyh (0.045 g, 0.01 mmol), and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.124 g, 0.01 mmol) was stirred in 8 ml demonized water and the pH value was adjusted to about 1.92 by 0.5 M HNO_3 solution. Then the suspension was transferred to a Teflon-lined autoclave (25 mL) and kept at 120 °C for 4 days. Transparent block crystals of **1** were obtained (Yield 53 % based on Mo) after cooling to room temperature.

$\{Cu_8(\mu_2\text{-}OH)_2(dpyh)_4[AlMo_6(OH)_7O_{17}]_3\cdot 8H_2O$ (3) Complex **3** was obtained employing a similar procedure to that for **2**, except that $Cu(NO_3)_2 \cdot 3H_2O$was used instead of $Zn(NO_3)_2 \cdot 6H_2O$ and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was replaced by $Na_3[AlMo_6(OH)_6O_{18}]\cdot 8H_2O$.The pH value was adjusted to about 2.50. Blue block

crystals of **3** were obtained (Yield 55 % based on Mo) after cooling to room temperature.

$Cu_4(H_2O)_6(dpyh)_2(TeMo_{12}O_{40})$ (2) Complex **4** was obtained employing a similar procedure to that for **3**, except that $Na_3[AlMo_6(OH)_6O_{18}]\cdot 8H_2O$ was replaced by $(NH_4)_6[TeMo_6O_{24}]\cdot 7H_2O$ and the pH value was adjusted to about 2.23. Blue block crystals of **4** were obtained (Yield 38 % based on Mo) after cooling to room temperature.

Electrochemical measurements

HER measurements at different electrolytes including alkaline (1 M KOH) and seawater (1 M KOH+0.5 M NaCl) media were carried out on an electrochemical station (CHI 760) with a three-electrode system.The mercury oxide electrode (in 1 M KOH and seawater) were used as reference electrodes. The platinum wire was used as counter electrode. **1-4**/CC (0.5 × 2 cm^2) was directly used as the working electrode with the average loading mass of 4 mg cm^{-2} for the grounded complex. The testing area was 1 cm^2. Working potentials were converted with respect to reversible hydrogen electrode (RHE) according to the equation: $E_{RHE} = E_{Hg/Hgo} + 0.098 + 0.059pH$. The measurement area was 1 cm^2.

Table S1 Crystallographic data for complex **1-4**

Complex	**1**	**2**	**3**	**4**
Empirical formula	$C_{14}H_{34}Mo_8N_6Ni_2O_{36}$	$C_{14}H_{20}Mo_4N_6O_{16}Zn$	$C_{56}H_{84}Al_3Cu_8Mo_{18}N_{24}O_{90}$	$C_{28}H_{44}Cu_4Mo_{12}N_{12}O_{50}Te$
Formula weight	1747.41	977.467	4849.65	2881.79
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	P2/n	$P2_1/c$	P-1	$P2_1/n$
a (Å)	15.7717(5)	9.7256(4)	15.0730(4)	18.3184(10)
b (Å)	7.8616(2)	16.1956(7)	15.3343(4)	22.4004(10)
c (Å)	19.9192(6)	17.6443(7)	17.7621(4)	19.0322(10)
α (°)	90	90	90.3450(10)	90
β (°)	111.6410(10)	103.292(2)	113.7870(10)	108.005(2)
γ (°)	90	90	105.2450(10)	90
V ($Å^3$)	2295.71(12)	2704.7(2)	3595.15(16)	7427.2(7)
Z	2	4	1	4

D_c (g/cm^3)	2.528	2.400	2.240	2.577
M (mm^{-1})	3.015	2.761	2.788	3.559
F(000)	1680.0	1862.7	2335.0	5472.0
Reflections collected	42475	96760	115469	125530
Unique reflections	4543	4754	12614	12986
R_{int}	0.0577	0.1027	0.0632	0.0657
GOF	1.062	1.115	1.034	1.039
R_1[a][I>=2σ(I)]	0.0217	0.0319	0.0247	0.0348
wR_2[b] (all data)	0.0531	0.0760	0.0630	0.0962

[a]$R_1=\sum||F_o|-|F_c||/\sum|F_o|$; [b]$wR_2=\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$

Table S2 Bond lengths [Å] and angles [°] for complex **1-4**

Complex **1**			
Ni1-O1	2.085(3)	O4W-Ni1-O1W	176.01(13)
Ni1-O1W	2.041(3)	O4W-Ni1-O2W	93.15(14)
Ni1-O2W	2.052(3)	O4W-Ni1-O3W	86.43(15)
Ni1-O3W	2.037(3)	O4W-Ni1-N1	88.33(13)
Ni1-O4W	2.021(3)	O3W-Ni1-O1	91.47(15)
Ni1-N1	2.047(3)	O3W-Ni1-O1W	89.85(15)
O1W-Ni1-O1	85.21(12)	O3W-Ni1-O2W	94.19(17)
O1W-Ni1-O2W	88.53(13)	O3W-Ni1-N1	168.77(17)
O1W-Ni1-N1	95.09(13)	N1-Ni1-O1	78.93(11)
O2W-Ni1-O1	171.55(13)	N1-Ni1-O2W	96.00(12)
O4W-Ni1-O1	93.45(13)		
Complex **2**			
Zn1-O2	2.104(4)	O1-Zn1-O15^3	103.41(17)
Zn1-O1W	2.129(4)	N1-Zn1-O2	91.82(16)
Zn1-O15^3	2.122(4)	N1-Zn1-O1W	96.85(17)

Zn1-O1	2.180(4)	N1-Zn1-O15^{3}	97.59(17)
Zn1-N1	2.069(5)	N1-Zn1-O1	76.85(17)
Zn1-N5^{3}	2.068(5)	N5^{3}-Zn1-O2	94.38(16)
O1W-Zn1-O2	83.44(15)	N5^{3}-Zn1-O1W	91.92(17)
O15^{3}-Zn1-O2	166.63(16)	N5^{3}-Zn1-O15^{3}	77.75(17)
O15^{3}-Zn1-O1W	86.02(17)	N5^{3}-Zn1-O1	95.25(17)
O1-Zn1-O2	87.92(15)	N5^{3}-Zn1-N1	169.79(18)
O1-Zn1-O1W	169.17(16)		
Complex **3**			
Cu4-O5	1.999(2)	N8-Cu3-O6	165.41(10)
Cu4-O4W	1.953(2)	N8-Cu3-O4	83.00(10)
Cu4-N5	1.939(3)	N7-Cu3-O6	95.66(10)
Cu4-N6	1.968(3)	N7-Cu3-O4	174.07(11)
Cu3-O6	1.964(2)	N7-Cu3-N8	98.63(11)
Cu3-O4	1.941(2)	O2-Cu1-O1	100.20(9)
Cu3-N8	1.933(3)	O1W-Cu1-O1	96.64(10)
Cu3-N7	1.921(3)	O1W-Cu1-O2	84.71(11)
Cu1-O1	2.323(2)	O1W-Cu1-N1	164.03(12)
Cu1-O2	1.997(2)	N1-Cu1-O1	93.26(10)
Cu1-O1W	1.947(3)	N1-Cu1-O2	81.21(11)
Cu1-N1	1.962(3)	N2-Cu1-O1	92.83(11)
Cu1-N2	1.943(3)	N2-Cu1-O2	166.96(12)
Cu2-O3	2.018(3)	N2-Cu1-O1W	93.39(13)
Cu2-O3W	2.326(3)	N2-Cu1-N1	98.63(12)
Cu2-O2W	1.957(3)	O3-Cu2-O3W	107.24(11)
Cu2-N3	1.959(3)	O2W-Cu2-O3	85.11(12)
Cu2-N4	1.952(3)	O2W-Cu2-O3W	93.37(13)
O4W-Cu4-O5	87.24(10)	O2W-Cu2-N3	94.62(12)
O4W-Cu4-N6	167.80(10)	N3-Cu2-O3	161.34(12)

N5-Cu4-O5	170.33(11)	N3-Cu2-O3W	91.40(11)
N5-Cu4-O4W	94.28(10)	N4-Cu2-O3	81.07(12)
N5-Cu4-N6	97.59(11)	N4-Cu2-O3W	90.34(11)
N6-Cu4-O5	81.53(10)	N4-Cu2-O2W	166.17(12)
O4-Cu3-O6	83.08(9)	N4-Cu2-N3	98.60(12)
Complex **4**			
Cu2-O2	1.977(4)	N8-Cu4-O4	81.67(17)
Cu2-O2W	1.969(4)	N8-Cu4-O6W	169.10(19)
Cu2-N4	1.937(5)	N8-Cu4-O5W	90.5(2)
Cu2-N3	1.954(5)	O6W-Cu4-O4	87.58(18)
Cu4-O4	1.991(4)	O6W-Cu4-O5W	93.5(2)
Cu4-N8	1.950(5)	N6-Cu4-O4	162.9(2)
Cu4-O6W	1.967(4)	N6-Cu4-N8	97.53(19)
Cu4-N6	1.934(5)	N6-Cu4-O6W	92.21(19)
Cu4-O5W	2.359(6)	N6-Cu4-O5W	95.3(3)
Cu3-O3	2.021(4)	O3-Cu3-O3W	95.6(2)
Cu3-O4W	1.949(4)	O4W-Cu3-O3	88.60(18)
Cu3-N5	1.943(5)	O4W-Cu3-O3W	92.9(3)
Cu3-N7	1.946(5)	N5-Cu3-O3	81.28(17)
Cu3-O3W	2.320(6)	N5-Cu3-O4W	169.8(2)
Cu1-O1	1.987(4)	N5-Cu3-N7	97.28(19)
Cu1-N1	1.940(5)	N5-Cu3-O3W	87.5(2)
Cu1-N2	1.930(5)	N7-Cu3-O3	160.7(2)
Cu1-O1W	1.941(4)	N7-Cu3-O4W	92.5(2)
O2W-Cu2-O2	88.95(17)	N7-Cu3-O3W	103.6(2)
N4-Cu2-O2	161.00(19)	N1-Cu1-O1	81.63(17)
N4-Cu2-O2W	92.31(18)	N1-Cu1-O1W	166.1(2)
N4-Cu2-N3	98.28(19)	N2-Cu1-O1	162.3(2)
N3-Cu2-O2	81.93(17)	N2-Cu1-N1	98.96(19)

N3-Cu2-O2W	169.07(19)	N2-Cu1-O1W	94.7(2)
O4-Cu4-O5W	101.7(2)	O1W-Cu1-O1	86.30(18)

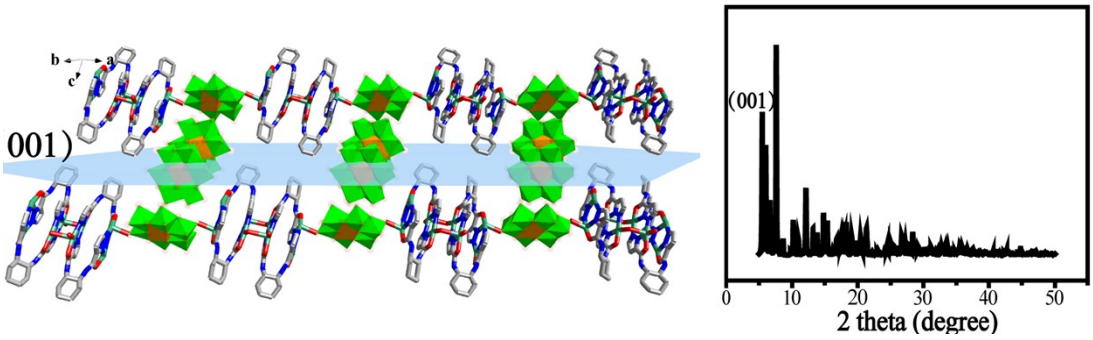

Fig. S1 The 1D inorganic chain and XRD data in **3**.

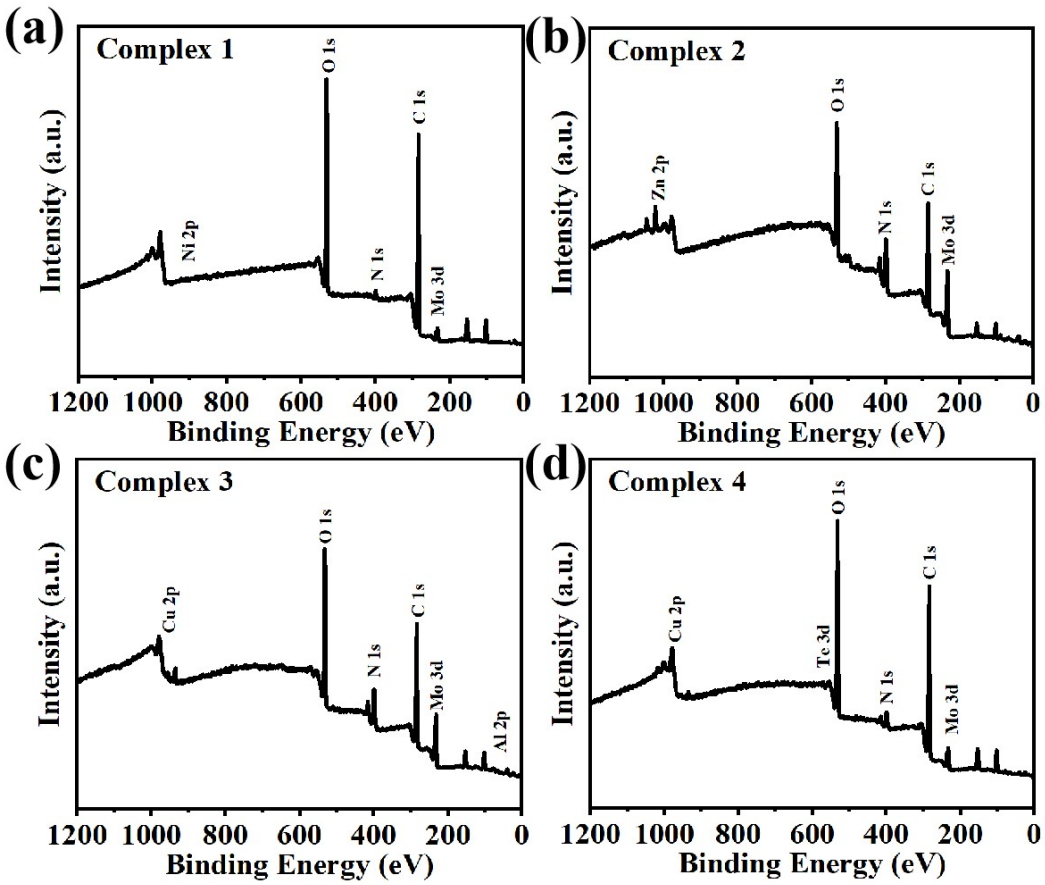

Fig. S2 X-ray photoelectron spectra (XPS) of complex **1-4**

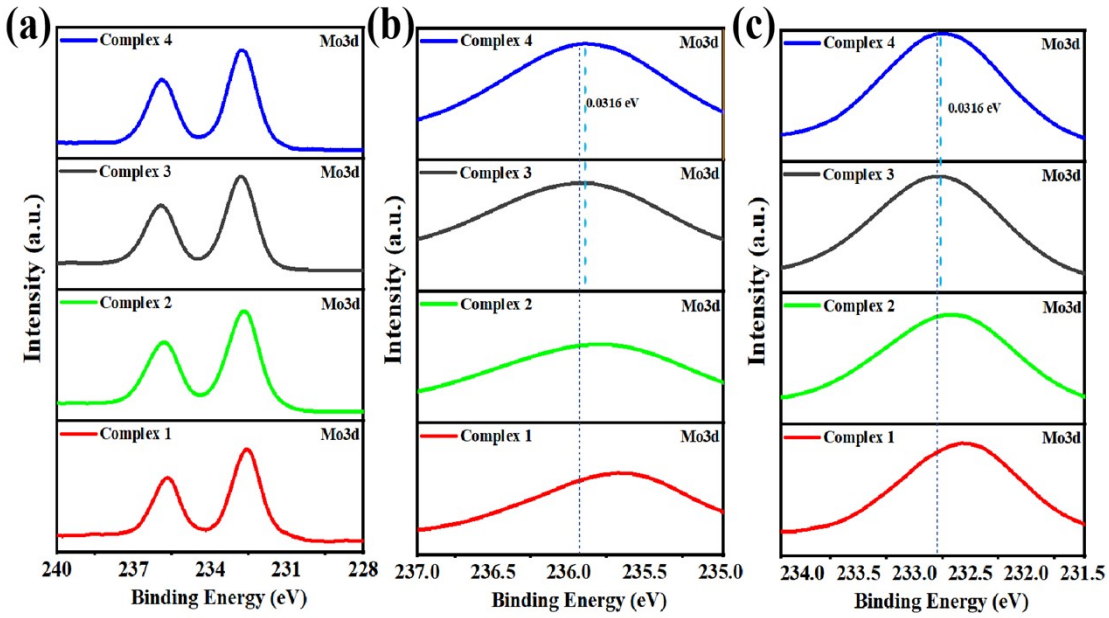

Fig. S3 The Mo3d XPS spectra of complex **1-4**

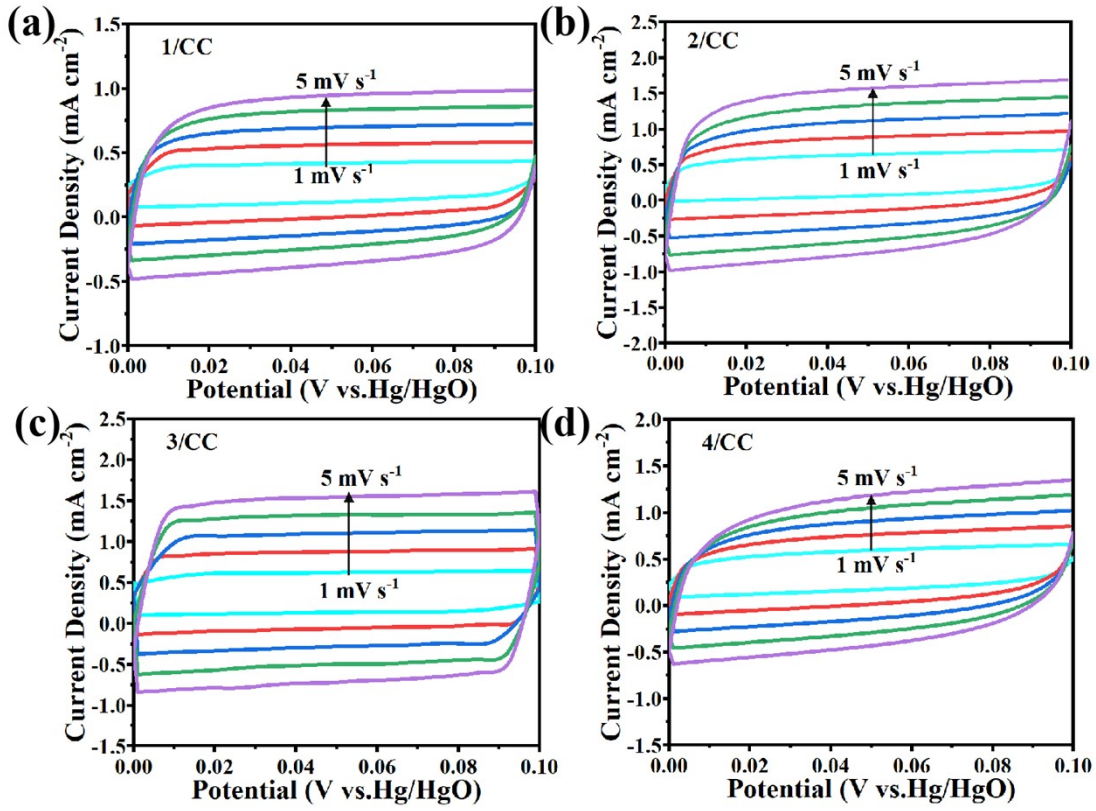

Fig. S4 CV curves for 1-4/CC at different rates from 1 mV/s to 5 mV/s in the region of 0~0.1 V in 1.0 mol/L KOH.

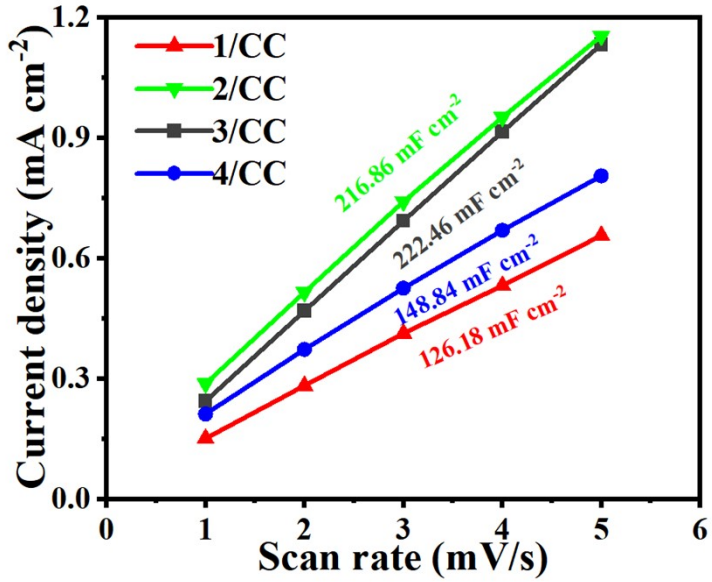

Fig. S5 Plots showing the extraction of the C_{dl} for **1-4**/CC.

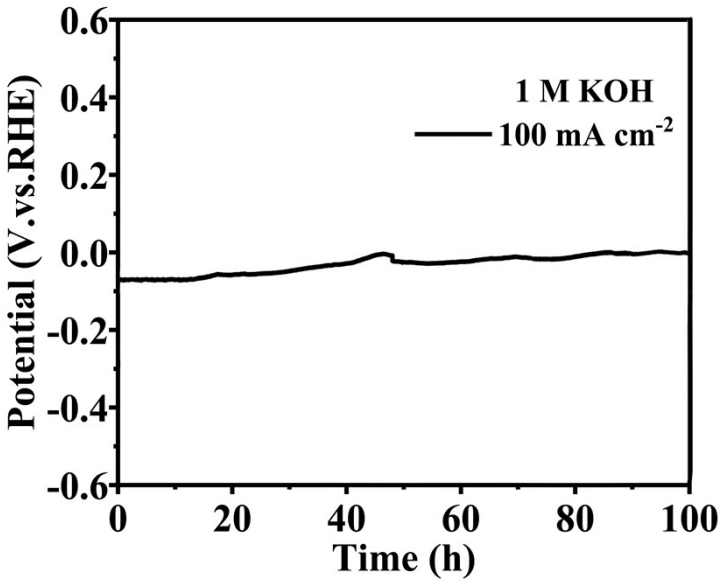

Fig. S6 Constant current test of 3/CC in 1M KOH at the current densities of 100 mA cm^{-2} for 100 h.

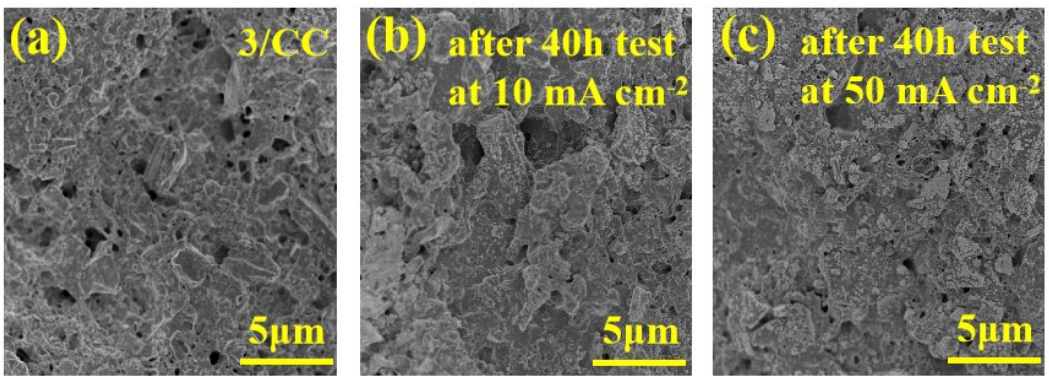

Fig. S7 (a) The SEM images of **3**/CC ; the SEM images of **3**/CC after long-term

stability test for 40 h in simulated seawater at (b) 10 mA cm^{-2} and (c) 50 mA cm^{-2}.

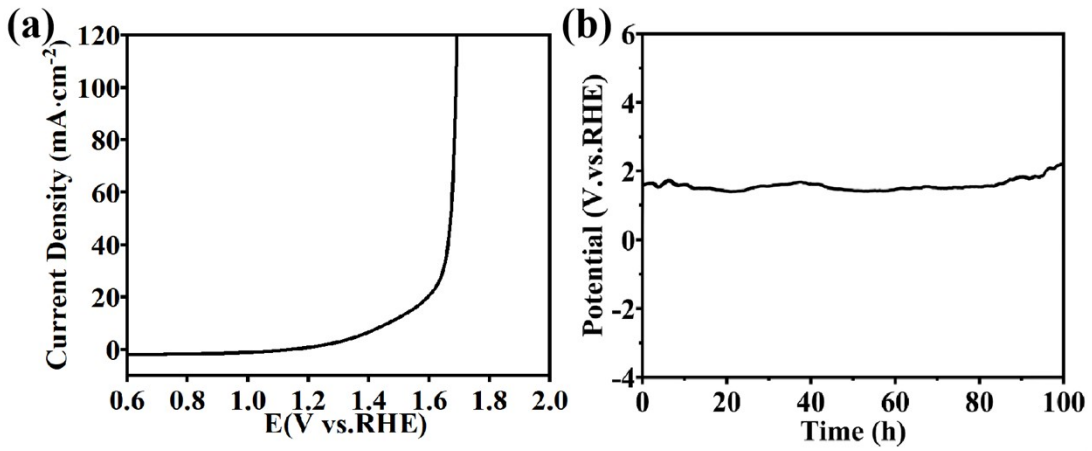

Fig. S8 (a) LSV curves of **3**/CC ‖ RuO_2 and LSV curves after fully electrolyzed water experiment in simulated seawater; (b) Fully electrolyzed water experiment of 3/CC ‖ RuO_2 in simulated seawater at 100 mA cm^{-2} for 100 h.

Table. S3 ICP-MS analysis results of the electrolyte before and after stability test

Sample	The amount of Mo in solution mg/L)
Solution of KOH	-0.00356
KOH solution after stability test	2.400
Simulated seawater solution before test	-0.0286
Simulated seawater solution after stability test	3.680