Supplementary Information

Tungstic Acid Integrated Metal-Organic Frameworks for Efficient

Oxygen Evolution Reaction

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Table S1. The amount of MOF and the corresponding solution used for the synthesis of WO_3 ·xH₂O-in-MIL-88.

| Samples | Precursor solution | EtOH | MIL-88 |
|--|--------------------|------|--------|
| MIL-88 | 0 µL | 5 mL | 50 mg |
| 7%-WO ₃ ·xH ₂ O-in-MIL-88 | 120 µL | 5 mL | 50 mg |
| 15%-WO ₃ ·xH ₂ O-in-MIL-88 | 240 µL | 5 mL | 50 mg |
| 30%-WO ₃ ·xH ₂ O-in-MIL-88 | 580 μL | 5 mL | 50 mg |
| 50%-WO ₃ ·xH ₂ O-in-MIL-88 | 1350 μL | 5 mL | 50 mg |

Synthesis of WO₃-in-MIL-88:

The WO₃-in-MIL-88 composites were obtained by a simple calcination process, where corresponding WO₃·xH₂O-in-MIL-88 composites were heated at 150 °C for 10 h in a vacuum with a heating rate of 2 °C/min, during which coordinated water of WO₃·xH₂O was removed entirely within the mesopores of MOF crystal.

Synthesis of MIL-88-H₂O₂:

MIL-88-H2O2 was obtained in a similar way to WO3·xH2O-in-MIL-88, just

replacing the precursor solution with pure H_2O_2 (30%).

| Samples | H_2O_2 | EtOH | MIL-88 |
|---|----------|------|--------|
| MIL-88 | 0 µL | 5 mL | 50 mg |
| MIL-88-H ₂ O ₂ -1 | 240 µL | 5 mL | 50 mg |
| MIL-88-H ₂ O ₂ -2 | 580 μL | 5 mL | 50 mg |
| MIL-88-H ₂ O ₂ -3 | 1350 µL | 5 mL | 50 mg |

Table S2. The amount of MOF and H_2O_2 used for the synthesis of MIL-88- H_2O_2 .

Electrochemical Measurements

In a typical preparation of catalyst ink, 10 mg of each catalyst (for the catalysts doped with KB, the formula is 9 mg catalyst and 1 mg KB) was blended with 1.0 mL Nafion ethanol solution (0.5 wt.%) in an ultrasonic bath for 30 min. Then, a fixed volume of catalyst ink (5 μ L, 10 mg mL⁻¹) was pipetted onto the glassy carbon electron with an area of 0.196 cm⁻² (loading: 0.255 mg cm⁻²). All the electrochemical measurements were carried out in a conventional three-electrode cell using the Gamry reference 600 workstations (Gamry, USA) at room temperature. A commercial reversible hydrogen electrode (RHE) was used as the reference electrode, and the graphite rod was used as the counter electrode. The measured OER polarization curves are carried out in an Ar-saturated 1.0 M KOH with a sweep rate of 10 mV s⁻¹ at 1600 rpm, which are automatically corrected with real-time iR.

The electrochemically active surface area was estimated by measuring by measuring the capacitance of the double layer at the solid-liquid interface with cyclic voltammetry. The measurement was performed in a potential window of 1.06-1.16 V versus RHE, where the Faradic current on the working electrode was negligible. The series of scan rates ranging from 5 to 25 mV s⁻¹ was applied to build a plot of the

charging current density differences against the scan rate at a fixed potential of 1.11 V. The slope of the obtained linear curve was twice of the double-layer capacitance (C_{dl}).

Electrochemical impedance spectroscopy (EIS) was carried out with a potentiostatic ESI method with a DC voltage of 1.495 V versus RHE in an Ar-saturated 1.0 M KOH electrolyte from 100 kHz to 0.1 Hz with a 10 mV AC potential at 1600 rpm. The stability tests for the catalysts were conducted using chronopotentiometry at the constant working current densities of 10, 50 mA cm⁻².

The mass activity values were calculated based on the following equation:

Mass activity
$$=\frac{1}{m}$$

Where I is the current, m is the weight of active site loaded on electrode.

The TOF values were calculated to reveal the number of oxygen molecules evolved per active site per second based on the following equation:

$$TOF = \frac{I}{2nF}$$

Where *I* is the current, *F* is Faraday constant (96485.3 C mol⁻¹), and *n* (mol) is the number of the active metal on the electrode. The TOFs data was calculated based on the weight content of Fe and Ni from XPS.

The simulated seawater was prepared by mixing 26.83 g of NaCl, 2.26 g of MgCl₂, 3.25 g of MgSO₄, 1.12 g of CaCl₂, 0.19 g of NaHCO₃, 3.48 g of Na₂SO₄ and 0.72 g of KCl in 1 L of ultrapure water. The pH value of simulated water is 8.20. The alkaline seawater was obtained by adding 500 mL of solution to 33 g KOH, followed by ultrasonic centrifugation.

Theoretical calculation model

The periodic boundary conditions were applied to all three directions. The MOFs were assumed to be rigid with nonbonding interactions. $\sum 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \sum \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}, \text{ where } \varepsilon_{ij} \text{ and } \sigma_{ij} \text{ are the well and collision}$ diameter of Lennard-Jones (LJ) potential, r_{ij} is the distance between atoms *i* and *j*, q_i is the atomic charges of atom *i*, and ε_0 is the permittivity of vacuum. The LJ potential parameters were adopted from the universal force field (UFF)¹ with the help of the OBGMX tool. ² The atomic charges of the MOFs were generated using modified EQeq ³ methods deployed by the Atomic Charge Calculator.⁴ Water was modeled by the SPC/E model.⁵ The electrostatic interactions were calculated using the Particle-Mesh Ewald method, while the LJ interactions were calculated using a cutoff of 1.2 nm. The temperature was maintained at 300 K using a v-rescale scheme, and the time step was 1 fs. After equilibration, a constant number of particles, volume, and temperature (NVT) ensemble was used for output simulation. The NVT simulation duration was 5 ns, and the latter 4 ns for data analysis. All the MD simulations were performed using GROMACS 2021,⁶ and the model was visualized using VMD 1.9.⁷

Supplementary Images



Figure S1. SEM images of 50%-WO₃·xH₂O-in-MIL-88.



Figure S2. SEM images and corresponding EDS elemental mappings of MIL-88.



Figure S3. SEM images and corresponding EDS elemental mappings of 7%- $WO_3 \cdot xH_2O$ -in-MIL-88.



Figure S4. SEM images and corresponding EDS elemental mappings of 15%-WO₃·xH₂O-in-MIL-88.



Figure S5. SEM images and corresponding EDS elemental mappings of 30%-WO₃·xH₂O-in-MIL-88.



Figure S6. SEM images and corresponding EDS elemental mappings of 50%-WO₃·xH₂O-in-MIL-88.



Figure S7. TEM image of (a)MIL-88 and (b)15%-WO₃·xH₂O-in-MIL-88.



Figure S8. TEM elemental mapping of MIL-88.



Figure S9. XPS survey scans of 7%-WO₃·xH₂O-in-MIL-88 and 30%-WO₃·xH₂O-in-MIL-88 and 50%-WO₃·xH₂O-in-MIL-88.



Figure S10. Fe 2p XPS spectra of MIL-88 with different tungstic acid loads.



Figure S11. Ni 2p XPS spectra of MIL-88 with different tungstic acid loads.



Figure S12. O 1s XPS spectra of MIL-88 with different tungstic acid loads.



Figure S13. W 4f XPS spectra of MIL-88 with different tungstic acid loads.



Figure S14. (a) Lsv of commercial RuO_2 in 1 M KOH. (b) Tafel plots of RuO_2 .



Figure S15. Cyclic voltammograms of (a) MIL-88, (b) 7%-WO₃·xH₂O-in-MIL-88,(c) 15%-WO₃·xH₂O-in-MIL-88, (d) 30%-WO₃·xH₂O-in-MIL-88, (e) 50%-WO₃·xH₂O-in-MIL-88 in 1 M KOH at different scan rates (5, 10, 15, 20 and 25 mV s⁻¹) in the non-Faradaic potential region (1.06–1.16 V versus RHE). (f) C_{dl} plots inferred from CV curves.



Figure S16. Nyquist plots of different catalysts.



Figure S17. XPS spectra of (a) Fe 2p, (b) Ni 2p for the 15%-WO₃·xH₂O-in-MIL-88/CC sample after OER tests in 1 M KOH.



Figure S18. SEM images of 15%-WO₃·xH₂O-in-MIL-88 deposited on carbon cloth (ac) before and (d-f) after 50 hours OER process.



Figure S19. (a) LSV curves of MIL-88 and MIL-88- H_2O_2 -1/2/3. (b) The overpotential of MIL-88 and MIL-88- H_2O_2 -1/2/3. (c) Tafel slope of MIL-88 and MIL-88- H_2O_2 -1/2/3.



Figure S20. Fourier-transform infrared (FTIR) spectra of MIL-88 and WO₃·xH₂O-in-MIL-88.



Figure S21. Thermogravimetric analysis and derivative thermos-gravimetric of 15%-WO₃·xH₂O-in-MIL-88 (red) and 15%-WO₃-in-MIL-88 (green).



Figure S22. Fourier-transform infrared (FTIR) spectra of 15%-WO₃·xH₂O-in-MIL-88 (red) and 15%-WO₃-in-MIL-88 (black).



Figure S23. SEM images of 15%-WO₃-in-MIL-88.



Figure S24. (a) Nyquist plots of 15%-WO₃·xH₂O-in-MIL-88 (red) and 15%-WO₃-in-MIL-88 (blue), (b)Tafel plots, and (c) Comparison of overpotentials at 10 mA cm⁻² and normalized current densities based on mass at 1.53 V versus RHE. (d) TOF for 15%-WO₃·xH₂O-in-MIL-88 and 15%-WO₃-in-MIL-88.



Figure S25. A slab model to estimate equilibrium water molecules inside MIL-88.



Figure S26. Radial distribution function g(r) of water molecules around Fe and Ni atoms in FeNi₂-MOF.



Figure S27. (a) LSV curves of 15%-WO₃·xH₂O-in-MIL-88 (red) and RuO₂ (black) in alkaline seawater. (b) Tafel slope.



Figure S28. (a) LSV curves of 7%-WO₃·xH₂O-in-MIL-88, 30%-WO₃·xH₂O-in-MIL-88, and 50%-WO₃·xH₂O-in-MIL-88 in alkaline seawater. (b) Tafel plots. (c) Overpotential and Tafel slope. (d) TOF values of 7%-WO₃·xH₂O-in-MIL-88, 30%-WO₃·xH₂O-in-MIL-88, and 50%-WO₃·xH₂O-in-MIL-88.

| 1 | | | 5 | | |
|--|-------|-------|-------|-------|-------|
| Samples | С | О | Fe | Ni | W |
| | (wt%) | (wt%) | (wt%) | (wt%) | (wt%) |
| MIL-88 | 43.53 | 28.99 | 13.51 | 12.38 | 0 |
| 7%-WO ₃ ·xH ₂ O-in-MIL-88 | 39.69 | 28.66 | 14.27 | 8.6 | 6.9 |
| 15%-WO ₃ ·xH ₂ O-in-MIL-88 | 36.86 | 29.96 | 13.73 | 7.5 | 9.69 |
| 30%-WO ₃ ·xH ₂ O-in-MIL-88 | 33.61 | 27.32 | 11.37 | 6.2 | 19.70 |
| 50%-WO ₃ ·xH ₂ O-in-MIL-88 | 27.47 | 25.87 | 8.07 | 3.48 | 33.10 |
| 15%-WO3-in-MIL-88 | 38.65 | 28.73 | 13.29 | 6.96 | 10.37 |
| | | | | | |

Table S3. The mass percent of the surface element determined by XPS.

| Samples | The impedance value (Ω) | | |
|--|--------------------------------|--|--|
| MIL-88 | 74.78 | | |
| 7%-WO ₃ ·xH ₂ O-in-MIL-88 | 16.83 | | |
| 15%-WO ₃ ·xH ₂ O-in-MIL-88 | 13.66 | | |
| 30%-WO ₃ ·xH ₂ O-in-MIL-88 | 31.75 | | |
| 50%-WO ₃ ·xH ₂ O-in-MIL-88 | 77.57 | | |
| 15%-WO3-in-MIL-88 | 31.27 | | |

 Table S4. The specific impedance value.

| Electrocatalysts | E _j =10 mA cm ⁻² (mV) | Tafel slope (mV dec ⁻¹) | electrolyte | substrate | references | |
|---|---|--|-------------|-----------|------------|--|
| 15%-WO ₃ ·xH ₂ O-in- | 263 | 39 | 1 M | GCE | This | |
| MIL-88 | | | КОН | | work | |
| α-Ni/CeO ₂ @NC | 286 | 49 | 1 M KOH | CFP | 8 | |
| CoTPA-D | 273 | 67 | 1 M KOH | CC | 9 | |
| S-CoNiFeMOF1 | 300 | 40.9 | 1 M KOH | GCE | 10 | |
| Ce@NiFe-MOF-5 | 258 | 54.44 | 1 M KOH | GCE | 11 | |
| NiFe ₂ O ₄ /KB | 258 | 43.01 | 1 M KOH | GCE | 12 | |
| Co ₃ Cu-Ni ₂ MOFs | 288 | 87 | 1 M KOH | GCE | 13 | |
| O-GOD-NiFe PBA | 259 | 52.5 | 1 М КОН | Nickel | 14 | |
| | 209 | 02.0 | 1 111 11011 | foam | | |
| CoFe-PTA/FDA | 295 | 62.85 | 1 M KOH | GCE | 15 | |
| NiN ₂ Cl ₂ @Fe-MIL-53 | 287 | 78 | 1 М КОН | Carbon | 16 | |
| 2 20 | | | | paper | | |
| Ni-MOF/Mkb14 | 294 | 31 | 1 M KOH | GCE | 17 | |
| Ni(Fe)MOF/Mkb14 | 279 | 25 | 1 M KOH | GCE | 17 | |
| N-NiCoP | 290 | 60.85 | 1 М КОН | Carbon | 18 | |
| | 00.00 | 1 101 10011 | paper | | | |

Table S5. The electrocatalytic performances of compared with some state-of-the-art

 catalytic electrodes.

Table S6. The mass percent of the surface element of 15%-WO₃·xH₂O-in-MIL-88 catalyst loading on carbon cloth before and after OER determined by XPS.

| Samples | Fe (wt %) | Ni (wt %) | W (wt %) |
|-----------|-----------|-----------|----------|
| Pristine | 46.70 | 25.67 | 27.63 |
| After OER | 49.06 | 27.60 | 23.34 |

| Electrocatalysts | Substrate | Cell voltage (V) at 10 mA cm ⁻² | Electrolyte | Reference |
|---|-----------|---|-------------|-----------|
| 15%-WO ₃ ·xH ₂ O-in-MIL-88 Pt/C | Ni foam | 1.50 | 1 M KOH | This work |
| $MoS_2/Ni_3S_2 MoS_2/Ni_3S_2 $ | Ni foam | 1.56 | 1 M KOH | 19 |
| Cu@NiFe LDH Cu@NiFe LDH | Cu foam | 1.54 | 1 M KOH | 20 |
| δ-FeOOH NSs δ-FeOOH NSs | Ni foam | 1.62 | 1 M KOH | 21 |
| NiVIr-LDH NiVIr-LDH | Ni foam | 1.49 | 1 M KOH | 22 |
| VOOH-3Fe VOOH-3Fe | Ni foam | 1.53 | 1 M KOH | 23 |
| $\label{eq:sigma_linear} \begin{split} Ni_3S_2@MoS_2/FeOOH Ni_3S_2@MoS_2/FeOO\\ H \end{split}$ | Ni foam | 1.57 | 1 М КОН | 24 |
| NiVIr-LDH NiVRu-LDH | Ni foam | 1.42 | 1 M KOH | 25 |
| Ni/Ni ₈ P ₃ Ni/Ni ₈ P ₃ | Ni foam | 1.61 | 1 M KOH | 26 |
| CoFeZr oxides CoFeZr oxides | Ni foam | 1.63 | 1 M KOH | 27 |
| Ni/Mo ₂ C Ni/Mo ₂ C | Ni foam | 1.64 | 1 M KOH | 28 |
| $Ni_3S_2 Ni_3S_2 $ | Ni foam | 1.76 | 1 M KOH | 29 |
| NiFe(DMBD)-MOF Pt/C | Ni foam | 1.50 | 1 M KOH | 30 |
| CdFe-BDC CdFe-BDC | Ni foam | 1.63 | 1 M KOH | 31 |
| Ir@Ni-BDC Ir@Ni-BDC | CC | 1.46 | 1 M KOH | 32 |

Table S7. Comparison of water splitting activity of 15%-WO₃·xH₂O-in-MIL-88/NF||Pt/C//NF cell in this work with other reported electrocatalysts in 1 M alkalinesolution.

References.

- A. K. Rappé, C. J. Casewit, K. Colwell, W. A. Goddard III and W. M. Skiff, Journal of the American Chemical Society, 1992, 114, 10024-10035.
- 2. G. Garberoglio, *Journal of computational chemistry*, 2012, **33**, 2204-2208.
- 3. G. C. Martin-Noble, D. Reilley, L. M. Rivas, M. D. Smith and J. Schrier, *Journal of chemical theory and computation*, 2015, **11**, 3364-3374.
- 4. T. Raček, O. Schindler, D. Toušek, V. Horský, K. Berka, J. Koča and R. Svobodová, *Nucleic acids research*, 2020, **48**, W591-W596.
- 5. H. Berendsen, J. Grigera and T. Straatsma, *Journal of Physical Chemistry*, 1987, **91**, 6269-6271.
- 6. M. J. Abraham, T. Murtola, R. Schulz, S. Páll, J. C. Smith, B. Hess and E. Lindahl, *SoftwareX*, 2015, **1**, 19-25.
- 7. W. Humphrey, A. Dalke and K. Schulten, *Journal of molecular graphics*, 1996, **14**, 33-38.
- 8. Z. H. Pei, H. B. Zhang, Z. P. Wu, X. F. Lu, D. Y. Luan and X. W. Lou, *Science Advances*, 2023, **9**, eadh1320.
- 9. G. Arunkumar, P. Nantheeswaran, M. Mariappan, R. K. Kamlekar, M. Pannipara, A. G. Al-Sehemi and S. P. Anthony, *New Journal of Chemistry*, 2023, **47**, 9654-9660.
- 10. P. Sayadi, S. Zeinali, S. Momeni, S. F. NamiAna and M. Tohidi, *Journal of Electronic Materials*, 2023, **52**, 3877-3891.
- 11. X. Wei, D. Liu, C. Wang, R. Yu, K. Zhang, S. Li, Z. Wu and Y. Du, *Inorganic Chemistry*, 2023, **62**, 3238-3247.
- C. Liu, X. Chen, X. Zhang, J. Li, B. Wang, Z. Luo, J. Li, D. Qian, J. Liu and G. I. N. Waterhouse, *The Journal of Physical Chemistry Letters*, 2023, 14, 6099-6109.
- 13. P. Dong, Y. Gu, G. Wen, R. Luo, S. Bao, J. Ma and J. Lei, *Small*, 2023, **19**, 2301473.
- 14. Y.-C. Lin, S. Aulia, M.-H. Yeh, L.-Y. Hsiao, A. M. Tarigan and K.-C. Ho, *Journal of Colloid and Interface Science*, 2023, **648**, 193-202.
- 15. Y. Gai, J. Hu, W. Deng, W. Xie, X. Li, J. Zhang, D. Long, S. Qiao, F. Jiang and K. Chhetri, *International Journal of Energy Research*, 2023, **2023**, 1-15.
- 16. Y. Wang, Z. Zhou, Y. Lin, Y. Zhang, P. Bi, Q. Jing, Y. Luo, Z. Sun, J. Liao and Z. Gao, *Chemical Engineering Journal*, 2023, **462**, 142179.
- T. H. Y. Beglau, L. Rademacher, R. Oestreich and C. Janiak, *Molecules*, 2023, 28, 4464.
- X. Lin, L. Chen, X. Zhong, A. BaQais, W. Dang, M. A. Amin, H. Huang, H. Li, G. Liang, G. Liu and Z. Yang, *Advanced Composites and Hybrid Materials*, 2023, 6, 79.
- 19. J. Zhang, T. Wang, D. Pohl, B. Rellinghaus, R. Dong, S. Liu, X. Zhuang and X. Feng, *Angewandte Chemie International Edition*, 2016, **55**, 6702-6707.
- 20. L. Yu, H. Zhou, J. Sun, F. Qin, F. Yu, J. Bao, Y. Yu, S. Chen and Z. Ren, *Energy & Environmental Science*, 2017, **10**, 1820-1827.

- 21. B. Liu, Y. Wang, H. Q. Peng, R. Yang, Z. Jiang, X. Zhou, C. S. Lee, H. Zhao and W. Zhang, *Advanced Materials*, 2018, **30**, 1803144.
- S. Li, C. Xi, Y.-Z. Jin, D. Wu, J.-Q. Wang, T. Liu, H.-B. Wang, C.-K. Dong, H. Liu, S. A. Kulinich and X.-W. Du, ACS Energy Letters, 2019, 4, 1823-1829.
- 23. J. Zhang, R. Cui, C. Gao, L. Bian, Y. Pu, X. Zhu, X. a. Li and W. Huang, *Small*, 2019, **15**, 1904688.
- 24. M. Zheng, K. Guo, W.-J. Jiang, T. Tang, X. Wang, P. Zhou, J. Du, Y. Zhao, C. Xu and J.-S. Hu, *Applied Catalysis B: Environmental*, 2019, **244**, 1004-1012.
- 25. D. Wang, Q. Li, C. Han, Q. Lu, Z. Xing and X. Yang, *Nature Communications*, 2019, **10**, 3899.
- 26. G. F. Chen, T. Y. Ma, Z. Q. Liu, N. Li, Y. Z. Su, K. Davey and S. Z. Qiao, *Advanced Functional Materials*, 2016, **26**, 3314-3323.
- L. Huang, D. Chen, G. Luo, Y. R. Lu, C. Chen, Y. Zou, C. L. Dong, Y. Li and S. Wang, *Advanced Materials*, 2019, **31**, 1901439.
- X. Luo, P. Ji, P. Wang, R. Cheng, D. Chen, C. Lin, J. Zhang, J. He, Z. Shi, N. Li, S. Xiao and S. Mu, *Advanced Energy Materials*, 2020, 10, 1903891.
- 29. L.-L. Feng, G. Yu, Y. Wu, G.-D. Li, H. Li, Y. Sun, T. Asefa, W. Chen and X. Zou, *Journal of the American Chemical Society*, 2015, **137**, 14023-14026.
- Y. Liu, X. Li, S. Zhang, Z. Wang, Q. Wang, Y. He, W. H. Huang, Q. Sun, X. Zhong, J. Hu, X. Guo, Q. Lin, Z. Li, Y. Zhu, C. C. Chueh, C. L. Chen, Z. Xu and Z. Zhu, *Advanced Materials*, 2023, 35, 2300945.
- 31. Y. Luo, X. Yang, L. He, Y. Zheng, J. Pang, L. Wang, R. Jiang, J. Hou, X. Guo and L. Chen, *ACS Applied Materials & Interfaces*, 2022, **14**, 46374-46385.
- 32. J. Yang, Y. Shen, Y. Sun, J. Xian, Y. Long and G. Li, *Angewandte Chemie International Edition*, 2023, **62**, e202302220.