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Supporting Information

Enhanced HOR catalytic activity of PGM-free catalysts in alkaline media: electronic effect induced by different heteroatoms doped carbon supports

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EXPERIMENTAL SECTION

Chemicals and Materials.

Sodium borohydride (NaBH₄, Sinopharm Chemical Reagent Co. Ltd., \geq 97.0 %), nickel sulfate hexahydrate (NiSO₄·6H₂O, Sinopharm Chemical Reagent Co. Ltd., \geq 98.5 %), ethanol absolute (EtOH, Sinopharm Chemical Reagent Co. Ltd., \geq 99.7 %), benzyl disulfide (C₁₄H₁₄S₂, Aladdin Industrual Co., 98 %), phenylboronic acid (C₆H₇BO₂, Changcheng chemical Co., 98 %), melamine (C₃H₆N₆, Sinopharm Chemical Reagent Co. Ltd., \geq 99.0 %), benzophenone (C₁₃H₁₀O, Sinopharm Chemical Reagent Co. Ltd., \geq 98.0 %), sulfuric acid (H₂SO₄, Sinopharm Chemical Reagent Co. Ltd., 95.0 ~ 98.0 %), potassium hydroxide (KOH, Aladdin Industrual Co., 99.999 % metals basis, except sodium), isopropanol (Sinopharm Chemical Reagent Co. Ltd., \geq 99.7 %) and Nafion® 117 solution (Sigma-Aldrich Co., ~5 % in a mixture of lower aliphatic alcohols and water) were utilized directly as received without any further purification. The ultrapure water (18.25 MΩ cm⁻¹) prepared from an up water purification system (Ulupure) was used throughout the whole experiment.

Synthesis of carbon supports (SC, NC, BC, and C).

The synthesis of heteroatoms doped carbon precursors was based on a thermal treatment process. Typically, 100 mg of Vulcan carbon powder (XC-72) was fully mixed with various heteroatom-containing precursors (the mass ratio of the initial XC-72 to the respective precursor is 1:10), which were ground in a mortar for more than half an hour. The obtained powder was put in a quartz boat in the center of a tube furnace. Then the system was heated up to an intermediate temperature (the decomposition temperature of each heteroatom precursor was selected: benzyl disulfide, 270 °C; phenylboronic acid, 280 °C; melamine, 550 °C), remained for 1 h. After that, continued to anneal at 900 °C and kept for 2 h in an Ar atmosphere, at a ramp rate of 5 °C min⁻¹. After cooling naturally at room temperature, the product was dissolved in 40 mL 0.5 M H₂SO₄ solution

in order to enhance the hydrophilicity of carbon materials. Finally, the product was separated by centrifugation and washed with ultrapure water and ethanol separately several times until a pH of 7, followed by vacuum drying at 60 °C for overnight. The resulting black powders (XC, X = S, N, or B) were obtained and directly used for further characterization and measurements. For comparison, we also synthesized non-doped carbon materials (C) by pyrolyzing the mixture of XC-72 and benzophenone. All the steps are the similar to that of the XC except for the intermediate temperatures (benzophenone, 240 °C).

Synthesis of Ni/XC (X = S, N, or B) and Ni/C.

The Ni/XC (X = S, N, or B) catalysts were synthesized by the hydrothermal method. 50 mg as-prepared carbon material was dissolved in a stand-up flask with about 10 mL H₂O, and ultrasonicated for 30 min to form a suspension liquid. Then, 0.262 g NiSO₄ was introduced in and maintained ultrasonic dispersion uniformity. After that, the system was transferred to a sink in an ice bath, 10 mL NaBH₄ ice-cold aqueous solution (10 mg mL⁻¹) was added into the suspension with drop by drop under the constant stirring. After reaction at 0 °C for 2 h, the suspension was poured into a 100-mL Teflon-lined stainless steel autoclave. The autoclave was sealed for hydrothermal treatment at 150 °C for 4 h. After cooling down to room temperature, the sample was washed thoroughly with plenty of water and ethanol, and then dried at room temperature under vacuum for 24 h. The product was collected and donated as Ni/XC or Ni/C for further testing and characterization.

Materials characterization.

Powder X-ray diffraction (XRD) patterns were carried out by using a Rigaku Miniflex600 X-ray diffractometer with a Cu K α radiation source ($\lambda = 0.154178$ nm) with a velocity of 8 °/min. The morphologies and sizes of the samples were observed by a Tecnai G20 U-Twin transmission electron microscope (TEM) equipped with an energy dispersive X-ray detector (EDX) at an acceleration voltage of 200 kV. Inductively

coupled plasma atomic emission spectroscopy (ICP-AES) was performed on a Thermo IRIS Intrepid II XSP atomic emission spectrometer. X-ray photoelectron spectroscopy (XPS) measurement was performed with a Kratos XSAM 800 spectrophotometer.

Preparation of working electrodes.

3.5 mg Ni/SC, Ni/NC, Ni/BC or Ni/C was mixed with 0.7 mL solvent of isopropyl alcohol containing 0.05 wt. % Nafion and ultrasonicated for more than 30 min to form a homogeneous ink. The glassy carbon (GC, 5 mm in diameter) electrode was polished with 1.0, 0.5 and 0.05 mm gamma alumina powder slurry to obtain a neat surface and then washed with ultrapure water and ethanol with sonication. Once the GC electrode was dried under air naturally, 12 μ L ink was drop-casted on the surface of the GC electrode (total loading: ~0.3 mg cm⁻²) and dried in air before any electrochemical measurements. The loadings of Ni on Ni/SC, Ni/NC, Ni/BC or Ni/C decorated electrodes could be calculated from the ICP-AES data, and are 137.6, 165.4, 168.4 or 166.9 μ g cm⁻², respectively.

Electrochemical measurements.

The electrocatalytic behaviors of all samples were measured at 303 (\pm 0.1) K, in a three-electrode system using a CHI 760E electrochemical workstation. The catalysts film decorated GC electrode, a mercury/mercury oxide electrode (Hg/HgO, filled with 0.1 M KOH), and a graphite rod were used as the working electrode, reference electrode, and counter electrode, respectively. All potentials reported in this work are referenced to the reversible hydrogen electrode (RHE) potential. For each electrochemical test, fresh 0.1 M KOH was used as the electrolyte.

Before hydrogen oxidation reaction (HOR) evaluation, we stabilized the GC disk surface at open circuit potential for more than 300 s in H_2 -saturated 0.1 M NaOH solution. Then, the polarization curves were

recorded by a rotating disk electrode (RDE) system (Pine Research Instruments) with the rotation rate of 2500 revolutions per minute (rpm). The potential was scanned from -0.08 V to 0.12 V (vs. RHE) at a scan rate of 5 $mV \cdot s^{-1}$.

Electrochemically active surface areas (ECSAs) were determined by cyclic voltammetry that conducted in an Ar-saturated electrolyte. The potential window was selected between -0.13 and 0.52 V at the scan rate of 50 mV·s⁻¹. The value of ECSA (cm_{metal} μ g_{metal}⁻¹) can be calculated via Eq.S1,

$$ECSA = \frac{Q_{Ni}}{Q_s \cdot m_{Ni}}$$
 Eq.S1

Where Q_{Ni} is the measured integral charge that corresponds the area of the shaded area as shown in Fig. S7, Q_s is the surface charge density of 514 μ C cm_{Ni}⁻² which is assumed for one monolayer of OH adsorption on Ni, m_{Ni} is the mass of the Ni on GC.

Electrochemical impedance spectra (EIS) tests was carried out after each RDE measurement with the AC impedance spectra from 200 kHz to 0.1 kHz and a voltage perturbation of 5 mV. The real part of the resistance at 1 kHz was taken as the uncompensated resistance (R_u) and was used to obtain the iR-free potential ($E_{iR-free}$) according to the following equation, Eq.S2,

$$E_{iR-free} = E - iR_{u}$$
 Eq.S2

where E is the measured potential and i is the corresponding current.

Theoretical Calculations

Computation details and theoretical models:

All the density functional theory (DFT) calculations for present study were implemented using DMol3 package in the Materials Studio. Generalized gradient approximation (GGA) method couple with the Perdew-Burke-Ernzerh (PBE) functional was applied to describe the exchange-correlation interactions. DFT Semi-core Pseudopots of core treatment were chose to conduct metal relativistic effect. The Grimme's DFT-D

correction was chose for the semi-empirical van der Waals correction owing to the dispersion. The basis set by using double numerical plus polarization were also employed. A smearing of 0.005 Ha, where 1 Ha = 27.21 eV, to the orbital occupation was implemented. The convergence tolerance is set as 1.0e-5 Ha for total energy, 0.002 Ha/Å for maximum force and 0.005 Å for maximum displacement, respectively. And the selfconsistent-field (SCF) tolerance is set as 1.0e-6 Ha to gain accurate electronic convergence. A 4×4 singlelayer graphene unit cell was used to simulate the XC-72 carbon layer. A vacuum layer of 15 Å was used in the z direction. Ni nanoparticle was simulated by Ni₄ cluster. In order to prevent the reconstruction of the Ni cluster, a rigid mode was used in this work.¹ In terms of N or B doping, threefold coordinated N and B configuration were considered at the concentration of 3.1 atomic % (the ratio between N/B and C is about 0.032). For S doping, two-fold coordinated S configuration with a defect site was considered at the concentration of 3.2 atomic % (the ratio between S and C is about 0.033). 4×4×1 Monkhorst-Pack grid kpoints were employed for geometric optimization. Spin-polarization was considered during all the calculations.

Calculation of free energies:

The adsorption free energy of H was calculated by this following formula: $\Delta G_{H^*} = \Delta E_{H^*} + \Delta ZPE - T\Delta S$, in which ΔE_{H^*} , ΔZPE and ΔS are on behalf of the binding energy, zero-point energy change as well as entropy change of H adsorption, respectively. Taking the small vibrational entropy for H* in the adsorbed state into consideration, ΔS can be calculated using the following equation: $\Delta S = S(H^*) - 1/2 S(H_2) \approx -1/2 S(H_2)$, where $S(H_2)$ represents the entropy of H₂ at the standard conditions in the gas phase. Moreover, ΔZPE can be gained by the equation $\Delta ZPE = ZPE(H^*) - 1/2 ZPE(H_2)$. Thus the overall corrections are simplified into $\Delta G_{H^*} = \Delta E_{H^*} + 0.24 \text{ eV}$. All the fcc adsorption sites of hydrogen on Ni₄ cluster were considered, and the corresponding ΔG_{H^*} values for different models are exhibited in Table S5.

To confirm the effect from the concentration of the dopants in carbon supports, we simply used the 5×5 and 4×5 single-layer graphene unit cell doped with a S atom as the supports at different concentrations (2.0 and 2.6 atomic %, the ratios between S and C are about 0.022 and 0.026, respectively), respectively (Fig. S16). The ΔG_{H^*} of the most stable adsorption site of hydrogen for these models were presented in Table S6.

SUPPLEMENTARY FIGURE:



Fig. S1 High-resolution XPS of (a) S 2p, (b) N 1s, and (c) B 1s in SC, NC, and BC, respectively.



Fig. S2 TEM images of (a) SC, (b) NC, (c) BC, (d) C, and (e) pristine XC-72.



Fig. S3 HR-TEM image of Ni/SC.



Fig. S4 High-resolution XPS of Ni in Ni/SC.



Fig. S5 High-resolution XPS of (a) S 2p, (b) N 1s, and (c) B 1s in Ni/SC, Ni/NC, and Ni/BC, respectively.



Fig. S6 (a) Polarization curves of Ni/SC in H₂-saturated 0.1 M KOH with a scan rate of 5 mV s⁻¹ at the rotating speeds varied from 2500 to 400 rpm. (b) Koutecky–Levich plot obtained from (a) at an overpotential of 50 mV. The value of $(j_{@50 mV})$ of Ni/SC is about 1.52 mA cm_{geo}⁻².



Fig. S7 CVs of (a) Ni/SC, (b) Ni/NC, (c) Ni/BC, and (d) Ni/C in Ar-saturated 0.1 M KOH at a scan speed of 50 mV s⁻¹. The integral charges assigned as the patterned areas are used to estimate the ECSA with a charge density of 514 μ C cm_{Ni}⁻² for monolayer of OH adsorption on the surface of Ni.



Fig. S8 Comparison of the ECSAs of Ni/SC, Ni/NC, Ni/BC, and Ni/C.



Fig. S9 Micropolarization region (- 10 to 10 mV) of Ni/SC, Ni/NC, Ni/BC, and Ni/C in H₂-saturated 0.1 M KOH. The dashed lines indicate the linear fittings. All the potentials are iR-corrected.



Fig. S10 Optimized model structures of H adsorption for (a and b) Ni/SC, (c and d) Ni/NC, (e and f) Ni/BC, and (g and i) Ni/C.



Fig. S11 High-resolution XPS of S 2p in (a) SC-1:5 and (b) SC-1:15.



Fig. S12 XRD of Ni/SC-1:5 and Ni/SC-1:15.



Fig. S13 CVs in Ar-saturated 0.1 M KOH (a, c) and LSV in H₂-saturated 0.1 M KOH (b, d) of (a, b) Ni/SC-1:5 and (c, d) Ni/SC-1:15.



Fig. S14 Comparison of *ECSA* and $j^{0,s}$ of Ni/SC-1:5 and Ni/SC-1:15.



Fig. S15 TEM images of (a) SC-1:15 and (b) Ni/SC-1:15.



Fig. S16 Optimized model structures of H adsorption for (a and b) Ni/SC-1:5 and (c and d) Ni/SC-1:15.

Sample	X : C $(X = S/N/B)$
SC	0.024
NC	0.023
BC	0.100
SC-1:5	0.014
SC-1:15	0.025

Table S1. The atomic ratio between the dopants and the carbon matrix of SC, NC, BC, SC-1:5, and SC-1:15 measured by XPS.

Table S2. The contents of Ni in Ni/SC, Ni/NC, Ni/BC, and Ni/C measured by ICP-AES.

Ni (wt. %)
45.04
54.12
55.10
54.62

 Table S3. Summary of the ECSAs, transfer coefficients, and HOR exchange current densities of Ni/SC,

 Ni/NC, Ni/BC, and Ni/C.

ECSA		Butler-Volmer fitting			Micropolarization	
Sample (cm ² µg _{Ni} ⁻¹)	α	j ^{θ,s} (μA cm _{Ni} ⁻²)	$j^{\theta,m}$ ($\mu A \mu g_{Ni}^{-1}$)	j ^{θ,s} (μA cm _{Ni} - ²)	$j^{ heta,m}$ ($\mu A \mu g_{Ni}^{-1}$)	
Ni/SC	0.169 ± 0.009	0.54 ± 0.05	40.2 ± 2.8	7.44 ± 0.88	38.4 ± 2.3	7.12 ± 0.94
Ni/NC	0.161 ± 0.003	0.59 ± 0.08	29.9 ± 5.1	4.82 ± 0.83	28.4 ± 4.3	4.58 ± 0.73
Ni/BC	0.154 ± 0.005	0.54 ± 0.07	13.0 ± 4.7	1.99 ± 0.73	12.7 ± 4.5	1.95 ± 0.69
Ni/C	0.071 ± 0.008	0.47 ± 0.05	13.8 ± 5.0	0.97 ± 0.25	14.7 ± 3.1	1.03 ± 0.10

Uncertainly values are the standard deviations of at least three sets of experimental repeats.

Sample	Temperature (K)	Loading	ECSA $(cm_{\rm ex}^2 u g_{\rm ex}^{-1})$	$j^{\theta,s}$	j ^{θ,m}	Reference
	(K)	(mg _{Ni} cm)	$(\operatorname{cm}_{\mathrm{Ni}} \mu \mathrm{g}_{\mathrm{Ni}})$	(µA cm _{Ni})	$(\mu A \mu g_{Ni})$	
Ni/SC		0.138	0.169	40.2	7.44	
Ni/NC	202	0.167	0.161	29.9	4.82	This work
Ni/BC	303	0.168	0.154	13.0	1.99	THIS WOLK
Ni/C		0.167	0.071	13.8	0.97	
Ni/N-CNT			0.126	28	3.53	
Ni/CNT	r.t.	0.25	0.106	9.2	0.98	<i>Nat. Commun.</i> , 2016 , <i>7</i> , 10141
Ni			0.112	1.3	0.15	
NiMo/KB	298	0.1 (Ni + Mo)		27	4.5 (Ni + Mo)	J. Mater. Chem. A, 2017, 5, 24433
Ni@(h-BN)/C		0.25	0.152	23	3.50	<i>Chem. Sci.</i> , 2017 , <i>8</i> , 5728
CoNiMo	293			15 ($\alpha = 0.5$) 7 ($\alpha = 1$)		Energy Environ. Sci., 2014 , 7, 1719
Ni _{0.95} Cu _{0.05} /C	298			14	1.5	Top Catal., 2015, 58, 1181
Ni _{0.95} Cu _{0.05} /C	298	0.025 (Ni + Cu)		14	2.5	J. Electroanal. Chem., 2016 , 783, 146
Non-activated Ni _{ED} /XC-72			0.924	6.2		
Ch-activated Ni _{ED} /XC-72	298		0.467	56		J. Power Sources, 2018, 402, 447
EC-activated Ni _{ED} /XC-72			0.446	39		

Table S4. ECSA, SA ($j^{0,s}$), and MA ($j^{0,m}$) of the Ni-based catalysts in alkaline medium (pH ~ 13).

	Carbon (total)	Heteroatoms	Ni ₄ clusters (total)
Ni/SC	-0.225	0.008	0.217
Ni/NC	0.240	-0.435	0.194
Ni/BC	-0.451	0.230	0.224
Ni/C	-0.237	/	0.235

Table S5. Mülliken population analysis for Ni_4 clusters on carbon matrix with different dopants.

S	Site	HBE/eV	$\Delta G_{H^{*}}/eV$
	Ni/SC-1	0.08	0.32
N:/00	Ni/SC-2	-0.24	0.00
NI/SC	Ni/SC-3	0.22	0.02
	Ni/SC-4	-0.20	0.04
	Ni/NC-1	-0.24	0.00
NUALC	Ni/NC-2	-0.29	-0.05
INI/INC	Ni/NC-3	-0.06	0.18
	Ni/NC-4	-0.30	-0.06
	Ni/BC-1	-0.32	-0.08
N:/DC	Ni/BC-2	-0.29	-0.05
NI/BC	Ni/BC-3	-0.38	-0.14
	Ni/BC-4	-0.30	-0.06
	Ni/BC-1	-0.44	-0.20
N:/C	Ni/BC-2	-0.24	0.00
INI/C	Ni/BC-3	-0.27	-0.03
	Ni/BC-4	-0.40	-0.16

Table S6. The values of HBE and ΔG of the H* adsorbed on the sites of different models.

Table S7. The values of HBE and ΔG of the H* adsorbed on the sites of different models.

Sample	HBE/eV	$\Delta G_{H^*}/eV$
Ni/SC-1:5	-0.25	-0.01
Ni/SC-1:15	-0.29	-0.04

Reference

(1) Z. Zhuang, S. A. Giles, J. Zheng, G. R. Jenness, S. Caratzoulas, D. G. Vlachos and Y. Yan, Nat. Commun.,

2016, 7, 10141.