Electronic Supplementary Information (ESI) for

Anion Exchange Strategy to Improve Electrocatalytic Hydrogen Evolution Reaction Performances in Cationic Metal Organic Frameworks

Bei Li, Qingjuan Lei, Tong Qin, Xiaoxian Zhang, Dongsheng Zhao, Feng Wang, Wenqian Li, Zhengguo Zhang^{*}, Liming Fan^{*}

Department of Chemistry, College of Science, North University of China, Taiyuan 030051, China. *E-mail: limingfan@nuc.edu.cn, zhengguozhang@nuc.edu.cn.*

Experimental Section

Materials and Methods. All chemicals used in this work were achieved and used as analytical-grade from commercial corporations. IR spectra were measured on a FTIR-8400S spectrometer in the range of 500-4000 cm⁻¹. Elemental analysis (EA) was carried out on a Vario MACRO cube elemental analyzer. TGA was measured from 30 to 800 °C on a PE analyzer at a heating rate 10 °C/min under nitrogen atmosphere. UV-vis absorption spectra were recorded on Shimadzu UV-2600 spectrophotometer. X-ray powder diffractions were measured on a Bruker APEX-II CCD diffractometer with Cu K α (λ = 1.54178 Å) radiation over the 2 θ range of 5-50 °C at room temperature. X-ray photoelectron spectra (XPS) were recorded by ThermoFisher Scientific XPS (NEXSA). Scanning electron microscope (SEM) images were measured on a Hitachi S-3500N equipped with an energy-dispersive X-ray spectroscopy (EDX) instrument. ICP was measured by ICP9000(N+M) (USA Thermo Jarrell-Ash Corp). All electrochemical measurements were performed at a standard three-electrode system CHI 660E electrochemical workstation at an ambient environment.

Synthesis of Synthesis of $\{[Ni(tipa)_2]SO_4 \cdot DMF \cdot 8H_2O\}_n$ (NiCP). A hybrid of NiSO₄ · 6H₂O (0.0158 g, 0.06 mmol), tipa (0.0177 g, 0.04 mmol), 10mL DMF/H₂O (V:V=1:3), 0.5 mL HNO₃ solution (1.2 mol/L), was transferred into a teflon lined stainless steel (25 mL) container which was heated at 130 °C for 3000 min, and then cooled to 25 °C with a descent rate of 10 °C/h. The dark green block crystals were collected by filtration with the yield of 58 % (based on tipa). Anal. Calcd (%) for NiCP: C 54.38; H 5.16; N 14.30. Found (%): C 58.21; H 5.05; N 14.27. IR (KBr, cm⁻¹): 3460 (s), 2357 (s), 1639 (s), 1518 (s), 1381 (s), 1263 (w), 1120 (w), 1065 (m), 968 (w), 829 (m), 735 (m), 663 (m), 540 (m).

Fabrication of Working Electrode and Suspension Solution. A mixture of catalysts powder (4 mg), super-P (1 mg) and polyvinylidene fluoride (PVDF, 1 mg), are added into a piece of cleaned nickel foam (NF, size 1cm \times 1cm), and then heated 60 °C for 1h. The nickel foam deposited with fabricated materials mixture are used as working electrode, and the carbon rod, saturated calomel electrode (SCE) served as counter electrode and reference electrode, respectively.

Electrochemical measurements. The electrochemical impedance spectroscopy (EIS) was measured at the amplitude of 5 mV with the frequency range 1.0×10^5 - 0.1 Hz. The linear scan voltammetry (LSV) was conducted at 5 mV s⁻¹ (iR compensation). All the measured potentials were calibrated to the reversible hydrogen electrode (RHE) potentials based on the equation: E (V vs. RHE) = E (V vs. SCE) + 0.059 × pH + 0.242. The electrochemical double-layer capacitance (C_{dl}) can be used to estimate the electrochemically active surface area (ECSA), which were measured by cyclic voltammetry (CV) curves at different scan rates 10 - 50 mV s⁻¹ in the non-Faraday region 1.068 - 1.168 (V vs RHE).

X-ray crystallography. Single crystals of **NiCP** were chosen and fixed on a glass fiber for data collection. Intensity data collection was carried out on a Bruker APEX-II CCD diffractometer equipped with a CCD detector using Cu $K\alpha$ monochromatized radiation ($\lambda = 1.54178$ Å). And the absorption correction was based on multiple and symmetry-equivalent reflections in the data set using the SADABS program. The structure was solved by direct methods, and refined by full-matrix

least-squares using the SHELXTL package. Anisotropic thermal parameters were applied to all non-hydrogen atoms. And all hydrogen atoms attached to C and N atoms were placed geometrically. The CCDC number is 2097257 for **NiCP**.



Scheme S1 The selected organic ligand in assembly of NiCP.







Fig. S2 The coordination environment of **NiCP** (Symmetric code: A 1+x-y, x, 1-z; B 2-y, 1+x-y, z; C 2-x, 2-y, 1-z; D 1-x+y, 2-x, z; E y, 1-x+y, 1-z; F -x+y, 1-x, z; G 1-y, 1+x-y, z).



Fig. S3 The reticular channels of NiCP.



Fig. S4 The pore size of NiCP in the *b* axis.



Fig. S6 (a) The UV-vis curves for the standard concentrations of MnO_4^- anion, (b) Fitting plot of MnO_4^- anion concentrations vs Abs values.

0.2



Fig. S7 (a) The UV-vis absorption spectrums of MnO_4^- anion in different time; (b) The removal percentage of NiCP towards MnO_4^- anion.



Fig. S8 (a) The UV-vis curves for the standard concentrations of CrO_4^{2-} anion; (b) Fitting plot of CrO_4^{2-} anion concentrations *vs* Abs values.



Fig. S9 (a) The UV-vis absorption spectrums of CrO_4^{2-} anion in different time; (b) The removal percentage of NiCP towards CrO_4^{2-} anion.



Fig. S10 Fitting curve of Cr@NiCP and Mn@NiCP based on pseudo-first-order kinetic model



Fig. S11 Fitting curve of Cr@NiCP and Mn@NiCP based on pseudo-second-order kinetic model.



Fig. S12 The EDX mapping images of NiCP (a), Mn@NiCP (b) and Cr@NiCP (c).



Fig. S13 The SEM images of NiCP (a), Mn@NiCP (b) and Cr@NiCP (c).



Fig. S14 Overpotentials of NiCP with different adsorptive capacity of CrO_4^{2-} anions towards HER (a) and corresponding Tafel plots (b).



Fig. S15 Overpotentials of NiCP with different adsorptive capacity of MnO_4 anions towards HER (a) and corresponding Tafel plots (b).



Fig. S16 The cyclic voltammetry of (a) NiCP@NF; (b) (Mn@NiCP)@NF; (c) (Cr@NiCP)@NF in varying scan rates 10-50 mV s⁻¹.



Fig. S17 (a) The LSV polarization curves of NiCP@NF (a), (Mn@NiCP)@NF (b) and (Cr@NiCP)@NF (c) before and after 1000 cycles.



Fig. S18 The PXRD patterns of different catalysts NiCP, Mn@NiCP, Cr@NiCP composite that are mixed with PVDF and super-P befer and after HER.



Fig. S19 The SEM images of NiCP (a), Mn@NiCP (b) and Cr@NiCP (c) before HER. And the corresponding images of NiCP (d), Mn@NiCP (e) and Cr@NiCP (f) after HER.

Table S1	Crystal da	ita, experimental	conditions, and	structure refinement	parameters of NiCP.
----------	------------	-------------------	-----------------	----------------------	---------------------

Empirical formula	C ₅₄ H ₄₂ N ₁₄ Ni
Formula weight	945.72
Crystal system	trigonal
Space group	R-3
a/Å	16.0135(6)
b/Å	16.0135(6)
c/Å	26.0061(14)
$\alpha/^{\circ}$	90
β/°	90
$\gamma^{/\circ}$	120
Volume/Å ³	5775.3(5)
Z	3
$\rho_{calc} g/cm^3$	0.816
μ/mm^{-1}	0.627
F (000)	1476.0
2Θ range for data collection/°	9.324 to 122.248
Index ranges	$-16 \le h \le 18, -18 \le k \le 17, -29 \le l \le 22$
Independent reflections	1968 [$R_{int} = 0.0226, R_{sigma} = 0.0209$]
Goodness-of-fit on F ²	1.144
Final R indexes [I>=2 σ (I)]	$R_1 = 0.0569, wR_2 = 0.1700$
Final R indexes [all data]	$R_1 = 0.0624, wR_2 = 0.1760$
a) $R_1 = \Sigma Fo - Fc / \Sigma Fo $. b)	$WR_2 = \{ [\Sigma w (Fo^2 - Fc^2)^2 / \Sigma w (Fo^2)^2] \}^{1/2}.$

Table S2 Selected bond length	ths (Å) and an	gles (°) for NiCP
Table 52 Science Joing leng	lins (11) and an	

Ni(1)-N(3)#1	2.128(19)	N(3)-Ni(1)-N(3)#2	89.89(8)
N(3)#1-Ni(1)-N(3)#3	90.11(8)	N(3) #4-Ni(1)-N(2)#3	180.00(9)
Symmetry code: #1 2-X	, 2-Y, 1-Z; #2	1+Y-X, 2-X, Z; #3 2-Y,1+X	K-Y, Z; #4 Y, 1-X+Y, 1-Z.

 Table S3 Fitting results based on the pseudo-first-order kinetic and pseudo-second-order kinetic models.

Sample	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
	q _{e, cal} (mg g ⁻¹)	k ₁ (min ⁻¹)	R ²	q _{e, cal} (mg g ⁻¹)	k ₂ (g mg ⁻¹ min ⁻¹)	R ²

Cr@NiCP	58.29	0.003	0.93	68.23	1.85 ×10-4	>0.99
Mn@NiCP	69.13	0.010	0.92	74.28	1.82×10^{-3}	>0.99

Electrocatalyst	Electrolyte	η ₁₀ (mV)	Tatel slope (mV dec ⁻¹)	Ref.
Fe ₂ Zn-MOF	0.1 M KOH	221	174	19
Fe ₂ Co-MOF	0.1 M KOH	229	205	19
Fe ₂ Ni-MOF	0.1 M KOH	262	466	19
Fe ₂ Mn-MOF	0.1 M KOH	214	193.8	19
Fe ₃ -MOF	0.1 M KOH	218	171.9	19
Co-MOFs	1.0 M KOH	595	84	20
Ni@Co-MOFs	1.0 M KOH	349	52	20
$CoS_x/Co-MOF$	1.0 M KOH	73	305	8
CoP/Co-MOF	1.0 M KOH	49	63	9
NiCoFeP/C	1.0 M KOH	149	108	10
NiCP	1.0 M KOH	190	173	This work
(Mn@NiCP)@NF	1.0 M KOH	173	165	This work
(Cr@NiCP)@NF	1.0 M KOH	161	154	This work

 Table S4 The corresponding HER performance of the reported electrocatalysts.

Table S5 The overpotentials of electrocatalyst with different adsorptive capacity of oxoanions.

Electrocatalyst	Contact time (min)	Adsorptive capacity of oxoanions (mg g ⁻¹)	Overpotential (mV)	Tafel slopes (mV dec ⁻¹)
(Cr@NiCP)@NF-1	240	19.78	174	160
(Cr@NiCP)@NF-2	480	33.44	168	157
(Cr@NiCP)@NF-3	2280	66.30	161	154
(Mn@NiCP)@NF-1	60	34.59	186	172
(Mn@NiCP)@NF-2	180	54.66	177	168
(Mn@NiCP)@NF-3	480	73.17	173	165

Table S6 ICP data for NiCP, Mn@NiCP and Cr@NiCP before and after HER.

	, 0	
Sample	Metal	l (wt%)
NiCP (Before HER)	Ni	3.18
NiCP (After HER)	Ni	3.16
Mn@NiCP (Before HER)	Ni 3.14	Mn 0.99
Mn@NiCP (After HER)	Ni 3.17	Mn 1.00
Cr@NiCP (Before HER)	Ni 3.12	Cr 0.86
Cr@NiCP (After HER)	Ni 3.15	Cr 0.87

The related calculation of capacity.

The adsorbed capacity $(Q_t, mg/g)$ was estimated with the help of following equation:

$$Q_t = \frac{(C_0 - C_t)V}{M}$$

where $C_0 (mg/L)$ is the initial concentration of anions in the solution, and the $C_t (mg/L)$ represents the concentration

of anions in the solution at the t time. V is the volume of the solution (mL). M is the mass of the adsorbent (g).

The remove percentage (%) of anions is calculated by the equation:

$$Q_{remove} = \frac{C_0 - C_t}{C_0} \times 100\%$$

Pseudo-first-order kinetic model:

Pseudo-second-order kinetic model:

$$\ln \left(Q_e - Q_t\right) = \ln Q_e - k_1 t_1$$
$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e}$$

where $Q_e (mg g^{-1})$ is the sorption capacity at equilibrium, and the $Q_t (mg g^{-1})$ represents sorption capacity of **NiCP** at time t. k_1 and $k_2 (mg g^{-1} min^{-1})$ represent the rate constants of pseudo-first-order and pseudo-second-order, respectively.