Supporting Information for

Bifunctional Single-Atomic Mn Sites for Energy-efficient Hydrogen

Production

Xianyun Peng,[†] Junrong Hou,[†] Yuying Mi, Jiaqiang Sun, Gaocan Qi,* Yongji Qin,* Shusheng Zhang, Yuan Qiu, Jun Luo, and Xijun Liu*

Experimental Section

Chemicals

All chemicals were bought from Sinopharm Chemical Reagent Co, Ltd. The commercial melamine foam (MF) was purchased from Vanguard supermarket with a brand of Clean rub. All the involved chemicals were analytic grade and used without any further purification.

Synthesis of Mn-SA/BNC

For the preparation of Mn-SA/BNC, 50 mg H_3BO_3 , 150 mg polyethylene glycol, 5 g urea were firstly added in 100 mL deionized water. Then, 10 µL manganous nitrate solution (50%) was injected into the resulting mixed solution. After stirring for 30 min at room temperature, a piece of melamine foam (3 cm x 3 cm x 5 cm) was immersed in the solution. After 24 h immersing, the solvent was removed. The enveloped melamine foam with the precursors was dried at 80 °C until completely dry, followed by annealing at 900 °C for 6 h in Ar atmosphere. For comparison, the pure BNC was synthesized at the same conditions without adding Mn precursor.

Materials Characterizations

The morphology and structure of the prepared sample were characterized by a scanning electron microscope (SEM, Verios 460L) operated at 20 kV and a transmission electron microscope (TEM, Talos F200X) operated at 200 kV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were taken

using an FEI Titan Cubed Themis G2 60-300 STEM with a probe corrector at 200 kV. Powder X-ray diffraction (XRD) patterns were tested on an X-ray diffractometer (Rigaku D/max 2500) at a scan rate of 10° min⁻¹ in a 2 ϑ range of 10–80°.

EAFS measurements

The X-ray absorption fine structure (XAFS) spectra at Mn K (6539 eV) edge were carried out in the fluorescence mode at the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF). The energy was standardized according to the adsorption edge of Mn foil. The obtained XAS spectra were analyzed using the Athena and Artemis software ver. 0.9.25 included in the Demeter package.

Catalytic ink preparation

For preparing the catalyst ink, 6 mg of as-prepared catalyst, 0.5 mL of 0.05 wt% Nafion were mixed with 0.5 mL absolute ethyl alcohol, and then the mixture was ultrasonicated for 30 min to obtain a well-dispersed suspension, namely the catalyst ink. For HER and HzOR tests, the electrode was prepared by dopping 20 μ L the catalyst ink onto a glassy carbon electrode with a diameter of 3 mm. For overall hydrazine splitting (OHzS) measurements, the electrode was prepared by the catalyst ink onto a carbon paper with a mass loading of 1 mg cm⁻².

Electrochemical measurements

Electrochemical measurements were carried out with a typical three-electrode system

by using an electrochemical workstation (CHI Instruments 760E) at room temperature. A graphite rod and Ag/AgCl electrode were used as counter and reference electrodes, respectively.

For HER tests, 1.0 M KOH aqueous solution was selected as the electrolyte. For HzOR tests, the electrolyte was 1 M KOH containing 0.5 M hydrazine hydrate solution. The polarization curves of catalysts were recorded by linear sweep voltammetry (LSV) at a scan rate of 10 mV s⁻¹. The HER stability was tested by the Amperometric *i-t* curve at the constant overpotential of –51 mV vs RHE with iR compensation similar to LSV.

For hydrazine-assisted water electrolysis, the symmetrical full electrolyzer was fabricated by using Mn-SA/BNC electrodes both as cathode and anode. LSV was measured at a scan rate of 10 mV s⁻¹ in 1.0 M KOH with 0.5 M N₂H₄. For comparison, the commercial noble metal Pt/C catalyst was measured in the same conditions. In this work, all potential was given versus reversible hydrogen electrode according to the following equation: $E_{RHE} = E_{Ag/AgCl} + 0.0591pH + 0.197$.

Electrochemical impedance spectra (EIS) for different samples were measured at an open-circuit potential in a frequency ranging from 100 kHz to 10 mHz with an AC voltage amplitude of 5 mV.

To determine the corresponding electrochemical surface area (ECSA), double layer capacitance (C_{dl}) of all the materials was measured in 1.0 M KOH solution. A potential range where no apparent Faradaic process occurred was determined first using cyclic voltammetry (CV) with different scan rates (10, 20, 30, 40, and 50 mV s⁻¹). The value of C_{dl} was then obtained from the linear curve versus scan rate.

Determine H₂ Faradic efficiency

The hydrogen evolved from the cathode could be measured by a water-gas displacing method. The volume of H_2 was calculated from the following relationships:

$$V_{\rm H2}$$
 (mL) = Q × 22.4 L mol⁻¹ × 1000 / (F × 2)

where Q is the cumulative charge (C), F is the Faraday constant (96485 C mol⁻¹).

Computational detail

The spin–unrestricted density functional theory (DFT) calculations are carried out by using the Dmol³ package (J. Chem. Phys., 2000, 113, 7756). Exchange–correlation functions are taken as generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) (P. Perdew et al. Phys. Rev. Lett. 1996, 77, 3865). To model the defective B, N-doped graphene monolayer, we first built a supercell containing 60 carbon atoms with a vacuum of at least 15 Å, and then removed six carbon atoms to create monovacancy and provide an anchoring site for a single Mn atom with one B and three N atoms. The convergence tolerances of energy, maximum force, and displacement were set to 1.0×10^{-5} Ha, 0.002 Ha/Å, and 0.005 Å, respectively. The free energy diagram for HER was obtained by calculating the change of the free energy with a hydrogen atom adsorbed on the surface.



Figure S1. XRD patterns of the as-prepared Mn-SA/BNC and BNC samples.



Figure S2. HAADF-STEM and elemental mapping images of Mn-SA/BNC.



Figure S3. $N_{\rm 2}$ adsorption/desorption isotherm curves and the corresponding pore

size distribution of Mn-SA/BNC.



Figure S4. The XPS survey of the as-prepared BNC and Mn-SA/BNC samples.



Figure S5. The corresponding EXAFS fitting curves of Mn-SA/BNC at *K*-space.



Figure S6. FT-EXAFS fittings of Mn-SA/BNC at Mn K-edge with (a) Mn-B₃N, (b) Mn-B₂N₂, and (c) Mnb-N₄. (d-f) The corresponding atomic model structures. Mn atom (red), B atom (pink), N atom (blue), C (grey). Compared to these possible atomic models, the Mn-B₁N₃ structure (the inset in Figure 1f) is calculated to be the most stable one and the Mn-B₁N₃ model fits best with the FT-EXAFS spectrum of Nb-SA/BNC (see more details in Table S1). This finding indicates that the Nb single atoms are more likely atomically dispersed as Mn-B₁N₃ on the carbon nanotubes.



Figure S7. The XRD pattern of the Mn-SA/BNC catalyst after HER stability test.



Figure S8. The atomic-resolution HAADF-STEM images of Mn-SA/BNC after HER

stability test. These images were taken from randomly selected regions of the sample.



Figure S9. The XRD pattern of the Mn-SA/BNC catalyst after HzOR stability test.



Figure S10. The atomic-resolution HAADF-STEM images of Mn-SA/BNC after OHzS

stability test. These images were taken from randomly selected regions of the sample.



Figure S11. Nyquist plot of the Mn-SA/BNC catalyst after the HER long-term stability

test.

Sample	Path	N	<i>R</i> (Å)	σ² (10 ⁻³ Ų)	Δ <i>Ε</i> ₀ (eV)	R factor
Mn-BN ₃	Mn-N	3.1 ± 0.1	1.99	2.49±0.18	-1.9±1.2	0.0015
	Mn-B	0.9 ± 0.2	2.15	2.49±0.18	-1.9±1.2	0.0015

Table S1. EXAFS data fitting results of the Mn-SA/BNC samples.

 S_0^2 is the amplitude reduction factor; *N* is the coordination number; *R* is the interatomic distance (the bond length between central atoms and surrounding coordination atoms); σ^2 is the Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances); ΔE_0 is an edge-energy shift (the difference between the zero kinetic energy value of the sample and that of the theoretical model). *R* factor is used to value the goodness of the fitting.

Catalysts	Electrolyte	η ₁₀ (mV)	Tafel slope (mV dec ⁻¹)	References
Mn-SA/BNC	1 M KOH	51	51.2	This and
Pt/C		27	29.7	Inis work
NiSe ₂ NSs	1 M KOH	207	186.5	Electrochim. Acta 2018, 279, 195
Ni ₃ Se ₂ /Ni foam	1 M KOH	97	79	Nano Energy 2016, 24, 103
Pt/C/ Ni foam		-	34	
NiSe ₂ /NF	1 M KOH	96	120	Angew. Chem. Int. Ed. 2015, 54, 9351
Pt/C/NF		40	43	
Ni ₃ Se ₂ /CF	1 M KOH	100	98	
Pt/C		-	63	Catal. Scl. Technol. 2015, 5, 4954
Ni _{0.85} Se	1 M NaOH	200	81	Int. J. Hydrogen. Energy 2016, 41, 10688

Table S2. Comparison of HER performance in the alkaline media for Mn-SA/BNC with other previously reported electrocatalysts.

NiSe/NF	1 M KOH	190	76.6	Electrochimica Acta 2017, 224, 412
NiSe ₂ NCs		540	139	ACS Appl. Mater. Interface 2016, 8,
Pt/C	IWKON	90	53	5327
Mn _{10%} -NiSe ₂	1 M KOH	128	63	Int. J. Hydrogen Energy 2020, 45,
Pt/C	I M KOH	-	38	12237
NiFeRu-LDH		29	31	Adv. Mater. 2018, 30, 1706279
Pt/C		31	32	
Cu NDs/Ni ₃ S ₂ NTs-CFs	1М КОН	128	76.2	J. Am. Chem. Soc. 2018, 140, 610
NC/CuCo/CuCoO _x	1М КОН	112	55	Adv. Funct. Mater. 2018, 28, 1704447
EG/Co _{0.85} Se/NiFeLDH	1 M KOH	260	160	From Fruiter (ci 2016 0 470
Pt/C		-	68	Energ. Environ. Sci. 2016, 9, 478
Se-(NiCo)S/OH	1 M KOH	101	87.3	Adv. Mater. 2018, 30, e1705538

Ru-MoO ₂		29	31	
Pt/C	1 M KOH	38	31	J. Water. Chem. A. 2017, 5, 5475
Ni ₂ P NPs/CC	1 M KOU	71	73	J. Mater. Chem. A. 2018, 6, 4088
Pt/C	I M KOH	71	63	
Ni@Ni ₂ P-Ru	1 M KOH	31	41	L Am Cham Sec 2018 140 2721
Pt/C		59	37	J. Am. Chem. Soc. 2018, 140, 2731
CoP/NCNHP	1 M KOH	115	66	J. Am. Chem. Soc. 2018, 140, 2610
Ru ₂ P@NPC	1 M KOH	52	69	Angew. Chem. Int. Ed. 2017,
Pt/C		-	57	56,11559
NH ₂ -BP	1 M KOH	290	63	1 Mator Cham A 2018 6 2404
Pt		32	42	J. Mater. Chem. A 2018, 6, 2494
NiCu@C	1 M KOH	740	94.5	Adv. Energy Mater. 2018, 8, 1701759

Ni ₂ P@NPCNFs	1 M KOH	104.2	79.7	Angew. Chem. Int. Ed. 2018, 57, 1963
P-Co ₃ O ₄	1 M KOH	120	52	Energ. Environ. Sci. 2017, 10, 2563
Mo ₂ N-Mo ₂ C/HGr	1 M KOH	154	68	Adv. Mater. 2018, 30, 1704156
Mo ₂ N-MoC		157	68	Adv. Mater. 2018, 30, 1704156
Pt/C	1 MI NAOH	-	51	
Cu@NiFe LDH	1 M KOH	116	58.9	Energ. Environ. Sci. 2017, 10, 1820
MoB/g-C ₃ N ₄	1 M KOH	0.133	46	Angew. Chem. Int. Ed. 2018, 57, 496
A-CoPt-NC	1 M KOH	50	48	Angew. Chem. Int. Ed. 2019, 58, 9404
Pt/C		65	56	
NP-MoS ₂ /CC	1 M KOH	78	51.6	Nano Energy 2019, 58, 862
Co/b-Mo ₂ C@N-CNTs	1 M KOH	170	92	Angew. Chem. Int. Ed. 2019, 58, 4923
Mn-Co-P/Ti	1 M KOH	76	52	Catal. Sci. Technol. 2018, 8, 4407

CoP nanowire/CC	1 M KOH	115	129	J. Am. Chem. Soc. 2014, 136, 7587
CoP ₂ /RGO		88	50	J. Mater. Chem. A 2016, 4, 4686
Pt/C	I M KOH	-	64	
np-CoP NWs/Ti	1 M KOH	100	71	Chem. Chem. Phys. 2014, 16, 16909
Co ₂ P NWs	1 M KOH	~140	-	Green Chem. 2016, 18, 1459
CoP/rGO-400	1 M KOH	340	38	Chem. Sci. 2016, 7, 1690
Co ₂ P nanorods	1 M KOH	99	72	Nano Energy 2014, 9, 373
Mn-Ni ₃ S ₂ /NF		10	152	Chem. Commun. (Camb) 2018, 54, 10100
Ni ₃ S ₂ /NF	1 М КОН	10	198	
Pt/C		83	80	
Ni ₃ S ₂	1 M KOH	10	233	J. Am. Chem. Soc. 2015, 137, 14023
Ni ₃ S ₂ /AT-NF	1 M KOH	10	200	Electrochim. Acta 2015, 174, 297

V–Ni ₃ S ₂ –NW	1 M KOH	10	~155	ACS Appl. Mater. Interface 2017, 9,
Pt/C		-	38	5959
Ni ₃ S ₂ –NW	1 M KOU	10	~199	Int. J. Hydrogen Energy 2017, 42,
Pt/C	I M KOH	-	29.8	7136
Fe _{0.1} -NiS ₂ NA/Ti	1 M KOH	10	~200	None Dec. 2016 0. 2246
Pt/C		-	60	Nano Res. 2016, 9, 3346
Ni ₃ S ₂ /NF covered with RGO	1 M KOH	10	157	Appl. Surf. Sci. 2017, 399, 769
NiCo ₂ S ₄ NW/NF	1 M KOH 1 M KOH	10	210	Adv. Funct. Mater. 2016, 26, 4661
40%Pt/C		32	41	
MoS ₂ /Mo		10	184	Electrochim. Acta. 2015, 168, 133
CoSe ₂ /Carbon Cloth	1 M KOH	10	190	Adv. Mater. 2016, 28, 7527
CoS ₂	1 M KOH	10	~255	Electrochim. Acta 2014, 148, 170

MoS ₂	1 M KOH	10	187	J. Am. Chem. Soc. 2013, 135, 10274
Ni-Mo nanopowder	1 M NaOH	79	-	ACS Catal. 2013, 3, 166
Mo ₂ N-MoC	1 M NaOH	157	68	Adv. Mater. 2018, 30, 1704156

 η_{10} is the overpotential at the current density of 10 mA cm⁻².

All of the "-" means that no values were reported for the corresponding parameters in the corresponding references.

Catalysts	Electrolyte	Potential (mV vs RHE)	References
Mn-SA/BNC	1 M KOH + 0.5 M N ₂ H ₄	$E_{10} = 132$	This work
Ni ₂ P-HNTs/NF	1 M KOH + 0.5 M N ₂ H ₄	$E_{100} = 166$	Nanoscale 2020, 12, 11526
Cu ₁ Ni ₂ -N	1 M KOH + 0.5 M N ₂ H ₄	<i>E</i> ₁₀₀ = ~200	Adv. Energy Mater. 2019, 9, 1900390
S-CuNiCo LDH-3	1 M KOH + 0.02 M N ₂ H ₄	<i>E</i> ₁₀₀ = ~700	J. Mater. Chem. A 2019, 7, 24437
Se/porous carbon membranes	1 M KOH + 0.1 M N ₂ H ₄	<i>E</i> ₁₀ = ~450	Angew. Chem. Int. Ed. 2019, 58, 13466
Fe ₂ MoC@NC	1 M KOH + 0.1 M N ₂ H ₄	$E_{10} = \sim 500$	Angew. Chem. Int. Ed. 2018, 57, 17168
CoSe ₂ /NF	1 M KOH + 0.5 M N ₂ H ₄	<i>E</i> ₁₀₀ = ~170	Angew. Chem. Int. Ed. 2018, 57, 7649
NiO _x -Pt/C	1 M KOH + 0.1 M N ₂ H ₄	<i>E</i> ₁₀₀ = ~200	Appl. Catal. B-Environ. 2017, 201, 22
N-doped carbon	1 M KOH + 0.1 M N ₂ H ₄	$E_{10} = ~700$	Angew. Chem. Int. Ed. 2017, 56, 13513

 Table S3. Comparison of HzOR performance in the alkaline media for Mn-SA/BNC with other previously reported electrocatalysts.

CoNi alloy@CoNi sulfide	1 M KOH + 2.0 M N ₂ H ₄	$E_{10} = ~150$	Adv. Mater. 2017, 29, 1604080
Vertical graphene nano- hills-45	1 M KOH + 0.05 M N ₂ H ₄	<i>E</i> ₁₀ = ~910	NPG Asia Mater. 2017, 9, e378.
FePc	0.2 М КОН + (-) N ₂ H ₄	$E_{100} = 0.35$	Talanta 2005, 67, 162
Cu nanoparticles	0.1 M KOH + 0.01 M N ₂ H ₄	E ₁₀₀ =~ 0.5	J. Mater. Chem. A 2014, 2, 4580
3D PNNF	$3.0 \text{ M KOH} + 0.5 \text{ M N}_2\text{H}_4$	$E_{100} = ~0.125$	Nano. Res. 2015, 8, 3365
FeN₄	0.2 M NaOH + (-)N ₂ H ₄	$E_{100} = 0.4$	Electrochem. Commun. 2013, 30, 34
Ni _{0.6} Co _{0.4} -ANSA	3.0 M KOH + 0.5 M N_2H_4	<i>E</i> ₁₀₀ = ~- 1 (V vs SCE)	Adv. Sci. 2017, 4, 1600179
Cu film	$3.0 \text{ M KOH} + 1.0 \text{ M N}_2\text{H}_4$	<i>E</i> ₁₀₀ = ~– 0.65 (V vs SCE)	Adv. Mater. 2015, 27, 2361
Fe-CoS ₂ nanosheets	$1.0 \text{ M KOH} + 0.1 \text{ M N}_2\text{H}_4$	$E_{100} = 0.129$	Nat. Commun. 2018, 9, 4365

 E_x is the potential at the current density of x mA cm⁻² except those specified else.

All of the "-" means that no values were reported for the corresponding parameters in the corresponding references.