Supporting Information

Efficient Alkaline Hydrogen Evolution on Atomically Dispersed Ni–N_x Species Anchored Porous Carbon with Embedded Ni Nanoparticles by Accelerating Water Dissociation Kinetics

Chaojun Lei,[a] Yu Wang,[d] Yang Hou,*[a] Pan Liu,[e] Jian Yang,[a] Tao Zhang,[b] Xiaodong Zhuang,[b] Mingwei Chen,[e] Bin Yang,[a] Lecheng Lei,[a] Chris Yuan,[f] Ming Qiu,*[c] Xinliang Feng*[b]

[a] Key Laboratory of Biomass Chemical Engineering of Ministry of Education, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China. E-mail: yhou@zju.edu.cn

[b] Center for Advancing Electronics Dresden (cfaed) & Department of Chemistry and Food Chemistry, Technische Universitaet Dresden, 01062 Dresden, Germany.
E-mail: xinliang.feng@tu-dresden.de

[c] Institute of Nanoscience and Nanotechnology, College of Physical Science and Technology, Central China Normal University, Wuhan 430079, China.
E-mail: qium@mail.ccnu.edu.cn

[d] Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201204, China

[e] WPI Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan & CREST, JST, 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan

[f] Department of Mechanical and Aerospace Engineering, Case Western Reserve University, 10900 Euclid Ave, Cleveland, OH 44106, United States

Experimental Section

Synthesis of Ni NP|Ni-N-C

For the synthesis of Ni NP|Ni-N-C, 0.07 g $NiCl_2$•$6H_2O$ and 0.35 g dicyanamide were dissolved in 20 mL water under stirring and then transferred into a Teflon-lined stainless steel autoclave. The autoclave was heated to 200 °C and maintained for 4 h. The resulting powder was pyrolyzed at 900 °C for 3 h under Ar atmosphere. The pyrolyzed sample was further soaked in 0.5 M H_2SO_4 for 10 h to remove accessible Ni species.

Synthesis of Ni NP|Ni-N-C after substantial acid etching (Ni-N-C)

For the synthesis of Ni-N-C, 0.07 g $NiCl_2$•$6H_2O$ and 0.35 g dicyanamide were dissolved in 20 mL water under stirring and then transferred into a Teflon-lined stainless steel autoclave. The autoclave was heated to 200 °C and maintained for 4 h. The resulting powder was pyrolyzed at 900 °C for 3 h under Ar atmosphere. The pyrolyzed sample was further soaked in 0.5 M H_2SO_4 for 48 h to remove the Ni-containing nanoparticles.

Synthesis of Ni NP

For the synthesis of Ni NP, 0.07 g $NiCl_2$•$6H_2O$ and 0.35 g dicyanamide were dissolved in 20 mL water under stirring and then transferred into a Teflon-lined stainless steel autoclave. The autoclave was heated to 200 °C and maintained for 4 h. The resulting powder was pyrolyzed at 900 °C for 3 h under Ar atmosphere. The pyrolyzed sample was further soaked in 0.5 M H_2SO_4 for 10 h to remove accessible Ni species. The obtained Ni NP|Ni-N-C powder was heated to 600 °C and maintained for 2 h under air atmosphere. The resulting product was finally annealed in mixture atmosphere of Ar/H_2 at 300 °C for 2 h to generate Ni NP.

Synthesis of Ni NP|Ni-N-C/EG

The EG was firstly prepared by anodization of graphite foil in 0.1 M $(NH_4)_2SO_4$ solution with a Pt foil as counter electrode under 10 V for 15 s.[1] Next, the obtained EG was immersed into 20 mL mixture solution of 0.07 g $NiCl_2$•$6H_2O$ and 0.35 g dicyanamide, and further transferred into a Teflon-lined stainless steel autoclave. The autoclave was heated to 200 °C and

maintained for 4 h. Finally, the resulting electrode was pyrolyzed at 900 °C for 3 h under Ar atmosphere, followed by acid etching treatment with 0.5 M H_2SO_4 for 10 h to remove accessible Ni species. The loading amount of Ni NP|Ni-N-C/EG on graphite foil was ~ 0.24 mg cm^{-2}.

Synthesis of Ni NP|Ni-N-C/EG (700 °C)

The EG was immersed into 20 mL mixture solution of 0.07 g $NiCl_2$•$6H_2O$ and 0.35 g dicyanamide, and further transferred into a Teflon-lined stainless steel autoclave. The autoclave was heated to 200 °C and maintained for 4 h. Finally, the resulting electrode was pyrolyzed at 700 °C for 3 h under Ar atmosphere, followed by acid etching treatment with 0.5 M H_2SO_4 for 10 h to remove accessible Ni species.

Synthesis of Ni NP|Ni-N-C/EG (800 °C)

The EG was immersed into 20 mL mixture solution of 0.07 g $NiCl_2$•$6H_2O$ and 0.35 g dicyanamide, and further transferred into a Teflon-lined stainless steel autoclave. The autoclave was heated to 200 °C and maintained for 4 h. Finally, the resulting electrode was pyrolyzed at 800 °C for 3 h under Ar atmosphere, followed by acid etching treatment with 0.5 M H_2SO_4 for 10 h to remove accessible Ni species.

Synthesis of Ni NP|Ni-N-C/EG (1000 °C)

The EG was immersed into 20 mL mixture solution of 0.07 g $NiCl_2$•$6H_2O$ and 0.35 g dicyanamide, and further transferred into a Teflon-lined stainless steel autoclave. The autoclave was heated to 200 °C and maintained for 4 h. Finally, the resulting electrode was pyrolyzed at 1000 °C for 3 h under Ar atmosphere, followed by acid etching treatment with 0.5 M H_2SO_4 for 10 h to remove accessible Ni species.

Synthesis of Ni-N-C/EG

The EG was immersed into 20 mL mixture solution of 0.07 g $NiCl_2$•$6H_2O$ and 0.35 g dicyanamide, and further transferred into a Teflon-lined stainless steel autoclave. The autoclave was heated to 200 °C and maintained for 4 h. Finally, the resulting electrode was

pyrolyzed at 900 °C for 3 h under Ar atmosphere, followed by acid etching treatment with 0.5 M H_2SO_4 for 48 h to remove the Ni-containing nanoparticles. The loading amount of Ni-N-C/EG on graphite foil was ~ 0.16 mg cm^{-2}.

Synthesis of Ni NP/EG

The EG was immersed into 20 mL mixture solution of 0.07 g $NiCl_2$•$6H_2O$ and 0.35 g dicyanamide, and further transferred into a Teflon-lined stainless steel autoclave. The autoclave was heated to 200 °C and maintained for 4 h. The resulting electrode was then pyrolyzed at 900 °C for 3 h under Ar atmosphere, followed by acid etching treatment with 0.5 M H_2SO_4 for 10 h to remove accessible Ni species. The obtained Ni NP|Ni-N-C/EG electrode was heated to 600 °C and maintained 600 °C for 2 h under air atmosphere. The resulting electrode was finally annealed in mixture atmosphere of Ar/H_2 at 300 °C for 2 h to generate Ni NP/EG. The loading amount of Ni NP/EG on graphite foil was ~ 0.10 mg cm^{-2}.

Synthesis of physical mixture of Ni NP and Ni-N-C supported on EG

As a reference, the Ni NP and Ni-N-C powders were ground together to form the physical mixture of Ni NP and Ni-N-C. The obtained mixture was further loaded on the surface of EG with the loading amount of ~ 0.24 mg cm^{-2} (physical mixture/EG).

Characterization

The morphology was characterized by field emission scanning electron microscope (FESEM, Carl Zeiss NVision 40), transmission electron microscopy (TEM, JEOL JEM-2001F and Carl Zeiss, Libra 120), high-resolution TEM (HRTEM, JEOL JEM-2001F and Carl Zeiss, Libra 120), high angle annular dark-field scanning TEM (HAADF-STEM), and energy dispersive spectra (EDX, JEOL JEM-2001F and Carl Zeiss, Libra 120). X-ray diffraction (XRD) pattern was performed on a Bruker D8 Advance powder diffractometer. Fourier transform infrared spectroscopy (FTIR) was carried out using a BRUKER TENSOR II spectrometer. Raman measurement was carried out on an NTEGRA Spectra system (NT-MDT). Thermogravimetric curve was recorded on a TA SDT 2960 thermoanalyzer. The Ni contents

of samples before and after HER reactions were recorded with inductively coupled plasma mass spectrometry (ICP-MS). Nitrogen sorption isotherms were measured with a Quadrasorb Adsorption Instrument. X-ray photoelectron spectra (XPS) were performed on an AXIS Ultra DLD system (Kratos). The contact wetting angles were characterized on a "DSA-10" Kruss goniometer. X-ray absorption near edge structure (XANES) and X-ray absorption fine structure (EXAFS) measurements were tested on the BL10C beam line of Pohang light source (PLS- II, Korea).

Electrochemical measurements

Electrochemical measurements of as-prepared samples were performed using CHI 760 E electrochemical analyzer in a three-electrode configuration, which was operated with a graphite rod and an Ag/AgCl electrode as counter electrode and reference electrode, respectively. Polarization curves were obtained with a scan rate of 1 mV s^{-1} in 1.0 M KOH electrolyte. Long-term durability test was performed using chronoamperometric measurement. All of the potentials are referenced to the reversible hydrogen electrode (RHE), and voltages are iR corrected unless noted. The solution resistances are measured by electrochemical impedance spectroscopy (EIS) in this work.[2]

For overall-water-splitting tests, the electrodes were directly used as both cathode and anode with a mass loading amount of 0.24 mg cm^{-2}. Polarization curves were obtained with a scan rate of 1 mV s^{-1} in 1.0 M KOH electrolyte. Durability of the samples was assessed via using constant current electrolysis. For comparison, the commercial Ir/C and Pt/C catalysts that were drop-dried onto the EG foil with mass loading amount of 0.24 mg cm^{-2}, respectively were measured under the same experimental conditions.

First-principles calculations

All first-principles-based calculations were conducted by applying the Cambridge Serial Total Energy Package (CASTEP) in Material Studio which performs the density functional theory (DFT) plane-wave pseudopotential method to carry out first principles quantum mechanics

calculations. In the calculation, the generalized gradient approximation (GGA) within Perdew–Burke–Ernzerhof (PBE) form was used as the exchange–correlation function. The convergence tests of the total energy with respect to the k-points sampling and the energy-cutoff were carefully examined, using 3 × 3 × 1 Monkhorst-Pack k-points grid and a 800 eV energy-cutoff for plane-wave expansion. Valence states used were Ni-$3s^2 3p^6 3d^8 4s^2$, C-$2s^2 2p^2$, N-$2s^2 2p^3$, O-$2s^2 2p^4$ and H-$1s^1$. In the super-cell configuration, a sufficiently large vacuum slab (about 15 Å) was maintained. The SCF tolerance was setup to 1e - 6eV·$atom^{-1}$ for the geometrical optimization and phonon calculations.

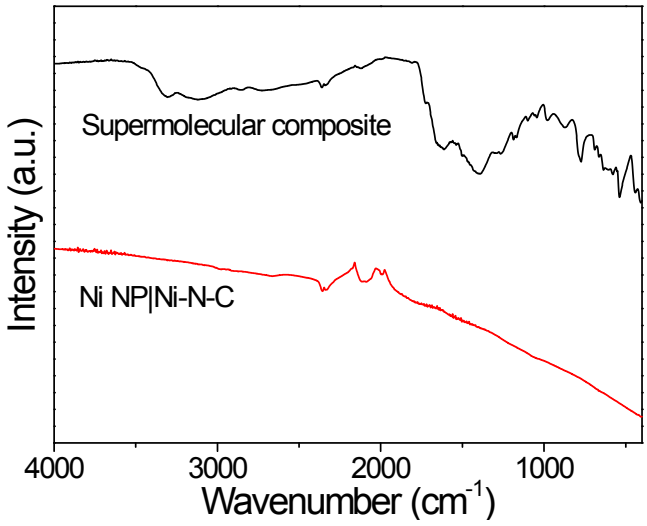


Figure S1. FTIR spectra of Ni NP|Ni-N-C and hydrothermally prepared supermolecular composite of dicyandiamide and Ni salt.

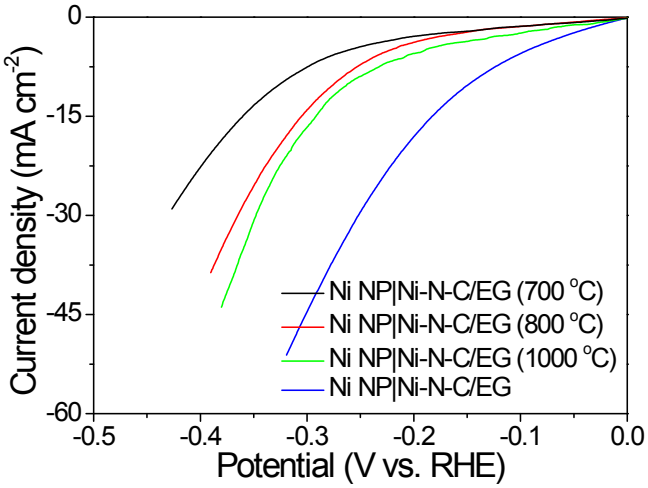


Figure S2. Polarization curves of Ni NP|Ni-N-C/EG, Ni NP|Ni-N-C/EG (700 °C), Ni NP|Ni-N-C/EG (800 °C), and Ni NP|Ni-N-C/EG (1000 °C) in 1.0 M KOH.

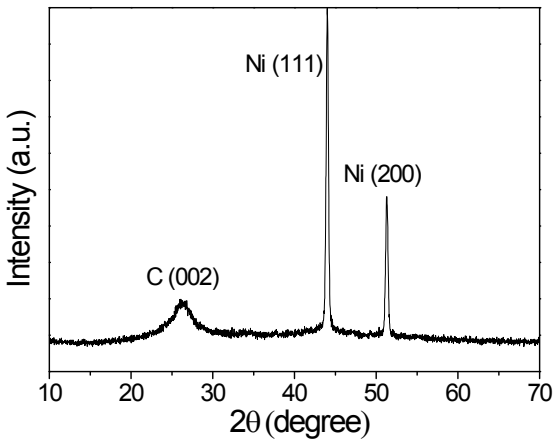


Figure S3. XRD pattern of Ni NP|Ni-N-C.

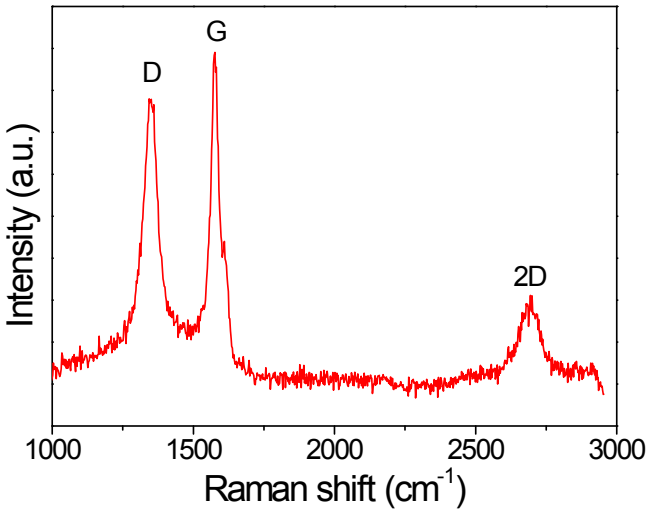


Figure S4. Raman spectrum of Ni NP|Ni-N-C.

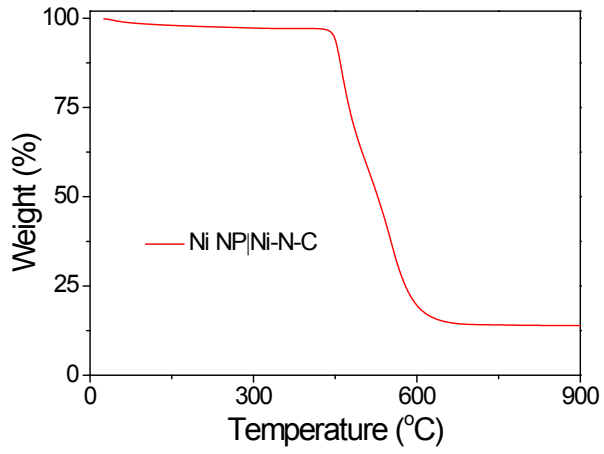


Figure S5. TGA curve of Ni NP|Ni-N-C under flowing air.

The TGA result also reveals that the content of Ni species in the Ni NP|Ni-N-C is about 11.8 wt.%, considering that the final product can be nickel oxide.

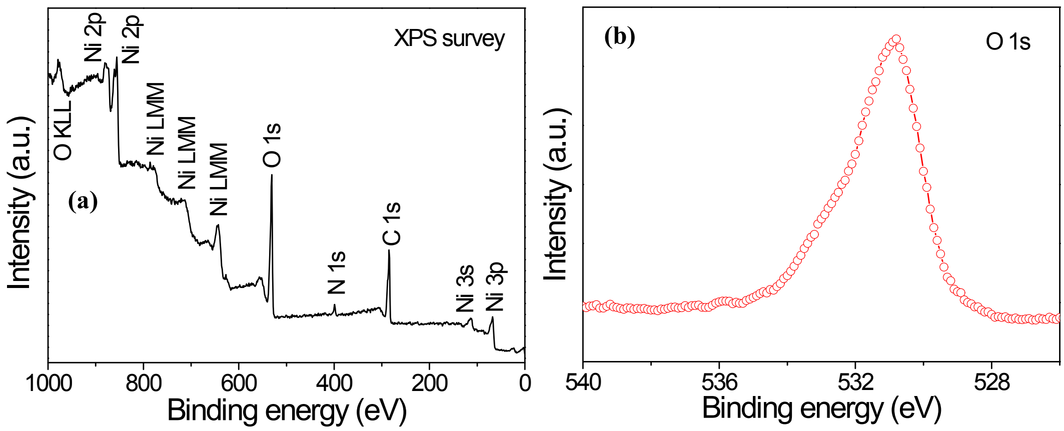


Figure S6. The XPS survey spectrum (a) and high-resolution O 1s XPS spectrum (b) of Ni NP|Ni-N-C.

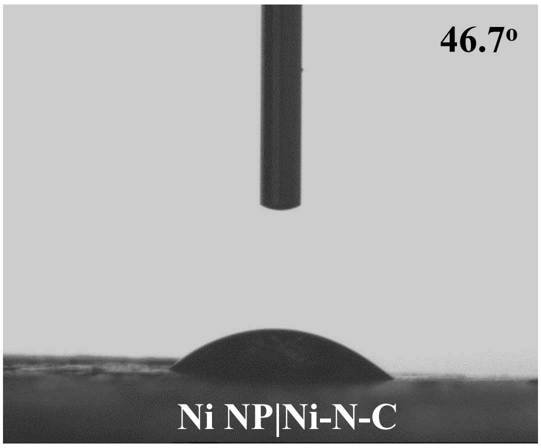


Figure S7. Contact wetting angel of Ni NP|Ni-N-C.

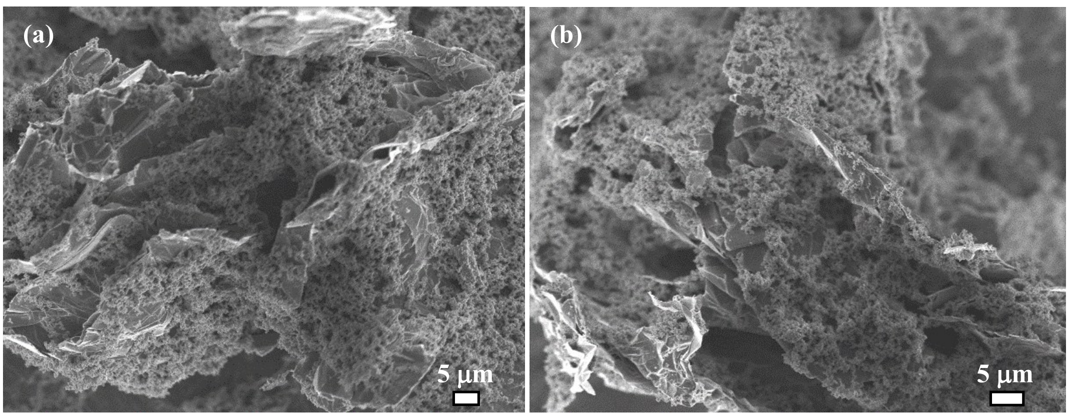
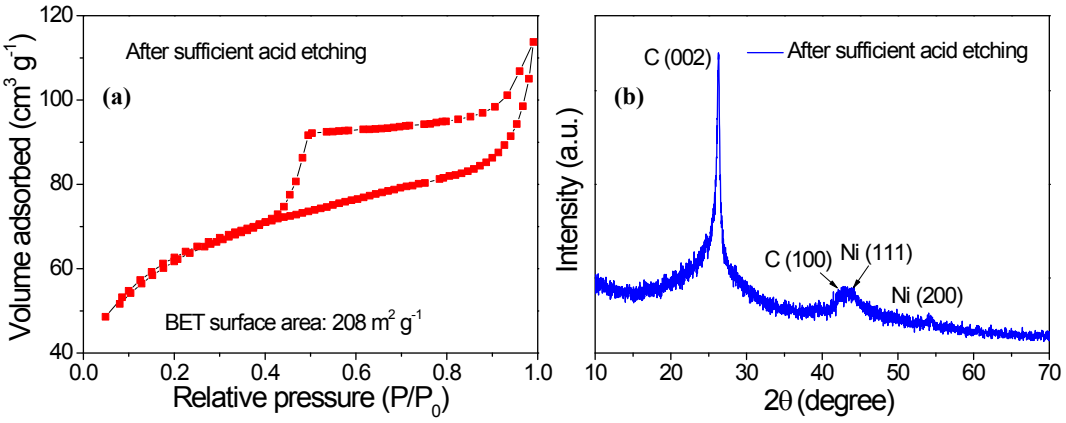


Figure S8. (a-b) FESEM images of Ni NP|Ni-N-C/EG.



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169 **Figure S9.** (a) N_2 adsorption-desorption isotherm and (b) XRD pattern of Ni NP|Ni-N-C after

170 sufficient acid etching treatment (Ni-N-C).

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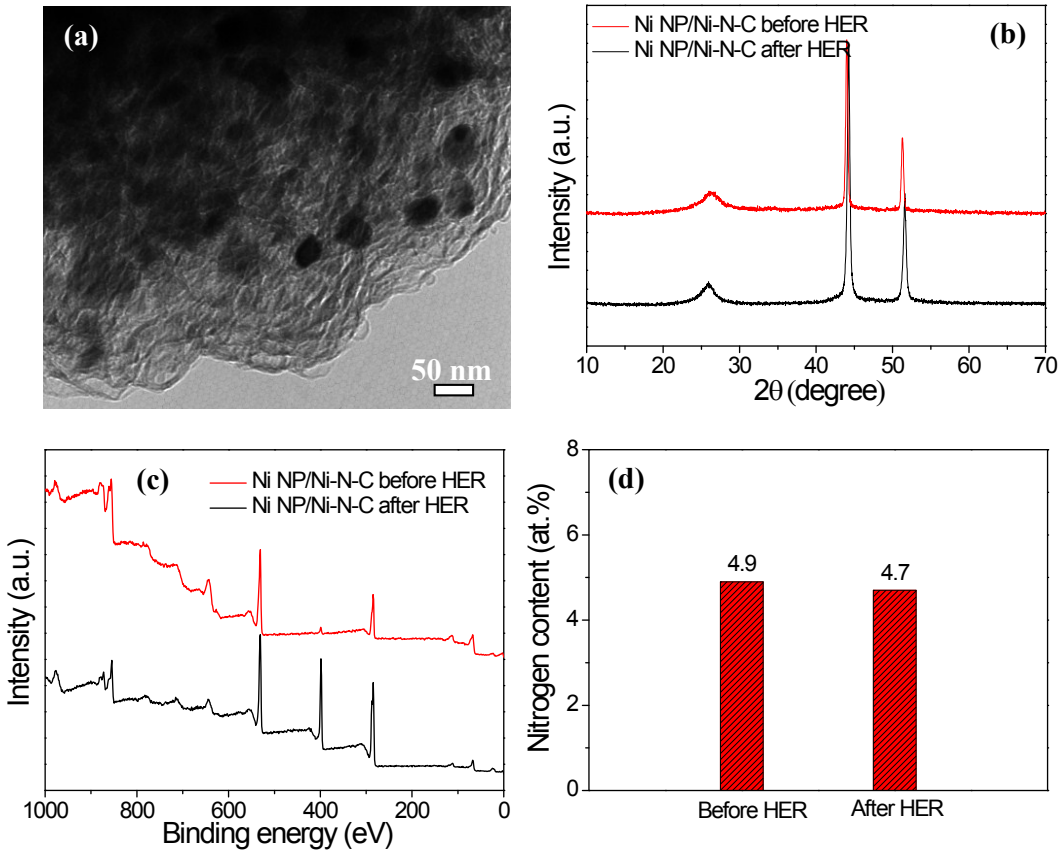

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173 **Figure S10.** (a) TEM image of Ni NP|Ni-N-C after HER test, (b) XRD patterns of Ni NP|Ni-

174 N-C before and after HER tests, (c) XPS survey spectra of Ni NP|Ni-N-C before and after

175 HER tests, and (d) N-content column bar graph of Ni NP|Ni-N-C before and after HER tests.

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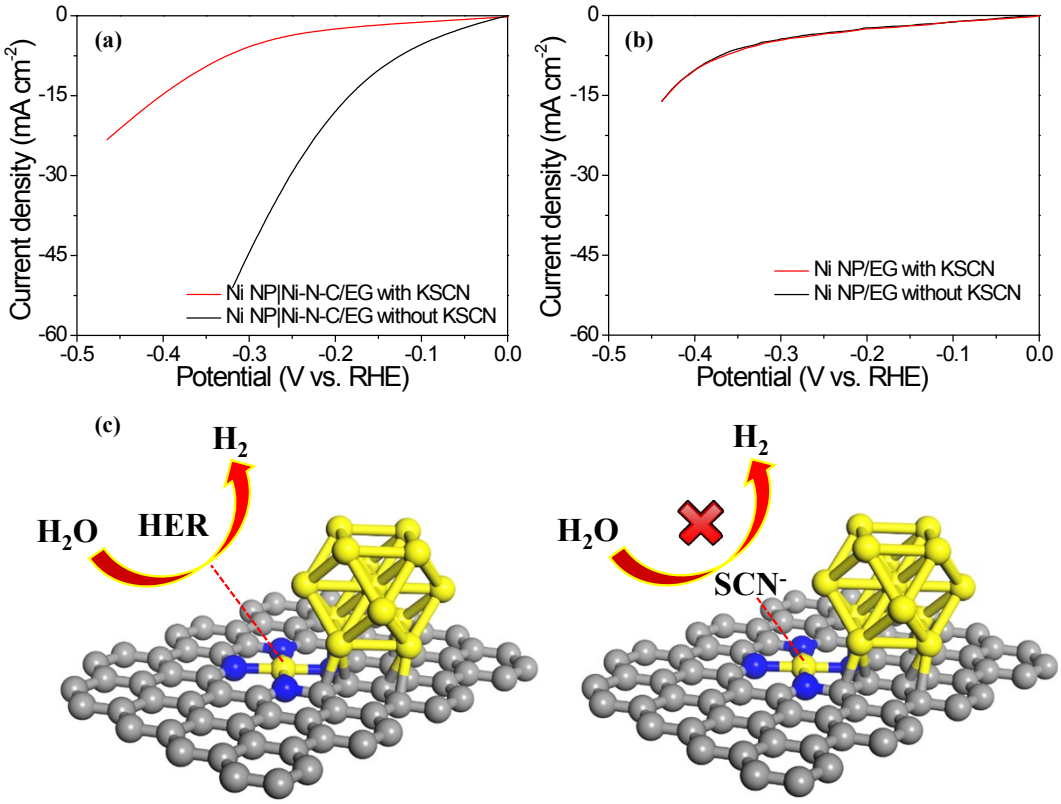

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178 **Figure S11.** HER polarization curves of Ni NP|Ni-N-C/EG (a) and Ni NP/EG (b) with and

179 without 10 mM KSCN in 1.0 M KOH. (c) Illustrations of Ni centers blocked by the SCN^-

180 ions.

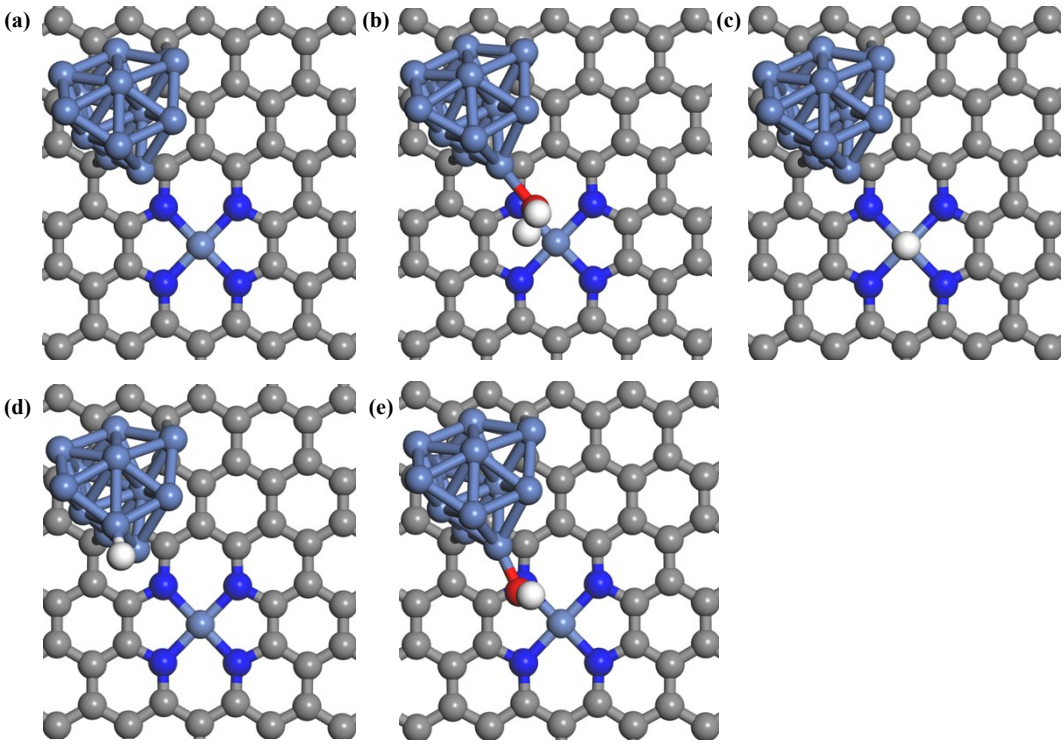

Figure S12. DFT calculated models (Volmer-Tafel-Heyrovsky mechanism) for NiN_4|NP1.

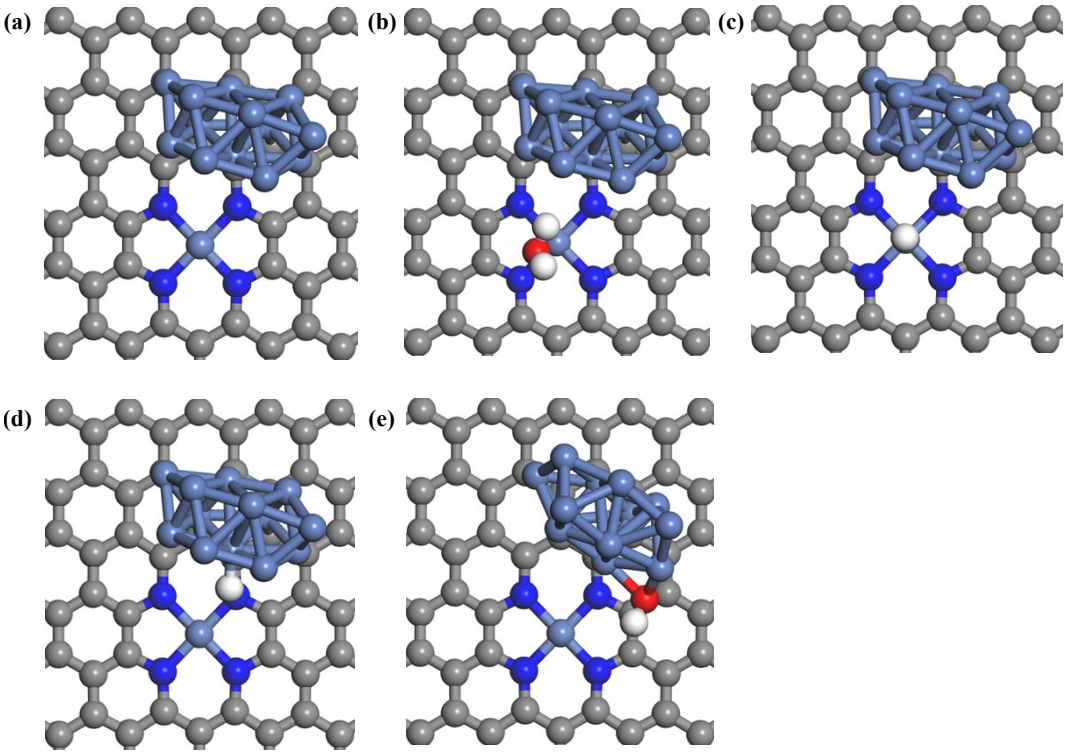

Figure S13. DFT calculated models (Volmer-Tafel-Heyrovsky mechanism) for NiN_4|NP3.

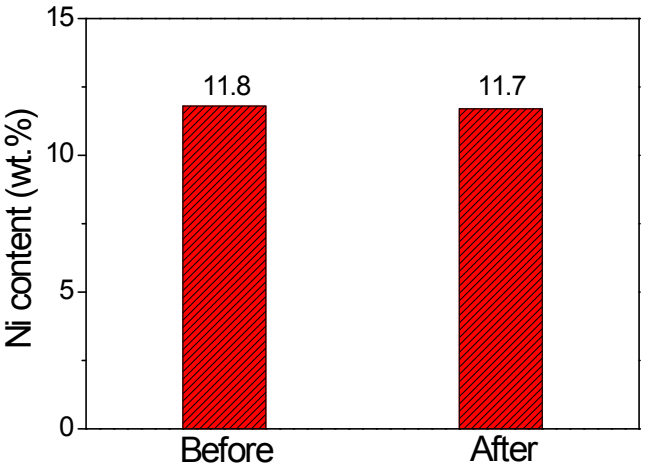

Figure S14. Ni content of Ni NP|Ni-N-C before and after HER stability test, as quantified by ICP-MS spectrometry.

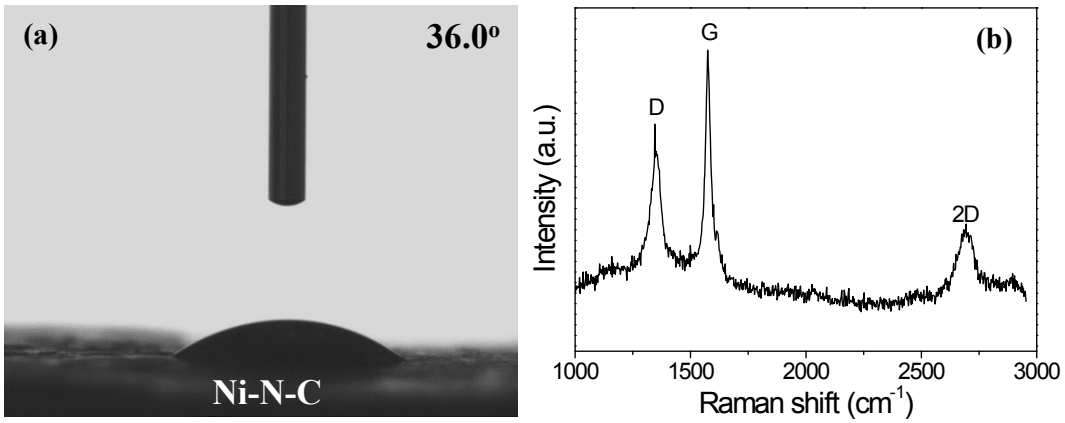

Figure S15. (a) Contact wetting angel and (b) Raman spectrum of Ni NP|Ni-N-C after sufficient acid etching treatment (Ni-N-C).

Table S1. Comparison of HER performance of Ni NP|Ni-N-C with some representative heteroatom-doped nanocarbon materials and transition-metal-based compounds.

Author	Catalyst (Loading density, mg cm^{-2})	Current density (J)	Potential at the correspondin g J	Electrolyte
This work	**Ni NP|Ni-N-C (0.24 mg cm^{-2})**	**10 mA cm^{-2}**	**147 mV**	**1.0 M KOH**
Adv. Mater. 2015, 27, 3175	PCPTF (0.1 mg cm^{-2})	10 mA cm^{-2}	~370 mV	1.0 M KOH
Energy Environ. Sci. 2016, 9, 1210	ONPPGC/OCC (0.1 mg cm^{-2})	10 mA cm^{-2}	~430 mV	1.0 M KOH
J. Am. Chem. Soc. 2015, 137, 15070	Co-C-N (2.0 mg cm^{-2})	10 mA cm^{-2}	~200 mV	1.0 M KOH
Angew. Chem. Int. Ed. 2014, 126, 4461	Co-NRCNTs (0.28 mg cm^{-2})	10 mA cm^{-2}	~370 mV	1.0 M KOH
J. Am. Chem. Soc. 2015, 137, 2688	CoO_x@CN (0.42 mg cm^{-2})	10 mA cm^{-2}	235 mV	1.0 M KOH
Adv. Mater. 2016, 28, 6442	$Pr_{0.5}$BSCF (0.232 mg cm^{-2})	10 mA cm^{-2}	237 mV	1.0 M KOH
Angew. Chem. Int. Ed. 2015, 54, 12361	Ni_5P_4 film (13.9 mg cm^{-2})	10 mA cm^{-2}	150 mV	1.0 M KOH
J. Am. Chem. Soc. 2013, 135, 9267	Ni_2P (1.0 mg cm^{-2})	10 mA cm^{-2}	210 mV	1.0 M KOH
Chem. Sci. 2016, 7, 1690	CoP/rGO-400 (0.28 mg cm^{-2})	10 mA cm^{-2}	~160 mV	1.0 M KOH
J. Am. Chem. Soc. 2014, 136,7587	CoP/CC (0.92 mg cm^{-2})	10 mA cm^{-2}	210 mV	1.0 M KOH
J. Am. Chem. Soc. 2014, 136, 15670	$CoSe_2$ nanosheets (0.142 mg cm^{-2})	10 mA cm^{-2}	320 mV	0.1 M KOH
Angew. Chem. Int. Ed. 2012, 51, 12703	MoB (0.9 mg cm^{-2})	10 mA cm^{-2}	~220 mV	1.0 M KOH
Angew. Chem. Int. Ed.	MoS_{2+x}/Ni foam	10 mA cm^{-2}	210 mV	0.1 M KOH

2015, 127, 674	(0.02 mg cm^{-2})			
Energy Environ. Sci. 2016, 9, 2789	Co-MoS_2 (0.89 mg cm^{-2})	10 mA cm^{-2}	200 mV	1.0 M KOH
Energy Environ. Sci. 2016, 9, 2789	MoS_2 nanosheets (0.89 mg cm^{-2})	10 mA cm^{-2}	310 mV	1.0 M KOH
Chem. Sci. 2016, 7, 3399	MoC-Mo_2C (0.14 mg cm^{-2})	10 mA cm^{-2}	~150 mV	1.0 M KOH
Nat. Mater. 2016, 15, 197	CoS_x/MoS_2 (0.05 mg cm^{-2})	5 mA cm^{-2}	210 mV	0.1 M KOH
Chem. Sci. 2011, 2, 1262	Amorphous MoS_x (---)	4 mA cm^{-2}	540 mV	0.1 M KOH
Adv. Funct. Mater. 2016, 26, 3314	Ni/NiS (11.04 mg cm^{-2})	10 mA cm^{-2}	~220 mV	1.0 M KOH
Nano Energy 2016, 24, 103	NF-Ni_3Se_2/Ni (8.87 mg cm^{-2})	10 mA cm^{-2}	203 mV	1.0 M KOH
Nano Energy 2016, 29, 37	CoP NPs (0.18 mg cm^{-2})	10 mA cm^{-2}	170 mV	1.0 M KOH
J. Mater. Chem. A, 2016, 4, 10114	u-CoP/Ti (6.32 mg cm^{-2})	10 mA cm^{-2}	60 mV	1.0 M KOH
Int. J. Hydrogen Energy, 2015, 40, 4727	Ni_3S_2/Ni foam (1.5 mg cm^{-2})	10 mA cm^{-2}	123 mV	1.0 M KOH

References

[1] K. Parvez, Z. S. Wu, R. Li, X. Liu, R. Graf, X. Feng, K. Müllen, *Journal of the American Chemical Society* **2014**, *136*, 6083.

[2] M. R. Gao, J. X. Liang, Y. R. Zheng, Y.-F. Xu, J. Jiang, Q. Gao, J. Li, S. H. Yu, *Nat Commun* **2015**, *6*.