## **Electronic Supplementary Information**

# Manipulating the Electronic State of Tungsten Carbide Using CoNi@N-doped Carbon Derived from Bimetallic MOF for Enhanced Electroreduction Reactions

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#### **S1. Materials and Instruments**

All chemicals were obtained from commercial sources and used without further purification. Methanol (CH<sub>3</sub>OH, AR), cobalt(II) nitrate hexahydrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 99%), nickel nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, AR), 2-methylimidazole (C<sub>4</sub>H<sub>6</sub>N<sub>2</sub>, AR), ammonium molybdate (99%, AM) and tungsten chloride (99%, WCl<sub>6</sub>) were purchased from Energy Chemical (Shanghai, China).

The contents of various metals in all samples were analyzed using an Agilent ICP-OES 730 inductively coupled plasma atomic emission spectrometer (ICP-AES). Power X-ray diffraction (PXRD) was carried out on a Rigaku Saturn 70 diffractometer at 113 K with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  A). Nitrogen sorption measurement was conducted using a Micromeritics ASAP 2020 system at 77 K. Scanning electron microscopy (SEM) images were acquired on JEOL JSM-7800F at an acceleration voltage of 10 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Thermo ESCALAB 250Xi high-performance electron spectrometer using monochromatized AlKa (hv = 1486.7 eV) as the excitation source. The transmission electron microscopy (TEM) images were obtained on Tecnai G2 20 with an electron acceleration energy of 200 kV. Raman scattering spectra were recorded with a Horiba LabRAM HR Evolution (Japan) using the 532 nm line of Ar<sup>+</sup> for excitation.

#### **S2. Experimental Section**

**Preparation of ZIF-8 nanocrystals:** The synthesis of ZIF-8 was based on the previous procedure with no modifications.<sup>1</sup> 1.68 g of  $Zn(NO_3)_2 \cdot 6H_2O$  is dissolved in 80 mL methanol. The solution is then mixed with 80 mL of methanol containing about 3.70 g of 2-Methylimidazole while stirring. Both the solutions are mixed for some time and then incubated for 24 h. The product was separated by centrifugation and washed thoroughly with methanol for twice, and finally dried overnight at 50 °C. The ZIF-8 powder was further activated at 200 °C under vacuum for 24 h prior to use.

Preparation of CoNi(1:1)-ZIF, CoNi(1:2)-ZIF, CoNi(2:1)-ZIF, ZnNi-ZIF, ZIF-67 nanocrystals: The synthesis of ZIF-8 was mainly based on a previous procedure with

simple modifications.<sup>1</sup> Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (3 mmol) and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (3 mmol) are dissolved in 80 mL methanol. The solution is then mixed with 80 mL of methanol containing about 3.7 g of 2-Methylimidazole while stirring. Both the solutions are mixed for some time and then incubated for 24 h. After that the resulting light purple precipitates were collected by centrifugation and washed with methanol in sequence for at least three times followed by overnight drying at 50 °C. The CoNi(1:1)-ZIF powder was further activated at 260 °C under vacuum for 24 h prior to use. CoNi(1:2)-ZIF and CoNi(2:1)-ZIF were synthesized by the same method, except the molar ratio of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O is different. The total molar amount of (Co + Ni) was fixed to be 6 mmol. ZIF-67 and ZnNi-ZIF were synthesized by the same method except that the selected salts were Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O.

**Preparation of AM@ZIF-8, WCl<sub>6</sub>@ZIF-8, AM-WCl<sub>6</sub>@ZIF-8, AM@CoNi-ZIF, AM-WCl<sub>6</sub>@CoNi-ZIF: 0.5 g of the dried sample ZIF-8 was placed into a small corundum crucible, 8 wt.% ammonium molybdate was weighed, and then water was added. The AM@ZIF-8 was obtained by dipping aqueous solution of ammonium molybdate into the precursor (ZIF-8) and drying for 12 h. The WCl<sub>6</sub>@ZIF-8 was obtained by dipping aqueous solution of tungsten chloride into the precursor (ZIF-8) and drying for 12 h. AM@CoNi-ZIF was synthesized by the same method, except the precursors ZIF-8 was adjusted to CoNi-ZIF. The 0.5 g dried sample CoNi-ZIF was placed in a small corundum crucible, weighed with 8wt.% ammonium molybdate and 8 wt.% tungsten chloride, and then added with deionized water. The precursor (ZIF-8) was immersed in ammonium molybdate and tungsten chloride and dried for 12 h to obtain AM-WCl<sub>6</sub>@ZIF-8. The precursor (CoNi-ZIF) was immersed in ammonium molybdate and tungsten chloride and dried for 12 h to obtain AM-WCl<sub>6</sub>@CoNi-ZIF.** 

Preparation of  $Mo_2C@NC$ , WC@NC, Co@NC, Ni@NC, CoNi@NC, CoNi@Mo\_2C@NC,  $M_xC@NC$ ,  $CoNi(x)@M_xC@NC$ ,  $CoNi@M_xC@NC$  (4 wt.%, 8wt.%, 16wt.%  $M_xC$ ): For the synthesis of  $Mo_2C@NC$  catalyst, 0.5 g of the dried sample AM@ZIF-8 was placed into a small corundum crucible. Then, the crucible was transferred to a tube furnace, and the sample was calcined at 800 °C (5 °C/min) for 2 h under an atmosphere of high-purity N<sub>2</sub>. After calcination, Mo<sub>2</sub>C@NC was obtained as black powders. WC@NC, Co@NC, Ni@NC, CoNi@NC, Mo<sub>2</sub>C-CoNi@NC, M<sub>x</sub>C@NC, CoNi(x)@M<sub>x</sub>C@NC and CoNi@xM<sub>x</sub>C@NC were synthesized by the same method, except the hybrid precursor AM@ZIF-8 was adjusted to WCl<sub>6</sub>@ZIF-8, ZIF-67, ZnNi-ZIF, CoNi-ZIF, AM@CoNi-ZIF, AM-WCl<sub>6</sub>@ZIF-8, AM-WCl<sub>6</sub>@CoNi-ZIF and xAM-WCl<sub>6</sub>@CoNi-ZIF.

Electrochemical measurements: All electrochemical measurements were performed by an electrochemical workstation (CHI 760E, CH Instruments Ins, Shanghai). Electrochemical tests were performed in a standard three-electrode system under alkaline condition (1 M KOH, pH = 13.8) with a prepared electrode as the working electrode, a graphite rod as the counter electrode, and a Hg/HgO as the reference electrode. Typically, 2 mg electrocatalyst was dispersed in 980  $\mu$ L ethanol, and then 10 µL of Nafion® solution (5 wt.%) were added. The suspension was immersed in an ultrasonic bath for 40 min to prepare a homogeneous ink. After ultrasonication, 28 µL of the homogeneous suspension was pipetted onto the surface of the carbon fiber (CF) (surface area: 1.0 cm<sup>2</sup>). Then, the working electrode was dried under the irradiation of infrared lamp. Cyclic voltammetry (CV), LSV, chronoamperometry (i-t) tests, and the electrochemical impedance spectroscopy (EIS) were conducted by CHI 760E electrochemical workstation. All the potentials were to a reversible hydrogen electrode (RHE) computed by the Nernst equation:  $E_{RHE} = E_{Hg/HgO} + 0.098 + 0.0592 pH$ . The electrodes were cycled 20 times so as to stabilize the electrochemical responses before the performance measurements. Then, the polarization curves were recorded by using LSV with a scan rate of 5 mV s<sup>-1</sup> in 1 M KOH solution. Electrochemical impedance spectra (EIS) were recorded in the frequency range from  $1 \times 10^5$  to 0.1 Hz. What's more, the measurements of double-layer capacitance (Cdl) were carried out by cycling the electrodes from 0.0268 to 0.1268 V (vs. RHE) (in 1 M KOH) at increasing sweep rates between 25 and 100 mV s<sup>-1</sup>. The electrochemical stability tests were conducted using the chronoamperometric i-t curve at a current density of 10 mA cm<sup>-2</sup> for 20 h.

**Catalytic tests for** *p***-NP electroreduction:** The electroreduction of *p*-NP experiment was carried out in a three-electrode system. The three-electrode system was carried out in an undivided electrolyzer. 1 M KOH containing 10 mM *p*-NP was used in the cathode compartment. In order to analyze the product, 20  $\mu$ L of the electrolyte solution was periodically collected from the electrolyte solution during reaction and diluted into appropriate concentration. The conversion rate of *p*-NP was measured by UV-vis spectrophotometer.

**Model construction:** In order to detect the charge transfer between WC/Mo<sub>2</sub>C and CoNi, three models of WC,  $M_xC@NC$  and CoNi@M<sub>x</sub>C@NC were constructed. Nine adsorption models were constructed to optimize the appropriate water reduction mechanism and the possible adsorption sites on the CoNi@M<sub>x</sub>C@NC.

**Computational methods:** All the calculations were performed in the framework of the density functional theory with the projector augmented plane-wave method, as implemented in the Vienna ab initio simulation package.<sup>2</sup> The generalized gradient approximation proposed by Perdew-Burke-Ernzerhof (PBE) was selected for the exchange-correlation potential.<sup>3</sup> The energy criterion was set to 10-6 eV in the iterative solution of the Kohn-Sham equation. The cut-off energy for plane wave was set to 500 eV. A vacuum spacing of 20 Å was applied perpendicular to the slab to quell the interlaminar interactions. All the structures were relaxed until the residual forces on the atoms decreased to less than 0.03 eV/Å. Visualization and data analysis were carried out with the help of VESTA<sup>4</sup> and VASPKIT<sup>5</sup> code.



Fig. S1. The corresponding EDS spectrum of  $Co_1Ni_1@M_xC@NC$  crystal shows the coexistence of Co, Ni, Mo, W, C and N in single particle.



Fig. S2. EDS elemental mapping images of single  $Co_1Ni_1@M_xC@NC$  particle. The Ni and Co elements are mainly concentrated on the center of the particle, and the Mo and W species are distributed in the whole particle.



**Fig. S3.** HRTEM image of Co<sub>1</sub>Ni<sub>1</sub>@M<sub>x</sub>C@NC.



Fig. S4. Raman spectra for  $Co_1Ni_1@M_xC@NC$ ,  $M_xC@NC$  and  $Co_1Ni_1@NC$ .



Fig. S5. Powder XRD patterns of simulated ZIF-8, as-synthesized ZIF-8 and CoNi-ZIF.



Fig. S6. (a)  $N_2$  sorption isotherms for CoNi-ZIF and Co<sub>1</sub>Ni<sub>1</sub>@M<sub>x</sub>C@NC. Filled and open symbols represent adsorption and desorption branches, respectively. (b) Pore size distribution for Co<sub>1</sub>Ni<sub>1</sub>@M<sub>x</sub>C@NC.



Fig. S7. High-resolution (a) XPS survey spectrum, (b) C 1s and (c) N 1s spectra of the  $Co_1Ni_1@M_xC@NC$ , WC@NC, Mo\_2C@NC and  $Co_1Ni_1@NC$  samples.



**Fig. S8.** (a) HER polarization curves of different catalysts. (b) Tafel plots at a scan rate of 5 mV/s.



Fig. S9. (a) PXRD patterns and (b) HER polarization curves of  $Co_1Ni_1@M_xC@NC$  with different  $M_xC$  contents in an electrolyte solution of 1 M KOH.



**Fig. S10.** CV curves in the non-Faradaic region from 0.0268 to 0.1268 V of (a)  $Co_1Ni_2@M_xC@NC$  and (c)  $Co_2Ni_1@M_xC@NC$ ; Capacitive current of (b)  $Co_1Ni_2@M_xC@NC$  and (d)  $Co_2Ni_1@M_xC@NC$  in 1 M KOH.



**Fig. S11.** EIS spectra of CoNi@M<sub>x</sub>C@NC with different Co/Ni ratios examined at the potential of -0.1 V in 1 M KOH.



Fig. S12. (a) XRD, (b) SEM, (c) TEM and (d) HRTEM images of  $Co_1Ni_1@M_xC@NC$  after cycling test.



**Fig. S13.** (a) The  $Co_1Ni_1@M_xC@NC$  model (CoNi-111 facet). (b and c) the adsorption of  $H_2O$  on WC models by DFT calculation.



**Fig. S14.** UV-vis absorption spectra of *p*-NP (10 mM) upon electrocatalytic time over different samples.

**Table S1.** The contents of various metals in  $Mo_2C@NC$ ,  $M_xC@NC$  and  $CoNi@M_xC@NC$  analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES).

Sample	Mo <sub>2</sub> C @NC	M <sub>x</sub> C@ NC	Co <sub>1</sub> Ni <sub>1</sub> @M <sub>x</sub> C @NC	Co <sub>1</sub> Ni <sub>2</sub> @M <sub>x</sub> C @NC	Co <sub>2</sub> Ni <sub>1</sub> @M <sub>x</sub> C @NC
W(mol%)	0	11.19	11.38	10.52	10.45
Mo(mol%)	9.64	11.47	9.65	8.12	8.21
Co(mol%)	0	0	26.57	17.59	37.87
Ni(mol%)	0	0	26.39	35.52	16.84

Entry	Catalysts	Loading	$\eta_{\rm 10}$	Reference
		(mg cm <sup>-2</sup> )	(mV)	
1	Co <sub>1</sub> Ni <sub>1</sub> @M <sub>x</sub> C@NC	0.06	103	This work
2	Pt/C	0.06	50	This work
3	Pt-MoO <sub>2</sub> @PC	11.6	20	6
4	(Mo <sub>2</sub> C) <sub>0.24</sub> -(WC) <sub>0.52</sub> - QDs/NG	0.28	133	7
5	Co-Mo <sub>2</sub> C-0.020	0.14	118	8
6	Bulk Mo <sub>2</sub> C	1.1	210	9
7	Mo <sub>2</sub> C/3D GF	0.285	177	10
8	Mo <sub>2</sub> C nanooctahedrons	0.8	151	11
9	NiCo-WC	20	145	12
10	MoP-Pv	0.05	162	13

Table S2. Performance comparison of the  $Co_1Ni_1@M_xC@NC$  with the related reported

electrocatalysts for HER.

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