Quantitative Electro-Reduction of CO₂ to Liquid Fuel over Electro-Synthesized Metal–Organic Frameworks

Xinchen Kang, Bin Wang, Kui Hu, Kai Lyu, Xue Han, Ben F. Spencer, Mark D. Frogley, Floriana Tuna, Eric J. L. McInnes, Robert A. W. Dryfe, Buxing Han,* Sihai Yang,* and Martin Schröder*

ABSTRACT: Efficient electro-reduction of CO₂ over metal–organic framework (MOF) materials is hindered by the poor contact between thermally synthesized MOF particles and the electrode surface, which leads to low Faradaic efficiency for a given product and poor electrochemical stability of the catalyst. We report a MOF-based electrode prepared via electro-synthesis of MFM-300(In) on an indium foil, and its activity for the electrochemical reduction of CO₂ is assessed. The resultant MFM-300(In)-e/In electrode shows a 1 order of magnitude improvement in conductivity compared with that for MFM-300(In)/carbon-paper electrodes. MFM-300(In)-e/In exhibits a current density of 46.1 mA cm⁻² at an applied potential of −2.15 V vs Ag/Ag⁺ for the electro-reduction of CO₂ in organic electrolyte, achieving an exceptional Faradaic efficiency of 99.1% for the formation of formic acid. The facile preparation of the MFM-300(In)-e/In electrode, coupled with its excellent electrochemical stability, provides a new pathway to develop efficient electro-catalysts for CO₂ reduction.

INTRODUCTION

Efficient conversion of CO₂ into chemical feedstocks and fuels is a highly desirable but extremely challenging target.¹⁻³ Reduction of CO₂ into useful chemicals via thermo-catalysis and photocatalysis has been studied very widely.⁴⁻⁷ However, the former often requires both high temperature and pressure to activate CO₂, while the latter relies heavily upon the use of sacrificial agents, typically organic amines, thus limiting long-term applications. Electro-catalysis enables the storage of intermittent renewable energy into chemical energy,⁸⁻¹⁰ and there are powerful drivers for the development of active, selective and stable electro-catalysts for the efficient reduction of anthropogenic CO₂ emission via conversion to valuable chemicals.¹¹⁻¹⁴ Electrocatalytic reduction of CO₂ normally relies upon the use of active transition metals (e.g., Cu, Co, and Pd) to reduce the high overpotentials required to activate CO₂ to the CO₂⁻⁻ radical anion or other intermediates that can be converted further.¹⁵⁻¹⁷

Metal–organic frameworks (MOFs) are crystalline hybrid materials constructed from metal ions or clusters bridged by polydentate organic ligands.¹⁸⁻⁻¹⁸⁻²⁰ Compared with conventional electro-catalysts, MOFs have unique features for the electro-chemical reduction of CO₂.¹⁻²² Metal sites (e.g., Co, Cu, Fe, and Ni) that show activity for CO₂ electro-reduction can be readily incorporated into MOF structures via single-site dispersion. Additionally, the intrinsic and tunable porosity of MOFs can lead to high capacity adsorption and selectivity to CO₂,²³⁻²⁸ thus promoting activation and further conversion. Gaseous products obtained from electro-reduction of CO₂ (e.g., CO and CH₄) often show lower adsorption in MOFs than CO₂ and can thus be readily recovered and the MOF electrode regenerated.²⁹ MOFs have inherent design flexibility via choice of metal ions and organic ligands, and therefore, their function and activity for electro-reduction of CO₂ can be optimized.³⁰⁻³ⁱ

To date, universal approaches to fabricate efficient MOF-based electrodes showing high charge-transfer capacity have been rarely reported.³⁰⁻³³ Normal methods are based upon the doping of MOF materials onto an electrode substrate.³⁴ Although various electrodes loaded with MOFs have been studied for the electro-reduction of CO₂, the poor contact between the catalyst and substrate surface limits their performance.³¹ Indium-based materials have demonstrated excellent performance for the electro-reduction of CO₂.³⁵⁻³⁶ Although electrodeposition of MOFs, particularly Cu- and Zn-based systems, has been described,³⁷⁻⁴⁰ the electro-synthesis of In-based MOFs has not been reported previously. We therefore sought to develop an In electrode decorated with a MOF film that might incorporate active defect sites and show high charge transfer capacity.

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Here, we report a facile route to the fabrication of such decorated electrodes via electro-synthesis of MOFs onto a metal foil substrate. The MFM-300(In)-e/In electrode ("e" is short for electro-synthesis) prepared in this way shows a 1 order of magnitude enhancement in electrical conductivity compared with electrodes prepared using MOFs prepared by thermo-chemical methods. More importantly, exceptional activities for the electro-reduction of CO₂ are observed with a current density of 46.1 mA cm⁻². (c and d) SEM images for MFM-300(In)-e. (e) Particle size distribution of MFM-300(In)-e. The scale bars of panels c and d are 200 and 2 μm, respectively.

**RESULTS AND DISCUSSION**

**Materials Preparation and Characterizations.** Samples of MFM-300(In)-t ("t" is short for thermo-synthesis) were obtained by solvothermal reaction of In(NO₃)₃·5H₂O and biphenyl-3,3',5,5'-tetracarboxylic acid (H₄L; Figure S1) in a mixture of DMF and MeCN at 85 °C for 3 days. The crystal structure of MFM-300(In) is shown in Figure S2. The electro-synthesis of MFM-300(In)-e was achieved using indium foil (In-foil) as both the cathode and anode in a solvent mixture of DMF/dioxane/water containing H₄L (Figure S1). The electro-synthesis was carried out rapidly at an applied potential of 10 V and 60 °C, and the In-foil anode was covered by particles of MFM-300(In)-e within 200 s. The MFM-300(In)-e electrode was then immersed in acetone for 2 h and dried before being used as the MFM-300(In)-e/In electrode. Scanning electron microscopy confirms that the In-foil metal surface is coated uniformly with MFM-300(In)-e, which has an octahedral morphology with a narrow particle size distribution centered at ~500 nm (Figures 1c–e). By comparison, MFM-300(In)-t shows cube-shaped crystals with an average particle size of ~2.5 μm (Figure S4). These differences in morphology result only in small differences in the relative intensity of powder X-ray diffraction (PXRD) peaks for MFM-300(In)-t and MFM-300(In)-e (Figure 2a).

Powder crystalline samples of MFM-300(In)-e were carefully scraped off the In-foil for characterizations. The crystal structure and phase purity of MFM-300(In)-e were confirmed by PXRD (Figure 2a); the increased peak width of MFM-300(In)-e compared with MFM-300(In)-t is consistent with their particle size distributions. Full chemical analysis suggests that the indium contents are 35.3 and 32.5 wt % in MFM-300(In)-e and MFM-300(In)-t, respectively. Negligible N content was detected in MFM-300(In)-e, indicating that the ionic liquid cations were removed completely during the solvent exchange process. The higher content of In³⁺ in MFM-300(In)-e suggests that acetate anions OAc⁻ introduced in the synthesis with EmimOAc are bound to the framework to balance the charge. The slightly higher residual solid observed in the thermogravimetric analysis (TGA) is consistent with the presence of additional In³⁺ in the framework of MFM-300(In)-e (Figure S5), while the slightly lower stability of MFM-300(In)-e compared with MFM-300(In)-t originates most likely from defects in the framework structure. The band observed near 1550 cm⁻¹ by Fourier-transform infrared (FTIR) spectroscopy is assigned to the vibration of the carboxylate group, but has an apparent red shift (20 cm⁻¹) for MFM-300(In)-e (Figure 2b), consistent with the presence of some coordinated acetate in this material. The Brunauer–Emmett–Teller (BET) surface areas of MFM-300(In)-t and MFM-300(In)-e are determined to be 1043 and 863 m² g⁻¹,

![Figure 1.](https://dx.doi.org/10.1021/jacs.0c05913)

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respectively (Figure 2c). The slightly reduced surface area of MFM-300(In)-e is attributed to the partial collapse of micropores during the rapid electro-synthesis. Pore size distributions of MFM-300(In)-t and MFM-300(In)-e estimated by nonlocal density functional theory (NLDFT) calculations (Figure 2d) confirm a micropore profile centered at 6.5 Å. In addition, there are two small peaks centered at 9.5 and 11.5 Å in MFM-300(In)-e owing to the presence of defects in the framework. During the electro-synthesis, we propose that the In-foil is oxidized to In3+ which binds OAc− anions from the EmimOAc electrolyte at the surface of the electrode thus preventing full dissolution of In3+. Binding of the tetracarboxylate ligand to In3+ occurs at the surface either directly or via replacement of OAc− to assemble the framework structure uniformly across the In-foil surface.42 Since there are abundant In3+ ions at and around the anode, the as-synthesized MFM-300(In)-e contains excess In3+ sites with some associated OAc−. Both MFM-300(In)-t and MFM-300(In)-e show typical features for In3+ at the surface as characterized by X-ray photoelectron spectroscopy (XPS) (Figure S6 and Table S1).

Electrochemical Reduction of CO2. Carbon paper (CP) has a very coarse surface that can support materials to fabricate electrodes. Samples of MFM-300(In)-t and MFM-300(In)-e were loaded onto CP substrates using Naﬁon D-521 as a binder to fabricate MFM-300(In)-t/CP and MFM-300(In)-e/CP electrodes, respectively. Indium foil has a very smooth surface, and we were thus unable to fabricate MFM-300(In)-t/In since loading thermally prepared MFM-300(In)-t onto this metal surface was unsuccessful. The surface structures of MFM-300(In)-e/In, MFM-300(In)-t/CP and MFM-300(In)-e/CP were characterized by XPS (Figure S7 and Table S1). These spectra show typical features of In3+ cations, and the shifts in binding energy [+0.5 and −0.5 eV for MFM-300(In)-t and MFM-300(In)-e, respectively] compared to powder samples originate from the different conductivities of the surface substrates.

All three electrodes were investigated for electrochemical reduction of CO2 in an H-type cell (Figure S8) with 0.5 M EmimBF4 (1-ethyl-3-methylimidazolium tetraﬂuoroborate) in MeCN and 0.5 M H2SO4 as catholyte and anolyte, respectively. Cyclic voltammetry (CV) of MFM-300(In)-e/In was studied as a function of gas loading (Figure 3a). Large current densities were generated in the CO2-saturated electrolyte, while negligible densities were observed for the electrolyte saturated with N2. Controlled potential electrolysis at −2.0~−2.3 V vs Ag/Ag+ was conducted at room temperature under a ﬂow of CO2 into the electrolyte. All liquid and gas-phase products were quantiﬁed by 1H NMR spectroscopy and gas chromatography (GC), respectively. Interestingly, only H2 was observed in the gas phase and formic acid was identiﬁed as the sole product in the liquid phase. The electrolysis was performed for 2 h and results are summarized in Figure 3b, 3c. The current density increases with increasing applied potential in all cases and the Faradaic efﬁciency for formic acid (FEHCOOH) reaches 99.1% with a current density of 46.1 mA cm−2 at −2.15 V vs Ag/Ag+ for MFM-300(In)-e/In. Signiﬁcantly, MFM-300(In)-e/In shows a higher current density compared with MFM-300(In)-e/CP and MFM-300(In)-t/CP at −2.15 V vs Ag/Ag+; the latter gives the lowest FEHCOOH at all potentials. The Faradaic efﬁciency for hydrogen (FEH2) has an inverse trend over these electrodes (Figure S9) with MFM-300(In)-t/CP higher than MFM-300(In)-e/CP, which is higher than MFM-300(In)-e/In. In-foil, as a smooth metallic electrode (Figure S10), exhibits a current density of 19.7 mA cm−2 and FEHCOOH of 50.7% in 0.5 M EmimBF4/MeCN at −2.15 V vs Ag/Ag+, lower than that.
observed for MFM-300(In)-e/In under the same conditions (Table 1).

The dependence of current density and \( \text{FE}_{\text{HCOOH}} \) on time was studied further (Figure 3d). \( \text{N}_2 \) was first charged into the electrolyte, and an imperceptible current density was observed for all electrodes investigated. Significant increases in current density were observed over all electrodes on charging \( \text{CO}_2 \) into the electrolyte, with MFM-300(In)-e/In showing the strongest response to \( \text{CO}_2 \) and reaching a maximum current density most rapidly. No obvious inflection point was observed for the

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**Figure 3.** Electrochemical reduction of \( \text{CO}_2 \) over MFM-300(In)-t/CP (black), MFM-300(In)-e/In (red), and MFM-300(In)-e/CP (blue) in 0.5 M \( \text{EmimBF}_4/\text{MeCN} \). (a) CV of MFM-300(In)-e/In in \( \text{N}_2 \)- and \( \text{CO}_2 \)-saturated electrolytes. (b) Plots of current density vs applied potential. (c) Plots of \( \text{FE}_{\text{HCOOH}} \) vs applied potential. (d) Plots of current density vs time before and after the introduction of \( \text{CO}_2 \). (e) Plots of current density vs time at \(-2.15 \text{ V vs Ag/Ag}^+\). (f) Plots of \( \text{FE}_{\text{HCOOH}} \) vs time at \(-2.15 \text{ V vs Ag/Ag}^+\). (g) Current density for five cycles of electrolysis at \(-2.15 \text{ V vs Ag/Ag}^+\) over 2 h. (h) \( \text{FE}_{\text{HCOOH}} \) for five cycles of electrolysis at \(-2.15 \text{ V vs Ag/Ag}^+\) over 2 h.
Table 1. Catalytic Performance for Electrochemical Reduction of CO2 to Formic Acid Using Different Cathodes in the Organic Electrolyte

| electrode | electrolyte | potential (V vs Ag/Ag⁺) | j (mA cm⁻²) | \( \text{FECOOH} \) (%) | ref |
|-----------|-------------|--------------------------|-------------|---------------------------|-----|
| MFM-300(In)-e/In | 0.5 M EmimBF₄/MeCN | –2.15 | 46.1 | 99.1 | this work |
| MFM-300(In)-t/CP | 0.5 M EmimBF₄/MeCN | –2.15 | 28.4 | 68.1 | this work |
| MFM-300(In)-e/CP | 0.5 M EmimBF₄/MeCN | –2.15 | 28.0 | 81.5 | this work |
| In-foil | 0.5 M EmimBF₄/MeCN | –2.15 | 19.7 | 50.7 | this work |
| MoP@In-PC | BmimPF₆/MeCN/H₂O (30/65/5) | –2.2 | 43.8 | 96.5 | 43 |
| Pb | 700 mM BmimTrizu/MeCN/5 wt %H₂O | –2.4 | 24.5 | 95.2 | 44 |
| Pb | BmimPF₆/MeCN/H₂O (30/65/5) | –2.2 | 17.8 | 95.3 | 45 |
| Sn | BmimPF₆/MeCN/H₂O (30/65/5) | –2.2 | 15.8 | 95.0 | 45 |
| Pb-PhyA | BmimBF₄/MeCN/H₂O (12.8/77.3/9.9) | –2.25 | 30.5 | 92.7 | 46 |
| SnO₂@N-PC | 0.5 M BmimPF₆/MeCN | –2.2 | 28.4 | 94.1 | 47 |
| Bi | 250 mM (DBU-H)PF₆/acetonitrile/0.1 M TBAPF₆ | –1.95⁻ | 27 | 77 | 56 |
| Sn powder | 0.5 M EmimN(CN)₂/H₂O | –1.2⁶ | 0.633 | 81.9 | 57 |

⁴² vs SCE, ⁶ vs RHE.

MFM-300(In)-t/CP electrode, indicating that H₂ evolution occurred initially, accompanied by CO₂ reduction throughout. The electro-reduction of CO₂ was conducted for 6 h at –2.15 V vs Ag/Ag⁺ to assess the long-term electrochemical stability of the electrodes (Figure 3e, 3f). After 6 h of electrolysis, the current density of MFM-300(In)-e/In had increased slowly to 57.6 mA cm⁻² with a slightly decrease in FEHCOOH to 91.2%. The average rate of production of formic acid is estimated to be 46 mg cm⁻² h⁻¹ for MFM-300(In)-e/In under these conditions (Figure S11). In contrast, the current density increased rapidly for MFM-300(In)-t/CP from 24.1 mA cm⁻² (1 h) to 52.3 mA cm⁻² (6 h) and for MFM-300(In)-e/CP from 24.1 mA cm⁻² (1 h) to 49.0 mA cm⁻² (6 h) but with notable decreases in FEHCOOH to 52.9% and 66.8%, respectively. No carbon-containing product was detected in the gas phase product. The increased current density is assigned to H₂ evolution over the extended period of electrolysis, but MFM-300(In)-e/In retains a high selectivity toward the activation of CO₂ vs H₂ evolution (Figure S12). A comparison of the electrolytic performance for the formation of formic acid for MFM-300(In)-based electrodes and other state-of-the-art electrodes in organic electrolytes is given in Table 1, with MFM-300(In)-e/In showing the best performance.⁴³⁻⁴⁷

**Reusability of Electrodes.** All three electrodes were reused over five cycles for electro-reduction of CO₂ (Figure 3g,h). Both the current density and Faradaic efficiency for formation of formic acid show excellent stability for all three electrodes. During the electrolysis over MFM-300(In)-e/In, the surface of the electrode is rendered flat as confirmed by SEM (Figures 1d and S13). PXRD studies confirm retention of the structure of MFM-300(In)-e in cycled samples after electrolysis (Figure S14). XPS was used to study the surface properties of used MFM-300(In)-t/CP and MFM-300(In)-e/In electrodes (Figure S15). During the electrolysis, both MFM-300(In)-t/CP and MFM-300(In)-e/In electrodes evolved and the change of surface structure was accompanied by shifts of the In 3d peak (~0.5 eV and +0.5 eV, respectively), moving to the energy of the as-prepared MOF sample (Table S1). Before the electrolysis, MOF particles are relatively isolated (Figure 1d), and intercrystallite charge-transfer is thus restricted, resulting in the difference observed in XPS spectra. As the MOF surface evolves during the electrolysis, the surface becomes flatter and increasingly uniform (Figure S13), and the energy difference is therefore minimized. The absence of In³⁺ at the electrode surface suggests that In³⁺ sites in MFM-300(In) are not reduced during electrolysis, consistent with the excellent electrochemical stability of MFM-300(In)-e/In.

**Mechanistic Studies.** Density functional theory (DFT) calculations afford the Gibbs free energy for the electro-reduction of CO₂ to formic acid over the pristine and defective MFM-300(In), representing MFM-300(In)-t and MFM-300(In)-e, respectively (Figure 4a). The formation of *COOH over pristine MFM-300(In) (an indicates an adsorption site on the MOF) involves a high energy barrier, indicating that this process is the rate-determining step. In contrast, the formation of *COOH is spontaneous over defective MFM-300(In)-e. The In³⁺ defects promote the adsorption of intermediate species, and therefore, higher Gibbs free energies are required for the desorption of *COOH and *HCOOH. The calculated reaction pathway of the electro-reduction of CO₂ over defective MFM-300(In) is shown in Figure S16. Furthermore, the Gibbs free energy for the formation of *COOH over In₂O₃, a benchmark indium-based catalyst, is very high (Figure S17), indicating that defective MFM-300(In) is a better candidate for the electro-reduction of CO₂. The adsorbed *COOH intermediate could be further reduced to *HCOOH or CO.⁴⁸ The calculation of Gibbs free energy of electro-reduction of CO₂ to CO over defective MFM-300(In) has also been conducted, and we find that the *HCOOH intermediate is more readily formed than *CO due to the lower energy barrier for the former. This rationalizes the formation of formic acid as the main product over MFM-300(In)-based electrodes.

We have used 5,5-dimethyl-1-pyrroline N-oxide (DMPO)⁴⁹ as a spin trap to identify any radical species involved in the catalytic reaction. Figure 4b shows the EPR spectra of the reaction solution measured after electrolysis at –2.15 V vs Ag/Ag⁺ using the different decorated electrodes. The EPR spectrum after electrolysis using MFM-300(In)-e/In shows three sets of radicals (Figure S19): two weak signals are assigned to oxidized DMPO radical-DMPO-OX, \( a_{\text{N}} = 1.5 \) mT, and to DMPO–OH radicals, \( a_{\text{N}} = 1.43 \) mT, \( a_{\text{H}} = 1.33 \) mT.⁵⁰⁻⁵² Based upon established pathways for CO₂ reduction, DMPO–COOH radicals are the intermediate products (Figure S16).⁵³,⁵⁴ In the above electrolysis we observe the formation of *COOH with \( a_{\text{N}} = 2.21 \) mT. The EPR spectra for the electrolysis reactions using MFM-300(In)-t/CP and MFM-300(In)-e/CP electrodes and their simulations are shown in Figures S20 and S21. The concentration of HCOOH intermediate could be further reduced to *HCOOH or *CO. The calculation of Gibbs free energy of electro-reduction of CO₂ to CO over defective MFM-300(In) has also been conducted, and we find that the *HCOOH intermediate is more readily formed than *CO due to the lower energy barrier for the former. This rationalizes the formation of formic acid as the main product over MFM-300(In)-based electrodes.
of DMPO−COOH radicals in solution using MFM-300(In)-e/In is notably higher than in reactions at the MFM-300(In)-t/CP and MFM-300(In)-t/CP electrodes under the same conditions, consistent with the higher activity of MFM-300(In)-e/In (Figure 4c).

The Tafel plot is an indicator of the reaction pathway with the ease of reduction reflected in a lower overpotential. The Tafel slope for reduction of CO₂ at MFM-300(In)-e/In, MFM-300(In)-t/CP and MFM-300(In)-e/CP electrodes are 138, 173, and 154 mV dec⁻¹, respectively (Figure 4d),
indicating that the initial electron-transfer to generate surface-adsorbed CO$_3^{2-}$ species is the rate-determining step.$^{12}$ Electrolysis using the MFM-300(In)-e/In electrode gives the lowest slope for the Tafel plot, indicating a higher absolute current density for a given overpotential compared with the other two electrodes. The MFM-300(In)-e/In electrode also shows more rapid kinetics for generation of radicals, consistent with the higher current density and higher $F_{\text{HCOOH}}$ for the electrolysis.

Electrochemical impedance spectroscopy (EIS) was conducted to investigate the properties of the electrode/electrolyte interface (Figures 4e, 4f).$^{43}$ Values for the interfacial charge-transfer resistance ($R_{\text{ct}}$) were obtained by fitting the experimental impedance data using Randles’ equivalent circuit (Figure S22). The interface between MOF particles and the substrate is a significant barrier to charge transfer. The electro-synthesized MOF on In-foil gives a better interfacial contact, resulting in a lower $R_{\text{ct}}$ for MFM-300(In)-e/In ($9.5 \ \Omega \ \text{cm}^2$) compared with MFM-300(In)-e/CP ($74.1 \ \Omega \ \text{cm}^2$). The lower $R_{\text{ct}}$ for MFM-300(In)-e/CP ($74.1 \ \Omega \ \text{cm}^2$) compared to MFM-300(In)-t/CP ($178.2 \ \Omega \ \text{cm}^2$) is consistent with the presence of In$_3^+$ defect sites, which enhances the charge transfer of the former electrode. The higher double-layer capacitance value of MFM-300(In)-e/In (1.06 mF cm$^{-2}$) compared to MFM-300(In)-t/CP (0.31 mF cm$^{-2}$) and MFM-300(In)-e/CP (0.46 mF cm$^{-2}$), as measured by CV curves at −0.6 to −0.65 V vs Ag/Ag$^+$ at different scan rate (Figure S23), indicates that MFM-300(In)-e/In has higher electrochemical surface area.$^{19}$

CO$_2$ adsorption isotherms of desolvated MFM-300(In)-t and MFM-300(In)-e show uptakes of 87.6 and 78.3 cm$^3$ g$^{-1}$, respectively, at 1 bar and 298 K (Figure 4g). The isosteric heat ($Q_{\text{st}}$) and entropies ($\Delta S$) of adsorption (Figure S24) were determined by fitting of the Van’t Hoff isochore from the adsorption isotherms of CO$_2$ at different temperatures (Figure S25). The value of $Q_{\text{st}}$ of MFM-300(In)-e is higher than that of MFM-300(In)-t suggesting a stronger interaction of CO$_2$ with MFM-300(In)-e.

Synchrotron FTIR microspectroscopy of MFM-300(In)-e was recorded as a function of CO$_2$ loading at 298 K (Figure 4h). The change in the stretching mode $\nu(\mu_2=\text{OH})$ at 3600 cm$^{-1}$ in the presence of CO$_2$ can provide direct insights into the strength of the host–guest binding. MFM-300(In)-t exhibits a red-shift of 5 cm$^{-1}$ of the $\nu(\mu_2=\text{OH})$ stretching band on binding of CO$_2$. In contrast, a red-shift of 25 cm$^{-1}$ is observed for this stretching vibration on CO$_2$-loading into MFM-300(In)-e under the same conditions, suggesting that MFM-300(In)-e interacts more strongly with CO$_2$. This is consistent with the DFT calculation and $Q_{\text{st}}$ analysis.

**CONCLUSIONS**

We have described a simple and effective strategy to prepare MOF-based electrodes via rapid electro-synthesis template by an ionic liquid. The as-prepared MFM-300(In)-e/In electrode incorporates active defect In$_3^+$ sites and shows high capacity for charge transfer and high electrochemical stability. This decorated electrode catalyzes the electro-reduction of CO$_2$ to formic acid with a current density of 46.1 mA cm$^{-2}$ and a Faradaic efficiency, $F_{\text{HCOOH}}$ of 99.1% in organic electrolyte. To the best of our knowledge, this performance exceeds all other MOF systems. Overall, the excess In$_3^+$ sites in MFM-300(In)-e combined with a strong contact between the MOF and the indium foil leads to reduction in interfacial resistance resulting in exceptional activity, selectivity and stability for the electro-reduction of CO$_2$.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c05913. Additional experimental details, results, Figures S1-S25, and Table S1 (PDF)

**AUTHOR INFORMATION**

**Corresponding Authors**

Buxing Han — Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Colloid, Interface and Chemical Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China; orcid.org/0000-0003-0440-809X; Email: hanbx@iccas.ac.cn

Sihai Yang — Department of Chemistry, The University of Manchester, Manchester M13 9PL, United Kingdom; orcid.org/0000-0002-1111-9272; Email: Sihai.Yang@manchester.ac.uk

Martin Schröder — Department of Chemistry, The University of Manchester, Manchester M13 9PL, United Kingdom; orcid.org/0000-0001-6992-0700; Email: M.Schroder@manchester.ac.uk

**Authors**

Xinchun Kang — Department of Chemistry, The University of Manchester, Manchester M13 9PL, United Kingdom

Bin Wang — Department of Chemistry, The University of Manchester, Manchester M13 9PL, United Kingdom

Kui Hu — Department of Chemistry, The University of Manchester, Manchester M13 9PL, United Kingdom

Kai Lyu — Department of Chemistry, The University of Manchester, Manchester M13 9PL, United Kingdom

Xue Han — Department of Chemistry, The University of Manchester, Manchester M13 9PL, United Kingdom

Ben F. Spencer — Department of Materials, The University of Manchester, Manchester M13 9PL, United Kingdom; orcid.org/0000-0002-1453-5327

Mark D. Frogley — Diamond Light Source, Oxfordshire OX11 9DD, United Kingdom

Floriana Tuna — Department of Chemistry and Photon Science Institute, The University of Manchester, Manchester M13 9PL, United Kingdom

Eric J. L. McInnes — Department of Chemistry, The University of Manchester, Manchester M13 9PL, United Kingdom; orcid.org/0000-0002-4090-7040

Robert A. W. Dryfe — Department of Chemistry, The University of Manchester, Manchester M13 9PL, United Kingdom

Complete contact information is available at: https://pubs.acs.org/10.1021/jacs.0c05913

**Notes**

The authors declare no competing financial interest.

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