Supporting Information

Tuning of tri-functional NiCu bimetallic nanoparticles confined in a porous carbon network with surface composition and local structural distortions for the electrocatalytic oxygen reduction, oxygen and hydrogen evolution reactions

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Computational methods

To investigate the catalytic activities of the NiCu alloys, five specific compositions were selected and studied in this project in accordance with the experiments. Overpotentials during the process of HER, OER and ORR were determined through first-principles calculations by calculating the Gibbs free energy of H^{*}, OH^{*} and OOH^{*} on the surfaces of different catalysts. These first-principles calculations were executed on the basis of DFT and were performed using the Vienna ab initio simulation package (VASP)^{S1, S2}. The core electrons were treated using projected augmented wave (PAW) pseudopotentials^{S3}, while the exchange correlation energies were evaluated by the formulations of Perdew-Burke-Ernzerhof (PBE) and ultra-soft potentials within the generalized gradient approximation (GGA)^{S4, S5}. The cut-off energy for the plane wave was set to be 400 eV, which was found to be sufficient for convergence of the adsorption energies. The FCC structures for each NiCu alloys (Cu, Ni_{0.25}Cu_{0.75}, Ni_{0.50}Cu_{0.50}, Ni_{0.75} Cu_{0.25} and Ni) were generated according to the experiment observation and tested with the VASP calculations. After relaxation the alloys showed a steady FCC structure, which matches the experimental observation. To simulate the free surface, a slab model with $2 \times 2 \times 2$ supercells of the five alloys was employed (Figure S2). A relatively large vacuum gap of 20 Å was set in the slab model to prevent its interaction with the periodic image of the lower layer. The bottom lattice of the model was fixed at the ground-state bulk distances, while the top lattice was set to be free to move in all directions. k-point meshes of $5 \times 3 \times 1$ were found to be sufficient to give a self-consistent field (SCF) convergence criterion of 1×10^{-5} eV. For each structure, atomic positions were relaxed first to reach their equilibrium. Thereafter, the adsorbate ion was placed on the top of the active sites (on the relaxed free surface) at a certain distance to calculate the total formation energy. The internal energy of the isolated adsorbates was also calculated. The adsorption energy E_{ad} was then calculated using Eq S1.^{S6, S7}

$$E_{ad} = E_{sub+adatom} - E_{sub} - E_{adatom}$$
(S1)

Where $E_{sub+adatom}$, E_{sub} , and E_{adatom} refer to the total energy of the NiCu alloy and adsorbate, the energy of the NiCu substrate and the energy of the isolated adsorbate, respectively. Based on this definition, the more negative value of E_{ad} represents a higher thermodynamic stability of the system. The Gibbs free energy difference ΔG was then calculated to describe the catalytic property by additional calculations. For HER, the Gibbs free energy difference ΔG_H is ^{S6, S7}

$$\Delta G_H = E_{ad-H} - \Delta E_{ZPE} - T \Delta S_H \tag{S2}$$

Where E_{ad-H} refers to the adsorption energy of H* (* denotes the uncertain ion state) on the NiCu surface. ΔE_{ZPE} refers to the difference of zero-point energy, which can be obtained from vibration frequency calculations. *T* is temperature and ΔS_H is the difference of entropy for the adsorbate, here is described as half of S_H , which is known thermodynamic properties for each adsorbate.

For OER and ORR, the Gibbs free energy difference ΔG also contains electron transfer and can be described as^{S6, S7}

$$\Delta G = E_{ad} - \Delta E_{ZPE} - T\Delta S + \Delta G_U + \Delta G_{pH}$$
(S3)

Where $\Delta G_U = -eU$, and *U* refers to the potential based on the standard hydrogen electrode. ΔG_{pH} represents the Gibbs free energy corrected by the *H*⁺ concentration. $\Delta G_{pH} = -kTln10 * pH$. For the four OER processes, the free energy changes can be described as ^{S6, S7}

$$\Delta G_1 = \Delta G_{OH*} \quad \Delta G_2 = \Delta G_{O*} - \Delta G_{OH*} \quad \Delta G_3 = \Delta G_{OOH*} - \Delta G_{O*} \quad \Delta G_4 = 4.92 - \Delta G_{OOH*} \tag{S4}$$

$$\Delta G_a = \Delta G_{OOH*} - 4.92 \qquad \Delta G_b = \Delta G_{O*} - \Delta G_{OOH*} \ \Delta G_c = \Delta G_{OH*} - \Delta G_{O*} \ \Delta G_d = -\Delta G_{OH*}$$
(S5)

The subscript numbers and letters in Eq. (S4) and (S5) indicate the free energy changes during OER and ORR, respectively. To evaluate the catalytic performance, the overpotential (η) of OER and ORR processes can be obtained by the following equations ^{S6, S7}

$$\eta^{OER} = \max\{\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4\} - 1.23$$
(S6)

$$\eta^{ORR} = \max\{\Delta G_a, \Delta G_b, \Delta G_c, \Delta G_d\} + 1.23$$
(S7)

Lattice constant for the prepared electrocatalysts:

The lattice constants for the Cu/C, Ni/C, Ni_{0.50}Cu_{0.50}/C, Ni_{0.75}Cu_{0.25}/C and Ni_{0.25}Cu_{0.75}/C electrocatalysts can be calculated according to the relationship between the d-spacing and lattice constants for a face centered cubic (FCC) crystal system:

$$d_{hkl} = \frac{\lambda}{2Sin(\theta_{hkl})} = \left[\frac{h^2 + k^2 + l^2 + l^2}{a^2}\right]^{-1/2}$$

Solving the above equation for the (111) peak gives the lattice constants as shown in Table S1. The lattice constants for the bimetallic electrocatalysts are in between of the monometallics.

Table S1: (111) peak positions and lattice constants for Cu/C, Ni/C, Ni_{0.50}Cu_{0.50}/C, Ni_{0.75}Cu_{0.25}/C and Ni_{0.25}Cu_{0.75}/C as determined by the XRD.

Catalyst	2θ 111 [°]	a [Aº]	Unit cell	Atoms per	# Surface sites
			volume [A ^{o 3}]	unit cell	[atoms cm- ² real]
Cu/C	43.40	3.607	46.93	4	1.94×10^{15}
Ni/C	44.50	3.522	43.68	4	2.03×10^{15}
Ni0.50Cu0.50/C	43.8	3.575	45.69	4	1.97×10^{15}
Ni _{0.75} Cu _{0.25} /C	44.05	3.556	44.97	4	1.99×10^{15}
Ni _{0.25} Cu _{0.75} /C	44.17	3.547	44.62	4	2.00×10^{15}

Turnover frequency (TOF) calculations:

To calculate the per-site turnover frequency, we have used the following formula as reported by Jaramillo et al.^{S8}

$$TOF = \frac{\# \text{ number of total hydrogen turnover per cm}^2}{\# \text{ number of active sites per cm}^2} = \frac{\# \text{ H}_2 \times |j|}{\text{active sites}}$$

The total number of hydrogen turn overs (#H₂) was calculated from the current density according to the following equation.

$$\begin{split} \#H_2 &= (j\frac{mA}{cm^2})(\frac{1\ Cs^{-1}}{1000\ mA})(\frac{1\ mol\ e^-}{96485.3\ C})(\frac{1\ mol\ H_2}{2\ mol\ e^-})(\frac{6.022\times10^{23}\ H_2\ molecules}{1\ mol\ H_2}) \\ &= 3.12\times10^{15}\ \frac{H_2\ /s}{cm^2}\ per\ \frac{mA}{cm^2} \\ \\ \#O_2 &= (j\frac{mA}{cm^2})(\frac{1\ Cs^{-1}}{1000\ mA})(\frac{1\ mol\ e^-}{96485.3\ C})(\frac{1\ mol\ O_2}{4\ mol\ e^-})(\frac{6.022\times10^{23}\ O_2\ molecules}{1\ mol\ O_2}) \\ &= 1.56\times10^{15}\ \frac{O_2\ /s}{cm^2}\ per\ \frac{mA}{cm^2} \\ \\ \#H_2O &= (j\frac{mA}{cm^2})(\frac{1\ Cs^{-1}}{1000\ mA})(\frac{1\ mol\ e^-}{96485.3\ C})(\frac{1\ mol\ H_2O}{4\ mol\ e^-})(\frac{6.022\times10^{23}\ O_2\ molecules}{1\ mol\ O_2}) \\ &= 1.56\times10^{15}\ \frac{O_2\ /s}{cm^2}\ per\ \frac{mA}{cm^2} \\ \\ \\ \#H_2O &= (j\frac{mA}{cm^2})(\frac{1\ Cs^{-1}}{1000\ mA})(\frac{1\ mol\ e^-}{96485.3\ C})(\frac{1\ mol\ H_2O}{4\ mol\ e^-})(\frac{6.022\times10^{23}\ H_2O\ molecules}{1\ mol\ H_2O}) \\ &= 1.56\times10^{15}\ \frac{H_2O/s}{cm^2}\ per\ \frac{mA}{cm^2} \end{split}$$

As the exact hydrogen binding sites are unknown, we predictably estimate the total number of surface sites or active sites by using the following equation. A similar approach was applied to estimate the TOF for Ni_2P and CoP.^{S9, S10}

number of active sites per real surface area (here calculated for $Ni_{0.25}Cu_{0.75}/C$):

number of active sites =
$$\left(\frac{\text{number of atoms/unit cell}}{\text{unit cell volume/unit cell}}\right)^{\frac{2}{3}}$$

= $\left(\frac{4 \text{ atoms/unit cell}}{44.62 \text{ A}^{03}/\text{unit cell}}\right)^{\frac{2}{3}}$ Fig. S1: FCC unit cell of Ni_{0.25}Cu_{0.75}

$$= 2.00 \times 10^{15}$$
 atoms cm⁻²_{real}

We have demonstrated the TOF calculations for the best $Ni_{0.25}Cu_{0.75}/C$ electrocatalyst in case of HER, OER and ORR processes. The other TOF values for the other electrocatalysts were also calculated accordingly.

For HER process: The current density at an overpotential of 0.15 V (vs RHE) is 5.76 mA·cm⁻² for the Ni_{0.25}Cu_{0.75}/C electrocatalyst.

$$\mathbf{TOF} = \frac{3.12 \times 10^{15} \frac{\text{H}_2/\text{s}}{\text{cm}^2} \text{ per } \frac{\text{mA}}{\text{cm}^2} \times 20 \frac{\text{mA}}{\text{cm}^2}}{2.00 \times 10^{15} \text{sites } \text{cm}^{-2}} = 8.98 \text{ s}^{-1}$$

For OER process: The current density at an overpotential of 1.65 V (vs RHE) is 12.40 mA·cm⁻² for the Ni_{0.25}Cu_{0.75}/C electrocatalyst.

$$\mathbf{TOF} = \frac{1.56 \times 10^{15} \frac{O_2/s}{cm^2} \text{ per } \frac{\text{mA}}{\text{cm}^2} \times 12.40 \frac{\text{mA}}{\text{cm}^2}}{2.00 \times 10^{15} \text{sites } \text{cm}^{-2}} = 9.67 \text{ s}^{-1}$$

For ORR process: The current density at an overpotential of 0.75 V (vs RHE) is 0.80 mA·cm⁻² for the $Ni_{0.25}Cu_{0.75}/C$ electrocatalyst.

$$\mathbf{TOF} = \frac{1.56 \times 10^{15} \frac{\text{H}_2\text{O/s}}{\text{cm}^2} \text{ per } \frac{\text{mA}}{\text{cm}^2} \times 0.80 \frac{\text{mA}}{\text{cm}^2}}{2.00 \times 10^{15} \text{sites } \text{cm}^{-2}} = 0.62 \text{ s}^{-1}$$

Finally, the plot of current density can be converted into a TOF plot based on the following equation:

For HER Process:

TOF =
$$\frac{(3.12 \times 10^{15}) \times |j|}{\# \text{ number of active sites } \times A_{ECSA}}$$

For OER Process:

$$\mathbf{TOF} = \frac{(1.56 \times 10^{15}) \times |\mathbf{j}|}{\# \text{ number of active sites } \times A_{\text{ECSA}}}$$

Electrocatalysts	C (wt%)	O (wt%)	Cu (wt%)	Ni (wt%)
Cu/C	62.52	18.22	19.26	/
Ni/C	53.64	16.12	/	30.24
Ni _{0.50} Cu _{0.50} /C	59.62	16.65	13.76	9.97
Ni _{0.75} Cu _{0.25} /C	65.88	13.77	10.90	9.45
Ni _{0.25} Cu _{0.75} /C	62.34	15.67	16.73	5.27

Table S2: The surface composition of the electrocatalysts obtained by the XPS measurements.

Table S3: Comparison of OER electrocatalytic performance of Cu/C, Ni/C, Ni_{0.50}Cu_{0.50}/C, Ni_{0.75}Cu_{0.25}/C and Ni_{0.25}Cu_{0.75}/C electrocatalysts in 0.5 M NaOH solution.

Catalyst	Onset Potential (V vs RHE)	η ₁₀ (mV vs RHE)	Tafel slope (mV/dec)	Mass Activity (mA/mg)	Specific Activity (mA/cm ²)	TOF (s ⁻¹)
Cu/C	1.64	/	147	4.69	0.03	0.53
Ni/C	1.62	/	144	6.51	0.05	0.72
Ni _{0.5} Cu _{0.5} / C	1.52	480	113	36.72	0.23	4.09
Ni _{0.75} Cu _{0.2} 5/C	1.49	470	93	43.77	0.25	4.82
Ni _{0.25} Cu _{0.7} 5/C	1.44	400	80	86.8	0.36	9.67

Catalyst	Onset Potential (mV)	η ₁₀ (mV)	Tafel slope (mV/dec)	Mass Activity (mA/mg)	Specific Activity (mA/cm ²)	TOF (s ⁻¹)
Cu/C	401	471	179	2.90	0.01	0.04
Ni/C	367	437	106	10.50	0.05	0.27
Ni _{0.5} Cu _{0.5} /C	327	400	125	24.71	0.10	0.33
Ni _{0.75} Cu _{0.25} / C	243	334	114	87.64	0.16	0.52
Ni _{0.25} Cu _{0.75} / C	75	186	84	641.20	0.79	8.98

Table S4: Comparison of HER electrocatalytic performance of Cu/C, Ni/C, Ni_{0.50}Cu_{0.50}/C, Ni_{0.75}Cu_{0.25}/C and Ni_{0.25}Cu_{0.75}/C electrocatalysts in 0.5 M H₂SO₄ solution.

Table S5: Comparison of ORR electrocatalytic performance of Cu/C, Ni/C, Ni_{0.50}Cu_{0.50}/C, Ni_{0.75}Cu_{0.25}/C and Ni_{0.25}Cu_{0.75}/C electrocatalysts in 0.5 M NaOH solution.

Catalyst	Onset Potential (V)	E _{1/2} (V)	Tafel slope (mV/dec)	Mass Activity (mA/mg)	Specific Activity (mA/cm ²)	TOF (s ⁻¹)
Cu/C	0.78	0.43	125	0.48	0.003	0.056
Ni/C	0.78	0.56	122	0.56	0.004	0.061
Ni _{0.5} Cu _{0.5} /C	0.81	0.60	120	0.84	0.006	0.10
Ni _{0.75} Cu _{0.25} / C	0.86	0.75	80	2.45	0.015	0.28
Ni _{0.25} Cu _{0.75} / C	0.95	0.80	51	5.60	0.023	0.62

Electrocatalytic	Catalyst	C_{dl}	ECSA	RF
Process		(mF·cm ⁻²)	(cm ²)	
	Cu/C	1.07	30.57	436.71
	Ni/C	1.13	32.28	461.14
HER	Ni _{0.5} Cu _{0.5} /C	1.24	35.42	506
	Ni _{0.75} Cu _{0.25} /C	2.71	77.42	1106
	Ni _{0.25} Cu _{0.75} /C	4.05	115.71	1653
	Cu/C	0.78	19.5	278.57
	Ni/C	0.80	20	285.71
OER	Ni _{0.5} Cu _{0.5} /C	0.87	21.75	310.71
	Ni _{0.75} Cu _{0.25} /C	0.98	24.5	350
	Ni _{0.25} Cu _{0.75} /C	1.4	35	500

Table S6: The obtained C_{dl} , ECSA and RF values for different electrocatalysts in HER and OER conditions.

Catalysts	Onset Potential (V vs RHE)	$\eta_{10} \ (mV)$	Reference
Ni _{0.25} Cu _{0.75} /C	1.44	400	This study
RuO ₂	1.48	410	This study
RuO ₂	1.51	370	S11
IrO ₂	1.50	340	S12
RuO ₂ NPs	1.54	460	S13
CoNi1@C	1.53	335	S14
FeNi4.34@FeNi-foil	1.45	283	S15
Pt-Ni@PCN920	1.50	290	S16
CCVG@CoNC ₈₀₀	1.40	357	S17
Co@NCNSs-900	1.51	360	S18
NiMo-FG	1.55	338	S19
Ni@Ni ₂ P/N-CNF-CN	1.46	269	S20
FCC@CNOs/GC	1.40	320	S21
CoFe@NC-SE	1.46	390	S22

Table S7: Comparison of OER performances with previously reported electrocatalysts.

Catalysts	Onset Potential (mV vs RHE)	η ₁₀ (mV vs RHE)	Reference
Ni _{0.25} Cu _{0.75} /C	75	184	This study
Ni@NC@MoS ₂	18	82	S23
0.02Ni–MoP	79	102	S24
Ni@NC-rGO	170	218	S25
Ni-Mo ₂ C-CNF	110	193	S26
CoSe ₂ /NPs	97	226	S27
Co@NPC	200	259	S28
NiCo ₂ S ₄ @NCNF	79	117	S29
NiFe@C	80	195	S30
CoP@NC	21	78	S31
NiCoOS	250	300	\$32

Table S8: Comparison of HER performances with previously reported electrocatalysts.

Catalysts	E _{Onset} (V vs RHE)	E _{1/2} (V vs RHE)	Reference
Ni _{0.25} Cu _{0.75} /C	0.95	0.80	This study
S-PtNiCu	0.89	0.767	S 33
Pt/C	0.98	0.872	S33
C ₆₀ -SWCNT ₁₅	0.91	0.84	S34
NiCo ₂ S ₄ @g-C ₃ N ₄ -CNT	0.87	0.76	S35
(Fe, Co) NCs	0.88	0.80	S 36
Zn/Co@C-NCNF	0.86	0.76	S37
CoNi/NG	0.97	0.85	S38
Cu@NCNT/Co _x O _y	0.95	0.82	S39
Pt ₂ Pd ₃ /CKN	0.90	0.82	S40
Zn ₆ Co_Fe	0.97	0.89	S41
N-C03O4@NC-2	0.89	0.77	S42
Fe ₂₈ /Ni ₂ -NPCF	0.96	0.88	S43

Table S9: Comparison of ORR performances with previously reported electrocatalysts.



with various composition

Figure S2. Slab model and OH adsorption on different electrocatalyst's surface.



Figure S3. (A-B), (C-D) and (E-F) EDS analysis and elemental mapping images of the $Cu_{0.5}Ni_{0.5}/C$, $Cu_{0.25}Ni_{0.75}/C$ and $Cu_{0.75}Ni_{0.25}/C$ electrocatalysts, respectively.



Figure S4. (A-B) TEM images of the Ni/C and Cu/C electrocatalysts, respectively.



Figure S5. XPS spectra of the Ni/C electrocatalyst: (A-D) survey spectra, C 1s, O 1s and Ni 2p, respectively.



Figure S6. XPS spectra of the Cu/C electrocatalyst: (A-D) survey spectra, C 1s, O 1s and Cu 2p, respectively.



Figure S7. XPS spectra of the $Cu_{0.5}Ni_{0.5}/C$ electrocatalyst: (A-E) survey spectra, C 1s, O 1s, Cu 2p and

Ni 2p, respectively.



Figure S8. XPS spectra of the $Cu_{0.25}Ni_{0.75}/C$ electrocatalyst: (A-E) survey spectra, C 1s, O 1s, Cu 2p and

Ni 2p, respectively.



Figure S9. LSVs of the $Ni_{0.75}Cu_{0.25}/C$ (green), $Ni_{0.50}Cu_{0.50}/C$ (wine) and $Ni_{0.25}Cu_{0.75}/C$ (purple) nanocatalysts showing the NiOOH formation peak use for area integration.



Figure S10. CVs of the as-synthesized electrocatalysts in N_2 and O_2 -saturated 0.5 M NaOH solution.

References

S1. Kresse, G., G. kresse and d. joubert, phys. rev. b 59, 1758 (1999). Phys. Rev. B 1758, 59, 1999.

S2. Kresse, G.; Furthmüller, J., Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996**, *54* (16), 11169-11186.

S3. Blöchl, P. E., Projector augmented-wave method. Phys. Rev. B 1994, 50 (24), 17953.

S4. Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C., Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation. *Phys. Rev. B* **1992**, *46* (11), 6671.

S5. Vanderbilt, D., Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. *Phys. Rev. B* **1990**, *41* (11), 7892.

S6. He, T.; Zhang, C.; Will, G.; Du, A., Cobalt porphyrin supported on graphene/Ni (111) surface:
Enhanced oxygen evolution/reduction reaction and the role of electron coupling. *Catal. Today* **2018**, *5*, 341-345.

S7. He, T.; Matta, S. K.; Will, G.; Du, A., Transition-metal single atoms anchored on graphdiyne as high-efficiency electrocatalysts for water splitting and oxygen reduction. *Small Methods* **2019**, *3* (9), 1800419.

S8. Kibsgaard, J.; Tsai, C.; Chan, K.; Benck, J. D.; Nørskov, J. K.; Abild-Pedersen, F.; Jaramillo,
T. F., Designing an improved transition metal phosphide catalyst for hydrogen evolution using experimental and theoretical trends. *Energ. Environ. Sci.* 2015, *8* (10), 3022-3029.

S9. Popczun, E. J.; Read, C. G.; Roske, C. W.; Lewis, N. S.; Schaak, R. E., Highly active electrocatalysis of the hydrogen evolution reaction by cobalt phosphide nanoparticles. *Angew. Chem. Id. Ed.* **2014**, *126* (21), 5531-5534.

S10. Popczun, E. J.; McKone, J. R.; Read, C. G.; Biacchi, A. J.; Wiltrout, A. M.; Lewis, N. S.; Schaak, R. E., Nanostructured nickel phosphide as an electrocatalyst for the hydrogen evolution reaction. *J. Am. Chem. Soc.* **2013**, *135* (25), 9267-9270.

S11. De Silva, U.; Masud, J.; Zhang, N.; Hong, Y.; Liyanage, W. P.; Zaeem, M. A.; Nath, M., Nickel telluride as a bifunctional electrocatalyst for efficient water splitting in alkaline medium. *J. Mater. Chem. A*, **2018**, *6*, 7608-7622.

S12. Wu, X.; Han, S.; He, D.; Yu, C.; Lei, C.; Liu, W.; Zheng, G.; Zhang, X.; Lei, L., Metal Organic Framework Derived Fe-Doped CoSe₂ Incorporated in Nitrogen-Doped Carbon Hybrid for Efficient Hydrogen Evolution. *ACS Sustainable Chem. Eng.* **2018**, *6*, 8672-8678.

S13. Leal-Rodríguez, C.; Rodríguez-Padrón, D.; Alothman, Z. A.; Cano, M.; Giner-Casares, J. J.; Muñoz-Batista, M. J.; Luque, R., Thermal and light irradiation effects on the electrocatalytic performance of hemoglobin modified Co 3 O 4-gC 3 N 4 nanomaterials for the oxygen evolution reaction. *Nanoscale*, **2020**, *12*(*15*), 8477-8484.

S14. Zhang, X.; Luo, J. S.; Wan, K.; Plessers, D.; Sels, B.; Song, J. X.; Chen, L. G.; Zhang,
T.; Tang, P. Y.; Morante, J. R.; Arbiol, J.; Fransaer, J., From rational design of a new bimetallic
MOF family with tunable linkers to OER catalysts. *J. Mater. Chem. A* 2019, *7* (4), 1616-1628.

S15. Qazi, U. Y.; Yuan, C. Z.; Ullah, N.; Jiang, Y. F.; Imran, M.; Zeb, A.; Zhao, S. J.; Javaid,
R.; Xu, A. W., One-Step Growth of Iron-Nickel Bimetallic Nanoparticles on FeNi Alloy Foils:
Highly Efficient Advanced Electrodes for the Oxygen Evolution Reaction. *ACS Appl. Mater. Interfaces* 2017, 9 (34), 28627-28634.

S16. Nadeem, M.; Yasin, G.; Bhatti, M. H.; Mehmood, M.; Arif, M.; Dai, L. M., Pt-M bimetallic nanoparticles (M = Ni, Cu, Er) supported on metal organic framework-derived N-doped

nanostructured carbon for hydrogen evolution and oxygen evolution reaction. *J. Power Sources* **2018**, *402*, 34-42.

S17. Zhang, Y. Y.; Sun, H. H.; Qiu, Y. F.; Ji, X. Y.; Ma, T. G.; Gao, F.; Ma, Z.; Zhang, B. X.; Hu, P. G., Multiwall carbon nanotube encapsulated Co grown on vertically oriented graphene modified carbon cloth as bifunctional electrocatalysts for solid-state Zn-air battery. *Carbon* **2019**, *144*, 370-381.

S18. Zheng, D. D.; Ci, S. Q.; Cai, P. W.; Wang, G. X.; Wen, Z. H., Nitrogen-Doped Carbon Nanosheets Encapsulating Cobalt Nanoparticle Hybrids as High-Performance Bifunctional Electrocatalysts. *ChemElectroChem* **2019**, *6* (10), 2683-2688.

S19. Jeong, S.; Hu, K. L.; Ohto, T.; Nagata, Y.; Masuda, H.; Fujita, J.; Ito, Y., Effect of Graphene Encapsulation of NiMo Alloys on Oxygen Evolution Reaction. *ACS Catal.* **2020**, *10* (1), 792-799.

S20. Tao, X.; Luo, S.; Tian, C. H.; Qing, Y.; Lu, X. H.; Yan, N.; Wu, Y. Q., Ni@Ni2P Encapsulation in Interconnected N-Doped Carbonized Cellulose Nanofibril Network for Efficient Oxygen Evolution Reaction. *ACS Sustainable Chem. Eng.* **2020**, *8* (4), 1859-1867.

S21. Xu, S. S.; Wang, M. Z.; Saranya, G.; Chen, N.; Zhang, L. L.; He, Y.; Wu, L. L.; Gong,
Y. T.; Yao, Z. Q.; Wang, G. K.; Wang, Z. B.; Zhao, S. J.; Tang, H.; Chen, M. Y.; Gou, H. Y.,
Pressure-driven catalyst synthesis of Co-doped Fe3C@Carbon nano-onions for efficient oxygen
evolution reaction. *Appl. Catal. B-Environ.* 2020, 268, 118385.

S22. Samanta, A.; Raj, C. R., Bifunctional nitrogen-doped hybrid catalyst based on onion-like carbon and graphitic carbon encapsulated transition metal alloy nanostructure for rechargeable zinc-air battery. *J. Power Sources* **2020**, *455*, 227975.

S23

S23. Shah, S. A.; Shen, X. P.; Xie, M. H.; Zhu, G. X.; Ji, Z. Y.; Zhou, H. B.; Xu, K. Q.; Yue,
X. Y.; Yuan, A. H.; Zhu, J.; Chen, Y., Nickel@Nitrogen-Doped Carbon@MoS2 Nanosheets: An
Efficient Electrocatalyst for Hydrogen Evolution Reaction. *Small* 2019, *15* (9), 1804545.

S24. Xiao, W. P.; Zhang, L.; Bukhvalov, D.; Chen, Z. P.; Zou, Z. Y.; Shang, L.; Yang, X. F.; Yan, D. Q.; Han, F. Y.; Zhang, T. R., Hierarchical ultrathin carbon encapsulating transition metal doped MoP electrocatalysts for efficient and pH-universal hydrogen evolution reaction. *Nano Energy* **2020**, *70*, 104445.

S25. Cao, Y. Y.; Lu, Y. D.; Ang, E. H.; Geng, H. B.; Cao, X. Q.; Zheng, J. W.; Gu, H. W., MOFderived uniform Ni nanoparticles encapsulated in carbon nanotubes grafted on rGO nanosheets as bifunctional materials for lithium-ion batteries and hydrogen evolution reaction. *Nanoscale* **2019**, *11* (32), 15112-15119.

S26. Sun, J. H.; Liu, J. N.; Chen, H.; Han, X.; Wu, Y.; He, J.; Han, C.; Yang, G. C.; Shan, Y.
P., Strongly coupled Mo2C and Ni nanoparticles with in-situ formed interfaces encapsulated by porous carbon nanofibers for efficient hydrogen evolution reaction under alkaline conditions. *J. Colloid Interf. Sci.* 2020, 558, 100-105.

S27. Liu, W. Q.; Zhou, Y. M.; Bao, J. H.; Wang, J. Q.; Zhang, Y. W.; Sheng, X. L.; Xue, Y.; Guo, C.; Chen, X. C., Co-CoO/ZnFe2O4 encapsulated in carbon nanowires derived from MOFs as electrocatalysts for hydrogen evolution. *J. Colloid Interf. Sci.* **2020**, *561*, 620-628.

S28. Wang, H. J.; Ma, N. M.; Cao, Y. H.; Yu, H.; Zuo, J. L.; Fan, W.; Peng, F., Cobalt and cobalt oxide supported on nitrogen-doped porous carbon as electrode materials for hydrogen evolution reaction. *Int. J. of Hydrogen Energ.* **2019**, *44* (7), 3649-3657.

S29. Xu, J. C.; Rong, J.; Qiu, F. X.; Zhu, Y.; Mao, K. L.; Fang, Y. Y.; Yang, D. Y.; Zhang, T., Highly dispersive NiCo2S4 nanoparticles anchored on nitrogen-doped carbon nanofibers for efficient hydrogen evolution reaction. *J. Colloid Interf. Sci.* **2019**, *555*, 294-303.

S30. Park, S. W.; Kim, I.; Oh, S. I.; Kim, J. C.; Kim, D. W., Carbon-encapsulated NiFe nanoparticles as a bifunctional electrocatalyst for high-efficiency overall water splitting. *J. Catal.* **2018**, *366*, 266-274.

S31. Yang, F. L.; Chen, Y. T.; Cheng, G. Z.; Chen, S. L.; Luo, W., Ultrathin Nitrogen-Doped Carbon Coated with CoP for Efficient Hydrogen Evolution. *ACS Catal.* **2017**, *7* (6), 3824-3831.

S32. Bai, Z. Y.; Li, S. S.; Fu, J.; Zhang, Q.; Chang, F. F.; Yang, L.; Lu, J.; Chen, Z. W., Metalorganic framework-derived Nickel Cobalt oxysulfide nanocages as trifunctional electrocatalysts for high efficiency power to hydrogen. *Nano Energy* **2019**, *58*, 680-686.

S33. Wu, D.; Zhang, W.; Lin, A.; Cheng, D., Low Pt-Content Ternary PtNiCu Nanoparticles with Hollow Interiors and Accessible Surfaces as Enhanced Multifunctional Electrocatalysts. *ACS Appl. Mater. Intefaces*, **2020**, *12*, 9600-9608.

S34. Gao, R.; Dai, Q.; Du, F.; Yan, D.; Dai, L., C60-Adsorbed Single-Walled Carbon Nanotubes as Metal-Free, pH Universal, and Multifunctional Catalysts for Oxygen Reduction, Oxygen Evolution, and Hydrogen Evolution. *J. Am. Chem. Soc.* **2019**, *141*, 11658–11666.

S35. Han, X.; Zhang, W.; Ma, X.; Zhong, C.; Zhao, N.; Hu, W.; Deng, Y., Identifying the Activation of Bimetallic Sites in NiCo2S4@ g-C3N4-CNT Hybrid Electrocatalysts for Synergistic Oxygen Reduction and Evolution. *Adv. Mater.*, **2019**, *31*(18), 1808281.

S36. Xi, J.; Xia, Y.; Xu, Y.; Xiao, J.; Wang, S. (Fe,Co)@Nitrogen-Doped Graphitic Carbon Nanocubes Derived from Polydopamine-Encapsulated Metal-Organic Frameworks as a Highly Stable and Selective Non-Precious Oxygen Reduction Electrocatalyst. *Chem. Commun.* **2015**, *51*, 10479-10482.

S37. Niu, Q.; Guo, J.; Chen, B.; Nie, J.; Guo, X.; Ma, G., Bimetal-organic frameworks/polymer core-shell nanofibers derived heteroatom-doped carbon materials as electrocatalysts for oxygen reduction reaction. *Carbon*, **2017**, *114*, 250-260.

S38. Yang, L.; Wang, D.; Lv, Y.; Cao, D., Nitrogen-doped graphitic carbons with encapsulated CoNi bimetallic nanoparticles as bifunctional electrocatalysts for rechargeable Zn–Air batteries. *Carbon*, **2019**, *144*, 8-14.

S39. Zhao, X.; Li, F.; Wang, R.; Seo, J.-M.; Choi, H.-J.; Jung, S.-M.; Mahmood, J.; Jeon, I.-Y.; Baek, J.-B. Controlled Fabrication of Hierarchically Structured Nitrogen-Doped Carbon Nanotubes as a Highly Active Bifunctional Oxygen Electrocatalyst. *Adv. Funct. Mater.* **2017**, *27*, 1605717.

S40. Li, D.; Fang, H.; Yu, J.; Xu, M.; Li, T.; Wang, J., Porous carbon supported PtPd alloy nanoparticles derived from N-Heterocyclic carbene bimetal complex as efficient bifunctional electrocatalysts. *Electrochim. Acta*, **2020**, *337*, 135855.

S41. Xiong, Y.; Yang, Y.; DiSalvo, F. J.; Abruña, H. D., Metal–organic-framework-derived Co– Fe bimetallic oxygen reduction electrocatalysts for alkaline fuel cells. *J. Am. Chem. Soc.*, **2019**, *141*(27), 10744-10750. S42. Wang, Z.; Xu, W.; Chen, X.; Peng, Y.; Song, Y.; Lv, C.; Liu, H.; Sun, J.; Yuan, D.; Li, X.;
Guo, X.; Yang, D.; Zhang, L. Defect-Rich Nitrogen Doped Co3O4/C Porous Nanocubes Enable
High-Efficiency Bifunctional Oxygen Electrocatalysis. *Adv. Funct. Mater.* 2019, *29*, 1902875.

S43. Guo, J.; Shu, J.; Nie, J.; Ma, G., Fe/Ni bimetal and nitrogen co-doped porous carbon fibers as electrocatalysts for oxygen reduction reaction. *J. Colloid. Interface Sci*, **2020**, *560*, 330-337.