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CoNi-Based Metal-Organic Frameworks Nanoarrays Supported on Carbon Cloth as Bifunctional Electrocatalysts for Efficient Water-Splitting[†]

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Experimental

Materials

Cobalt acetate tetrahydrate (Co(OAc)₂·4H₂O), acetate tetrahydrate (Ni(OAc)₂·4H₂O), cobalt chloride hexahydrate (CoCl₂·6H₂O), nickel chloride hexahydrate (NiCl₂·6H₂O), terephthalic acid (H₂BDC) and potassium hydroxide (KOH) were purchased from Energy Chemical (Shanghai). Nafion, RuO₂, N, N-Dimethylformamide (DMF) and ethanol (C₂H₅OH) were purchased from Sinopharm Chemical Reagent Co., Ltd. The water used in this work was deionized water. All chemicals used in this study were of analytical grade and used without further purification.

Preparation of 2D CoNiBDC-MOF arrays onto carbon cloth by spray method: (CoNiBDC/CC)

H₂BDC (66.4 mg, 0.4 mmol) was dissolved in 18 mL of mixture of DMF, C₂H₅OH and H₂O (V:V:V =16:1:1) in a vial. Then the clean carbon cloth was soaked in the above transparent solution for 2min. After that, Co(OAc)₂·4H₂O (50 mg) and Ni(OAc)₂·4H₂O (50 mg) were dissolved in 18 mL of mixture of DMF, C₂H₅OH and H₂O (V:V:V =16:1:1), and 0.1 mL of the metal ions solution was uniformly sprayed onto the wet carbon cloth with the flow rate of 2 μ L/sec. The resulting carbon cloth was dried naturally and then heated at 80 °C for 6 hours in a vacuum.

Synthesis of bulk CoNiBDC onto carbon cloth by hydrothermal method: (CoNiBDC-H/CC)

0.75 mmol (124.5 mg) H₂BDC was dissolved into the 18 mL of mixed solution of DMF, C₂H₅OH and H₂O (V:V:V =16:1:1) under ultrasonication. Subsequently, 0.375 mmol (89.3 mg) CoCl₂·6H₂O and 0.375 mmol (89.3 mg) NiCl₂·6H₂O were dissolved into the 18 mL of mixed solution of DMF, C₂H₅OH and H₂O (V:V:V =16:1:1). Finally, the two solutions and a clean carbon cloth were mixed and transferred into a 45 ml Teflon-lined autoclave at 140 °C for 48 h under airtight conditions. The resulting carbon cloth was dried naturally and then heated at 80 °C for 6 hours in a vacuum.

Characterization

Morphologies of samples were characterized by field-emission scanning electron

microscopy (FESEM, Hitachi SU8010) and transmission electron microscopy (TEM, JEOL JEM2100PLUS). The elemental mapping was done by energy-dispersive X-ray (EDX, Oxford Instruments). The crystallographic information was analyzed by X-ray diffraction (XRD, PANalytical Empyrean) equipped with a Cu K α radiation source (λ = 1.5406 Å). The organic groups in the CoNiBDC-MOF was characterized by Fourier transform infrared spectroscopy (FT-IR, Bruker VERTEX 70). The composition of the materials was analyzed through quantitative X-ray photoelectron spectroscopy (XPS) which gave information about the surface electronic states of the elements (THERMO VG ESCALAB250). The ultraphonic spray nozzle & system was manufactured by Siansonic Technology Co., Ltd. The ultraphonic generator was DP30 and the nozzle is ZPQ-S-95.

Electrochemical Tests

The electrochemical test for OER and HER were performed on a CHI 660E electrochemical workstation in a standard three-electrode system using CoNiBDC/CC, CoNiBDC-H/CC and RuO₂/CC as working electrode, a Platinum sheet (OER) / carbon rod (HER) as counter electrode, and an Ag/AgCl as reference electrode. A twoelectrode cell was constructed by using CoNiBDC/CC as both the anode and the cathode material for the water splitting electrochemical test. RuO₂/CC was prepared by ultrasonication of the mixture of 3 mg of RuO₂, 1 mL of ethanol and 50 µL of 5 wt % Nafion. Then, the RuO₂ ink was loaded on carbon cloth to achieve a mass loading of 1 mg cm⁻². Linear sweep voltammetry (LSV) curves of the samples were recorded in 1 M KOH at a scan rate of 5 mV s⁻¹, and the potentials reported here were calibrated with respect to the reversible hydrogen electrode (RHE): $E(RHE) = E(Ag/AgCl) + 0.059 \times$ pH + 0.197. For OER: (1) Polarization curves were expressed as the potential (η) vs log current (log |j|) to obtain the Tafel plots. By fitting the linear portion of the Tafel plots to the Tafel equation $[\eta = blog(j) + a]$, the Tafel slope (b) was obtained. (2) Electrochemical impedance spectra (EIS) were recorded in the frequency range from 0.1 to 10⁵ Hz with an AC amplitude of 5 mV at an applied potential of 1.479 V 1.481 V and 1.576 V (vs the RHE) for RuO₂/CC, CoNiBDC/CC and CoNiBDC-H/CC, respectively. (3) The effective surface area of CoNiBDC/CC was tested by estimating the electrochemical double layer capacitance (C_{dl}) with CV. CV curves were performed at a potential range of 0.2-0.3 V vs RHE where no obvious electrochemical features corresponding to the Faradaic current were observed. The capacitive currents at 0.25 V were plotted against the scan rate (0.02 mV/s-0.1m V/s). Durability of the CoNiBDC/CC for OER, HER and water splitting catalysis were evaluated by chronoamperometry at a potential of 1.48 V, -0.135 V and 1.625 V (vs the RHE), respectively.

The Faradaic efficiency (FE) was obtained according to:

$$FE = \frac{Iring}{Ce \times Idisk}$$

Here, Idisk is the given current on the disk electrode. Iring is the collection current on the Pt ring electrode at a constant potential of 0.4V versus RHE. Ce is the oxygen collection coefficient (\sim 0.2) for this type of electrode configuration.



Fig. S1. The photograph of bare carbon cloth and CoNiBDC/CC



Fig. S2. TEM images of CoNiBDC nanosheets.



Fig. S3. SEM images of bulk CoNiBDC onto carbon cloth by hydrothermal method (CoNiBDC-H/CC).



Fig. S4. Crystalline structure of CoNiBDC. Cobalt, nickel, oxygen, hydrogen and carbon atoms are shown in purple, green, red, white and grey, respectively.



Fig. S5. XPS survey spectrum CoNiBDC.



Fig. S6. Energy dispersive X-ray (EDX) elemental analysis of CoNiBDC.



Fig. S7. High-resolution Ni 2p XPS spectra of NiBDC and CoNiBDC.



Fig. S8. (a) The LSV curves of CoxNiyBDC/CC with different proportion (x y) of Co and Ni. (b) The comparison of overpotential of CoNiBDC/CC with different Co/Ni proportions at 10 and 100 mA cm⁻².



Fig. S9. SEM image of Co_{0.6}Ni_{1.4}BDC/CC.

Catalyst	Current	Overpot	Tafel slope	Substrate	reference
	Density	ential	[mV dec ⁻¹]		
	[mA]	[V]			
Ni-BDC@NiS	20	330	62	Ni substrate	1
UTSA-16	10	408	62	GCE	2
Co _{0.6} Fe _{0.4} -MOF-74	10	280	56	Ni foam	3
FeNi-DOBDC	50	270	49	RDE	4
MIL-53(FeNi)	50	233	31.3	Ni foam	5
A _{2.7} B-MOF-FeCo _{1.6}	10	288	39	Ni foam	6
Ni-MOF@Fe-MOF	10	265	82	GCE	7
(Ni ₂ Co ₁) _{0.925} Fe _{0.075} -MOF	10	257	41.3	Ni foam	8
CTGU-10c2	10	240	58	GCE	9
Co/NiMOFs@Fe	10	264	53.4	Fe foam	10
Ni-MOF	10	346	64	carbon	11
Ni@JXUN-4-NA	20	310	102	Cu foam	12
NiFe-MOF-74	10	223	71.6	Ni foam	13
Co/Fe-MOFs	10	410	60	FTO	14
Fe(OH) ₃ @Co-MOF-74	10	292	44	carbon paper	15
Co ₂ Fe-MOF	10	280	44.7	GCE	16
Ni-MOF	100	320	123	Ni foam	17
Fe-MOF	50	240	72	Ni foam	18
Fe/Ni-MOFs	10	236	49	Ni foam	19
Fe ₁ Ni ₄ -HHTP	150	300	96	carbon cloth	20
Co-Fe/Ni@HPA-MOF	10	320	58	GCE	21
FeNi-MIL-101	20	237	44.2	Ni foam	22
CoBDC-Fc	10	178	51	Ni foam	23
NiCo-UMOFNs	10	250	42	GCE	24
NiCu-MOFNs	100	309	47.9	Ni foam	25
Co-MOFs	10	398	59		26
FN-2	10	275	56.7	carbon paper	27
Co-MONs	10	309	75.71	carbon paper	28
CoNiBDC/CC	10	251	42	carbon cloth	This work

 Table S1. The catalytic activity of different MOFs-catalysts for OER



Fig. S10. The Overpotential at $10 \text{ mA} \cdot \text{cm}^{-2}$ and Tafel slope for OER of different MOFscatalysts.

References:

- P. He, Y. Xie, Y. Dou, J. Zhou, A. Zhou, X. Wei and J.-R. Li, *ACS Appl. Mater. Interfaces*, 2019, 11, 41595-41601.
- 2. J. Jiang, L. Huang, X. Liu and L. Ai, ACS Appl. Mater. Interfaces, 2017, 9, 7193-7201.
- X. Zhao, B. Pattengale, D. Fan, Z. Zou, Y. Zhao, J. Du, J. Huang and C. Xu, ACS Energy Lett., 2018, 3, 2520-2526.
- 4. F. Zheng, D. Xiang, P. Li, Z. Zhang, C. Du, Z. Zhuang, X. Li and W. Chen, ACS Sustainable Chem. Eng., 2019, 7, 9743-9749.
- 5. F. Sun, G. Wang, Y. Ding, C. Wang, B. Yuan and Y. Lin, Adv. Energy Mater., 2018, 8, 1800584.
- Z. Xue, Y. Li, Y. Zhang, W. Geng, B. Jia, J. Tang, S. Bao, H.-P. Wang, Y. Fan, Z.-w. Wei, Z. Zhang, Z. Ke, G. Li and C.-Y. Su, *Adv. Energy Mater.*, 2018, 8, 1801564.
- K. Rui, G. Zhao, Y. Chen, Y. Lin, Q. Zhou, J. Chen, J. Zhu, W. Sun, W. Huang and S. X. Dou, *Adv. Funct. Mater.*, 2018, 28, 1801554.
- 8. Q. Qian, Y. Li, Y. Liu, L. Yu and G. Zhang, Adv. Mater., 2019, 31, 1901139.
- W. Zhou, D.-D. Huang, Y.-P. Wu, J. Zhao, T. Wu, J. Zhang, D.-S. Li, C. Sun, P. Feng and X. Bu, Angew. Chem. Int. Ed., 2019, 58, 4227-4231.
- 10. P. Luo, S. Li, Y. Zhao, G. Ye, C. Wei, Y. Hu and C. Wei, *Chemcatchem*, 2019, DOI: 10.1002/cctc.201900972.
- 11. V. Maruthapandian, S. Kumaraguru, S. Mohan, V. Saraswathy and S. Muralidharan, *Chemelectrochem*, 2018, **5**, 2795-2807.
- Z.-Q. Jiang, Y.-F. Li, X.-J. Zhu, J. Lu, T. Wen and L. Zhang, *Chem. Commun.*, 2019, 55, 4023-4026.
- 13. J. Xing, K. Guo, Z. Zou, M. Cai, J. Du and C. Xu, Chem. Commun., 2018, 54, 7046-7049.
- B. Iqbal, M. Saleem, S. N. Arshad, J. Rashid, N. Hussain and M. Zaheer, *Chem. Eur. J.*, 2019, 25, 10490-10498.
- 15. Z. Gao, Z. W. Yu, F. Q. Liu, C. Yang, Y. H. Yuan, Y. Yu and F. Luo, *Chemsuschem*, 2019, **12**, 4623-4628.
- 16. S. Xie, F. Li, S. Xu, J. Li and W. Zeng, Chinese Journal of Catalysis, 2019, 40, 1205-1211.
- 17. Q. Liu, L. Xie, X. Shi, G. Du, A. M. Asiri, Y. Luo and X. Sun, *Inorg. Chem. Front.*, 2018, 5, 1570-1574.
- 18. X. Zhang, Q. Liu, X. Shi, A. M. Asiri and X. Sun, Inorg. Chem. Front., 2018, 5, 1405-1408.
- F. Zheng, Z. Zhang, D. Xiang, P. Li, C. Du, Z. Zhuang, X. Li and W. Chen, J. Colloid Interface Sci., 2019, 555, 541-547.
- W.-H. Li, J. Lv, Q. Li, J. Xie, N. Ogiwara, Y. Huang, H. Jiang, H. Kitagawa, G. Xu and Y. Wang, J. Mater. Chem. A, 2019, 7, 10431-10438.
- M. Lu, Y. Li, P. He, J. Cong, D. Chen, J. Wang, Y. Wu, H. Xu, J. Gao and J. Yao, J. Solid State Chem., 2019, 272, 32-37.
- 22. Q. Wang, C. Wei, D. Li, W. Guo, D. Zhong and Q. Zhao, *Microporous Mesoporous Mater.*, 2019, 286, 92-97.
- 23. Z. Xue, K. Liu, Q. Liu, Y. Li, M. Li, C.-Y. Su, N. Ogiwara, H. Kobayashi, H. Kitagawa, M. Liu and G. Li, *Nat. Commun.*, 2019, **10**.
- 24. S. Zhao, Y. Wang, J. Dong, C.-T. He, H. Yin, P. An, K. Zhao, X. Zhang, C. Gao, L. Zhang, J. Lv, J. Wang, J. Zhang, A. M. Khattak, N. A. Khan, Z. Wei, J. Zhang, S. Liu, H. Zhao and Z. Tang, *Nat. Energy*, 2016, 1, 16184.

- 25. X. Zheng, X. Song, X. Wang, Z. Zhang, Z. Sun and Y. Guo, *New J. Chem.*, 2018, **42**, 8346-8350.
- 26. D. Han, K. Huang, X. Li, M. Peng, L. Jing, B. Yu, Z. Chen and D. Qin, *RSC Adv.*, 2019, **9**, 33890-33897.
- 27. M. Liu, L. Kong, X. Wang, J. He and X.-H. Bu, Small, 2019, 15, 1903410.
- 28. X. Wang, H. Zhang, Z. Yang, C. Zhang and S. Liu, Ultrason. Sonochem., 2019, 59, 104714.



Fig. S11. Ring current of CoNiBDC on RRDE at a ring potential of 0.4 V in N2-saturated 1 M KOH solution.



Fig. S12. (a) the chronoamperometry curves of CoNiBDC/CC at the current density of -10 mA cm⁻² for HER. (b) the chronoamperometry curves of the full electrolytic cell at the current density of 20 mA cm⁻² for water overall splitting.



Figure S13. SEM images (a)/(b) and XRD pattern (c) of CoNiBDC/CC after long-term tests.