

# Facile synthesis of CeO<sub>2</sub>-decorated W@Co-MOF heterostructures as a highly active and durable electrocatalyst for overall water splitting

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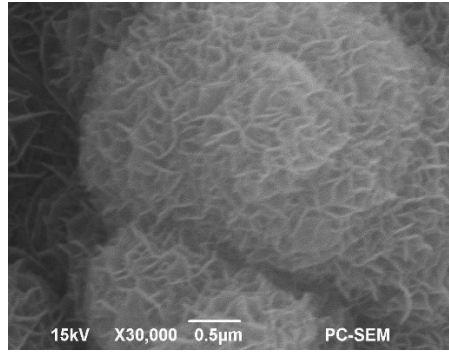
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## **Materials and Reagents**

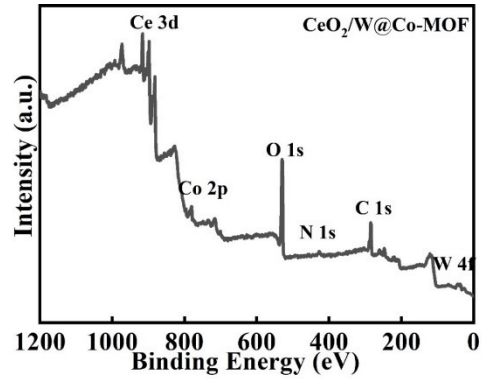
The cobalt nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), Cerium nitrate hexahydrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ) and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) were obtained from Sinopharm Chemical Reagent Co. Ltd. The 2-aminoterephthalic acid (2-NH<sub>2</sub>-BDC) and Sodium metatungstate ( $\text{Na}_6\text{W}_{12}\text{O}_{39} \cdot x\text{H}_2\text{O}$ ) were purchased from Sigma-Aldrich Co. Ltd. The potassium hydroxide (KOH) and N,N-dimethylformamide (DMF) were purchased from Shanghai Maclean Biochemical Technology Co., Ltd. Besides, ultrapure water (18.2 M $\Omega$ ) was utilized throughout the whole experiment. The purity of all reagents more than 99%.

## **Materials characterization**

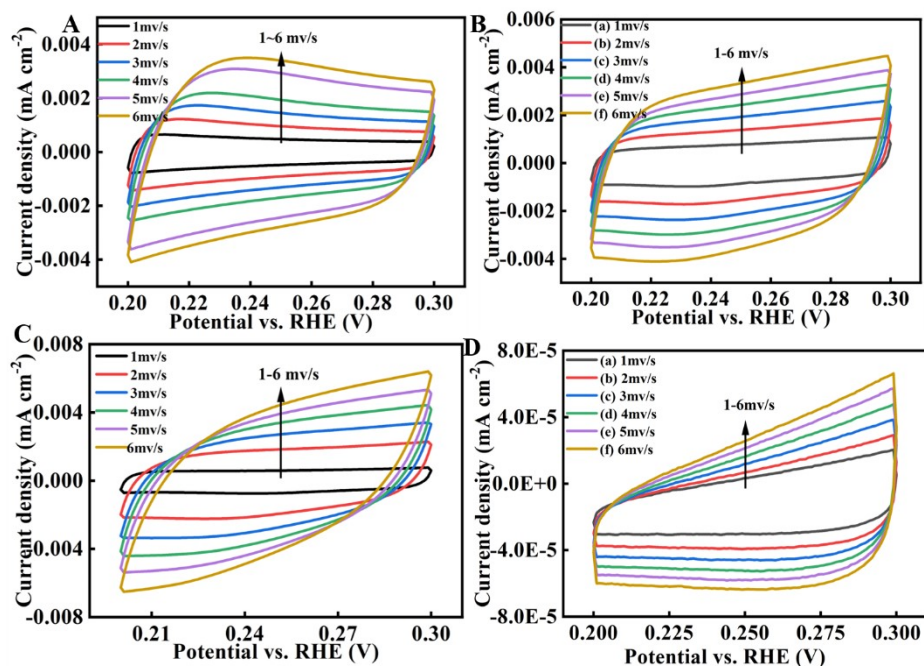
The morphologies and microstructures of the prepared products were tested by scanning electron microscope (SEM, JSM-6360LA, Japan) and transmission electron microscopy (TEM, JEM-2010, Japan). The X-ray diffraction (XRD) was used to identify the crystal phases of products on the Max-2000 (Rigaku Co., Ltd., Japan) and X-ray photoelectron spectroscopy (XPS) can be used to analyze the elemental chemical states of the catalyst materials on the AXIS-Ultra DLD (Shimazu, Japan). The surface pore size adsorption instrument was used to calculate the specific surface area and pore size distribution of the material.



**Fig. S1.** The SEM images of Co-MOF/NF.



**Fig. S2.** XPS full spectrum image of CeO<sub>2</sub>/W@Co-MOF/NF



**Fig. S3.** CV curves of various electrodes in the potential window from 0.05 to 0.15 V (vs. RHE) at 1, 2, 3, 4, 5 and 6 mV s<sup>-1</sup>: (A) Co-MOF/NF, (B) W@Co-MOF/NF, (C) CeO<sub>2</sub>/W@Co-MOF/NF and (D) CeO<sub>2</sub>/NF.

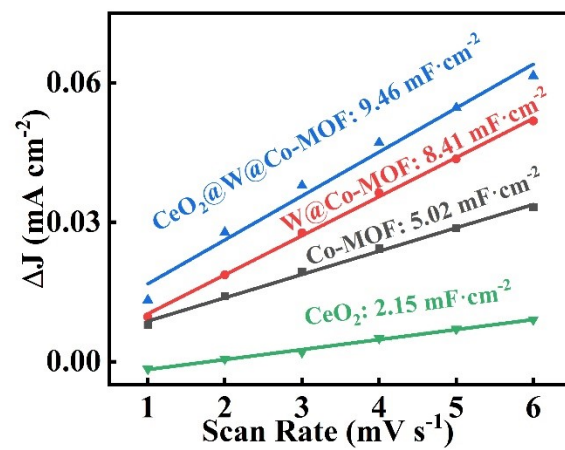


Fig. S4. Double-layer capacitances ( $C_{dl}$ ) of the four samples derived from the cyclic voltammograms.

**Table S1.** Comparison of OER activity at 10 mA cm<sup>-2</sup> and stability of various MOF-based catalysts.

Catalyst	$\eta_{10}/\text{mV}$	Tafel slope/ $\text{mV dec}^{-1}$	Electrolyte	Reference
<b>CeO<sub>2</sub>/W@Co-MOF/NF</b>	<b>239</b>	<b>29.39</b>	<b>1M KOH</b>	<b>This work</b>
Ce/Cu-MOF/GO	386	98.1	1M KOH	1
Co/CoS <sub>2</sub> @NC	349	237.8	1M KOH	2
Co/CoP@HOMC	260	151	1M KOH	3
Hollow CoS <sub>2</sub> -MoS <sub>2</sub>	266	104	1M KOH	4
FeCo-P	240	38.24	1M KOH	5
Fe-Co-Ni MOF	254	51.3	1M KOH	6
(Ni <sub>2</sub> Co <sub>1</sub> ) <sub>0.925</sub> Fe <sub>0.075</sub> -MOF	257	41.3	1M KOH	7
Co-BPDC/Co-BDC-3	335	72.1	1M KOH	8
Co-Ni@HPA-MOF	320	58	1M KOH	9
BaTiO <sub>3</sub> @MOF-Fe/Co	247	38.4	1M KOH	10

**Table S2.** Comparison of HER activity at 10 mA cm<sup>-2</sup> and stability of various Co-based MOFs catalysts.

Catalyst	$\eta_{10}/\text{mV}$	Tafel slope/ mV dec <sup>-1</sup>	Electrolyte	Reference
<b>CeO<sub>2</sub>/W@Co-MOF/NF</b>	<b>87</b>	<b>32.25</b>	<b>1M KOH</b>	<b>This work</b>
Co-Fe-P/CeO <sub>2</sub>	320	69.7	1M KOH	11
Co/CoS <sub>2</sub> @NC	188	54.9	1M KOH	2
Co/CoP@HOMC	120	78	1M KOH	3
FeCo-P	131	89.9	1M KOH	5
NiCo-MOF-P	195	105	1M KOH	12
MXene@Ce-MOF	220	149.9	1M KOH	13
Fe-MOF@MoS <sub>2</sub>	118	68	1M KOH	14



**Table S3.** Comparison of overall water splitting at 10 mA cm<sup>-2</sup> and stability of various Co-based MOFs catalysts.

<b>Catalyst</b>	<b>Volatage/ V</b>	<b>Electrolyte</b>	<b>Reference</b>
<b>CeO<sub>2</sub>/W@Co-MOF/NF</b>	<b>1.54</b>	<b>1M KOH</b>	<b>This work</b>
NiFe-MOF-5	1.57	1M KOH	15
Fe-Co-Ni-MOF	1.60	1M KOH	6
FeCo-P	1.47	1M KOH	16
CoNiP/NF	1.62	1M KOH	17
FeCoMnNi-MOF-74/NF	1.62	1M KOH	18
Co,Fe-MOF-74/Co/CC	1.65	1M KOH	19

## Notes and references

1. Y. Chen, N. Huang and Y. Liang, *Ionics*, 2021, **27**, 4347-4360.
2. G. Gao, B. Fang, Z. Ding, W. Dong, Y.-X. Li, X. L. Wang and Y.-F. Yao, *International Journal of Hydrogen Energy*, 2023, **48**, 1831-1841.
3. W. Li, J. Liu, P. Guo, H. Li, B. Fei, Y. Guo, H. Pan, D. Sun, F. Fang and R. Wu, *Advanced Energy Materials*, 2021, **11**.
4. Y. Li, W. Wang, B. Huang, Z. Mao, R. Wang, B. He, Y. Gong and H. Wang, *Journal of Energy Chemistry*, 2021, **57**, 99-108.
5. H. Jiang, Z. Zhao, G. Li, M. Wang, P. Chen, X. Liu, X. Tu, Y. Hu, Z. Shen and Y. Wu, *Advanced Science*, 2023, **11**.
6. F. Shahbazi Farahani, M. S. Rahmanifar, A. Noori, M. F. El-Kady, N. Hassani, M. Neek-Amal, R. B. Kaner and M. F. Mousavi, *Journal of the American Chemical Society*, 2022, **144**, 3411-3428.
7. Q. Qian, Y. Li, Y. Liu, L. Yu and G. Zhang, *Adv Mater*, 2019, **31**, e1901139.
8. Q. Zha, F. Yuan, G. Qin and Y. Ni, *Inorg Chem*, 2020, **59**, 1295-1305.
9. M. Lu, Y. Li, P. He, J. Cong, D. Chen, J. Wang, Y. Wu, H. Xu, J. Gao and J. Yao, *Journal of Solid State Chemistry*, 2019, **272**, 32-37.
10. S. Wang, Q. Li, S. Sun, K. Ge, Y. Zhao, K. Yang, Z. Zhang, J. Cao, J. Lu, Y. Yang, Y. Zhang, M. Pan, Z. Lin and L. Zhu, *Journal of Materials Chemistry A*, 2022, **10**, 5350-5360.
11. Y. Hu, F. Li, Y. Long, H. Yang, L. Gao, X. Long, H. Hu, N. Xu, J. Jin and J. Ma, *Journal of Materials Chemistry A*, 2018, **6**, 10433-10440.
12. M. M. Rajpure, H. A. Bandal, H. S. Jadhav and H. Kim, *Journal of Electroanalytical Chemistry*, 2022, **923**, 116825.
13. S. Li, H. Chai, L. Zhang, Y. Xu, Y. Jiao and J. Chen, *Journal of Colloid and Interface Science*, 2023, **642**, 235-245.
14. R. Velayutham, C. J. Raj, H. M. Jang, W. J. Cho, K. Palanisamy, C. Kaya and B. C. Kim, *Materials Today Nano*, 2023, **24**.
15. Q. Mou, Z. Xu, G. Wang, E. Li, J. Liu, P. Zhao, X. Liu, H. Li and G. Cheng, *Inorganic Chemistry Frontiers*, 2021, **8**, 2889-2899.
16. D. Ji, S. Peng, L. Fan, L. Li, X. Qin and S. Ramakrishna, *Journal of Materials Chemistry A*, 2017, **5**, 23898-23908.
17. H. Liu, R. Huang, W. Chen, Y. Zhang, M. Wang, Y. Hu, Y. Zhou and Y. Song, *Applied Surface Science*, 2021, **569**.
18. M. Zhang, W. Xu, T. Li, H. Zhu and Y. Zheng, *Inorganic Chemistry*, 2020, **59**, 15467-15477.
19. Q. Zha, M. Li, Z. Liu and Y. Ni, *ACS Sustainable Chemistry & Engineering*, 2020, **8**, 12025-12035.