Supporting Information

MOFs-derived Hierarchical 3D Bi-doped CoP Nanoflower Eletrocatalyst

for Hydrogen Evolution Reaction in Both Acidic and Alkaline Media

Lei Guo,^{a+} Xue Bai,^{a+} Hui Xue^{*a}, Jing Sun^a, Tianshan Song,^a Shuai Zhang,^a Ling Qin,^a Keke Huang,^b Feng He,^c and Qin Wang^{*a}

^a College of Chemistry and Chemical Engineering, Inner Mongolia University

Hohhot 010021, P. R. China

^b State Key Laboratory of Inorganic Synthesis and Preparative Chemistry

Jilin University, Changchun 130022, P. R. China

^c Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China

University of Chinese Academy of Sciences, Beijing 100190, P. R. China

*Corresponding author: Prof. Dr. Q. Wang

Email: qinwang@imu.edu.cn

Synthesis of ZIF-67

All the chemicals were directly used after purchase without further purification. In a typical synthesis, $1.092 \text{ g } \text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 15 mL methanol to form solution A, and solution B was composed of 0.616 g 2-methylimidazole and 15 mL methanol. Then, solution A was adding to solution B drop by drop under sonication, and maintained sonication for 10 minutes. Afterwards, the mixed solution was transferred into a Teflon-lined stainless steel autoclave and maintained at 120 °C for 4 h. After the autoclave cooled down to room temperature, the as-obtained powder was washed with methanol for several times and dried at 80 °C overnight.

Synthesis of CoP

0.1 g NaH₂PO₂ was placed at the upstream side of the quartz crucible and 0.02 g ZIF-67 was placed at the downstream side. Then, it was calcined at 350 °C for 2 h in N₂ atmosphere with the heating rate of 2 °C/min.

Synthesis of 3% Bi/ZIF-67

In a typical synthesis, 1.092 g Co(NO₃)₂·6H₂O and 0.057 g Bi(NO₃)₃·5H₂O were dissolved in 15 mL absolute methanol to form solution A, and solution B was composed of 0.616 g 2-methylimidazole and 15 mL methanol. Then, solution A was adding to solution B drop by drop under sonication, and maintained sonication for 10 minutes. Afterwards, the mixed solution was transferred into a Teflon-lined stainless steel autoclave and maintained at 120 °C for 4 h. After the autoclave cooled down to room temperature, the as-obtained powder was washed with methanol for several times and dried at 80 °C overnight. In addition, other Bi doped ZIF-67 precursors were also prepared by the same experimental process only mass fraction of bismuth was changed.

Synthesis of 3% Bi/CoP

0.1 g NaH₂PO₂ was placed at the upstream side of the quartz crucible and 0.02 g 3% Bi/ZIF-67 was placed at the downstream side. Then, it was calcined at 350 °C for 2 h in N₂ atmosphere with the heating rate of 2 °C/min. Other comparison sample with different amount of Bi content were prepared by the same experimental process.

Materials characterization

X-ray powder diffraction (XRD) was performed using a PuXi XD3 diffractometer with graphite monochromatized Cu-K α radiation (λ =0.15406 nm). Thermogravimetric Analysis (TG) data were collected on a Netzsch STA449 instrument from room temperature (25°C) to 900°C with a heating rate of 10 °C/min under compressed N₂ flow. The scanning electron microscopy (SEM) images were performed on JEOL-JSM 6700-F SEM. The transmission electron microscopy (TEM) images and scanning transmission electron microscopy (STEM) elemental mapping were taken on JEM-2010 system and a HITACHI 800 operating at acceleration voltages of 120 kV and 200 kV, respectively. X-ray photoelectron spectra (XPS) were obtained on an ESCALAB 250 X-ray electron spectrometer using Al-K α radiation.

Electrochemical measurements.

Electrochemical measurements were carried out using a CHI 760E electrochemical workstation (ChenHua, Shanghai, China) with a three-electrode system at room temperature. Typically, 5 mg catalyst mixed with 25 μ L Nafion® solution (5 %) were dispersed in 250 μ L water and 250 μ L ethanol, and ultrasonicated for 30 min to form a homogeneous ink. Then, 2 μ L dispersion solution was deposited onto the glassy-carbon electrode with an area of 0.0707 cm² (3.0 mm in diameter). The reference electrode was Hg/HgCl electrode and the counter electrode was carbon rod. In alkaline solution: Linear-sweep voltammetry was performed at a scan rate of 5 mV s⁻¹ in N₂-saturated 1.0 M KOH solutions. The electrochemical impedance spectroscopies (EIS) were carried out at -1.1 V (vs. Hg/HgCl) in a frequency from range 100 KHz to 100 MHz with an amplitude of 5 mV. To evaluate the electrochemical active surface

area of the catalysts, the electrochemical double-layer capacitance (Cdl) of the samples in 1.0 M KOH solution was measured by using cyclic voltammetry (CV) in a nonFaradaic region at different scan rates. All electrochemical measurements were carried out at room temperature.

In acid solution: Linear-sweep voltammetry was performed at a scan rate of 5 mV s⁻¹ in N₂-saturated 0.5 M H₂SO₄ solutions. The electrochemical impedance spectroscopies (EIS) were carried out at -0.1 V (vs. Hg/HgCl) in a frequency from range 100 KHz to 100 MHz with an amplitude of 5 mV. To evaluate the electrochemical active surface area of the catalysts, the electrochemical double-layer capacitance (Cdl) of the samples in 0.5 M H₂SO₄ solution was measured by using cyclic voltammetry (CV) in a nonFaradaic region at different scan rates. All electrochemical measurements were carried out at room temperature. The Faradaic efficiency can be calculated by follow equation:

Faradaic efficiency
$$= \frac{mnF}{Q}$$

F is the Faraday constant, *m* is number of moles for total amount of hydrogen produced, *n* is number of electrons in electrode reaction, n = 2. Q(C) is the total amount of charge passed through the electrode. To determine the faradic efficiency, H₂ was collected by the water-gas displacing method. Then, the theoretical amount of H₂ was calculated by the Faraday law with an I-t curves

Computational details

All calculations were based on density functional theory (DFT) using the Vienna Abinitio Simulation Package (VASP).^{1, 2} The Perdew-Burke-Ernzerhof functional (PBE) of generalized gradient approximation functional (GGA) was used for the electronic exchange and correlation effects.³ The core electrons were approximated with the projector-augmented wave (PAW) method.⁴ The plane wave energy cutoff was set as 450 eV, and the first Brillouin zone was sampled in the Monkhorst-Pack grid with a $3\times3\times1$ k-points mesh.⁵ Geometries were optimized until the energy was converged to 1.0×10^{-6} eV/atom and the force was converged to 0.01 eV/Å. A 2×2 supercell and four layers of CoP (202) and Bi doped CoP (202) surface were chosen to construct the investigated sample. A 15 Å vacuum above the surface was chosen to avoid the periodic interaction. The dispersion corrections DFT-D3 was employed in order to describe the vdw interaction in this work.

As known, the key reaction steps in alkaline HER include the H_2O splitting to form H* intermediate process (the Volmer step) and the H_2 generation process (the Tafel step or the Heyrovsky step), which are shown as follow:

(1) $H_2O + e^- + * \rightarrow H^* + OH^-$ (Volmer step)

(2) $2H^* \rightarrow H_2 \uparrow (Tafel step)$

(3)
$$H^* + H_2O + e^- \rightarrow * + OH^- + H_2\uparrow$$
 (Heyrovsky step)

where * represents the catalyst surface. The free energy of elementary reaction was calculated using the following equation⁶:

ΔG =Etotal-Esurface-EH2/2+ $\Delta EZPE$ -T ΔS

where G, E, ZPE and TS represent the free energy, total energy from DFT calculations, zero point energy and entropic contributions (T was set to be 300K), respectively. ZPE values could be derived after frequency calculation by⁷:

$$ZPE = \frac{1}{2} \sum hv_i$$

TS values of adsorbed species were calculated after obtaining the vibrational frequencies⁸:

$$TS_{\nu} = k_{B}T \left[\sum_{K} \ln(\frac{1}{1 - e^{-h\nu/k_{B}T}}) + \sum_{K} \frac{h\nu}{k_{B}T} \frac{1}{(e^{h\nu/k_{B}T} - 1)} \right]$$



Fig. S1 XRD patterns of ZIF-67 and 3% Bi/ZIF-67 precursor.



Fig. S2 XRD patterns of different content of Bi on CoP.



Fig. S3 SEM images: (a) and (b) 3% Bi/CoP; (c) and (d) 7% Bi/CoP; (e) and (f) 10% Bi/CoP.



Fig. S4 TGA-DTG of 3% Bi/ZIF-67 under nitrogen atmosphere with a heating rate of 10 °C min⁻¹.

As show in Fig. S4, the 3% Bi/ZIF-67 sample begins to lose mass above 200 °C, which probably corresponds to loss of inserted water molecules and the decomposition of the hydroxide composition. A sharp drop in mass at 250 °C can be ascribed to structural degradation. The TGA results indicated that imidazole molecules in 3% Bi/ZIF-67 should be decomposed during phosphination step. Furthermore, the characteristic peak of N 1s from XPS survey spectra has disappeared after phosphating process, indicting that the imidazole molecules were removed from catalyst (Fig. S5).



Fig. S5 XPS survey spectra of the 3% Bi/CoP.



Fig. S6 HER polarization curves and (a) Tafel slopes (b) of different content of Bi /CoP in 1 M KOH.



Fig. S7 CV curves at various scan rates in the potential range -0.08-0.02 V of different content of Bi/CoP in 1 M KOH: (a) 1% Bi/CoP; (b) 3% Bi/CoP; (c) 5% Bi/CoP; (d) 7% Bi/CoP; (e) 10% Bi/CoP; (f) 20% Bi/CoP; (g) 30% Bi/CoP.



Fig. S8 EIS Nyquist plots of the of the prepared phosphorized Bi/CoP in 1 M KOH.

Fig. S9 HER polarization curves (a) and Tafel slopes (b) of different content of Bi /CoP in 0.5 M H_2SO_4 .



Fig. S10 CV curves at various scan rates in the potential range -0.05-0.05 V of different content of Bi/CoP in 0.5 M H₂SO₄: (a) 1% Bi/CoP; (b) 3% Bi/CoP; (c) 5% Bi/CoP; (d) 7% Bi/CoP; € 10% Bi/CoP; (f) 20% Bi/CoP; (g) 30% Bi/CoP.



Fig. S11 EIS Nyquist plots of the of the prepared phosphorized Bi/CoP in 0.5 M H_2SO_4 .



Fig. S12 Photographs of Faradaic efficiency measurement device.



Fig. S13 The amount of gas (theoretically calculated and experimentally measured) vs. time for hydrogen production in (a) alkaline media, and (b) acid media.



Fig. S14 SEM images of 3% Bi/CoP after the stability test (a) in $0.5 \text{ M H}_2\text{SO}_4$ and (b) in 1.0 M KOH, respectively.



Fig. S15 XPS survey spectra of the 3% Bi/CoP after durability tests in 0.5 M $\rm H_2SO_4$



Fig. S16 XPS spectra of 3% Bi/CoP after durability tests in 0.5 M H_2SO_4 and 1.0 M KOH: (a) Co 2p, (b) Bi 4f, (c) P 2p, and (d) O 1s.



and acidic media.

Catalysts	Electrolyte	Overpotential at 10 mA cm ⁻² (η ₁₀ / mV)	Tafel slope (mV dec ⁻¹)	Ref.
3% Bi/CoP	1.0 M KOH	122	60.2	This work
MoC _x	1.0 M KOH	151	59	9
CoP/rGO	1.0 M KOH	120	38	10
NiSe@NC	1.0 M KOH	250	55.3	11
Ni ₂ P nanosheets	1.0 M KOH	168	63	12
Co-P/NC	1.0 M KOH	154	51	13
CoNiP-4	1.0 M KOH	138	65	14
Co ₄ Ni ₁ P	1.0 M KOH	129	52	15
Ni@NC-800	1.0 M KOH	205	160	16
3D-CNTA	1.0 M KOH	185	135	17
C/LDH/S	1.0 M KOH	142	62	18
Mo ₂ C/C	1.0 M KOH	165	63.6	19
NiSe ₂ @NG	1.0 M KOH	171	72.4	20
HC800	1.0 M KOH	123	83	21
Co@NCNTs-800	1.0 M KOH	240	83	22
Ni/CoO@CoNC	1.0 M KOH	190	98	23
CoO@CoP	1.0 M KOH	201	37	24
CoP/NCNT-CP	1.0 M KOH	165	96	25
Co-NC-800	1.0 M KOH	242	94	26
Co@N-Carbon	1.0 M KOH	305	107	27

NGO/Ni ₇ S ₆	1.0 M KOH	370	145.5	28
3% Bi/CoP	0.5 M H ₂ SO ₄	150	64.5	This work
ZnxCo1-xMoS ₃	0.5 M H ₂ SO ₄	160	85	29
CoSx@MoS ₂	0.5 M H ₂ SO ₄	347	103	30
C-MoS ₂	0.5 M H ₂ SO ₄	200	53	31
NiMo ₂ C@C	0.5 M H ₂ SO ₄	169	100	32
Co-SAC	0.5 M H ₂ SO ₄	260	80	33
CTGU-5	0.5 M H ₂ SO ₄	388	125	34
FeCo@NGC	0.5 M H ₂ SO ₄	262	174	35
MoC@GS	0.5 M H ₂ SO ₄	124	43	36
Ni-Co-MoS ₂ @NC	0.5 M H ₂ SO ₄	155	51	37
NiMo/NiMoO ₄ @NC/NF	0.5 M H ₂ SO ₄	80	98.9	38

Reference

- 1. Kresse, G.; Hafner, J, Phys. Rev. B. 1993, 47, 558-561.
- 2. Kresse, G.; Hafner, J, Phys. Rev. B. 1994, 49, 14251-14269.
- 3. Perdew, J. P.; Burke, K.; Ernzerhof M, Phys. Rev. Lett. 1996, 77, 3865-3868.
- 4. Kresse, G.; Joubert, D, Phys. Rev. B: Condens. *Matter Mater. Phys.* 1999, **59**, 1758-1775.
- 5. Monkhorst, H. J.; Pack, J. D, Phys. Rev. B. 1976, 13, 5188-5192.
- 6. J. K. Norskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandelov,

U. Stimming, PLoS One. 2005, 5, e12154-e12154.

- J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard, H. Jónsson, J. Chem. Phys. B. 2004, 108, 17886-17892.
- 8. L. I. Bendavid and E. A. Carter, J. phys. chem. C. 2013, 117, 26048-26059.
- H. B. Wu, B. Y. Xia, L. Yu, X. Y. Yu and X. W. Lou, *Nat. Commun.* 2015, 6, 6512.
- 10. L. Jiao, Y. X. Zhou and H. L. Jiang, Chem. Sci. 2016, 7, 1690-1695.
- Z. Huang, J. Liu, Z. Xiao, H. Fu, W. Fan, B. Xu, B. Dong, D. Liu, F. Dai and D. Sun, *Nanoscale*. 2018, **10**, 22758-22765.
- Q. Wang, Z. Liu, H. Zhao, H. Huang, H. Jiao and Y. Du, J. Mater. Chem. A. 2018, 6, 18720-18727.
- B. You, N. Jiang, M. Sheng, S. Gul, J. Yano and Y. Sun, *Chem. Mater.* 2015, 27, 7636-7642.
- Y. Lu, Y. Deng, S. Lu, Y. Liu, J. Lang, X. Cao and H. Gu, *Nanoscale*. 2019, 11, 21259-21265.
- L. Yan, L. Cao, P. Dai, X. Gu, D. Liu, L. Li, Y. Wang and X. Zhao, *Adv. Funct. Mater.* 2017, 27,1703455.
- Y. Xu, W. G. Tu, B. W. Zhang, S. M. Yin, Y. Z. Huang, M. Kraft, R. Xu, *Adv. Mater.* 2017, 29, 1605957
- 17. S. J. Wang, J. W. Qin, T. Meng, M. H. Cao, Nano Energy. 2017, 39, 626
- G. Yilmaz, K. M. Yam, C. Zhang, H. J. Fan and G. W. Ho, *Adv. Mater.* 2017, 29, 1606814.
- M. Qamar, A. Adam, B. Merzougui, A. Helal, O. Abdulhamid and M. N. Siddiqui, J. Mater. Chem. A. 2016, 4, 16225-16232.

- W. Li, B. Yu, Y. Hu, X. Wang, D. Yang and Y. Chen, ACS Sustain Chem. Eng. 2019, 7, 4351-4359.
- 21. X. Xu, F. Nosheen and X. Wang, Chem. Mater. 2016, 28, 6313-6320.
- J.-S. Li, B. Du, Z.-H. Lu, Q.-T. Meng and J.-Q. Sha, New J Chem. 2017, 41, 10966-10971.
- 23. G. Cai, W. Zhang, L. Jiao, S.-H. Yu and H.-L. Jiang, Chem. 2017, 2, 791-802.
- M. Lu, L. Li, D. Chen, J. Li, N. I. Klyui and W. Han, *Electrochimica Acta*, 2020, 330, 135210.
- L. Wang, J. Cao, X. Cheng, C. Lei, Q. Dai, B. Yang, Z. Li, M. A. Younis, L. Lei, Y. Hou and K. Ostrikov, ACS Sustain Chem. Eng. 2019, 7, 10044-10051.
- R. Wang, P. Sun, Q. Yuan, R. Nie and X. Wang, *Inter J Hydrogen Energ*. 2019, 44, 11838-11847.
- J. Cong, H. Xu, M. Lu, Y. Wu, Y. Li, P. He, J. Gao, J. Yao and S. Xu, *Chem Asian J.* 2018, 13, 1485-1491.
- K. Jayaramulu, J. Masa, O. Tomanec, D. Peeters, V.Ranc, A. Schneemann, R. Zboril, W.Schuhmann, R. Fische, *Adv. Funct. Mater.* 2017, 27, 1700451.
- L. Zhang, L. Yang, G. Xu, W. Wang, H. Song, C. Wang and D. Jia, ACS Sustain Chem. Eng. 2019, 7, 9800-9807.
- L. Yang, L. Zhang, G. Xu, X. Ma, W. Wang, H. Song and D. Jia, ACS Sustain Chem. Eng. 2018, 6, 12961-12968.
- J. Feng, H. Zhou, J. Wang, T. Bian, J. Shao and A. Yuan, *Int J Hydrogen Energ*. 2018, 43, 20538-20545.
- X. Li, L. Yang, T. Su, X. Wang, C. Sun and Z. Su, J. Mater. Chem. A. 2017, 5, 5000-5006.

- 33. W. Zhao, G. Wan, C. Peng, H. Sheng, J. Wen and H. Chen, *ChemSusChem*. 2018, 11, 3473-3479.
- Y. P. Wu, W. Zhou, J. Zhao, W. W. Dong, Y. Q. Lan, D. S. Li, C. Sun and X. Bu, Angew. Chem., Int. Ed. 2017, 56, 13001-13005.
- Y. Yang, Z. Lun, G. Xia, F. Zheng, M. He and Q. Chen, *Energ Environ. Sci.* 2015, 8, 3563-3571.
- Z. Shi, Y. Wang, H. Lin, H. Zhang, M. Shen, S. Xie, Y. Zhang, Q. Gao and Y. Tang, J. Mater. Chem. A. 2016, 7,7301-7327.
- X. Y. Yu, Y. Feng, Y. Jeon, B. Guan, X. W. Lou and U. Paik, *Adv. Mater.* 2016, 28, 9006-9011.
- K. Karuppasamy, V. R. Jothi, D. Vikraman, K. Prasanna, T. Maiyalagan, B.-I. Sang, S.-C. Yi and H.-S. Kim, *Appl. Surf. Sci.* 2019, 478, 916-923.