Supporting Information

for


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Supplementary Note:

Fourier transform infrared (FTIR) spectra were obtained to analyze the surface functional groups (Fig. 2c). The absorption peaks at 1370 and 1427 cm\(^{-1}\) corresponding to the asymmetric vibrations, while the peak at 1514 cm\(^{-1}\) represents the symmetric vibrations of carboxylic group in the MOFs. Similarly, a broad peak centered at 3450 cm\(^{-1}\) indicating the stretching mode of OH group originates from the surface-absorbed water molecules in MOFs. In addition, the peaks observed at 724 and 1313 cm\(^{-1}\) are assigned to the -C-H- and C-C stretching vibrations of the benzene ring in the organic linker. Peaks at 540 and 1643 cm\(^{-1}\) are attributed to bond between metal ions and COO- groups of BTC, which reveals the successful coordination of Ni/Fe with the BTC linker.

The surface characteristics of NiFe-BTC-GNPs are also evaluated using Raman spectroscopy (Fig. 2d). All MOF samples exhibit characteristic Raman active mode at 1000 and 3085 cm\(^{-1}\) corresponding to \(\nu(CH)\) stretching of the organic linker. Similarly, the bands at 1610 and 1006 cm\(^{-1}\) are related to \(\nu(C=C)\) modes of the benzene ring; the peaks at 824 and 724 cm\(^{-1}\) are attributed to out-of-plane ring (C−H) bending vibrations and out-of-plane ring bending, respectively. Further, the doublet located at 1550 and 1460 cm\(^{-1}\) indicate the presence of asym(C−O\(_2\)) and asym(C−O\(_2\)) groups. In the case of NiFe-BTC-GNPs and NiFe-BTC MOFs, three additional bands at 480, 565 and 719 cm\(^{-1}\) are assigned to the characteristic bands of M-O-M and M-O (M=Ni\(^{2+}\)/ Fe\(^{3+}\)) in the corresponding MOF. These results are consistent with FTIR-spectral data in Fig. 2c. Particularly, the absence of the COOH peak around 1760–1690 cm\(^{-1}\) would be a direct evidence of metal coordination with BTC. Furthermore, the Raman spectra of NiFe-BTC-GNPs displays the major Raman features of graphene at 1350, 1582 and 2708 cm\(^{-1}\) corresponding to D, G and 2D bands, respectively. The appearance of low-intensity D band indicates the high quality of the graphene in NiFe-BTC-GNPs. Besides, the sharp narrow 2D band
along with an \( I_{2D}/I_G \) value of 5.0 implies the presence of few-layer graphene in the composite material.\textsuperscript{11,12}
Supplementary Figures

Fig. S1 SEM and HRTEM images of NiFe-BTC and NiFe-BTC-GNPs MOFs. a, SEM images of NiFe-BTC. b-d, SEM (b,c) and HRTEM (d) images of NiFe-BTC-GNPs. f, HRTEM-EDS mapping of NiFe-BTC-GNPs.
Fig. S2 Elemental analysis Of NiFe-BTC-GNPs MOF. EDAX-XRF Analysis of NiFe-BTC-GNPs at different locations.
Fig. S3 Electrochemical and Physical characterization of the MOF samples. 

a, Polarization curves of the NiFe-BTC-GNPs MOF loaded on Nickel Foam (NF) in 1M KOH Solution. 
b, Nyquist plots of NiFe-BTC-GNPs electrode measured as a function of applied potential in 1M KOH solution. 
c, Four Point Probe analysis of MOF samples. 
d, Contact angle measurements of the MOF samples (from bottom to top: Ni-BTC, NiFe-BTC, and NiFe-BTC-GNPs MOF).
**Fig. S4** Faradaic efficiency calculation measured through ORR-OER method. 

**a,** RRDE Setup.  

**b,** Rotating ring disk electrode (RRDE) voltammogram of NiFe-BTC-GNPs.  

**C,** Electron-transfer number (n) as a function of applied potential calculated from fig.b.
Fig. S5 Elemental and crystal Phase analysis of NiFe-BTC-GNPs MOF after long-term stability studies. a, HRTEM image of NiFeBTC-GNPs after continuous electrolysis. b, ICP-MS analysis as – prepared sample and after stability. c, XRD Pattern of NiFe-BTC-GNPs. d,e, High-resolution O1S spectra of NiFe-BTC-GNPs MOF (d) after and (e) before continuous electrolysis.
Theoretical overpotential of OER | DFT+U+TS

NiFe-BTC

Fig. S6 DFT-predicted structures of each intermediates on the active sites, their free energy differences and overpotentials. Fe site of NiFe-BTC (Fe: yellow, Ni: grey, C: brown, O: red, and H: cyan, respectively).
**Fig. S7** OER activity of MOF in Conventional Electrolyser: OER Performance of MOF measured in the conventional electrolyser using 20 wt% Pt/C as a cathode. 

**a**, Polarization plots of the electrolyser obtained in 1M aqueous KOH solution at RT with scan rate of 1mV S$^{-1}$

**b**, Long-term stability of the electrolyser with NiFe-BTC-GNPs anode measured by applying a constant potential of 1.55 V for 12 days. The conventional electrolyser (fine frit-separator) was fabricated by utilizing the as-synthesized BTC-derived catalysts on CFP as anode electrodes and the commercial 20% Pt/C on CFP as cathode electrodes. For comparison, the state-of-the-art IrO$_2$ and Co$_3$O$_4$ based anodes were also fabricated. NiFe-BTC-GNPs based electrolyzer exhibits excellent performance compared to other anode catalysts, requiring smaller $\eta=250/330$mV to reach $j=10/100$ mA cm$^{-2}$ (a). These values are even better than the state-of-the-art IrO$_2$/(Pt/C) electrodes which demands larger $\eta$ to achieve similar current densities. The NiFe-BTC-GNPs based electrolyzer demonstrates excellent long-term stability for 12 days on continuous electrolysis operation (b).
Fig. S8 Components of Prototype AAEMWE. (a) AAEMWE setup used in this study. (b) Demonstration of AAEMWE for practical hydrogen generation.

Fig. S9 Electrochemical characterization of Commercial AAEMWE. a, LSV curves of AAEMWE and PEM electrolyser with Commercial 20% Pt/C cathode and IrO$_2$ anode in ultrapure water electrolyte at 70°C. b, Stability of MEA with commercial catalysts (20% Pt/C cathode and IrO$_2$ anode) at 25°C. c, Polarization curve obtained with commercial Pt/C loaded on CFP in 1M KOH solution.
Fig. S10  Electrochemical characterization of NiFe-BTC-GNPs based AAEMWE  

a, Nyquist plots of AEM water electrolyser measured as a function of applied potential in the ultra-pure water.  

b, Long-term durability of the cell with pt/C cathode at constant potential 1.8 V.  

c, Faradaic efficiency measured through water displacement method.
Fig. S11 Solar-to-hydrogen (STH) conversion: Demonstration of PV-powered AAEMWE for solar hydrogen production. Experimental set up used for the Solar to Hydrogen Efficiency (STH) Measurements. The single cell comprising NiFe-BTC-GNPs MOF as anode catalyst was integrated with commercial silicon solar cell.
### Supplementary Tables

**Table S1.** Summary of the OER performance of our catalysts compared with high performance catalysts reported in the literature.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Electrolyte</th>
<th>$\eta_{O_2}$ @ $j=10$ mA cm$^{-2}$ (mV)</th>
<th>Stability (hrs)</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>NiFe-BTC-GNPs MOF/CFP</td>
<td>1M KOH</td>
<td>220</td>
<td>1000*</td>
<td>This work</td>
</tr>
<tr>
<td>NiFe-BTC-GNPS MOF/NF</td>
<td>1M KOH (j=20)</td>
<td>180</td>
<td>1000*</td>
<td>This Work</td>
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<tr>
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<td>1M KOH</td>
<td>250</td>
<td>96</td>
<td>This work</td>
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<td>IrO$_2$/CFP</td>
<td>1M KOH</td>
<td>280</td>
<td>32</td>
<td>This Work</td>
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<td>Ultrathin NiCo-MOF/NF</td>
<td>1M KOH</td>
<td>189</td>
<td>11</td>
<td>13</td>
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<tr>
<td>Ultrathin NiFe-MOF/NF</td>
<td>1M KOH</td>
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<td>5.5</td>
<td>14</td>
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<tr>
<td>Fe$_1$Ni$_2$-BDC MOF/GCE</td>
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<td>10</td>
<td>3</td>
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<td>Co$<em>{0.6}$Fe$</em>{0.4}$-MOF-74/GCE</td>
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<td>280</td>
<td>12</td>
<td>15</td>
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<td>NaNi$<em>{0.8}$Fe$</em>{0.2}$O$_2$</td>
<td>1M KOH</td>
<td>320</td>
<td>30</td>
<td>16</td>
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<td>O$_2$-Cat-1/Fe Plate</td>
<td>1M KOH</td>
<td>269</td>
<td>100</td>
<td>17</td>
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<td>NiFe hydroxide/Nickel Foam</td>
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<td>10</td>
<td>18</td>
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<tr>
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<td>240</td>
<td>10</td>
<td>19</td>
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<td>Ni–Co–P Hollow Nano bricks</td>
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<td>20</td>
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<td>Ni$<em>{0.75}$V$</em>{0.25}$-LDH</td>
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<td>320</td>
<td>25</td>
<td>22</td>
</tr>
</tbody>
</table>

Some of the information was not specified in the literature and was estimated according to the data graphs.

CFP: Carbon Fiber Paper, NF: Nickel Foam

GCE: Glassy carbon electrode

*Overall stability: cv cycles, half-cell stability and electrolyser stability
References:


18. X. Lu and C. Zhao, *Nature Communications*, 2015, 6, 6616.


