

Supporting Information

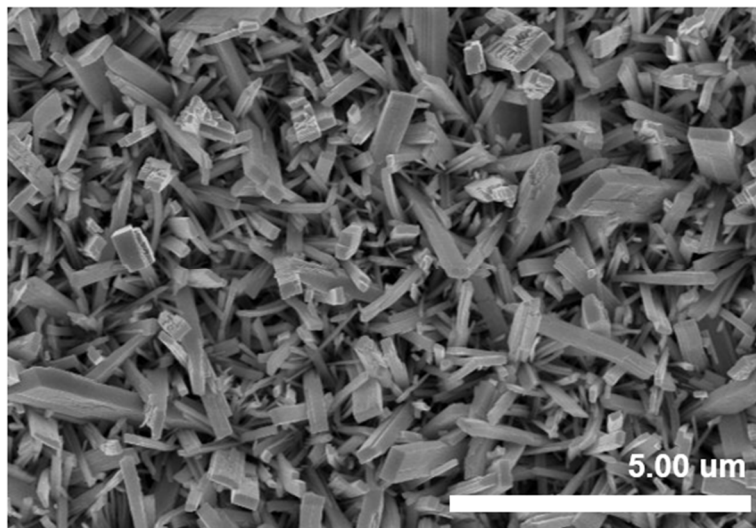


Figure S1. Top-view SEM images of WO₃ on FTO.

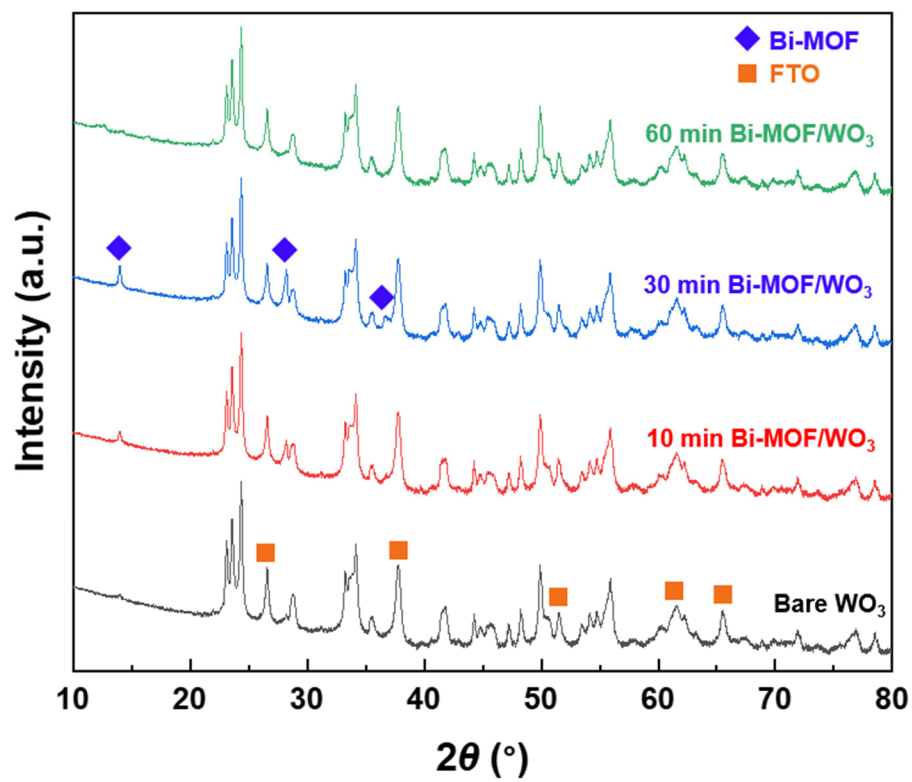


Figure S2. Out-of-plane θ - 2θ scans of Bi-MOF/ WO_3 at different synthesis times of MOF.

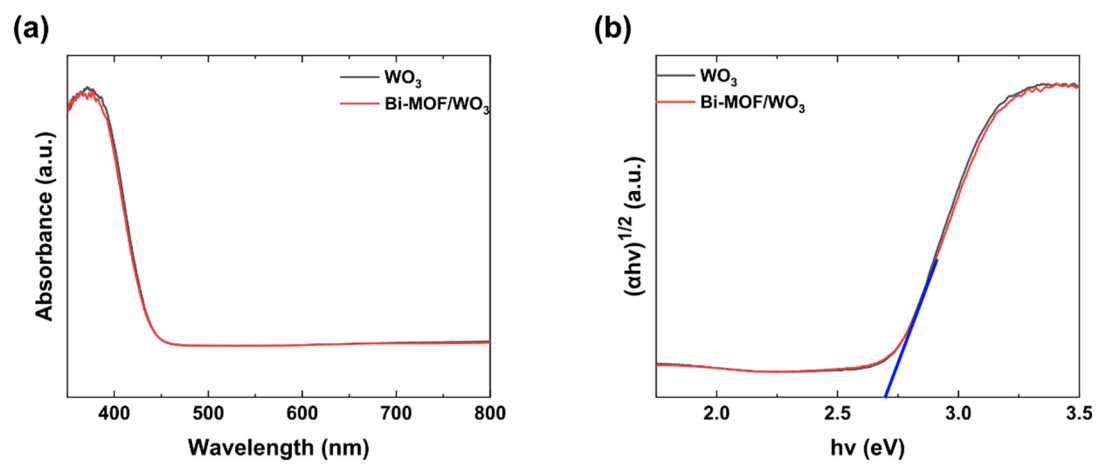


Figure S3. (a) UV-vis absorbance spectra, (b) Tauc plot

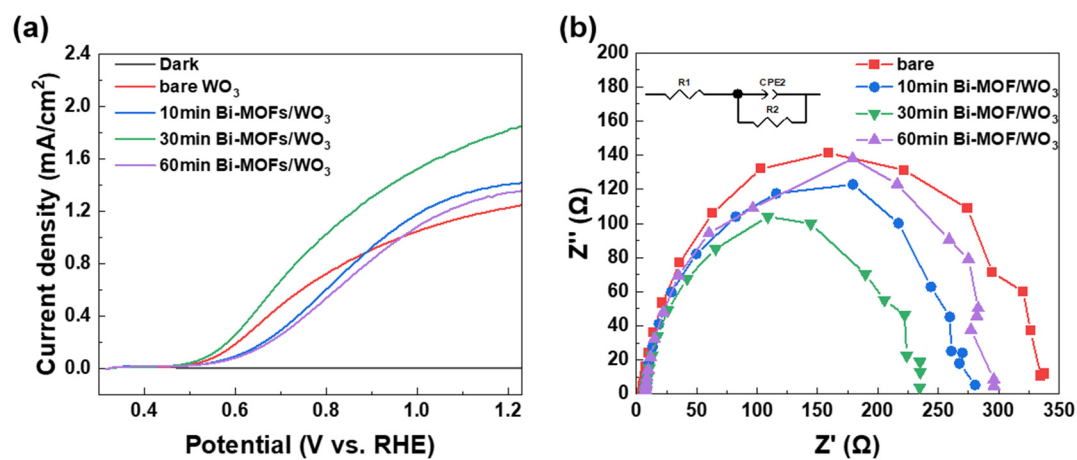


Figure S4. PEC performance of WO_3 and Bi-MOF/ WO_3 in 0.5 M Na_2SO_4 electrolytes, with pH adjusted to 2 using sulfuric acid, with 0.1 M glycerol. (a) LSV polarization curves, (b) Nyquist plots with different synthesis times of MOF.

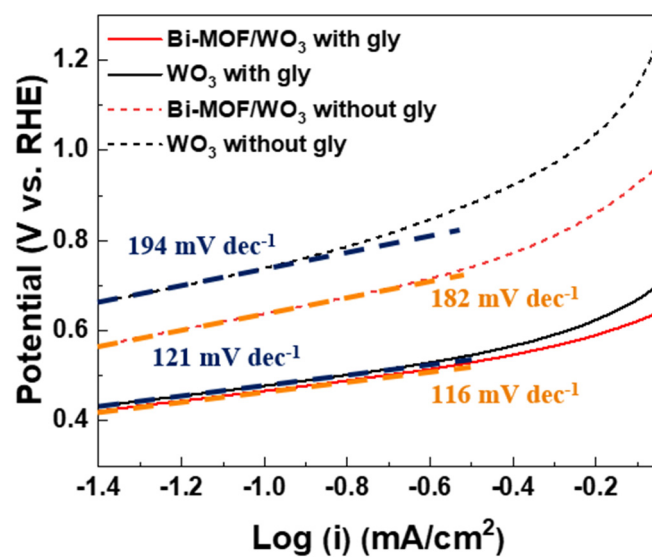


Figure S5. Tafel plots of WO₃ and Bi-MOF/WO₃ in 0.5 M Na₂SO₄ electrolytes, with pH adjusted to 2 using sulfuric acid, with and without 2 M glycerol.

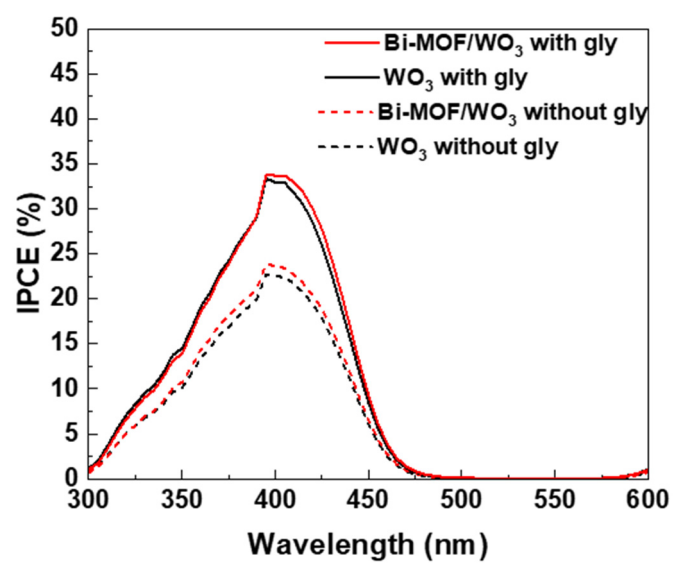


Figure S6. IPCE values at 1.2 V vs. RHE with 2 M glycerol.

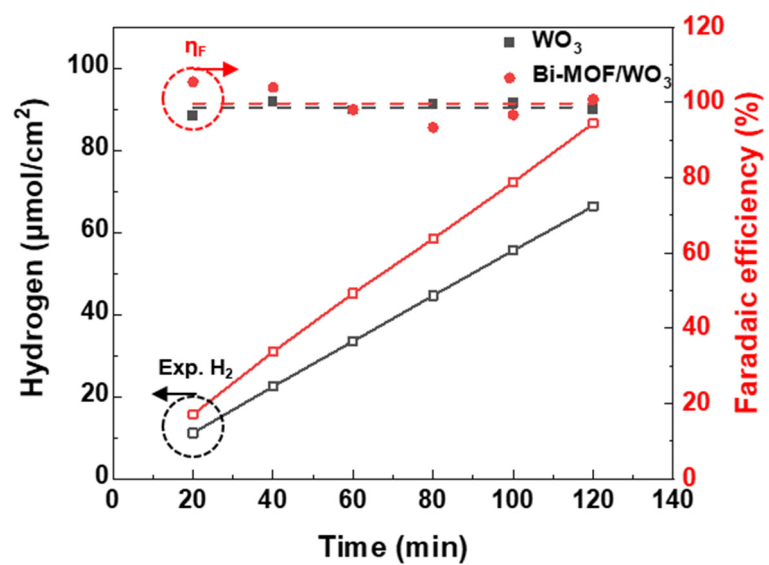


Figure S7. Faradaic efficiency and production rate of hydrogen at 1.2 V vs. RHE

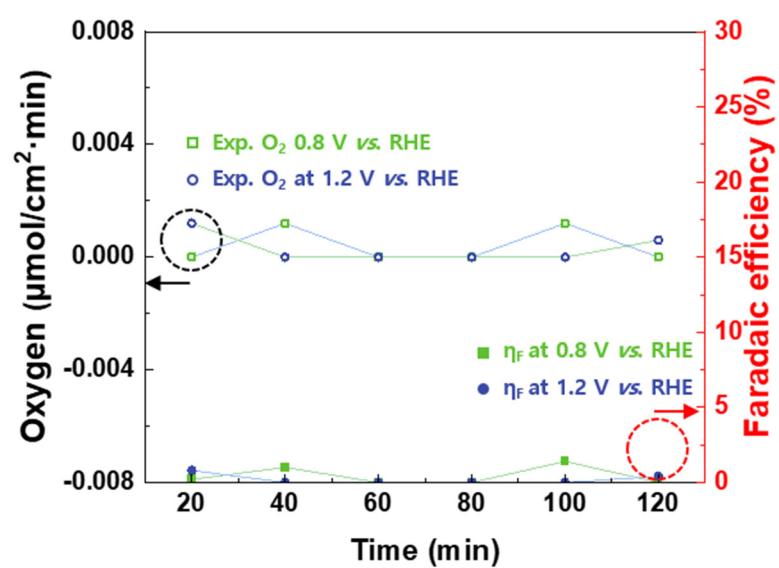


Figure S8. Faradaic efficiency and production rate of oxygen.

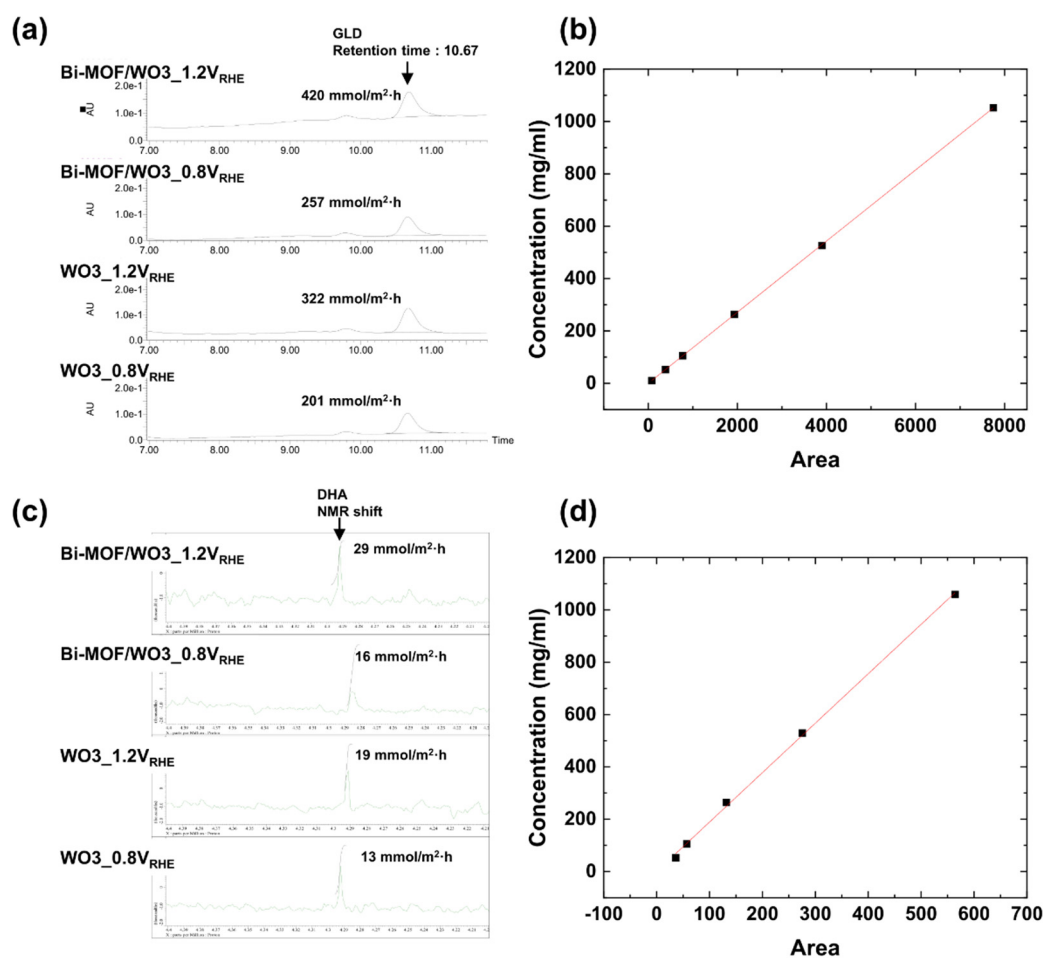


Figure S9. (a) Liquid chromatography of produced glyceraldehyde, (b) calibration curve of standard glyceraldehyde (c) NMR spectra of produced dihydroxyacetone, (d) calibration curve of standard dihydroxyacetone.

Table S1. Reaction rate, production rate, and faradaic efficiency from WO₃ and Bi-MOF/WO₃.

| Electrode | Applied potential (V _{RHE}) | Glycerol | Glyceraldehyde | | Dihydroxyacetone | |
|------------------------|---------------------------------------|---|---|-------------------------|---|-------------------------|
| | | Conversion rate (mmol/m ² , μmol/cm ²) | Production rate (mmol/m ² , μmol/cm ²) | Faradaic efficiency (%) | Production rate (mmol/m ² , μmol/cm ²) | Faradaic efficiency (%) |
| WO ₃ | 0.8 | 215 | 201 | 94 | 13 | 6 |
| | | 21.5 | 20.1 | | 1.3 | |
| WO ₃ | 1.2 | 356 | 322 | 90 | 19 | 5 |
| | | 35.6 | 32.2 | | 1.9 | |
| Bi-MOF/WO ₃ | 0.8 | 278 | 257 | 93 | 17 | 6 |
| | | 27.8 | 25.7 | | 1.7 | |
| Bi-MOF/WO ₃ | 1.2 | 467 | 420 | 90 | 29 | 6 |
| | | 46.7 | 42.0 | | 2.9 | |

Table S2. Photocatalyst, and photoelectrode for the selective oxidation of glycerol.

| Material | Medium (total volume) | Time | Major product | FE (%) | Selectivity (%) | Ref. |
|--|--|-------------|----------------------|---------------|------------------------|------------------|
| BiVO₄ | 0.1 M glycerol, 0.5 M Na₂SO₄ | 1 h | DHA | 50 | 50 | [40] |
| BiVO₄ | 0.1 M glycerol, 0.1 M NaBi | 2 h | DHA | - | 60 | [41] |
| Ag/LDH/TiO₂ | 0.1 M glycerol, 0.5 M Na₂SO₄ | 4 h | DHA | 55 | 72 | [87] |
| Bi₂O₃/TiO₂ | 0.1 M glycerol, 0.5 M Na₂SO₄, H₂SO₄ | 1h | DHA | 62 | 75 | [88] |
| TiO₂ | 10 mM glycerol, 20 mM Na₂SO₄ | 4 h | GAD | - | 44 | [89] |
| H-WO₃/TiO₂ | Na₂SO₄, NaBi, | 1 h | GAD | 51 | 56 | [90] |
| WO₃ | 1 M glycerol, 0.1 M Na₂SO₄ | 2 h | GAD | 75 | 80 | [91] |
| Bi-MOF/WO₃ | 2 M glycerol, 0.5 M Na₂SO₄, | 1 h | GAD | 93 | 94 | This work |

