Supporting Information

Assembling Metal Organic Layer Composites for High-Performance Electrocatalytic CO₂ Reduction to Formate

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Section 1. Materials and characterizations

S1.1 Materials
Ligand H$_3$TATB (4,4’,4’’-s-triazine-2,4,6-triyl-tribenzoic acid) was synthesized according to the publication of Feng et al. The successful synthesis is confirmed by proton nuclear magnetic resonance spectroscopy ($^1$H-NMR) (δ, DMSO): 8.22 (d, 6 H), 8.88 (d, 6 H), 13.39 (s, 3 H). All other chemicals were purchased from commercial suppliers and used without further purification, unless mentioned.

S1.2 Characterizations
Metal contents were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Varian Vista-MPX). Gas (N$_2$) sorption measurements were conducted on an Autosorb 3B (Quantachrome) at 77K. Field emission scanning electron microscopy (FE-SEM) images were collected using a Zeiss Supra 40 with a field S3 emission scanning electron microanalyzer. Powder X-ray diffraction (PXRD) patterns were analyzed by a BrukerD8 Advance diffractometer of 35 kV and 40 mA with a Cu Kα (λ = 0.154 nm) radiation. Atomic force microscopy (AFM) analysis was conducted on a Bruker Multi-mode 8 Atomic Force Microscope, using mica as a support.

The liquid products, especially formate, were detected by high performance liquid chromatography (HPLC, Agilent 1260 Infinity) equipped with a NUCLEOGEL Sugar 810 H column and a refractive index detector (RID), using 0.5 mM H$_2$SO$_4$ as an eluent. The concentration can be calculated using a calibration plot. Other liquid products were detected by NMR (Bruker Advance 500) with a solvent suppression method, using $d4$-trimethylsilylpropanoic acid ($d4$-TMSP) sodium salt of known concentration as the internal standard. The gaseous products were analyzed by offline/online gas chromatography (GC, Agilent 7890A), equipped with PLOT&MOLESIEVE columns, a thermal conductivity detector (TCD) and a flame ionization detector (FID), using He as carrier gas.

X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis Ultra, equipped with a monochromated Al Kα x-ray source (hv = 1486.6 eV). A charge neutralizer was applied, to compensate for the poor conductivity of the samples. The calibration was done by setting C 1s from adventitious carbon to 284.8 eV. Survey scans are performed before and after detailed scans to check for potential beam damage. The fitting conditions and results were listed in Table S2.
Transmission electron microscopy (TEM) images were collected by Philips CM-200 FEG TEM. Aberration corrected HRTEM was performed using a JEOL ARM200F TEM equipped with a cold-field emission gun and a post specimen spherical aberration corrector (Cs) operated at an acceleration voltage of 80 kV. The TEM sample was prepared using the drop-casting method: a drop of sample dispersion was placed on a carbon-coated Cu grid and dried in air. For STEM and EELS, we used a JEOL ARM200F equipped with a DCOR corrector (CEOS GmbH), a cold-field emission electron gun, and a Gatan GIF Quantum ERS electron energy-loss spectrometer. The acceleration voltage was set to 200 kV. HAADF-STEM imaging was performed with a convergent semi-angle of 20.4 mrad and the collection semi-angle of 70-300 mrad. A collection semi-angle of 111 mrad was used for EELS measurements with a Gatan K2 Summit camera. EELS spectrum imaging was performed with a dispersion of 0.5 eV/channel and 1900 eV drift tube energy with a 4000-pixel wide detector for the simultaneous acquisition of Zr and Bi spectrum images. The raw spectrum image data were first denoised by applying the principal component analysis (PCA) with a multivariate statistical analysis (MSA) plugin (HREM Research Inc.) in Gatan DigitalMicrograph and then smoothed using a spatial filter in Gatan DigitalMicrograph. 4D-STEM datasets were acquired with a Merlin direct electron detector (256 ×256 pixels, Quantum Detectors), operating in the 1-bit mode with continuous reading/writing at a pixel dwell time of 4.8 ×10^{-5} s.
Section 2. Synthesis and electrocatalytic CO\textsubscript{2} reduction test

S2.1 Synthesis of Zr-TATB MOL
Generally, 190 mg ZrOCl\textsubscript{2}·8H\textsubscript{2}O (99.9\%, Alfa Aesar) was dissolved into a mixture of 6 mL DMF (99.8\%, Sigma-Aldrich) and 4 mL glacial HOAc (99.7\%, Sigma-Aldrich), further transferred into a 20 mL vial with cap. The vial was placed in an oven at 85 °C for 2 hours, to accelerate cluster formation. Then, 44 mg H\textsubscript{3}TATB was added into the above solution, followed by ultrasonic. The vial was solvothermally treated in an oven at 120 °C for 12 hours. After the reaction, as-synthesized Zr-TATB MOL can be separated by centrifugation and washed with DMF and acetone (p.a. Merck). After drying in an oven at 85 °C, the white powder can be harvested. Besides static synthesis, continuously stirring at 100 °C in an oil bath for 12 hour also works.

S2.2 Synthesis of UiO-66\textsuperscript{53}
Generally, 186 mg ZrCl\textsubscript{4} (98\%, TCI) and 138 mg terephthalic acid (TPA, Acros, 98\%) were dissolved in 50 mL DMF and 6 mL HOAc in a flask. After adding two drops of water, the flask was sealed and placed into an oil bath of 120 ºC for 12 h under continuously stirring. After the reaction, the solid can be separated by centrifugation and washed with DMF and acetone. The white powder can be harvested after drying at 85 °C.

S2.3 Synthesis of Bi\textsubscript{2}O\textsubscript{3}/MOL, BiO\textsubscript{x}/MOL, Bi\textsubscript{2}O\textsubscript{3}/UiO and Bi\textsubscript{2}O\textsubscript{3}/AB
Generally, 40 mg support (MOL, UiO-66 or Acetylene Black (99.9\%, Alfa Aesar)) and 60 mg Bi(NO\textsubscript{3})\textsubscript{3}·5H\textsubscript{2}O (98\%, Carl Roth) were dispersed in 4 mL DMF. The mixture was transferred into a 20 mL vial with cap and solvothermally treated in an oven at 85 °C for 12 hours. The catalysts can be harvested by centrifugation, washing with DMF, H\textsubscript{2}O and acetone, and were finally dried at 85 °C. The catalysts were denoted as Bi\textsubscript{2}O\textsubscript{3}/MOL, Bi\textsubscript{2}O\textsubscript{3}/UiO and Bi\textsubscript{2}O\textsubscript{3}/AB, respectively. For BiO\textsubscript{x}/MOL, the synthesis was conducted at room temperature, while all other parameters were kept the same as Bi\textsubscript{2}O\textsubscript{3}/MOL.

S2.4 Synthesis of Bi\textsubscript{2}O\textsubscript{3}/MOL, Bi\textsubscript{2}O\textsubscript{3}/UiO and Bi\textsubscript{2}O\textsubscript{3}/AB with controlled Bi loading
The loading procedures are consistent with Bi\textsubscript{2}O\textsubscript{3}/MOL described in the above S2.3, except for the amount of added precursors Bi(NO\textsubscript{3})\textsubscript{3}·5H\textsubscript{2}O: 8 mg for Bi\textsubscript{2}O\textsubscript{3}/MOL-0.6 (0.6 wt% loading), 72 mg for Bi\textsubscript{2}O\textsubscript{3}/UiO-2.6 (2.6 wt% loading), 128 mg for Bi\textsubscript{2}O\textsubscript{3}/AB-2.6 (2.6 wt% loading).
S2.5 Synthesis of MOLs loaded with different active metals (Bi, Sn and In)

Generally, 20 mg Zr-TATB MOL and 10 mg metal precursors (SnCl$_2$·2H$_2$O (p.a., Merck) or In(NO$_3$)$_3$·xH$_2$O (99.99%, Alfa Aesar)) were dispersed into 4 mL DMF. The mixture was sealed into an autoclave and solvothermally treated at 160 °C for 10 hours. The products were separated by centrifugation, washed by H$_2$O/acetone and dried, giving SnO$_2$/MOL or In$_2$O$_3$/MOL.

S2.6 Synthesis of MOLs loaded with different Bi species (Bi$_2$O$_3$, BiOCl and metallic Bi)

BiOCl/MOL can be obtained by a post hydrothermal treatment of Bi$_2$O$_3$/MOL. To be precise, 20 mg Bi$_2$O$_3$/MOL was dispersed into 5 mL tap water and sealed into an autoclave. The hydrothermal treatment was done at 160 °C for 10 hours in an oven. A white powder can be harvested by centrifugation, washed with acetone and dried. The chloride from natural water is enough for the phase transformation to BiOCl (Figure S50).

Metallic Bi/MOL was prepared by post-synthetic treatment of Bi$_2$O$_3$/MOL. First, 30 mg NaBH$_4$ (98%, Merck) was dissolved into 2 mL cold Methanol (MeOH, 99.8% Sigma Aldrich) as a reductant. Then, 20 mg Bi$_2$O$_3$/MOL was dispersed into 8 mL MeOH, followed by a quick addition of the reductant solution. After 30 seconds, the resulting black powder was separated through centrifugation, washed with MeOH and dried at room temperature under vacuum.

S2.7 Preparation of working electrodes for the H-type cells

The catalyst ink was prepared by dispersing 1 mg catalyst, 1 mg acetylene black and 10 μL Nafion solution (5 wt%, Sigma Aldrich) into 1 mL isopropanol. After thorough ultrasonication, 200 μL ink was drop-casted onto carbon paper (Toray paper, TGP-H-060) with an area of 1.0 × 1.0 cm$^2$, followed by drying overnight in an oven at 85 °C. The loading of the catalyst is 0.2 mg·cm$^{-2}$.

S2.8 Electrocatalytic tests in the H-type cells

Electrocatalytic CO$_2$ reduction reactions were conducted in a typical H-type cell with a three-electrode system (Scheme S1). The reference electrode and counter electrode is saturated Ag/AgCl and Pt foil respectively. The 0.5 M KHCO$_3$ (99%, Carl Roth) was adopted as an electrolyte for both anode and cathode. The electrochemical workstation is from Origalys (OGF500 pack). All applied potentials, with auto IR compensation, were converted from vs. saturated Ag/AgCl to vs.
RHE, using equation: \( E \ (\text{vs. RHE}) = E \ (\text{vs. Ag/AgCl}) + 0.199 + 0.0591 \times \text{pH} \). The pH value of CO\(_2\) saturated 0.5 M KHCO\(_3\) was adopted as 7.23.\(^{54}\)

**Scheme S1.** Scheme of the H-type cell.

Pre-conditioning is required before measurements, which is cyclic voltammetry (-1.5 to +1.0 V, vs. Ag/AgCl, 50 mV/s, 10 cycles) and pre-electrolysis at -1.8 V vs. Ag/AgCl for 10 min under CO\(_2\) atmosphere. LSV measurements were conducted with a scan rate of 10 mV/s with CO\(_2\) or Ar bubbling. Before chrono-amperometric measurements, the electrolyte was purged with CO\(_2\) to remove air. During the reaction, the CO\(_2\) was recirculated by bubbling within the cell by a peristaltic pump. The magnetic stirring speed was controlled to be 1000 rpm for every experiment. After certain reaction times, the gas samples were taken and analyzed by offline GC. The liquid product was quantified by HPLC, and further confirmed by \(^1\)H-NMR with a solvent suppression method. The experiments were repeated to determine an error margin.

**S2.9 Preparation of gas diffusion electrode as working electrode**

Gas diffusion electrodes were prepared by drop-casting the ink on the home-made gas diffusion layers (GDLs). The home-made GDLs were prepared by dry-pressing methods as follows\(^{55}\): (1) Knife-milling of a mixture containing 35 wt% polytetrafluoroethylene powder (PTFE, 350 μm) and 65 wt% acetylene black; (2) Dry-pressing 400 mg PTFE/AB mixture (10 kN cm\(^{-2}\)); 3. Sintering at 340 °C under N\(_2\) atmosphere for 10 min. The ink was the same as the one used for H-type cell test. The catalyst loading was controlled to be 1.4 mg per cm\(^2\).
**S2.10 Electrocatalytic tests by gas diffusion electrode**

The experimental setup for gas diffusion electrode tests was demonstrated in a previous work.\(^5\) The reference and counter electrodes are Hg/HgO (1M KOH) electrode and a Ni mesh, respectively. The 1.0 M KHCO\(_3\) (99%, Carl Roth) and 5.0 M KOH (99%, Carl Roth) were adopted as electrolytes for the cathode and anode, respectively. The electrochemical workstation was a Gamry Reference 3000 potentiostat. All the applied potentials, with auto IR compensation, were converted from vs. Hg/HgO to vs. RHE, using the equation: 
\[
E (\text{vs. RHE}) = E (\text{vs. Hg/HgO}) + 0.140 + 0.0591 \times \text{pH}
\]
The pH value of 1.0 M KHCO\(_3\) was adopted as 8.4.\(^6\)

Pre-conditioning is required before measurements, which is cyclic voltammetry (-1.6 to +0.3 V, vs. Hg/HgO, 50 mV/s, 5 cycles) under CO\(_2\) atmosphere. The flow rate of the gas inlet (CO\(_2\)) is adjusted by a mass flow controller (MFC), which is determined by the instantaneous current density. The flow rate of the gas outlet was monitored by a mass flow meter (MFM). After a certain reaction time, the gas sample was analyzed by online GC. The liquid product was quantified by HPLC. The experiments were repeated to determine an error margin.
Section 3. Characterizations of Zr-TATB MOL

Figure S1. (a) Scheme illustrating the structure of the Zr-TATB MOL viewed from the $a$ axis. (b) 2D-$k_{gd}$ topology of Zr-TATB MOL, where the 6-connected Zr$_6$-oxo clusters and the 3-connected TATB ligands were simplified as blue hexagons and orange triangles, respectively.

Figure S2. SEM images of the as-synthesized Zr-TATB MOL.
Figure S3. (a) N$_2$ sorption isotherms (solid symbols: adsorption curve; open symbols: desorption curve) of Zr-TATB MOL and Bi$_2$O$_3$/MOL at 77 K (Inserted table: BET surface area and pore volume ($V_p$)). (b) DFT pore size distribution of Zr-TATB MOL and Bi$_2$O$_3$/MOL. The pore size distribution was calculated via DFT by the mode of N$_2$ at 77 K on silica (cylindr./sphere. pore, NLDFT ads. Model).

Compared with the UiO based composites, the Bi loading did not significantly decrease the surface area and pore volume for the MOL based composites (Figure S23). This can be attributed to the insertion of Bi nanowires, which act as pillars between MOL layers to support pore space.

Figure S4. TGA plot of the Zr-TATB MOL under air with a ramping rate of 2 °C·min$^{-1}$.

The weight loss below 160 °C could be attributed to the evaporation of water and DMF, which serve as reactant/solvent during synthesis. Starting from 180 °C, the dehydration of the surface -O/OH group will occur.$^{31}$ Decomposition of acetate and ligand happens at around 310 and 450 °C respectively, finally resulting in ZrO$_2$.
Figure S5. PXRD patterns of the Zr-TATB MOL exposed to different electrolytes.

Figure S6. Scheme of the structure of the Zr-TATB MOL. Zr light blue, O red, C grey, N blue, H white. The (001) and (110) planes are highlighted by red and olive colors, respectively. Acetates are capped to the Zr₆-oxo clusters from the c axis direction.

The crystal structure of Zr-TATB MOL was constructed through modifications of the Zr-BTB MOL from a former publication for a similar topology. After the energy and geometry optimization by Forcite calculation, the detailed parameters can be given. Space group: C2/m, a 19.52 Å, b 34.18 Å, c 12.57 Å, α 90°, β 97.29°, γ 90°. The PXRD pattern of the preferred (001) orientation was extracted by the Mercury software.
Figure S7. Scheme of possible 3D MOFs constructed by Zr$_6$-oxo SBUs and TATB ligands. (a) PCN-777, view along [111]. Yellow balls highlight the void of cages. (b) Interlocked Zr-TATB, view along c axis. Blue and orange polyhedrons indicate interlocked layers of Zr-TATB.

Figure S8. PXRD patterns of the simulated Zr-TATB MOL, PCN-777, interlocked Zr-TATB and as-synthesized Zr-TATB MOL.
Figure S9. $^1$H-NMR spectrum of the dissolved Zr-TATB MOL after being treated under different conditions, using $d_4$-trimethylsilylpropanoic acid ($d_4$-TMSP) sodium salt as an internal standard. The intensities are normalized by the area of the TATB$^{3-}$ signal.

The significant decrease of acetate concentration after thermal-vacuum treatment can be attributed to the condensed removal of the acetate groups with the proton sources ($\mu_3$-OH, $H_2$O, etc), indicating its flexible coordination. The slight shift of the peaks of TATB$^{3-}$ can be a result of the difference in pH and water content.$^{S10}$

Figure S10. (a-e) TEM images of the Zr-TATB MOL. (f) Corresponding FFT patterns of the box region in (e), where a monolayer MOL is displayed.
Figure S11. (a) TEM image of the Zr-TATB MOL. (b) Selected area electron diffraction (SAED) pattern of the Zr-TATB MOL.

The diffraction spots show a hexagonal symmetry, which is well-matched with the FFT pattern of MOL (Figure 1d, S3f).

Figure S12. (a) Low-magnification annular dark-field scanning transmission electron microscopy (ADF-STEM) image of the Zr-TATB MOL. (b,c) Ptychography reconstructed modulus and phase images of the Zr-TATB MOL using a 4D dataset acquired with a Merlin electron detector.
Figure S13. Atomic force microscopy (AFM) image of the Zr-TATB MOL and the corresponding height profiles (marked in red numbers).
Section 4. Characterizations and formation mechanism of Bi$_2$O$_3$/MOL

![Diagram of Zr$_6$-oxo cluster and ion modifications](image)

Figure S14. (a) Structure of the Zr$_6$-oxo cluster, with open anchoring sites. Symbols with green/blue nets represent -OH/OH$_2$ and -μ$_3$-O/OH, respectively. (b) Scheme illustrating the ion modifications upon Zr$_6$-oxo cluster. The flexible coordination of capping acetate groups can also be verified by the dissolved NMR results (Figure S9).
Figure S15. (a) Bright field and (b) dark field STEM images of Bi$_2$O$_3$/MOL. (c,d) High-resolution HAADF images of the selected areas marked with red and orange borders.

Some ultrafine clusters highlighted by blue circles can be observed, independent of nanowires.

Figure S16. PXRD patterns of the β-Bi$_2$O$_3$, as-synthesized Zr-TATB MOL, Bi$_2$O$_3$/MOL and BiO$_x$/MOL.
Figure S17. (a-c) Annular dark-field scanning transmission electron microscopy (ADF-STEM) images of the Zr-TATB MOL. (d-f) The STEM-EELS maps for Bi, Zr and the composite map, respectively.

The exact dispersion of Bi on BiO$_x$/MOL can be confirmed by the elemental maps by HAADF-STEM combined with EELS. Contrasted by the background, we can conclude the uniform and extensive dispersion of Bi on the MOL (Figure 2e). Besides, only a few heterogeneous nanoparticles are recognized by the HAADF-STEM and the corresponding EELS maps.
Figure S18. *Ex-situ* TEM images of Bi$_2$O$_3$/MOL at the different hydrothermal times (scale bar: 50 nm). For the *ex-situ* TEM study of the formation of Bi$_2$O$_3$/MOL, several samples were taken after different synthesis time. Except for time, all other parameters were kept the same as general synthesis of Bi$_2$O$_3$/MOL.

Figure S19. Loading diagram of Bi$_2$O$_3$/MOL over reaction times.
Section 5. Investigation on the support effect of Bi-based catalysts

**Figure S20.** PXRD patterns of standard β-Bi$_2$O$_3$, simulated UiO-66, as-synthesized UiO-66 and Bi$_2$O$_3$/UiO.

**Figure S21.** TEM images of (a) bare UiO-66 and (b) Bi$_2$O$_3$/UiO.
Figure S22. XPS Bi 4f spectrum of Bi$_2$O$_3$/UiO.

In contrast to Bi$_2$O$_3$/MOL and BiO$_x$/MOL, two different Bi components in Bi$_2$O$_3$/UiO are visible (Table S2). The state at lower binding energy (159.3 eV) can be ascribed to crystalline Bi$_2$O$_3$. Another state at higher binding energy (160.2 eV) can be ascribed to ultrafine BiO$_x$ binding to the Zr clusters (Figure 2f).$^{12,13}$ The larger proportion of BiO$_x$ can be ascribed to the hindered growth of nanowires in the interior pore space within UiO-66 (pore size < 2 nm) (Figure S23). Thus, it can be inferred that the nanowires are more concentrated on the external surface, consistent with the TEM images (Figure S21).
Figure S23. (a,c) N\textsubscript{2} sorption isotherms (solid symbols: adsorption curve; open symbols: desorption curve) of UiO-66, Bi\textsubscript{2}O\textsubscript{3}/UiO and acetylene black (AB) at 77 K (Inserted table: BET surface area and pore volume (V\textsubscript{p})). (b,d) DFT pore size distribution of UiO-66, Bi\textsubscript{2}O\textsubscript{3}/UiO and acetylene black (AB). (b) The DFT calculation mode: N\textsubscript{2} at 77 K on silica (cylindr./sphere. pore, NLDFT ads. Model). (d) The DFT calculation mode: N\textsubscript{2} at 77 K on carbon (slit/cylindr. pores, QSDFT ads. branch).

For UiO based composites, there is a noticeable decrease in the surface area and pore volume after Bi loading. The change in DFT pore size distribution can also prove the occupation of interior pore volume (d = ~ 2 nm) by Bi species. For the acetylene black, it presents a non-porous structure.
Figure S24. PXRD patterns of standard $\beta$-$\text{Bi}_2\text{O}_3$ and as-synthesized $\text{Bi}_2\text{O}_3$/AB.

Figure S25. HAADF-STEM images of $\text{Bi}_2\text{O}_3$/AB. The $\text{Bi}_2\text{O}_3$ appears as nanowires and nanoparticles. Compared to $\text{Bi}_2\text{O}_3$/MOL, $\text{Bi}_2\text{O}_3$/AB possesses a smaller proportion of nanowires.

Acetylene black with \(\geq99.9\%\) purity level was purchased from Alfa Aesar. The porosity is out of the stacking of the AB nanoparticles, verified by the N\(_2\) sorption experiments (Figure S23). The proposed principle of loading Bi on AB is the impregnation effect. And then, partial hydrolysis can happen by the water residue from solvent or Bi precursors ($\text{Bi(NO}_3\text{)}_3\cdot5\text{H}_2\text{O}$) during the solvotherm treatment, which results in the deposition of Bi species on AB.
**Figure S26.** HAADF-STEM and EELS maps of Bi$_2$O$_3$/AB. The Bi mapping evidences the presence of Bi in the form of nanowires and nanoparticles.

**Figure S27.** XPS Bi 4f spectrum of Bi$_2$O$_3$/AB. The binding energy of Bi 4$f_{7/2}$ (160.0 eV) can be ascribed to the crystalline Bi$_2$O$_3$, combined with its PXRD pattern (**Figure S24**).
Figure S28. LSV curves over Bi$_2$O$_3$/MOL with different AB content (0%, 16% and 50%) under Ar/CO$_2$. The catalyst loadings were fixed at 0.2 mg·cm$^{-2}$. The AB amount was controlled to be 0 mg·cm$^{-2}$, 0.04 mg·cm$^{-2}$ or 0.2 mg·cm$^{-2}$, denoted as 0% AB, 16% AB and 50% AB, respectively.
Figure S29. (a,b) FEₘ and (c) formate partial current densities and (d) formate partial currents per mg Bi at different potentials over Bi₂O₃/MOL with different AB content (0%, 16%, 50%). The catalyst was fixed at 0.2 mg·cm⁻². The AB amount was controlled to be 0 mg·cm⁻², 0.04 mg·cm⁻² or 0.2 mg·cm⁻², denoted as 0% AB, 16% AB and 50% AB, respectively.

The improved performance after adding AB can be attributed to the inhibited stacking of Bi₂O₃/MOL and enhanced conductivity.⁷⁴
Figure S30. (a) LSV curves in Ar/CO$_2$, (b) FEs and current densities of ECR at different potentials over Zr-TATB MOL.

The slight enhancement in current response in CO$_2$ than Ar may be caused by the decrease of pH, when saturated with CO$_2$.\textsuperscript{54}
**Figure S31.** Chrono-amperometric I-t plot at different potentials (V vs. RHE) over (a/b) Bi$_2$O$_3$/MOL without/with AB as additive, (c) Bi$_2$O$_3$/UiO and (d) Bi$_2$O$_3$/AB.

**Figure S32.** NMR detection of liquid products by Bi$_2$O$_3$/MOL. Formate is the only liquid product detected. TMSP was adopted as an internal standard.
Figure S33. (a) FEs towards CO/H\(_2\) and (b) formate partial current per mg Bi at different potentials over Bi\(_2\)O\(_3\)/MOL, Bi\(_2\)O\(_3\)/UiO and Bi\(_2\)O\(_3\)/AB.

Figure S34. PXRD pattern of Bi\(_2\)O\(_3\)/MOL after a 10-hours durability test.

The durability test was conducted by using a glassy carbon plate (2.5 \(\times\) 2.5 cm\(^2\)) as the working electrode, while other parameters remained unchanged. The sample for the post-reaction PXRD test was collected by scrapping the catalysts off the glassy carbon electrode. These steps were aimed to avoid the interference from carbon paper or glassy carbon. The peaks of Zr-TATB MOL remain well after reaction, indicating a good structural stability. The appearance of Bi\(_2\)O\(_2\)CO\(_3\) can be ascribed to the reaction of bismuth oxide with bicarbonate from electrolyte.\(^{S15}\) The appearance of metallic Bi are from the reduction of Bi species.\(^{S16}\)
**Figure S35.** TEM images of Bi$_2$O$_3$/MOL after a 10-hours durability test.

The morphology of the MOL layer or Bi-based nanowires remains intact after the durable test. Owing to the use of Nafion binders, the stacking of the catalysts observed from TEM images is inevitable.

**Figure S36.** (a) Bi 4f XPS and (b) Zr 3d XPS spectra of Bi$_2$O$_3$/MOL after a 10-hours durability test.

The sample for post-reaction XPS test shares the same procedure as that in Figure S34. The energies are calibrated by carbon (C 1s) fitting and Si signal from the Kapton tape. Compared with the signal before test, the overall reduction of Bi species after test can be observed clearly. The Bi(III) occurred because of the fast oxidation process at the Bi surface, once the reaction was
terminated. The reduction can also be proved by the PXRD post-reaction (Figure S34). As for the Zr signal, there is no apparent change in binding energy (Zr 3d$_{5/2}$: 182.6 eV) and peak shape before and after the reaction.

![Figure S37. PXRD patterns of the β-Bi$_2$O$_3$, as-synthesized Zr-TATB MOL, Bi$_2$O$_3$/MOL-0.6 (0.6 wt%) and BiO$_x$/MOL.](image)

To alleviate the effect of different Bi loadings, we synthesized a Bi$_2$O$_3$/MOL with ultra-low loading (0.6 wt%) as a reference. From the PXRD test, the Bi$_2$O$_3$/MOL contained apparently crystalline Bi$_2$O$_3$, while BiO$_x$/MOL showed non-crystalline bismuth species.

![Figure S38. LSV curves over BiO$_x$/MOL and Bi$_2$O$_3$/MOL-0.6 (0.6 wt%) under Ar/CO$_2$.](image)
Figure S39. (a,b) FEs and (c) formate partial current densities and (d) formate partial currents per mg Bi at different potentials over BiO\textsubscript{x}x/MOL and Bi\textsubscript{2}O\textsubscript{3}/MOL-0.6 (0.6 wt%).

Even though BiO\textsubscript{x}x/MOL exhibits better Faradic efficiencies, Bi\textsubscript{2}O\textsubscript{3}/MOL-0.6 still has better performance when comparing the partial current densities. From this dataset, we can conclude the positive effect of the crystallinity of Bi\textsubscript{2}O\textsubscript{3} on ECR performance.
Figure S40. LSV curves over Bi$_2$O$_3$/MOL, Bi$_2$O$_3$/UiO and Bi$_2$O$_3$/AB with controlled Bi loadings of 2.6 wt% under Ar/CO$_2$. 
Figure S41. (a,b) FEs and (c) formate partial current densities and (d) formate partial currents per mg Bi at different potentials over Bi$_2$O$_3$/MOL, Bi$_2$O$_3$/UiO and Bi$_2$O$_3$/AB with controlled Bi loadings of 2.6 wt%.

The activities increased along with the higher loading for all the samples. Bi$_2$O$_3$/MOL still exhibits the best performance, both in terms of selectivity and partial current density, exceeding other counterparts. Besides, there was no apparent difference in Faradaic efficiencies compared to the results in Figure 4b, indicating that the selectivity depends mainly on the nature of the catalyst.
Figure S42. (a) Chrono-amperometric I-t plot at different potentials (V vs. RHE) over Bi$_2$O$_3$/MOL using gas diffusion electrode (GDE). (b) FEs under different applied potentials over BiOx/MOL using GDE. Comparisons of (c) formate partial current densities and (d) formate partial currents per mg Bi for GDE and H-type cell.

The partial current density (to formate) can reach above 300 mA·cm$^{-2}$ using GDE. Additionally, the currents per mg Bi also significantly exceed the performance by the H-type. The reason for much enhanced performance by GDE is to improve the CO$_2$ mass transfer significantly and avoid the dilemma of CO$_2$ depletion in the H-type cell.$^{85}$
Figure S43. Cyclic voltammetry (CV) plots of fresh Bi$_2$O$_3$/MOL, Bi$_2$O$_3$/UiO and Bi$_2$O$_3$/AB under CO$_2$ with a scan rate of 50 mV/s. The current responses were normalized by the mass of casted Bi.

The area of the oxidative peak (Bi$^0$→Bi$^{3+}$) can be an indicator of the amount of electroactive Bi.$^{517}$ Bi$_2$O$_3$/UiO exhibits a much smaller electroactive area than Bi$_2$O$_3$/MOL. Considering their similar Bi loadings, Bi$_2$O$_3$/UiO possesses significantly worse utilization of the loaded Bi, which can be attributed to the insulating nature of bulk UiO-66.
**Figure S44.** Oxidative LSV plots of (a) Bi$_2$O$_3$/MOL, (b) Bi$_2$O$_3$/UiO and (c) Bi$_2$O$_3$/AB after chrono-amperometric ECR reactions (V vs. RHE, 30 min) with a scan rate of 100 mV/s. The current responses were normalized by the mass of casted Bi.

The area of the peak (Bi$^0$→Bi$^{3+}$) can be an indicator of the amount of electroactive active Bi.$^{17}$ For Bi$_2$O$_3$/ MOL, the oxidative Bi peak did not show an apparent decrease after CO$_2$RR, indicating its good stability. In contrast, Bi$_2$O$_3$/UiO presented gradually attenuated peaks, implying the deactivation under too negative potentials. The moderate decrease in Bi$_2$O$_3$/AB can be attributed to the limited anchoring sites to prevent agglomeration, despite having a large conductive area.$^{18}$
**Section 6. Investigation on the effect of different metal species of MOL composites**

**Figure S45.** PXRD patterns and TEM images of (a,b) SnO$_2$/MOL and (c,d) In$_2$O$_3$/MOL.

The identification of the phases was done by comparison with standards and simulated MOL. The TEM images confirm the good dispersion of guest nanoparticles. The loadings of Sn and In were determined to be 18.2 wt% and 13.2 wt% respectively by ICP-AES (*Table S1*).
Figure S46. (a) Sn 3d XPS and (b) In 3d XPS spectra of SnO$_2$/MOL and In$_2$O$_3$/MOL. The XPS spectra confirm the formation of SnO$_2$ and In$_2$O$_3$, respectively.

Figure S47. LSV curves over Bi$_2$O$_3$/MOL, SnO$_2$/MOL and In$_2$O$_3$/MOL under Ar/CO$_2$. 
Figure S48. (a) FEs towards CO/H$_2$ and (b) formate partial current per mg M (M = Bi, Sn or In) at different potentials over Bi$_2$O$_3$/MOL, SnO$_2$/MOL and In$_2$O$_3$/MOL.

Figure S49. Chrono-amperometric I-t plot at different potentials (V vs. RHE) over (a) SnO$_2$/MOL and (b) In$_2$O$_3$/MOL.
Section 7. Investigation on the effect of different bismuth species of MOL composites

Figure S50. PXRD patterns and TEM images of (a,b) BiOCl/MOL and (c,d) Bi/MOL.

The identification of the phases was done by comparison with the standard cards and simulated MOL. The TEM images confirm the good dispersion of guest nanoparticles. The loadings of Bi were determined to be 2.66 wt% and 1.93 wt%, respectively, by ICP-AES (Table S1).
Figure S51. LSV curves over Bi$_2$O$_3$/MOL, BiOCl/MOL and Bi/MOL under Ar/CO$_2$.

Figure S52. (a) FEs towards CO/H$_2$ and (b) formate partial current per mg Bi at different potentials over Bi$_2$O$_3$/MOL, BiOCl/MOL and Bi/MOL.
**Figure S53.** Chrono-amperometric I-t plot at different potentials (V vs. RHE) over (a) BiOCl/MOL and (b) Bi/MOL.
Table S1. ICP-AES results of MOL composites.

| Catalyst           | Loading/wt% |
|--------------------|-------------|
| Bi_2O_3/MOL (12 h)| Bi: 2.61 ± 0.03 |
| BiO_x/MOL RT      | Bi: 0.56 ± 0.00 |
| Bi_2O_3/MOL-0.6   | Bi: 0.61 ± 0.01 |
| Bi_2O_3/UiO        | Bi: 2.38 ± 0.01 |
| Bi_2O_3/UiO-2.6   | Bi: 2.60 ± 0.01 |
| Bi_2O_3/AB        | Bi: 1.76 ± 0.02 |
| Bi_2O_3/AB-2.6    | Bi: 2.63 ± 0.01 |
| Bi_2O_3/MOL 30 min| Bi: 0.87 ± 0.00 |
| Bi_2O_3/MOL 2 h   | Bi: 1.45 ± 0.01 |
| Bi_2O_3/MOL 5 h   | Bi: 1.63 ± 0.02 |
| Bi_2O_3/MOL 24 h  | Bi: 2.59 ± 0.00 |
| In_2O_3/MOL       | In: 13.20 ± 0.05 |
| SnO_2/MOL         | Sn: 18.20 ± 0.06 |
| BiOCl/MOL         | Bi: 2.67 ± 0.01 |
| Bi/MOL            | Bi: 1.93 ± 0.01 |
### Table S2. Summary of XPS fitting results.\[^a\]

| Samples         | Peaks | Fitting State | Binding Energy (eV) | FWAH (eV) | Area % |
|-----------------|-------|---------------|---------------------|-----------|--------|
| Bi₂O₃/MOL       | Bi 4f\textsubscript{7/2} | Bi\textsubscript{2}O₃ | 159.1               | 1.30      | 76.3%  |
|                 |       | Bi(ІІІ)O\textsubscript{x} | 159.9               | 1.37      | 23.7%  |
| BiO\textsubscript{x}/MOL | Bi 4f\textsubscript{7/2} | Bi(ІІІ)O\textsubscript{x} | 159.6               | 1.56      | 100%   |
| Bi₂O₃/UiO\[^b]\] | Bi 4f\textsubscript{7/2} | Bi\textsubscript{2}O₃ | 159.3               | 1.48      | 61.9%  |
|                 |       | Bi(ІІІ)O\textsubscript{x} | 160.2               | 1.36      | 38.1%  |
| Bi₂O₃/AB        | Bi 4f\textsubscript{7/2} | Bi\textsubscript{2}O₃ | 160.0               | 1.29      | 100%   |
| Bi₂O₃/MOL before test | Bi 4f\textsubscript{7/2} | Bi\textsubscript{2}O₃ | 159.2               | 1.46      | 76.5%  |
|                 | Zr 3d\textsubscript{5/2} | Zr(ІV) | 182.6               | 1.88      | 100%   |
| Bi₂O₃/MOL after test | Bi 4f\textsubscript{7/2} | Bi(ІІІ) | 159.3               | 1.28      | 100%   |
|                 | Zr 3d\textsubscript{5/2} | Zr(ІV) | 182.6               | 1.59      | 100%   |

\[^a\] The fitting of the XPS spectra were performed by XPSPEAK with a Shirley-type background. The area ratio of Bi 4f\textsubscript{7/2} and Bi 4f\textsubscript{5/2} was fixed to 4:3 during the fitting process. \[^b\] Considering the limited detective depth of XPS, the actual proportion of Bi(ІІІ)O\textsubscript{x} in Bi₂O₃/UiO would be apparently higher than 38.1%. The formation of Bi₂O₃ nanowires would be subject to steric hindrance in the inner pores.
Table S3. Summary of MOFs/MOF composites direct for ECR to formate.

| Catalyst                | Current Density[a] by area (mA·cm\(^{-2}\)) | Current Density[a] by mass[b] (mA·mg\(^{-1}\)) | TOF[a,c] (h\(^{-1}\)) | FE (%) | Potential (V vs. RHE) | Stability (h) | Ref. |
|-------------------------|---------------------------------------------|-------------------------------------------------|------------------------|--------|----------------------|---------------|------|
| CR-MOF                 | 1.1                                         | 1.11                                            | 7.4                    | 30     | -1.19                | 2.2           | S19  |
| Cu/NU-1000             | 0.3                                         | -                                               | -                      | 28     | -0.82                | 0.5           | S20  |
| CAU-17                 | 8.2                                         | 8.20                                            | 136                    | 41     | -0.32                | 5             | S21  |
| HNTM-Cu[d]             | 2.2                                         | 2.18                                            | 3520                   | 77     | -0.7                 | -             | S22  |
| In-BDC                 | 12.1                                        | 12.1                                            | 4500                   | >80    | -0.42 to -0.77       | 21            | S23  |
| Bi-BTC                 | 10.7                                        |                                           | >80                    |        | -0.76 to -1.06       | 12            | S24  |
| Cu-TCPP(Cu)            | 1.7                                         | 3.40                                            | 50                     | 80.9   | -0.7                 | 5             | S25  |
| Sn/ZIF-8               | 20                                          | 20.0                                            | 14750                  | 74     | -1.1                 | -             | S26  |
| MOF-ns-Cu[d]           | 2.0                                         | 3.98                                            | 334                    | 83     | -0.6                 | 12            | S27  |
| CPs@In(BCP)            | 6.9                                         | 6.9                                             | 158                    | 90.1   | -0.84                | 20            | S28  |
| In-MOF[NiS\(_4\)]     | 36.0                                        | 36.0                                            | 1174                   | 89.6   | -1.3                 | 12            | S29  |
| Su-100                 | 7.2                                         | 72                                              | 1645                   | 90.0   | -0.97                | 0.5           | S30  |
| Bi\(_2\)O\(_3\)/MOL[e] | 11.8                                        | 59.18                                           | 17676                  | >85    | -0.87 to -1.17       | 22            |      |
|                         | 329.8                                       | 235.6                                           | 70360                  | >85    | -0.96 to -1.16       | -             |      |
| In\(_2\)O\(_3\)/MOL   | 9.8                                         | 48.91                                           | 1587                   | 70     | -1.07                | -             |      |
|                         | 3.4                                         | 17.09                                           | 416                    | 45     | -1.07                | -             |      |
| SnO\(_2\)/MOL          | 7.6                                         | 38.15                                           | 11141                  | >80    | -0.87 to -1.17       | -             |      |
| BiOCl/MOL              | 5.5                                         | 27.65                                           | 11172                  | >80    | -0.87 to -1.07       | -             |      |
| Bi/MOL                 | 5.5                                         | 27.65                                           | 11172                  | >80    | -0.87 to -1.07       | -             |      |

[a] Partial current density to formate at the potential of the FE\(_{\text{max}}\). [b] The current responses are normalized by the mass of catalyst, not mass of active sites. [c] Turnover frequency was calculated by 1/2 HCOO\(^-\) (number of electrons) per metal site, divided by reaction time (h). [d] Light promoted ECR. [e] Activities obtained using the H-type cell and GDE, respectively.
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