

Cite this: *Chem. Sci.*, 2019, 10, 2199

All publication charges for this article have been paid for by the Royal Society of Chemistry

# Cathodized copper porphyrin metal–organic framework nanosheets for selective formate and acetate production from CO<sub>2</sub> electroreduction†

Jian-Xiang Wu, Shu-Zhen Hou, Xiang-Da Zhang, Ming Xu, Hua-Fei Yang, Pei-Sheng Cao and Zhi-Yuan Gu \*

An efficient and selective Cu catalyst for CO<sub>2</sub> electroreduction is highly desirable since current catalysts suffer from poor selectivity towards a series of products, such as alkenes, alcohols, and carboxylic acids. Here, we used copper(II) paddle wheel cluster-based porphyrinic metal–organic framework (MOF) nanosheets for electrocatalytic CO<sub>2</sub> reduction and compared them with CuO, Cu<sub>2</sub>O, Cu, a porphyrin–Cu(II) complex and a CuO/complex composite. Among them, the cathodized Cu–MOF nanosheets exhibit significant activity for formate production with a faradaic efficiency (FE) of 68.4% at a potential of –1.55 V *versus* Ag/Ag<sup>+</sup>. Moreover, the C–C coupling product acetate is generated from the same catalyst together with formate at a wide voltage range of –1.40 V to –1.65 V with the total liquid product FE from 38.8% to 85.2%. High selectivity and activity are closely related to the cathodized restructuring of Cu–MOF nanosheets. With the combination of X-ray diffraction, X-ray photoelectron spectroscopy, high resolution transmission electron microscopy and Fourier transform infrared spectroscopy, we find that Cu(II) carboxylate nodes possibly change to CuO, Cu<sub>2</sub>O and Cu<sub>4</sub>O<sub>3</sub>, which significantly catalyze CO<sub>2</sub> to formate and acetate with synergistic enhancement from the porphyrin–Cu(II) complex. This intriguing phenomenon provides a new opportunity for the rational design of high-performance Cu catalysts from pre-designed MOFs.

Received 30th September 2018  
Accepted 14th December 2018

DOI: 10.1039/c8sc04344b

rsc.li/chemical-science

## Introduction

The reduction of CO<sub>2</sub> to useful chemicals holds great promise for reducing humanity's enormous carbon footprint.<sup>1–5</sup> Electrochemical conversion of CO<sub>2</sub> using electricity generated from renewable energy sources could provide a viable solution to the production of carbon-neutral fuels and chemicals.<sup>6–8</sup> Current products from the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) include carbon monoxide, alkenes, acids, and alcohols.<sup>9</sup> Although many research studies focus on the production of potential fuels, such as C<sub>2</sub>H<sub>4</sub>, CH<sub>3</sub>OH, and C<sub>2</sub>H<sub>5</sub>OH,<sup>10–12</sup> a recent gross-margin model counter-intuitively revealed that HCOOH and CO are the most economically viable products.<sup>13</sup> Compared with gaseous CO,<sup>14–20</sup> the liquid products HCOOH and CH<sub>3</sub>COOH are easy to collect and store.<sup>21</sup> However, the formate and acetate production from the CO<sub>2</sub>RR still remains a scientific challenge.<sup>22</sup> Major Sn-based catalysts usually suffer from limited reaction selectivity and a narrow range of active voltage,<sup>23–25</sup> although a recent Bi-based catalyst has shown

high potential for formate generation.<sup>26,27</sup> In addition, very few electrocatalysts perform CO<sub>2</sub> reduction to acetate due to the low activity of C–C coupling.<sup>28</sup> Therefore, it is urgent to develop new catalysts for the transformation of CO<sub>2</sub> to formate and acetate. Copper-based CO<sub>2</sub>RR catalysts are well-known for their capability of producing C<sub>2</sub><sup>+</sup> products, but they suffer from low selectivity and product diversity.<sup>29,30</sup> Recent Cu-based catalysts have demonstrated great potential for the production of formate and acetate,<sup>28,29</sup> however, with lower faradaic efficiency (FE).

Metal–organic frameworks (MOFs) with high porosity and designable metal clusters and organic linkers arouse significant research interest in biomedical, energy and environmental applications, such as drug delivery, enzyme inhibition, separation and catalysis.<sup>31–34</sup> The atomic-level periodicity of metal complexes or metal clusters in MOFs allows the precise control over the rational design of the active metals as potential electrocatalysts for the CO<sub>2</sub>RR.<sup>15,19,35–38</sup> The successful application of most bulk MOFs as electrocatalysts is largely hindered by their poor electrical conductivity and inevitable gas diffusion barrier,<sup>39</sup> which could be significantly improved by adjusting the synthetic method to form nano-MOFs, especially two-dimensional (2-D) MOF nanosheets.<sup>40,41</sup> Nevertheless, to the best of our knowledge, 2-D MOF nanosheets have not yet been explored in the CO<sub>2</sub> electroreduction.

It is now well accepted that an electrocatalyst undergoes *in situ* structural transformation under reaction conditions, which

Jiangsu Key Laboratory of Biofunctional Materials, Jiangsu Collaborative Innovation Center of Biomedical Functional Materials, Jiangsu Key Laboratory of New Power Batteries, School of Chemistry and Materials Science, Nanjing Normal University, Nanjing, 210023, P. R. China. E-mail: guzhiyuan@njnu.edu.cn; Fax: +86-25-85891952; Tel: +86-25-85891952

† Electronic supplementary information (ESI) available: Synthetic experimental details and additional figures (XRD and SEM data). See DOI: 10.1039/c8sc04344b



has been largely underestimated.<sup>42,43</sup> 2-D MOF nanosheets under cathodization conditions have not been studied before. Thus, we choose copper(II)-5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin-Cu(II) ( $\text{Cu}_2(\text{CuTCPP})$ ) nanosheets with two different copper chemical environments as a potential  $\text{CO}_2$  electrocatalyst. One is the porphyrinic Cu, which has been shown as an electrocatalyst for the formation of  $\text{CH}_4$ .<sup>44</sup> The other is the Cu paddle wheel, the cluster in the famous HKUST-1, which is efficient in  $\text{CH}_4$  and  $\text{C}_2\text{H}_4$  production.<sup>44,45</sup>

Here, we report the efficient and selective electroreduction of  $\text{CO}_2$  to formate and acetate by a 2-D Cu-MOF nanosheet catalyst. The FE for the formation of two liquid products reached up to 85.2% with a total current density of  $4.5 \text{ mA cm}^{-2}$ . The turnover frequency (TOF) of the catalyst for formate and acetate formation could reach as high as  $2037 \text{ h}^{-1}$  and  $148 \text{ h}^{-1}$ , respectively. This high efficiency is significantly different from that of common Cu catalysts, such as  $\text{Cu}_2\text{O}$ ,  $\text{CuO}$ ,  $\text{Cu}$  and a porphyrin-Cu(II) complex ( $\text{CuTCPP}$ ). *Ex situ* powder X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FT-IR) confirmed the cathodized reconstruction of 2-D MOF nanosheets to the heterostructures of  $\text{CuO}$ ,  $\text{Cu}_2\text{O}$  and  $\text{Cu}_4\text{O}_3$  through the  $\text{Cu}(\text{HCOO})_2$  and  $\text{Cu}(\text{OH})_2$  intermediates. Meanwhile, the  $\text{CuTCPP}$  complex was still anchored on the catalyst and could enhance the activity of the catalyst. This result reveals the fundamental significance of cathodized restructuring for highly selective production of formate and acetate on pre-designed MOF electrocatalysts.

## Results and discussion

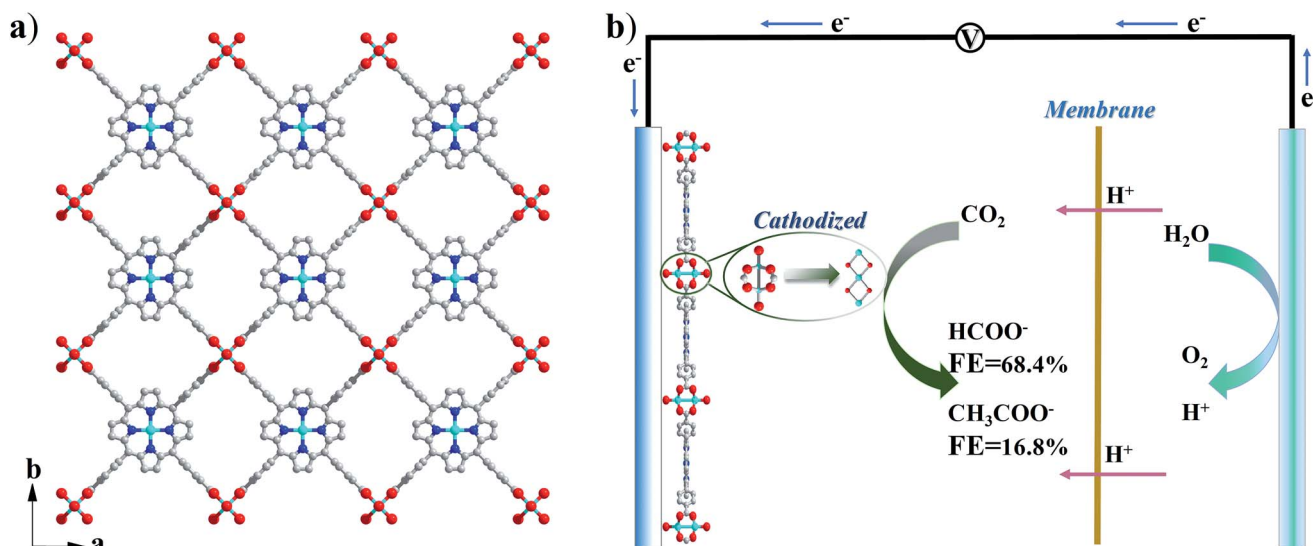
### Preparation and characterization of $\text{Cu}_2(\text{CuTCPP})$ nanosheets

$\text{Cu}_2(\text{CuTCPP})$  has a porous 2D layered reticular framework structure with Cu porphyrin ligands connected through  $\text{Cu}_2(\text{COO})_4$  paddle wheels (Scheme 1a and Fig. S1†). The

adjacent layers stack in parallel, generating vertical 1D channels along the *c* axis. The XRD pattern of the as-prepared product was consistent with that of  $\text{Cu}_2(\text{CuTCPP})$  (Fig. 1a).<sup>46,47</sup> The broad peaks in the XRD pattern were due to the nanosheet feature. After dispersion in ethanol by ultrasonication, these nanosheets showed layered structures with thin thickness in the SEM image (Fig. 1c). The TEM image revealed that the  $\text{Cu}_2(\text{CuTCPP})$  nanosheets had a smooth surface, and uniform and ultrathin thickness with high aspect ratio, which resulted in the partial curling of nanosheet edges (Fig. 1d). Atomic force microscopy (AFM) measurements showed that the nanosheets had a homogeneous thickness of  $\sim 3.7 \text{ nm}$ , indicating only 8 layers (Fig. 1b and S1†). Notably, the direct synthesis of few-molecular-layer MOF nanosheets on a large scale is rarely reported,<sup>46,47</sup> although this type of flat and high-aspect-ratio nanosheet is very desirable for electrocatalysis because of its advantages over bulk materials in regard to reducing the diffusion kinetics barrier and enhancing the electron transfer.

### Electrochemical $\text{CO}_2$ reduction by $\text{Cu}_2(\text{CuTCPP})$ nanosheets

The electrocatalytic  $\text{CO}_2\text{RR}$  activity of  $\text{Cu}_2(\text{CuTCPP})$  nanosheets on a FTO electrode was evaluated in  $\text{CH}_3\text{CN}$  solution with 1 M  $\text{H}_2\text{O}$  and 0.5 M ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ( $\text{EMIMBF}_4$ ) in a two-compartment electrochemical H-type cell (Scheme 1b).<sup>3</sup> The organic electrolyte with water and ionic liquid components was chosen to control proton concentration and enhance  $\text{CO}_2$  solubility, respectively.<sup>48–50</sup> The linear sweep voltammetry (LSV) curves of  $\text{Cu}_2(\text{CuTCPP})$  in  $\text{N}_2$ -saturated and  $\text{CO}_2$ -saturated electrolytes showed different cathodic waves from 0.5 V to  $-2.0 \text{ V versus Ag/Ag}^+$  (Fig. S2†). In the  $\text{CO}_2$ -saturated electrolyte, a steep increase of current density in the negative sweep started from  $-1.2 \text{ V versus Ag/Ag}^+$  indicating significant  $\text{CO}_2$  reduction (Fig. S2†). Meanwhile, a blank experiment with a FTO electrode was also performed since FTO



Scheme 1 (a) Crystal structure of  $\text{Cu}_2(\text{CuTCPP})$  nanosheets along the *c* axis. Red is O, blue is N, grey is C and cyan is Cu; (b)  $\text{CO}_2$  electrochemical reduction system with  $\text{Cu}_2(\text{CuTCPP})$  nanosheets as the catalyst.



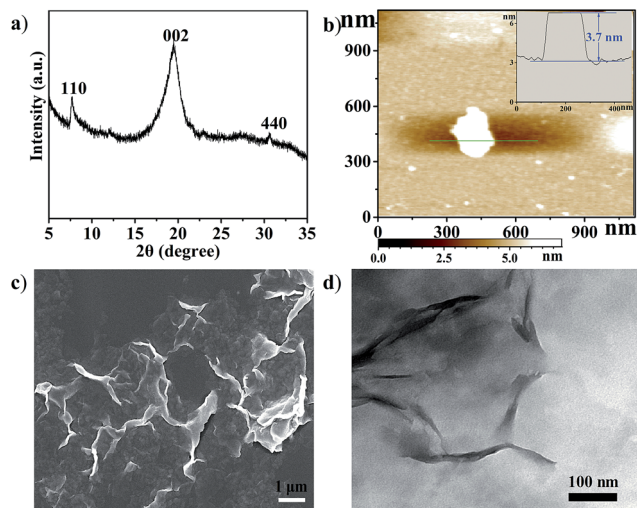


Fig. 1 (a) XRD pattern of  $\text{Cu}_2(\text{CuTCPP})$  nanosheets; (b) AFM image of the nanosheets, inset: the thickness curve; (c) SEM image of  $\text{Cu}_2(\text{CuTCPP})$  nanosheets; (d) TEM image of  $\text{Cu}_2(\text{CuTCPP})$  nanosheets.

is F-doped  $\text{SnO}_2$ , which is also the active material for the  $\text{CO}_2\text{RR}$  (Fig. S3<sup>†</sup>). We found that only a small amount of CO (FE < 10%) was produced as the reduction product, ruling out the possible formate generation from the FTO substrate.

In order to identify and quantify the reduction products, electrolysis was performed at different potentials between  $-1.40$  V and  $-1.65$  V *versus*  $\text{Ag}/\text{Ag}^+$  for 5 h. Resultant gaseous products were periodically sampled and examined using gas chromatography (GC), while the liquid products were analyzed after electrolysis by nuclear magnetic resonance (NMR) spectroscopy. We found that formate and acetate were the two dominant reduction products, accompanied by a small amount of CO and  $\text{CH}_4$  from the  $\text{CO}_2\text{RR}$  as well as  $\text{H}_2$  from the HER. The FEs for the formation of different products at various potentials were calculated and are shown in Fig. 2a. Formate and acetate were reliably and reproducibly detected at as positive as  $-1.40$  V *versus*  $\text{Ag}/\text{Ag}^+$ . Initially, the faradaic efficiencies were 28.1% and 11.6%, respectively, which then quickly rose to 61.5% and 12.3% at  $-1.55$  V *versus*  $\text{Ag}/\text{Ag}^+$ . The faradaic efficiency for the formation of the two gaseous products, CO and  $\text{CH}_4$ , remained small (<5%) in this range of potentials. Moreover,  $\text{H}_2$  production from the competing HER was well controlled from  $-1.50$  V to  $-1.65$  V.

However, the catalyst delivered a significant decrease of cathodic current density during the first 1 h and then a stable cathodic current density of  $4.5 \text{ mA cm}^{-2}$  (Fig. 2b). The first 1 h changes of current density indicated possible chemical restructuring of the catalyst under the cathodization conditions. It is also worth noting that the decrease from a total FE of 100% at  $-1.60$  V and  $-1.65$  V might indicate the hidden consumption of electrons by the side reactions as well (Fig. 2a). The initial increase in *i-t* curves and the insufficient total FE values both indicated the possible redox-based chemical restructuring of the  $\text{Cu}_2(\text{CuTCPP})$  catalyst. Thus, the production of formate and acetate as a function of electrolysis time was



Fig. 2  $\text{CO}_2\text{RR}$  performance in  $\text{CO}_2$ -saturated  $\text{CH}_3\text{CN}$  solution with 1 M  $\text{H}_2\text{O}$  and 0.5 M EMIMBF<sub>4</sub>. (a) Faradaic efficiencies of  $\text{Cu}_2(\text{CuTCPP})$  nanosheets; (b) faradaic efficiencies of  $\text{Cu}_2(\text{CuTCPP})$  nanosheets at different times; (c) faradaic efficiencies of pre-electrolyzed  $\text{Cu}_2(\text{CuTCPP})$  nanosheets; and (d) total and partial current densities for  $\text{CO}_2\text{RR}$  products on pre-electrolyzed  $\text{Cu}_2(\text{CuTCPP})$ .

investigated at  $-1.55$  V (Fig. 2b). In the first 1 h, the HER became the dominant cathodic process with a small amount of CO and  $\text{CH}_4$ . Then, after 90 min, formate appeared, while  $\text{H}_2$  from the HER decreased. After 3 h, acetate appeared. After that, stable production of formate and acetate occurred.

To eliminate the side reactions during the initial process and further confirm the activity of the final cathodized catalyst,  $\text{Cu}_2(\text{CuTCPP})$  nanosheets were pre-electrolyzed at  $-1.55$  V. Then, the  $\text{CO}_2\text{RR}$  was performed with fresh electrolyte at various potentials (Fig. 2c). The highest faradaic efficiencies for formate and acetate formation were increased to 68.4% and 16.8% at  $-1.55$  V *versus*  $\text{Ag}/\text{Ag}^+$ , respectively, with a total faradaic efficiency of 85.2%. Furthermore, the partial current densities for  $\text{CO}_2\text{RR}$  products on the  $\text{Cu}_2(\text{CuTCPP})$  catalyst were calculated and plotted against the working potentials (Fig. 2d). The maximum values of  $j_{\text{formate}}$  and  $j_{\text{acetate}}$  are  $3.5 \text{ mA cm}^{-2}$  and  $1.0 \text{ mA cm}^{-2}$ , respectively, at  $-1.60$  V *versus*  $\text{Ag}/\text{Ag}^+$ . What's more, at  $-1.55$  V *versus*  $\text{Ag}/\text{Ag}^+$ , with a maximum total faradaic efficiency of 85.2% and a surface active site density of  $3.16 \times 10^{-8} \text{ mol cm}^{-2}$  (Fig. S4<sup>†</sup>), the TOF of the catalyst for formate and acetate production could reach as high as  $2037 \text{ h}^{-1}$  and  $148 \text{ h}^{-1}$ , respectively (Fig. S5<sup>†</sup>), which outperformed that of most of the reported catalysts.<sup>51,52</sup>

To confirm the carbon source of the  $\text{CO}_2\text{RR}$  process, a control experiment under a  $\text{N}_2$  atmosphere was performed (Fig. S6<sup>†</sup>).  $\text{H}_2$  was the only product, which demonstrated that formate and acetate were produced from the reduction of  $\text{CO}_2$ , but not from the organic part or the impurities in the electrolyte or MOF material. The continual production of formate and acetate as shown by the kinetic data also supports that the carbon source was  $\text{CO}_2$ . Water concentration was also an important factor and was optimized since the competitive HER also uses  $\text{H}_2\text{O}$  as the proton source (Fig. S7<sup>†</sup>). Without  $\text{H}_2\text{O}$ , no





products could be detected, for both the HER and CO<sub>2</sub>RR. The CO<sub>2</sub>RR is significant because of the unusually low FE for the HER at a water concentration of 1.0 M, indicating that H<sub>2</sub>O is not only the proton source but also important in the cathodization procedure to generate an effective catalyst (Fig. S8†). Since CO is a possible intermediate,<sup>53</sup> we explored the direct CO reduction. However, only the HER occurred with Cu<sub>2</sub>(CuTCPP) as the catalyst for the electrocatalytic CO reduction (Fig. S9†).

### Comparison with other Cu catalysts

The restructuring of a Cu catalyst to other active Cu-containing species is not rare in electrocatalyst research.<sup>42</sup> Before the elucidation of structural changes of the Cu<sub>2</sub>(CuTCPP) catalyst, we first surveyed the CO<sub>2</sub>RR activity of Cu, CuTCPP, Cu<sub>2</sub>O, and CuO, which are common Cu catalysts (Fig. 3 and S10†). The catalysts were confirmed by XRD (Fig. S11–S14†) and were evaluated as CO<sub>2</sub> electrocatalysts under identical conditions compared to those of Cu<sub>2</sub>(CuTCPP) nanosheets.

Control experiments with Cu, CuTCPP, CuO, and Cu<sub>2</sub>O suggested that although in the presence of CO<sub>2</sub>, the HER became the dominant cathodic process for all four catalysts, accompanied by the co-generation of a small amount of CO, CH<sub>4</sub>, HCOOH and CH<sub>3</sub>COOH. The FE and yield of products at different potentials were calculated and are shown in Fig. 3 and Table S1,† respectively. Negligible CO<sub>2</sub>RR was observed on the Cu catalyst with mainly CO and CH<sub>4</sub> as products (FE < 5%) while no formate and acetate were observed. The CuTCPP complex was chosen as the counterpart since it is one of two Cu components in Cu<sub>2</sub>(CuTCPP). However, although CO was produced with a FE of 20% at potentials from –1.50 V to –1.65 V, H<sub>2</sub> from the HER was still the major product. CuO and Cu<sub>2</sub>O were two common forms of copper oxides for the CO<sub>2</sub>RR.<sup>54</sup> In our results, CuO was significant to generate both HCOOH (an FE of 14.7% at –1.5 V) and CH<sub>3</sub>COOH (an FE of 5.8% at –1.45 V), while only HCOOH was

obtained with Cu<sub>2</sub>O with an FE up to 21.5% (Table S1†). The above results indicated that the production of formate and acetate on Cu<sub>2</sub>(CuTCPP) was superior to that on the four individual Cu counterparts. Thus, no single component was possibly responsible for the high activity and selectivity of formate and acetate production, while the functionalities of the porphyrin ligand and copper paddle wheel clusters should be reconsidered.

### Cathodized reconstruction of Cu<sub>2</sub>(CuTCPP) nanosheets

The high selectivity and activity towards formate and acetate production with the reductive formation from Cu<sub>2</sub>(CuTCPP) encouraged us to pursue the “real catalyst”. These structural changes were explored with *ex situ* XRD, SEM, TEM, XPS and FT-IR characterization.

The potential Cu species from the Cu(II) paddle-wheel nodes during cathodized reconstruction were first revealed at –1.55 V with different reaction times (Fig. 4a and S15†). After the optimal electrocatalysis at –1.55 V for 15 min, the XRD peak of the Cu<sub>2</sub>(CuTCPP) catalyst on FTO electrodes shifted from 20.39° to a lower value of 20.04° with the appearance of three new peaks (Cu(HCOO)<sub>2</sub> at 13.40°, an unassigned peak at 21.37°, and Cu(OH)<sub>2</sub> at 23.42°). At 15 min, the morphology changed from well-shaped nanosheets to partially amorphous layered structures (Fig. S16a and S16b†). Then, after 30 min, two XRD peaks disappeared (21.37° and 23.42°), and the peak intensity of Cu(HCOO)<sub>2</sub> at 13.40° increased, while three new peaks (Cu(HCOO)<sub>2</sub> at 26.55°, 40.68° and 53.74°) appeared. At 30 min, the morphology changed from partially amorphous layered structures to amorphous solid (Fig. S16c†). Next, after 60 min, other XRD peaks of Cu(HCOO)<sub>2</sub> disappeared with only one peak at 13.40° remaining, while two peaks at 21.37° and 23.42° were observed again. At the same time, new dendritic structures appeared (Fig. S16d†). Finally, after 90 min, the XRD showed multiple peaks of CuO, Cu<sub>2</sub>O and Cu<sub>4</sub>O<sub>3</sub>, while the amorphous morphology was observed again (Fig. S16e†). These resultant products could be the real active catalysts in regard to the CO<sub>2</sub>RR results at the same time interval (Fig. 2b).

Meanwhile, we also performed *ex situ* XRD and SEM characterization at different voltages (Fig. S17 and S18†). Similar intermediate species, Cu(HCOO)<sub>2</sub>, and morphology changes were observed with the same confirmed final catalysts CuO, Cu<sub>2</sub>O and Cu<sub>4</sub>O<sub>3</sub>. These continual changes in XRD patterns and SEM pictures at different reaction times and working potentials showed that the Cu<sub>2</sub>(CuTCPP) catalyst had changed to CuO, Cu<sub>2</sub>O and Cu<sub>4</sub>O<sub>3</sub> with confirmed intermediates Cu(HCOO)<sub>2</sub> and Cu(OH)<sub>2</sub>. It is worth noting that the above *ex situ* XRD and SEM monitored cathodization process was fully consistent with the first 1 h current density fluctuation in electrolysis and the CO<sub>2</sub>RR time course experiment, further confirming the reliability of *ex situ* characterization techniques in our system.

To further elucidate the final catalyst and active sites of cathodized Cu<sub>2</sub>(CuTCPP) nanosheets, TEM and XPS were utilized. HRTEM images with *d* = 0.230 nm for Cu<sub>2</sub>O (111) and *d* = 0.257 nm for CuO (111), Cu<sub>2</sub>O (–111) and/or Cu<sub>4</sub>O<sub>3</sub> (211) were obtained from *ex situ* cathodized catalysts with a longer electrolysis time of 5 h. Furthermore, the Cu<sub>2</sub>(CuTCPP)

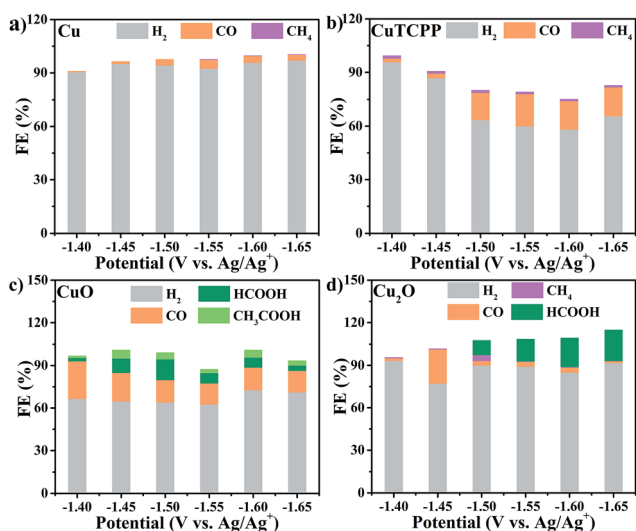


Fig. 3 Faradaic efficiencies for formation of different products in the CO<sub>2</sub>RR with different catalysts: (a) Cu, (b) CuTCPP, (c) CuO, and (d) Cu<sub>2</sub>O.



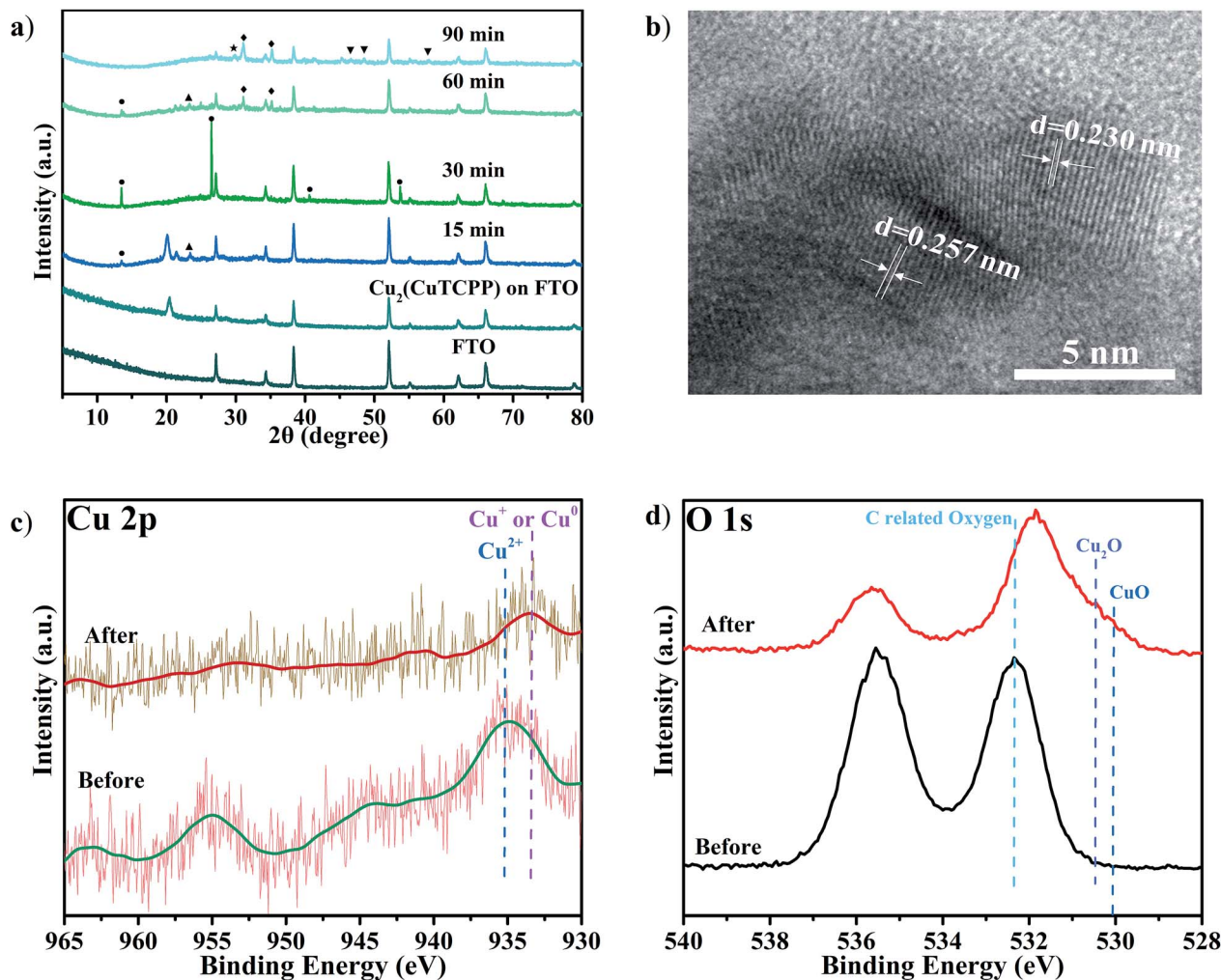


Fig. 4 (a) XRD of  $\text{Cu}_2(\text{CuTCPP})$  nanosheets on a FTO electrode with different reaction times ( $\bullet$   $\text{Cu}(\text{HCOO})_2$ ;  $\blacklozenge$   $\text{Cu}_4\text{O}_3$ ;  $\blacktriangle$   $\text{Cu}(\text{OH})_2$ ;  $\blacktriangledown$   $\text{CuO}$ ;  $\star$   $\text{Cu}_2\text{O}$ ); (b) HRTEM after 5 h reaction; (c) Cu 2p XPS spectra and (d) O 1s XPS spectra of  $\text{Cu}_2(\text{CuTCPP})$  on FTO before and after 5 h reaction. All potentials were set at  $-1.55$  V vs.  $\text{Ag}/\text{Ag}^+$ .

nanosheets and cathodized  $\text{Cu}_2(\text{CuTCPP})$  on FTO electrodes before and after the  $\text{CO}_2\text{RR}$  were characterized by XPS (Fig. 4c and d). The spectra of Cu 2p clearly showed that the as-prepared  $\text{Cu}_2(\text{CuTCPP})$  surface has  $\text{Cu}^{2+}$  states which are distinct from their lower binding energy states, the  $\text{Cu}^+$  or  $\text{Cu}^0$ , after 5 h electrocatalysis. Although the binding energies of the  $\text{Cu}^+$  and  $\text{Cu}^0$  states were very close in the XPS spectra, Auger spectra could possibly distinguish these two states with overlapped peaks at 569.5 eV and 572.5 eV, which were ascribed to the kinetic energy of  $\text{Cu}^+$  and  $\text{Cu}^{2+}$ , respectively.<sup>55</sup> Only  $\text{Cu}^+$  was observed, ruling out the possible existence of metallic copper (Fig. S19<sup>†</sup>). Meanwhile, XPS O1s spectra also showed that the as-prepared  $\text{Cu}_2(\text{CuTCPP})$  surface has C related oxygen, which was distinctively reduced to the lower binding energy O states associated with  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  after 5 h reaction (Fig. 4d).<sup>42</sup> Additional peaks in O 1s spectra were related to chemisorbed oxygen in carboxylic groups or water.<sup>56,57</sup>

The strong intensity of O 1s XPS peaks indicated the existence of O-containing species. Thus, it is crucial to elucidate the

status and possible functionality of the TCPP ligand. First, from the pictures of the electrolyte before and after electrocatalysis, we could exclude the possibility that the porphyrin ligand dissolved in the electrolyte after reaction (Fig. S20<sup>†</sup>). The NMR spectra further showed no TCPP peaks for the electrolyte samples (Fig. S21<sup>†</sup>). Second, the peak at  $1650\text{ cm}^{-1}$  in the FT-IR spectrum confirmed that the ligand was still anchored to the surface of the catalyst during the reaction (Fig. S22<sup>†</sup>).<sup>46,47,58</sup> Third, a control experiment in which a physical mixture of  $\text{CuO}$  and  $\text{CuTCPP}$  with a molar ratio of 2 : 1 was tested as a catalyst for the  $\text{CO}_2\text{RR}$  (Fig. S23<sup>†</sup>) showed that  $\text{CuO}/\text{CuTCPP}$  was significant to generate both  $\text{HCOOH}$  (FE of 31.1% at  $-1.55$  V) and  $\text{CH}_3\text{COOH}$  (FE of 17.3% at  $-1.55$  V), the FEs being higher than that of individual  $\text{CuO}$  and  $\text{CuTCPP}$  (Fig. 3). It is worth noting that our cathodized catalyst was possibly anchored by TCPP through chemical bonds, in which the activity was even better than that of the physical mixture of  $\text{CuO}/\text{CuTCPP}$ . Thus, the inorganic species of the cathodized  $\text{Cu}_2(\text{CuTCPP})$  nanosheets were confirmed as  $\text{CuO}$ ,  $\text{Cu}_2\text{O}$  and  $\text{Cu}_4\text{O}_3$ , while the



anchored CuTCPP could synergistically enhance the activity of the final catalyst and result in different selectivities compared to traditional Cu catalysts as well as Cu-MOFs such as HKUST-1.<sup>45</sup>

## Conclusions

This research discovered the high selectivity and efficiency in electrocatalytic CO<sub>2</sub> reduction to formate and acetate with cathodized copper porphyrin MOF nanosheets. The comparison with CuO, Cu<sub>2</sub>O, Cu and CuTCPP counterparts and XRD, XPS, FT-IR and HRTEM studies confirmed the cathodized reconstruction to a mixture of CuO, Cu<sub>2</sub>O and Cu<sub>4</sub>O<sub>3</sub> anchored with the TCPP ligand. Although inevitable structural changes occurred in the cathodization process, this pre-designed feature of 2-D MOF nanosheets will bring precise control over the preparation of electrocatalysts.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work is financially supported by the NSFC (No. 21505076), the Young Elite Scholar Support (YESS) Program from CAST, the Program of Jiangsu Specially-Appointed Professor, the NSF of Jiangsu Province of China (No. BK20150967), the Innovation Team Program of Jiangsu Province of China, and the Priority Academic Program Development of Jiangsu Higher Education Institutions.

## Notes and references

- H. Takeda, K. Ohashi, A. Sekine and O. Ishitani, *J. Am. Chem. Soc.*, 2016, **138**, 4354–4357.
- J. Bonin, M. Robert and M. Routier, *J. Am. Chem. Soc.*, 2014, **136**, 16768–16771.
- S. Zhang, P. Kang, M. Bakir, A. M. Lapides, C. J. Dares and T. J. Meyer, *Proc. Natl. Acad. Sci. U. S. A.*, 2015, **112**, 15809–15814.
- U. Kang, S. K. Choi, D. J. Ham, S. M. Ji, W. Choi, D. S. Han, A. Abdel-Wahab and H. Park, *Energy Environ. Sci.*, 2015, **8**, 2638–2643.
- X. Yang, E. A. Fugate, Y. Mueanngern and L. R. Baker, *ACS Catal.*, 2017, **7**, 177–180.
- F. Li, L. Chen, M. Xue, T. Williams, Y. Zhang, D. R. MacFarlane and J. Zhang, *Nano Energy*, 2017, **31**, 270–277.
- S. Huo, Z. Weng, Z. Wu, Y. Zhong, Y. Wu, J. Fang and H. Wang, *ACS Appl. Mater. Interfaces*, 2017, **9**, 28519–28526.
- Y. Wu, J. Jiang, Z. Weng, M. Wang, D. L. J. Broere, Y. Zhong, G. W. Brudvig, Z. Feng and H. Wang, *ACS Cent. Sci.*, 2017, **3**, 847–852.
- Z. Sun, T. Ma, H. Tao, Q. Fan and B. Han, *Chem*, 2017, **3**, 560–587.
- Y. Huang, A. D. Handoko, P. Hirunsit and B. S. Yeo, *ACS Catal.*, 2017, **7**, 1749–1756.
- W. Zhang, Q. Qin, L. Dai, R. Qin, X. Zhao, X. Chen, D. Ou, J. Chen, T. T. Chuong and B. Wu, *Angew. Chem., Int. Ed.*, 2018, **57**, 9475–9479.
- Y. Liu, Y. Zhang, K. Cheng, X. Quan, X. Fan, Y. Su, S. Chen, H. Zhao, Y. Zhang and H. Yu, *Angew. Chem., Int. Ed.*, 2017, **129**, 15813–15817.
- S. Verma, B. Kim, H.-R. M. Jhong, S. Ma and P. J. A. Kenis, *ChemSusChem*, 2016, **9**, 1972–1979.
- H. Tao, X. Sun, S. Back, Z. Han, Q. Zhu, A. W. Robertson, T. Ma, Q. Fan, B. Han, Y. Jung and Z. Sun, *Chem. Sci.*, 2018, **9**, 483–487.
- I. Hod, M. D. Sampson, P. Deria, C. P. Kubiak, O. K. Farha and J. T. Hupp, *ACS Catal.*, 2015, **5**, 6302–6309.
- N. Han, Y. Wang, L. Ma, J. Wen, J. Li, H. Zheng, K. Nie, X. Wang, F. Zhao, Y. Li, J. Fan, J. Zhong, T. Wu, D. J. Miller, J. Lu, S.-T. Lee and Y. Li, *Chem*, 2017, **3**, 652–664.
- X. Zhang, Z. Wu, X. Zhang, L. Li, Y. Li, H. Xu, X. Li, X. Yu, Z. Zhang, Y. Liang and H. Wang, *Nat. Commun.*, 2017, **8**, 14675.
- C. Costentin, S. Drouet, M. Robert and J.-M. Savéant, *Science*, 2012, **338**, 90–94.
- N. Kornienko, Y. Zhao, C. S. Kley, C. Zhu, D. Kim, S. Lin, C. J. Chang, O. M. Yaghi and P. Yang, *J. Am. Chem. Soc.*, 2015, **137**, 14129–14135.
- C. Zhao, X. Dai, T. Yao, W. Chen, X. Wang, J. Wang, J. Yang, S. Wei, Y. Wu and Y. Li, *J. Am. Chem. Soc.*, 2017, **139**, 8078–8081.
- Y. Liu, S. Chen, X. Quan and H. Yu, *J. Am. Chem. Soc.*, 2015, **137**, 11631–11636.
- Y. Deng, Y. Huang, D. Ren, A. D. Handoko, Z. W. Seh, P. Hirunsit and B. S. Yeo, *ACS Appl. Mater. Interfaces*, 2018, **10**, 28572–28581.
- F. Li, L. Chen, G. P. Knowles, D. R. MacFarlane and J. Zhang, *Angew. Chem., Int. Ed.*, 2017, **56**, 505–509.
- Y. Zhang, L. Chen, F. Li, C. D. Easton, J. Li, A. M. Bond and J. Zhang, *ACS Catal.*, 2017, **7**, 4846–4853.
- J. Gu, F. Héroguel, J. Luterbacher and X. Hu, *Angew. Chem., Int. Ed.*, 2018, **130**, 2993–2997.
- X. Sun, Q. Zhu, X. Kang, H. Liu, Q. Qian, Z. Zhang and B. Han, *Angew. Chem., Int. Ed.*, 2016, **55**, 6771–6775.
- N. Han, Y. Wang, H. Yang, J. Deng, J. Wu, Y. Li and Y. Li, *Nat. Commun.*, 2018, **9**, 1320.
- Y. Wang, D. Wang, C. J. Dares, S. L. Marquard, M. V. Sheridan and T. J. Meyer, *Proc. Natl. Acad. Sci. U. S. A.*, 2017, 201713962.
- K. P. Kuhl, E. R. Cave, D. N. Abram and T. F. Jaramillo, *Energy Environ. Sci.*, 2012, **5**, 7050–7059.
- C. W. Li and M. W. Kanan, *J. Am. Chem. Soc.*, 2012, **134**, 7231–7234.
- M. Xu, S. Yuan, X.-Y. Chen, Y.-J. Chang, G. Day, Z.-Y. Gu and H.-C. Zhou, *J. Am. Chem. Soc.*, 2017, **139**, 8312–8319.
- T. Rodenas, I. Luz, G. Prieto, B. Seoane, H. Miro, A. Corma, F. Kapteijn, F. X. Llabrés i Xamena and J. Gascon, *Nat. Mater.*, 2014, **14**, 48.
- L. Zhu, X.-Q. Liu, H.-L. Jiang and L.-B. Sun, *Chem. Rev.*, 2017, **117**, 8129–8176.



- 34 H. Zheng, Y. Zhang, L. Liu, W. Wan, P. Guo, A. M. Nyström and X. Zou, *J. Am. Chem. Soc.*, 2016, **138**, 962–968.
- 35 R. S. Kumar, S. S. Kumar and M. A. Kulandainathan, *Electrochem. Commun.*, 2012, **25**, 70–73.
- 36 J. Albo, D. Vallejo, G. Beobide, O. Castillo, P. Castaño and A. Irabien, *ChemSusChem*, 2017, **10**, 1100–1109.
- 37 R. Hinogami, S. Yotsuhashi, M. Deguchi, Y. Zenitani, H. Hashiba and Y. Yamada, *ECS Electrochem. Lett.*, 2012, **1**, H17–H19.
- 38 L. Ye, J. Liu, Y. Gao, C. Gong, M. Addicoat, T. Heine, C. Wöll and L. Sun, *J. Mater. Chem. A*, 2016, **4**, 15320–15326.
- 39 W. H. Li, K. Ding, H. R. Tian, M. S. Yao, B. Nath, W. H. Deng, Y. Wang and G. Xu, *Adv. Funct. Mater.*, 2017, **27**, 1702067.
- 40 Y. Wang, P. Hou, Z. Wang and P. Kang, *ChemPhysChem*, 2017, **18**, 3142–3147.
- 41 S. Zhao, Y. Wang, J. Dong, C.-T. He, H. Yin, P. An, K. Zhao, X. Zhang, C. Gao and L. Zhang, *Nat. Energy*, 2016, **1**, 16184.
- 42 S. Y. Lee, H. Jung, N.-K. Kim, H.-S. Oh, B. K. Min and Y. J. Hwang, *J. Am. Chem. Soc.*, 2018, **140**, 8681–8689.
- 43 P. Grosse, D. Gao, F. Scholten, I. Sinev, H. Mistry and B. Roldan Cuenya, *Angew. Chem., Int. Ed.*, 2018, **130**, 6300–6305.
- 44 Z. Weng, Y. Wu, M. Wang, J. Jiang, K. Yang, S. Huo, X.-F. Wang, Q. Ma, G. W. Brudvig, V. S. Batista, Y. Liang, Z. Feng and H. Wang, *Nat. Commun.*, 2018, **9**, 415.
- 45 D.-H. Nam, O. S. Bushuyev, J. Li, P. De Luna, A. Seifitokaldani, C.-T. Dinh, F. P. García de Arquer, Y. Wang, Z. Liang, A. H. Proppe, C. S. Tan, P. Todorović, O. Shekhah, C. M. Gabardo, J. W. Jo, J. Choi, M.-J. Choi, S.-W. Baek, J. Kim, D. Sinton, S. O. Kelley, M. Eddaoudi and E. H. Sargent, *J. Am. Chem. Soc.*, 2018, **140**, 11378–11386.
- 46 G. Xu, K. Otsubo, T. Yamada, S. Sakaida and H. Kitagawa, *J. Am. Chem. Soc.*, 2013, **135**, 7438–7441.
- 47 G. Xu, T. Yamada, K. Otsubo, S. Sakaida and H. Kitagawa, *J. Am. Chem. Soc.*, 2012, **134**, 16524–16527.
- 48 Q. Zhu, J. Ma, X. Kang, X. Sun, H. Liu, J. Hu, Z. Liu and B. Han, *Angew. Chem., Int. Ed.*, 2016, **128**, 9158–9162.
- 49 B. A. Rosen, A. Salehi-Khojin, M. R. Thorson, W. Zhu, D. T. Whipple, P. J. Kenis and R. I. Masel, *Science*, 2011, 1209786.
- 50 X. Sun, X. Kang, Q. Zhu, J. Ma, G. Yang, Z. Liu and B. Han, *Chem. Sci.*, 2016, **7**, 2883–2887.
- 51 T. N. Huan, P. Simon, A. Benayad, L. Guetaz, V. Artero and M. Fontecave, *Chem.–Eur. J.*, 2016, **22**, 14029–14035.
- 52 T. N. Huan, E. S. Andreiadis, J. Heidkamp, P. Simon, E. Derat, S. Cobo, G. Royal, A. Bergmann, P. Strasser and H. Dau, *J. Mater. Chem. A*, 2015, **3**, 3901–3907.
- 53 K. J. P. Schouten, Y. Kwon, C. J. M. van der Ham, Z. Qin and M. T. M. Koper, *Chem. Sci.*, 2011, **2**, 1902–1909.
- 54 H. Mistry, A. S. Varela, C. S. Bonifacio, I. Zegkinoglou, I. Sinev, Y.-W. Choi, K. Kisslinger, E. A. Stach, J. C. Yang, P. Strasser and B. R. Cuenya, *Nat. Commun.*, 2016, **7**, 12123.
- 55 F. Deng, N. Li, S. Tang, C. Liu, H. Yue and B. Liang, *Chem. Eng. J.*, 2018, **334**, 1943–1953.
- 56 L.-Z. Fan, S. Qiao, W. Song, M. Wu, X. He and X. Qu, *Electrochim. Acta*, 2013, **105**, 299–304.
- 57 L.-Z. Fan, J.-L. Liu, R. Ud-Din, X. Yan and X. Qu, *Carbon*, 2012, **50**, 3724–3730.
- 58 W. Tu, J. Lei, P. Wang and H. Ju, *Chem.–Eur. J.*, 2011, **17**, 9440–9447.

