



## RESEARCH ARTICLE

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# Steady Cu<sup>+</sup> species *via* magnesium and boron co-modification for enhanced CO<sub>2</sub> electroreduction to C<sub>2+</sub> products: an *in situ* Raman spectroscopic study†

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The electrochemical carbon dioxide reduction reaction (CO<sub>2</sub>RR) to produce high-value multi-carbon (C<sub>2+</sub>) compounds holds significant practical importance in realizing carbon neutrality. Copper-based electrocatalysts are promising for CO<sub>2</sub>-to-C<sub>2+</sub> conversion. However, the labile Cu valence at high current densities impedes C<sub>2+</sub> product generation. Here, we present an electrocatalyst derived from CuO, featuring a heterostructure of Cu/Cu<sub>2</sub>O/CuO/Mg(OH)<sub>2</sub> *via* the co-addition of Mg and B during the preparation (referred to as Cu<sub>5</sub>(B<sub>0.02</sub> M)Mg<sub>1</sub>). The Cu<sub>5</sub>(B<sub>0.02</sub> M)Mg<sub>1</sub> shows an impressive C<sub>2+</sub> yield, with a Faraday efficiency (FE<sub>C<sub>2+</sub></sub>) of 79.59% at −1.57 V vs. RHE (reversible hydrogen electrode). Additionally, the partial current density of C<sub>2+</sub> on the Cu<sub>5</sub>(B<sub>0.02</sub> M)Mg<sub>1</sub> catalyst is −317.03 mA cm<sup>−2</sup>, 2.7 and 3.5 times higher than those catalysts lacking B (Cu<sub>5</sub>Mg<sub>1</sub> catalyst) or Mg (Cu(B<sub>0.02</sub> M) catalyst), respectively. Over a wide potential range of 600 mV between −1.17 and −1.77 V vs. RHE, the overall FE<sub>C<sub>2+</sub></sub> surpasses 60% on the Cu<sub>5</sub>(B<sub>0.02</sub> M)Mg<sub>1</sub> catalyst. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and high-resolution transmission electron microscopy (HRTEM) characterization studies indicate the NaBH<sub>4</sub> reactant could promote the formation of crystalline Mg(OH)<sub>2</sub> in the catalyst structure, which is found to better stabilize Cu<sup>+</sup> at negative potentials compared to the amorphous phase. Further *in situ* Raman spectroscopy reveals that at increasingly negative potentials, the higher copper species (Cu<sup>2+</sup>) is inevitably reduced to the lower copper species (Cu<sup>0</sup>/Cu<sup>+</sup>). However, the synergy of Mg and B prolongs the presence of Cu<sup>+</sup> on the catalyst surface across a broad potential range, and \*CO and \*CO<sub>2</sub><sup>−</sup> could still be recorded at quite negative reduction potentials. This suggests enhanced binding strength of \*CO intermediates on the catalyst surface, promoting the C–C coupling process.

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## 1. Introduction

The electrocatalytic carbon dioxide reduction reaction (CO<sub>2</sub>RR) represents a pathway for producing high-value-added chemicals and fuels, offering a means to reduce global carbon dioxide (CO<sub>2</sub>) emissions and alleviate the shortage of non-renewable carbon resources.<sup>1–3</sup> The CO<sub>2</sub>RR yields primarily hydrocarbons and oxygen-containing compounds. Among them, multi-carbon (C<sub>2+</sub>) products such as ethylene (C<sub>2</sub>H<sub>4</sub>) and ethanol (C<sub>2</sub>H<sub>5</sub>OH) have broader industrial applications and higher energy densities compared with C<sub>1</sub> products like

carbon monoxide (CO) and methane (CH<sub>4</sub>), thus commanding a higher economic value per unit mass.<sup>4–6</sup> However, challenges persist due to the requirement of a significant amount of energy to break the C=O bond with the high dissociation energy of CO<sub>2</sub> (about 750 kJ mol<sup>−1</sup>). Furthermore, the multi-step proton-coupling process contributes to the poor selectivity and yield of target products during the CO<sub>2</sub>RR.<sup>7–9</sup> Addressing these issues requires the exploration and design of electrocatalysts with enhanced efficiency to facilitate CO<sub>2</sub> conversion while minimizing product distribution variability during the CO<sub>2</sub>RR process.

To date, copper-based materials, which have been found crucial for C–C coupling, remain the major electrocatalysts for efficiently converting CO<sub>2</sub> to long-chain hydrocarbons and multi-carbon oxygenates.<sup>10–12</sup> Previous studies suggest that Cu<sup>+</sup> species on Cu-based materials could enhance the selectivity of C<sub>2+</sub> products.<sup>13,14</sup> However, under high-current electrolysis, particularly at the negative potentials required for C<sub>2+</sub>

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product formation, the catalyst structure becomes unstable, and  $\text{Cu}^+$  is readily reduced to  $\text{Cu}^0$  during the  $\text{CO}_2\text{RR}$ . Consequently, prolonging the lifetime of  $\text{Cu}^+$  at reduction potentials is a current research focus. To preserve  $\text{Cu}^+$  during the  $\text{CO}_2\text{RR}$  so as to enhance  $\text{C}_{2+}$  formation, essential steps involve generating  $\text{Cu}^+$  sites and optimizing intermediate adsorption. Researchers have developed several strategies for this purpose, including doping modification,<sup>15,16</sup> addition of different metallic elements,<sup>17,18</sup> heterogeneous interface engineering,<sup>19,20</sup> oxidation state regulation,<sup>21–23</sup> defect control,<sup>21,24–26</sup> *etc.* Until now, nonmetallic elements such as B, C, F, and S have been reported to effectively regulate the electronic structure and stabilize  $\text{Cu}^+$  in Cu lattices, facilitating the reduction of  $\text{CO}_2$  to  $\text{C}_{2+}$  products at large current densities.<sup>27–29</sup> For example, Yao *et al.* devised a B- $\text{Cu}_2\text{O}$  catalyst which showed high selectivity for ethanol product. Their oxygen programmed desorption and density functional theory (DFT) calculations confirmed that B prevented lattice oxygen from separating out from  $\text{Cu}_2\text{O}$ , thereby stabilizing  $\text{Cu}^+$  species on the B- $\text{Cu}_2\text{O}$  surface. This was believed to strengthen Cu–O bonds, significantly enhancing C–C coupling and facilitating the formation of  $\text{C}_{2+}$  products.<sup>30</sup> Alkaline-earth metals such as Mg, Ba and Ca were found to not only maintain  $\text{Cu}^+$  on catalyst surfaces, but also enhance the adsorption of intermediates at active centers, thereby influencing the reaction kinetics of the  $\text{CO}_2\text{RR}$  process.<sup>31</sup> For instance, Peng *et al.* synthesized a nano- $\text{Cu}_2\text{Mg}$  intermetallic catalyst predominantly oriented along the (111) crystal face on a carbon black substrate (denoted as  $\text{Cu}_2\text{Mg}(111)$ ). *In situ* Raman spectroscopy and DFT calculations confirmed that the  $\text{Cu}_3^{\delta-}\text{Mg}^{\delta+}$  active sites in  $\text{Cu}_2\text{Mg}(111)$  enhanced the coverage of  $\ast\text{CO}$  on the catalyst surface, lowered the energy barrier for  $\ast\text{CO}$ – $\text{CO}$  coupling, and stabilized the  $\ast\text{CHCHOH}$  intermediates to promote ethanol production.<sup>32</sup> In addition, Xie *et al.* engineered a Mg-modified  $\text{Cu}_x\text{O}$  nanoparticle catalyst targeting the  $\text{C}_2\text{H}_4$  product. *In situ* XRD, *in situ* Raman spectroscopy and DFT calculations demonstrated that the amorphous  $\text{Mg}(\text{OH})_2$  species stabilized  $\text{Cu}^+$  species, promoting the presence of vital high  $\ast\text{CO}$  intermediates for  $\text{C}_{2+}$  products.<sup>33</sup> However, challenges still exist regarding these Cu-based materials specially designed for  $\text{C}_{2+}$  products. Under current modification measures,  $\text{Cu}^+$  has a relatively short lifetime and could only exist within a narrow potential window, significantly limiting its effectiveness during the  $\text{CO}_2\text{RR}$ . Furthermore, there is a lack of literature on the combined effects of alkaline-earth metals and non-metals on copper catalysts. Additionally, the influence of the crystalline or amorphous state of alkaline-earth metal oxides on the stability of  $\text{Cu}^+$  has not been thoroughly studied.

Based on the above considerations, we have designed a B-Cu/ $\text{Cu}_2\text{O}$ / $\text{CuO}$ / $\text{Mg}(\text{OH})_2$  catalyst through a simple two-step protocol involving calcination and wet chemical reduction, aiming to enhance  $\text{C}_{2+}$  products at high current densities across wide potential ranges. The target catalyst is referred to as  $\text{Cu}_5(\text{B}_{0.02}\text{M})\text{Mg}_1$ , named according to the content of the elements during its preparation. X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM) and *ex*

*situ* X-ray photoelectron spectroscopy (XPS) reveal that the addition of  $\text{NaBH}_4$  during catalyst synthesis could promote the formation of crystalline  $\text{Mg}(\text{OH})_2$  in the catalyst structure, which we suggest would better stabilize  $\text{Cu}^+$  compared to the amorphous  $\text{Mg}(\text{OH})_2$  phase. Further *in situ* Raman investigation confirms that  $\text{Cu}^+$  on the  $\text{Cu}_5(\text{B}_{0.02}\text{M})\text{Mg}_1$  catalyst could persist across a much broader potential window compared to those catalysts lacking crystalline  $\text{Mg}(\text{OH})_2$  or B. Additionally, the  $\ast\text{CO}$  intermediate, a significant precursor of  $\text{C}_{2+}$  products, is recorded on the  $\text{Cu}_5(\text{B}_{0.02}\text{M})\text{Mg}_1$  surface even at rather negative potentials during the  $\text{CO}_2\text{RR}$ . Benefiting from the stabilized  $\text{Cu}^+$ ,  $\text{Cu}_5(\text{B}_{0.02}\text{M})\text{Mg}_1$  shows high selectivity towards  $\text{C}_{2+}$  within  $-1.17$  to  $-1.77$  V vs. RHE (unless specified, all potentials in this work are referenced against RHE). Overall, our work reveals the significance of morphologies of  $\text{Mg}(\text{OH})_2$  in  $\text{Cu}^+$  stabilization and provides a comprehensive understanding of the role of  $\text{Cu}^+$  in the efficient  $\text{CO}_2\text{RR}$  towards  $\text{C}_{2+}$  products.

## 2. Results and discussion

### 2.1 Morphological and structural characterization of the catalysts

The typical fabrication process of  $\text{Cu}_5(\text{B}_{0.02}\text{M})\text{Mg}_1$  is depicted in Fig. 1, with detailed synthesis described in the ESI.† The XRD pattern indicates diffraction peaks of Cu,  $\text{Cu}_2\text{O}$ , CuO and  $\text{Mg}(\text{OH})_2$  in the  $\text{Cu}_5(\text{B}_{0.02}\text{M})\text{Mg}_1$  catalyst (Fig. 2a). The characteristic peaks at  $42.3^\circ$ ,  $50.4^\circ$ , and  $74.1^\circ$  correspond to the (111), (200) and (220) planes of Cu (PDF#04-0836), respectively. Additionally, four peaks at  $29.5^\circ$ ,  $36.4^\circ$ ,  $42.3^\circ$  and  $61.3^\circ$  correspond to the (110), (111), (200) and (220) planes of  $\text{Cu}_2\text{O}$  (PDF#05-0667), respectively. Peaks at  $35.4^\circ$ ,  $39.7^\circ$ ,  $48.7^\circ$ ,  $53.5^\circ$  and  $66.4^\circ$  are attributed to the (002), (111), (202), (020) and (310) planes of CuO (PDF#48-1548), respectively. Furthermore, peaks at  $18.5^\circ$ ,  $32.9^\circ$ ,  $58.6^\circ$  and  $68.2^\circ$  align well with the (001), (100), (110) and (103) planes of  $\text{Mg}(\text{OH})_2$  (PDF#44-1482), respectively. The XRD pattern demonstrates that the  $\text{Cu}_5(\text{B}_{0.02}\text{M})\text{Mg}_1$  catalyst mainly comprises Cu,  $\text{Cu}_2\text{O}$ , CuO and  $\text{Mg}(\text{OH})_2$  crystal phases. On the other hand, XRD patterns of the corresponding reference  $\text{Cu}_5\text{Mg}_1$ ,  $\text{Cu}_5(\text{B}_{0.1}\text{M})\text{Mg}_1$ ,  $\text{Cu}(\text{B}_{0.02}\text{M})$ ,  $\text{Cu}_{10}(\text{B}_{0.02}\text{M})\text{Mg}_1$  and  $\text{Cu}_1(\text{B}_{0.02}\text{M})\text{Mg}_1$  catalysts are provided in Fig. S1.† The  $\text{Cu}_5(\text{B}_{0.1}\text{M})\text{Mg}_1$ ,  $\text{Cu}_{10}(\text{B}_{0.02}\text{M})\text{Mg}_1$  and  $\text{Cu}_1(\text{B}_{0.02}\text{M})\text{Mg}_1$  catalysts also consist of Cu,  $\text{Cu}_2\text{O}$ , CuO and  $\text{Mg}(\text{OH})_2$ . The  $\text{Cu}(\text{B}_{0.02}\text{M})$  catalyst comprises three phases: Cu,  $\text{Cu}_2\text{O}$  and CuO. Notably, for the  $\text{Cu}_5\text{Mg}_1$  catalyst (lacking the  $\text{NaBH}_4$  reactant during its preparation), XRD only reveals the existence of CuO (PDF#48-1548), while the  $\text{Mg}(\text{OH})_2$  (PDF#44-1482) crystalline phases are absent. We propose that this results from the generation of amorphous  $\text{Mg}(\text{OH})_2$  rather than crystalline  $\text{Mg}(\text{OH})_2$  when the reducing agent  $\text{NaBH}_4$  is absent (Fig. S1a†).<sup>34</sup>

Scanning electron microscopy (SEM) and TEM reveal that the as-prepared  $\text{Cu}_5(\text{B}_{0.02}\text{M})\text{Mg}_1$  catalyst is constructed of nanoclusters (Fig. S2† and Fig. 2b). Energy-dispersive X-ray spectroscopy (EDS) elemental mappings demonstrate a uniform distribution of Cu, Mg, B and O elements on the cata-

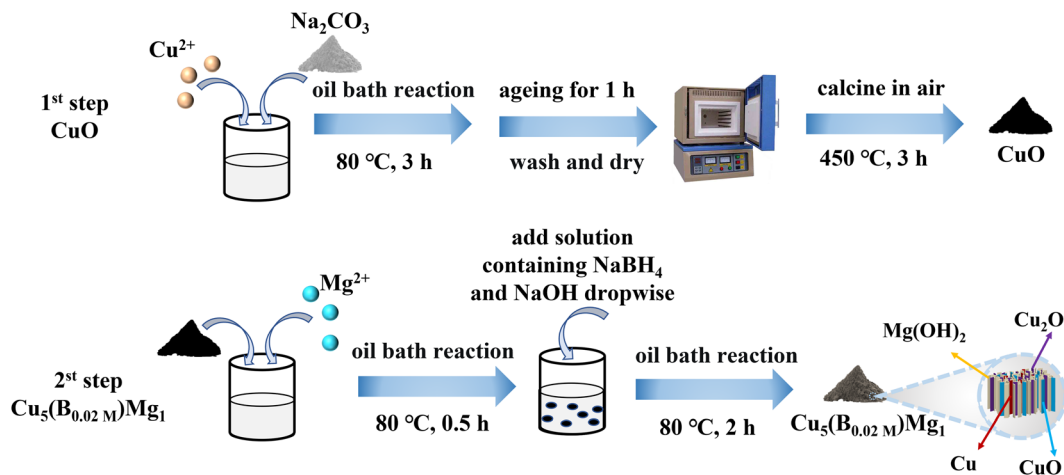


Fig. 1 Graphical scheme for the synthesis of the  $\text{Cu}_5(\text{B}_{0.02\text{M}})\text{Mg}_1$  catalyst.

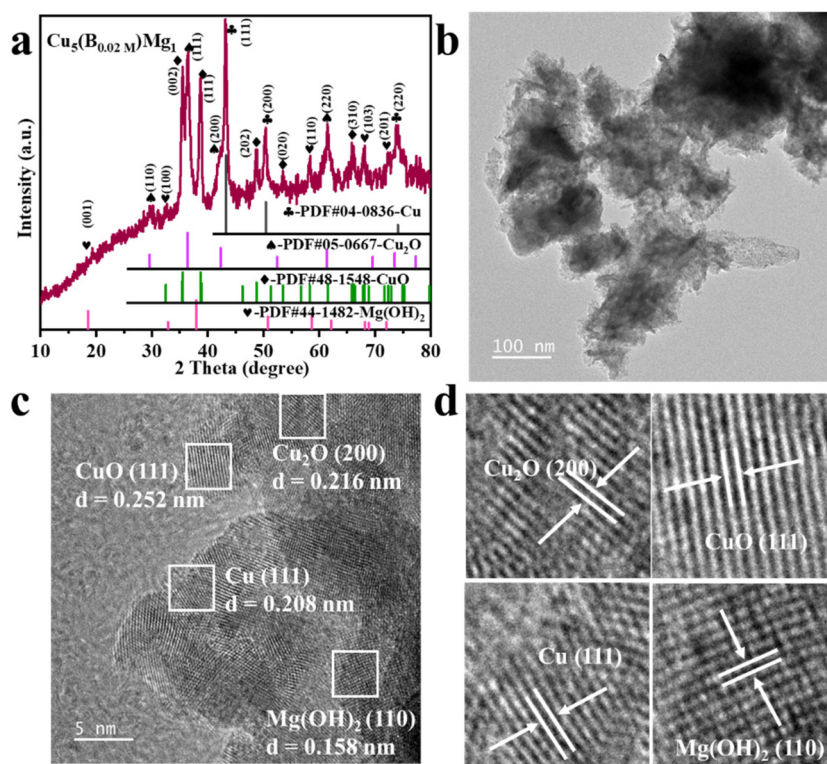


Fig. 2 (a) XRD, (b) TEM and (c) HRTEM characterization of the  $\text{Cu}_5(\text{B}_{0.02\text{M}})\text{Mg}_1$  catalyst. (d) is the enlarged view of (c).

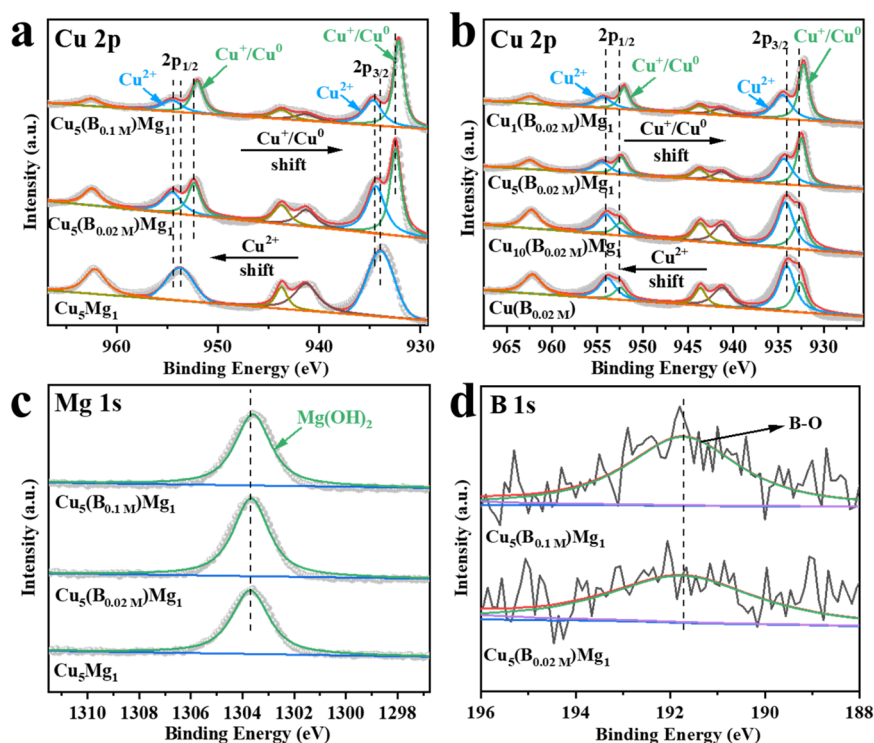
lyst surface (Fig. S2c and d<sup>†</sup>). SEM and EDS characterization studies were performed on the  $\text{Cu}_5\text{Mg}_1$ ,  $\text{Cu}_5(\text{B}_{0.1\text{M}})\text{Mg}_1$ ,  $\text{Cu}(\text{B}_{0.02\text{M}})$ ,  $\text{Cu}_{10}(\text{B}_{0.02\text{M}})\text{Mg}_1$  and  $\text{Cu}_1(\text{B}_{0.02\text{M}})\text{Mg}_1$  catalysts as well, with the corresponding results shown in Fig. S3–S7.<sup>†</sup> Further HRTEM analysis reveals interplanar spacings of 0.208 (Cu (111)), 0.216 ( $\text{Cu}_2\text{O}$  (200)), 0.252 (CuO (111)) and 0.158 nm ( $\text{Mg}(\text{OH})_2$  (110)) in the  $\text{Cu}_5(\text{B}_{0.02\text{M}})\text{Mg}_1$  catalyst, consistent with its XRD result (Fig. 2c and d). TEM and HRTEM were also conducted on  $\text{Cu}(\text{B}_{0.02\text{M}})$  and  $\text{Cu}_5\text{Mg}_1$  to explore the effect of

Mg and B on the structure of the catalyst (Fig. S8 and S9<sup>†</sup>). For the  $\text{Cu}(\text{B}_{0.02\text{M}})$  catalyst, the HRTEM image reveals crystal lattices with interfacial spacings of 0.209, 0.247, and 0.253 nm, coinciding with the Cu (111),  $\text{Cu}_2\text{O}$  (111), and CuO (111) lattices (Fig. S8<sup>†</sup>). Conversely, the  $\text{Cu}_5\text{Mg}_1$  catalyst primarily exhibits the CuO (111) crystalline phase, along with some amorphous species (Fig. S9<sup>†</sup>). Considering TEM and XRD results collectively, we may speculate that the observed amorphous substance in  $\text{Cu}_5\text{Mg}_1$  arises from some Mg-based amorphous

species formed due to the absence of the  $\text{NaBH}_4$  reagent (Fig. S9b†).

The electronic structures of the catalysts with different ratios of Cu, Mg and B additions were characterized by XPS (Fig. 3). The Cu 2p XPS spectra demonstrate two peaks corresponding to Cu  $2p_{3/2}$  and Cu  $2p_{1/2}$  (Fig. 3a and b).<sup>35,36</sup> The peaks at 933.98 and 953.78 eV are attributed to the  $\text{Cu}^{2+}$  of CuO in  $\text{Cu}_5\text{Mg}_1$  (Fig. 3a and Table S1†),<sup>37–39</sup> indicating that in the absence of  $\text{NaBH}_4$  reducing agent, the Cu species in the catalyst mainly exists in the form of  $\text{Cu}^{2+}$ . Notably, upon  $\text{NaBH}_4$  addition, the  $\text{Cu}^{2+}$  bands of  $\text{Cu}_5(\text{B}_{0.02\text{ M}})\text{Mg}_1$  and  $\text{Cu}_5(\text{B}_{0.1\text{ M}})\text{Mg}_1$  catalysts shift to higher electron binding energies by 0.55 and 0.64 eV, respectively, and at the same time  $\text{Cu}^0/\text{Cu}^+$  is produced. Additionally, with increasing  $\text{NaBH}_4$  content, the  $\text{Cu}^0/\text{Cu}^+$  electron binding energies decrease from 932.43/952.23 eV ( $\text{Cu}_5(\text{B}_{0.02\text{ M}})\text{Mg}_1$ ) to 932.17/951.97 eV ( $\text{Cu}_5(\text{B}_{0.1\text{ M}})\text{Mg}_1$ ) (Fig. 3a and Table S1†).<sup>40–42</sup> These results demonstrate that the  $\text{NaBH}_4$  content is a key factor affecting the electronic structure of Cu centers. To further differentiate between  $\text{Cu}^0$  and  $\text{Cu}^+$ , Cu LMM Auger electron spectroscopy analysis was performed on  $\text{Cu}_5(\text{B}_{0.02\text{ M}})\text{Mg}_1$  and  $\text{Cu}_5(\text{B}_{0.1\text{ M}})\text{Mg}_1$  catalysts (Fig. S10†). The two peaks at around 568.00 and 569.75 eV correspond to  $\text{Cu}^0$  and  $\text{Cu}^+$ ,<sup>43,44</sup> respectively, confirming the co-existence of  $\text{Cu}^0$  and  $\text{Cu}^+$  species on these two catalysts. According to previous studies,  $\text{Cu}^0$  and  $\text{Cu}^+$  played different roles during the  $\text{CO}_2\text{RR}$ .  $\text{Cu}^0$  contributed to activating

$\text{CO}_2$  molecules.<sup>45</sup> At the initial stage of the reaction,  $\text{CO}_2$  tended to be above the  $\text{Cu}^0$  zone. After  $\text{CO}_2$  activation,  $\text{Cu}^{\delta+}$  ( $0 < \delta \leq 1$ ) was proposed to stabilize  $\text{CO}_2$  molecules, which can promote the dimerization process between  $^*\text{CO}$  intermediates and enhance the subsequent C–C coupling.<sup>46,47</sup> In addition, we have investigated the effects of Mg on the valence state of Cu compounds, as provided in Fig. 3b and Table S2.† It can be seen that Mg plays a similar role to B, since with the increasing Mg content, the characteristic XPS band of  $\text{Cu}^{2+}$  shifts to a higher electron binding energy, while the  $\text{Cu}^0/\text{Cu}^+$  peak shifts in the opposite direction. These results suggest that the introduced B and Mg elements interact with the surrounding atoms, altering the electron density at the Cu sites. Fig. 3c shows that regardless of the presence of  $\text{NaBH}_4$ , the  $\text{Mg}(\text{OH})_2$  species persists on the catalysts, as indicated by its characteristic peak at  $\sim 1303.60$  eV.<sup>48</sup> Taking the XPS and the above XRD/TEM results into comprehensive consideration, it is suggested that the  $\text{NaBH}_4$  reactant plays a significant role in tuning the crystalline state of the  $\text{Mg}(\text{OH})_2$  species. In the absence of  $\text{NaBH}_4$ ,  $\text{Mg}(\text{OH})_2$  exists in an amorphous phase, while with  $\text{NaBH}_4$  addition,  $\text{Mg}(\text{OH})_2$  exists as crystals. We propose that the existing form of  $\text{Mg}(\text{OH})_2$  could be a critical influencing factor on the  $\text{CO}_2\text{RR}$  performance of the catalyst. Nonetheless, the high-resolution B 1s spectra of  $\text{Cu}_5(\text{B}_{0.02\text{ M}})\text{Mg}_1$  and  $\text{Cu}_5(\text{B}_{0.1\text{ M}})\text{Mg}_1$  show two peaks at 191.92 and 191.81 eV, belonging to B–O (Fig. 3d).<sup>49,50</sup> Additionally, the contents



**Fig. 3** XPS spectra of Cu 2p in (a)  $\text{Cu}_5\text{Mg}_1$ ,  $\text{Cu}_5(\text{B}_{0.02\text{ M}})\text{Mg}_1$ ,  $\text{Cu}_5(\text{B}_{0.1\text{ M}})\text{Mg}_1$  (varying the  $\text{NaBH}_4$  feeding amount while keeping the Cu/Mg ratio at 5 : 1) and (b)  $\text{Cu}(\text{B}_{0.02\text{ M}})$ ,  $\text{Cu}_{10}(\text{B}_{0.02\text{ M}})\text{Mg}_1$ ,  $\text{Cu}_5(\text{B}_{0.02\text{ M}})\text{Mg}_1$  and  $\text{Cu}_1(\text{B}_{0.02\text{ M}})\text{Mg}_1$  (varying the ratio of Cu/Mg while keeping the  $\text{NaBH}_4$  feeding amount the same at 0.02 M). (c) XPS spectra of Mg 1s in  $\text{Cu}_5\text{Mg}_1$ ,  $\text{Cu}_5(\text{B}_{0.02\text{ M}})\text{Mg}_1$ , and  $\text{Cu}_5(\text{B}_{0.1\text{ M}})\text{Mg}_1$ . (d) The corresponding B 1s XPS spectra of  $\text{Cu}_5(\text{B}_{0.02\text{ M}})\text{Mg}_1$  and  $\text{Cu}_5(\text{B}_{0.1\text{ M}})\text{Mg}_1$  catalysts.

of Cu, Mg and B elements on the  $\text{Cu}_5(\text{B}_{0.02 \text{ M}})\text{Mg}_1$  catalyst surface were determined *via* XPS analysis, as provided in Table S3.†

## 2.2 Electrochemical $\text{CO}_2\text{RR}$ performance in a flow cell

The  $\text{CO}_2\text{RR}$  performances of  $\text{Cu}_5(\text{B}_{0.02 \text{ M}})\text{Mg}_1$ ,  $\text{Cu}_5(\text{B}_{0.1 \text{ M}})\text{Mg}_1$ ,  $\text{Cu}_5\text{Mg}_1$ ,  $\text{Cu}_{10}(\text{B}_{0.02 \text{ M}})\text{Mg}_1$ ,  $\text{Cu}_1(\text{B}_{0.02 \text{ M}})\text{Mg}_1$  and  $\text{Cu}(\text{B}_{0.02 \text{ M}})$  catalysts were evaluated in 1.0 M KOH electrolyte saturated with  $\text{CO}_2$  at potentials ranging from  $-0.77$  to  $-1.97$  V. Typical gaseous products ( $\text{C}_2\text{H}_4$ ,  $\text{CH}_4$ ,  $\text{CO}$ , and  $\text{H}_2$ ) and liquid products ( $\text{CH}_3\text{CH}_2\text{OH}$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{CH}_3\text{OH}$ , and  $\text{HCOOH}$ ) were analyzed (Fig. S11 and S12†). Among these different materials,  $\text{Cu}_5(\text{B}_{0.02 \text{ M}})\text{Mg}_1$  ( $\text{Cu} : \text{Mg} = 5 : 1$ ,  $\text{NaBH}_4 = 0.02 \text{ M}$ ) shows excellent selectivity towards  $\text{C}_{2+}$  products (Fig. 4 and S13†).

Linear sweep voltammetry (LSV) was first employed to determine the current densities of these Cu catalysts modified by Mg and/or B under  $\text{CO}_2\text{RR}$  conditions (Fig. 4a). It is found that the  $\text{Cu}_5(\text{B}_{0.02 \text{ M}})\text{Mg}_1$  catalyst exhibits a significantly higher current density as compared to the  $\text{Cu}_5\text{Mg}_1$  and  $\text{Cu}(\text{B}_{0.02 \text{ M}})$  catalysts, suggesting a potentially better  $\text{CO}_2\text{RR}$  activity. The electrocatalytic products of the three catalysts were then collected during chronoamperometry measurements, and their Faraday efficiencies (FEs) are presented in Fig. 4b–d. Among all the catalysts,  $\text{Cu}_5(\text{B}_{0.02 \text{ M}})\text{Mg}_1$  shows the highest  $\text{C}_{2+}$

product selectivity (Fig. 4b). Notably, the  $\text{FE}_{\text{C}_{2+}}$  for the  $\text{Cu}_5(\text{B}_{0.02 \text{ M}})\text{Mg}_1$  catalyst remains  $>60\%$  across a wide potential range of 600 mV (from  $-1.17$  to  $-1.77$  V), significantly outperforming  $\text{Cu}_5\text{Mg}_1$  and  $\text{Cu}(\text{B}_{0.02 \text{ M}})$  (Fig. 4b–d). It should be noted that the  $\text{Cu}_5(\text{B}_{0.02 \text{ M}})\text{Mg}_1$  catalyst also shows a low FE for  $\text{H}_2$  ( $\text{FE}_{\text{H}_2}$ ) of  $<15\%$  within the potential range of  $-0.77$  to  $-1.57$  V, indicating that the hydrogen evolution reaction is effectively inhibited on the catalyst. In particular, a maximal  $\text{FE}_{\text{C}_{2+}}$  of 79.59% at  $-1.57$  V is recorded for  $\text{Cu}_5(\text{B}_{0.02 \text{ M}})\text{Mg}_1$  ( $\text{FE}_{\text{C}_2\text{H}_4} = 50.31\%$ ,  $\text{FE}_{\text{C}_2\text{H}_5\text{OH}} = 28.58\%$ , with a small amount of  $\text{CH}_3\text{COOH}$ ), significantly higher than those of  $\text{Cu}_5\text{Mg}_1$  ( $\text{FE}_{\text{C}_{2+}} = 49.53\%$ ) and  $\text{Cu}(\text{B}_{0.02 \text{ M}})$  catalysts ( $\text{FE}_{\text{C}_{2+}} = 31.21\%$ ) (Fig. 5a and Table S4†). Furthermore,  $\text{Cu}_5(\text{B}_{0.02 \text{ M}})\text{Mg}_1$  shows prominently enhanced partial current densities for  $\text{C}_{2+}$  products ( $j_{\text{C}_{2+}}$ ). As depicted in Fig. 5b,  $j_{\text{C}_{2+}}$  of  $\text{Cu}_5(\text{B}_{0.02 \text{ M}})\text{Mg}_1$  ( $-317.03 \text{ mA cm}^{-2}$ ) is 2.7 and 3.5 times higher than those of  $\text{Cu}_5\text{Mg}_1$  ( $-116.74 \text{ mA cm}^{-2}$ ) and  $\text{Cu}(\text{B}_{0.02 \text{ M}})$  ( $-91.09 \text{ mA cm}^{-2}$ ) at the same working potential of  $-1.57$  V, suggesting the synergistic promotion of  $\text{C}_{2+}$  formation on Cu surfaces by Mg and B. In addition,  $j_{\text{C}_{2+}}$  of  $\text{Cu}_5(\text{B}_{0.02 \text{ M}})\text{Mg}_1$ ,  $\text{Cu}_5\text{Mg}_1$  and  $\text{Cu}(\text{B}_{0.02 \text{ M}})$  at more different voltages are shown in Table S5.† Additionally, we have investigated the influence of different ratios of B and Mg during preparation on the electrocatalytic  $\text{CO}_2\text{RR}$  activities of the catalysts (Fig. S13†). The results reveal that appropriate amounts of



Fig. 4 (a) LSVs of  $\text{Cu}(\text{B}_{0.02 \text{ M}})$ ,  $\text{Cu}_5\text{Mg}_1$  and  $\text{Cu}_5(\text{B}_{0.02 \text{ M}})\text{Mg}_1$ . The Faraday efficiencies (FEs) of all products for different catalysts: (b)  $\text{Cu}_5(\text{B}_{0.02 \text{ M}})\text{Mg}_1$ , (c)  $\text{Cu}_5\text{Mg}_1$ , and (d)  $\text{Cu}(\text{B}_{0.02 \text{ M}})$ .

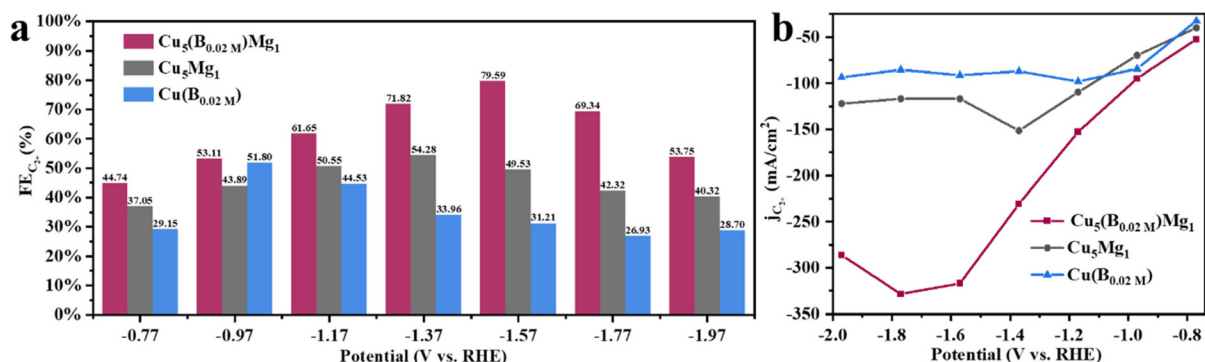


Fig. 5 Electrochemical CO<sub>2</sub>RR performance of the Cu<sub>5</sub>(B<sub>0.02</sub> M)Mg<sub>1</sub> catalyst: (a) FEs of C<sub>2+</sub> (C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>5</sub>OH and CH<sub>3</sub>COOH) at different potentials and (b) partial current densities of C<sub>2+</sub>.

NaBH<sub>4</sub> and Mg reactants during synthesis are conducive to enhanced C<sub>2+</sub> selectivity, while excessive usage will reduce C<sub>2+</sub> products. This could be because the selective promoting and blocking effects of these elements in Cu<sub>5</sub>(B<sub>0.02</sub> M)Mg<sub>1</sub> reach a relatively balanced state for efficient CO<sub>2</sub>RR catalysis (Table S4†).<sup>33</sup> Furthermore, we have compared the CO<sub>2</sub>RR activities of Cu<sub>5</sub>(B<sub>0.02</sub> M)Mg<sub>1</sub> with other different catalysts in previous literature, which shows that the synergy of Mg and B contributes to a competitive selectivity towards C<sub>2+</sub> products (Table S6†).

The long-term catalytic performance of Cu<sub>5</sub>(B<sub>0.02</sub> M)Mg<sub>1</sub> for the CO<sub>2</sub>RR was measured through chronoamperometry at -1.57 V (Fig. S14†). Within a 10 h period, the current density shows negligible attenuation, but the yield of C<sub>2</sub>H<sub>4</sub> gradually decreases over time. After the long-term CO<sub>2</sub>RR measurement, Cu<sub>5</sub>(B<sub>0.02</sub> M)Mg<sub>1</sub> was subjected to XRD characterization. The results indicate that the bulk of the catalyst post CO<sub>2</sub>RR is primarily composed of Cu (PDF#04-0836), Cu<sub>2</sub>O (PDF#05-0667) and Mg(OH)<sub>2</sub> (PDF#44-1482), with CuO completely reduced. Notably, the XRD peaks of Mg(OH)<sub>2</sub> diminish post CO<sub>2</sub>RR, which we believe leads to the decline in the stability of Cu<sub>5</sub>(B<sub>0.02</sub> M)Mg<sub>1</sub> (Fig. S15†). Besides, previous literature studies have suggested that the accumulation of impurities like NO<sub>x</sub>, SO<sub>x</sub>, and carbon on the catalyst surface can also affect the active sites for the CO<sub>2</sub>RR, thereby resulting in a gradual decrease in performance.<sup>51–53</sup> In addition to XRD, XPS characterization was employed to analyze the elemental distribution on the Cu<sub>5</sub>(B<sub>0.02</sub> M)Mg<sub>1</sub> catalyst surface (Fig. S16†). As depicted in Fig. S16a,† copper species, in the form of Cu<sup>0</sup> and Cu<sup>+</sup>, predominantly exist on the catalyst surface. The crystalline Mg(OH)<sub>2</sub> species nearly vanishes after the long-term CO<sub>2</sub>RR, therefore contributing to the decline in the performance of the Cu<sub>5</sub>(B<sub>0.02</sub> M)Mg<sub>1</sub> catalyst (Fig. S16b†). Additionally, XPS results show that the B element still exists on the catalyst (Fig. S16c†).

To study the enhanced CO<sub>2</sub>RR performance of the Cu<sub>5</sub>(B<sub>0.02</sub> M)Mg<sub>1</sub> catalyst, the electrochemically active surface areas of all the electrocatalysts were estimated by calculating their double layer capacitances (C<sub>dl</sub>) (Fig. S17 and S18†). Obviously, compared with Cu<sub>5</sub>Mg<sub>1</sub> (2.83 mF cm<sup>-2</sup>), Cu<sub>5</sub>(B<sub>0.1</sub> M)

Mg<sub>1</sub> (1.61 mF cm<sup>-2</sup>), Cu(B<sub>0.02</sub> M) (0.99 mF cm<sup>-2</sup>), Cu<sub>10</sub>(B<sub>0.02</sub> M)Mg<sub>1</sub> (2.20 mF cm<sup>-2</sup>) and Cu<sub>1</sub>(B<sub>0.02</sub> M)Mg<sub>1</sub> (1.19 mF cm<sup>-2</sup>), Cu<sub>5</sub>(B<sub>0.02</sub> M)Mg<sub>1</sub> (3.28 mF cm<sup>-2</sup>) has the largest C<sub>dl</sub> value, revealing that the Cu<sub>5</sub>(B<sub>0.02</sub> M)Mg<sub>1</sub> catalyst can provide more active sites for the CO<sub>2</sub>RR. Meanwhile, it is worth noting that the active surface area of Cu<sub>5</sub>Mg<sub>1</sub> is lower than that of Cu<sub>5</sub>(B<sub>0.02</sub> M)Mg<sub>1</sub>, which may be due to the formation of amorphous Mg(OH)<sub>2</sub> on the catalyst surface, causing part of the active sites to be covered due to the “stacking” effect, thus reducing the overall catalytic activity of Cu<sub>5</sub>Mg<sub>1</sub>.<sup>54</sup> Electrochemical impedance spectroscopy measurements have also been performed to investigate the charge transfer properties of the catalysts (Fig. S19†). It is obvious that an appropriate co-modification of Mg and B could accelerate the charge transfer process during the CO<sub>2</sub>RR.

*In situ* Raman spectroscopy was further conducted to examine the effects of B and/or Mg on the valence of Cu (Cu<sup>0</sup>, Cu<sup>+</sup> or Cu<sup>2+</sup>) as well as to probe probable intermediates during the CO<sub>2</sub>RR (Fig. 6). Fig. 6a presents the *in situ* Raman spectra of the Cu<sub>5</sub>(B<sub>0.02</sub> M)Mg<sub>1</sub> catalyst in 1.0 M KOH electrolyte (saturated with CO<sub>2</sub>) during the CO<sub>2</sub>RR. At the open circuit voltage, three characteristic peaks are observed at around 147, 522 and 626 cm<sup>-1</sup>, attributed to Cu<sub>2</sub>O.<sup>55–57</sup> After applying a cathodic potential of -0.37 V, a new Raman band appears at 703 cm<sup>-1</sup> on the Cu<sub>5</sub>(B<sub>0.02</sub> M)Mg<sub>1</sub> catalyst, corresponding to surface δCO<sub>2</sub><sup>-</sup>, which represents the umbrella motion of oxygen atoms of the \*CO<sub>2</sub><sup>-</sup> intermediate. Previous studies recognized \*CO<sub>2</sub><sup>-</sup> as the initial intermediate just after CO<sub>2</sub> activation.<sup>58</sup> At the same time, Raman peaks at 290 and 374 cm<sup>-1</sup> are recorded, assigned to the frustrated rotation and tensile vibrations of Cu-CO, respectively.<sup>59–61</sup> Besides, the band at 1071 cm<sup>-1</sup> corresponds to the symmetric C-O stretching band of CO<sub>3</sub><sup>2-</sup> from the electrolyte.<sup>62,63</sup> It is worth noting that over the wide potential range of -0.37 to -1.37 V, Cu<sub>2</sub>O peaks at 147, 522 and 626 cm<sup>-1</sup> consistently appear on the Cu<sub>5</sub>(B<sub>0.02</sub> M)Mg<sub>1</sub> catalyst, indicating that the CuO species on the catalyst surface has been completely reduced, while Cu<sup>+</sup> persists, probably being the reactive sites during the electrochemical CO<sub>2</sub>RR. We propose that the robust stability of Cu<sub>2</sub>O species over a wide potential window is attributed to the synergy of B and crystal-



Fig. 6 The *in situ* Raman spectra of (a)  $\text{Cu}_5(\text{B}_{0.02\text{M}})\text{Mg}_1$ , (b)  $\text{Cu}_5\text{Mg}_1$  and (c)  $\text{Cu}(\text{B}_{0.02\text{M}})$  catalysts at various potentials in 1.0 M KOH electrolyte during  $\text{CO}_2\text{RR}$  catalysis.

line  $\text{Mg}(\text{OH})_2$ . According to previous literature, the  $\text{Cu}^+$  on the catalyst surface is crucial for the formation of multi-carbon products.<sup>64–67</sup> The Raman spectra over  $-1.37$  V cannot be collected because of the accumulation of gaseous products on the catalyst surface that block signals. Nevertheless, Raman signals for  $\text{Cu}_5\text{Mg}_1$  and  $\text{Cu}(\text{B}_{0.02\text{M}})$  are also recorded under the same conditions as  $\text{Cu}_5(\text{B}_{0.02\text{M}})\text{Mg}_1$  to explore the influences of Mg and B on the Cu catalysts, as shown in Fig. 6b and c. In contrast to the  $\text{Cu}_5(\text{B}_{0.02\text{M}})\text{Mg}_1$  catalyst,  $\text{Cu}_2\text{O}$  peaks vanish at only  $-0.87$  V and  $-0.97$  V for  $\text{Cu}_5\text{Mg}_1$  and  $\text{Cu}(\text{B}_{0.02\text{M}})$  catalysts, respectively. In addition, unlike the  $\text{Cu}_5(\text{B}_{0.02\text{M}})\text{Mg}_1$  catalyst which displays characteristic bands of  $^*\text{CO}$  and  $^*\text{CO}_2^-$  at  $-0.37$  V, neither  $\text{Cu}_5\text{Mg}_1$  nor the  $\text{Cu}(\text{B}_{0.02\text{M}})$  catalyst shows these bands until  $-0.47$  V. Hence, it is evident that compared to the  $\text{Cu}_5\text{Mg}_1$  and  $\text{Cu}(\text{B}_{0.02\text{M}})$  catalysts, the collaborative effect of Mg and B, which induces the formation of crystalline  $\text{Mg}(\text{OH})_2$  species in the catalyst structure, facilitates the early formation of  $^*\text{CO}_2^-$  and  $^*\text{CO}$  intermediates during the  $\text{CO}_2\text{RR}$ .

A previous study by Yang *et al.* utilized cerium as a self-sacrificing agent to stabilize  $\text{Cu}^+$  in their catalyst, taking advantage of the easy redox properties of  $\text{Ce}^{3+}/\text{Ce}^{4+}$ . Their *in situ* Raman and Fourier transform infrared spectroscopy results demonstrated that the stabilized  $\text{Cu}^+$  components promoted C–C coupling under the  $\text{CO}_2\text{RR}$ . DFT calculations further revealed that strong  $^*\text{CO}$  adsorption and low C–C coupling energy were conducive to the formation of  $\text{C}_2\text{H}_5\text{OH}$ .<sup>61</sup> Wang *et al.* prepared an ultra-thin 2D  $\text{Cu}_2\text{O}$  nanosheet ( $\text{Cu}_2\text{O}\text{-NS}$ ) catalyst with abundant oxygen vacancies. *In situ* Raman spectroscopy and DFT calculations supported that  $\text{Cu}_2\text{O}\text{-NS}$  prevented the reduction of surface Cu oxides, thereby stabilizing  $\text{Cu}^+$  and enhancing the conversion of  $\text{CO}_2$  to  $\text{C}_{2+}$ .<sup>68</sup> Similarly, in our work,  $\text{Cu}^+$  stabilization is achieved through the introduction of appropriate Mg and B into Cu materials. We found that the addition of the  $\text{NaBH}_4$  reactant can tune the amorphous or crystalline phases of  $\text{Mg}(\text{OH})_2$ . Crystallized  $\text{Mg}(\text{OH})_2$  is crucial for prolonging the lifetime of  $\text{Cu}^+$  during the  $\text{CO}_2\text{RR}$  and facilitating the activation of  $\text{CO}_2$  on the Cu surface to

generate key  $^*\text{CO}$  intermediates for C–C coupling. Consequently, this enhances the selectivity towards  $\text{C}_{2+}$  products of our catalyst.

### 3 Conclusion

Overall, a simple two-step method involving calcination and subsequent wet chemical reduction is developed to construct a Cu-based electrocatalyst modified by crystalline  $\text{Mg}(\text{OH})_2$  and B. XRD, TEM, and XPS analyses indicate that the addition of the  $\text{NaBH}_4$  reactant can induce the formation of crystalline  $\text{Mg}(\text{OH})_2$ , which is proposed to enhance the conversion of  $\text{CO}_2$  to  $\text{C}_{2+}$  during the  $\text{CO}_2\text{RR}$  compared to amorphous  $\text{Mg}(\text{OH})_2$ . In support of this, *in situ* Raman spectroscopy reveals that the synergy of crystalline  $\text{Mg}(\text{OH})_2$  and B can stabilize  $\text{Cu}^+$  at rather cathodic potentials during the  $\text{CO}_2\text{RR}$  process, effectively producing and preserving the  $^*\text{CO}$  intermediates, therefore greatly enhancing the  $^*\text{CO}\text{-CO}$  coupling. As a result, the  $\text{FE}_{\text{C}_{2+}}$  surpasses 60% on the  $\text{Cu}_5(\text{B}_{0.02\text{M}})\text{Mg}_1$  electrocatalyst over a wide potential window of 600 mV ( $-1.17$  to  $-1.77$  V). In particular, at  $-1.57$  V, the catalyst exhibits a  $\text{FE}_{\text{C}_{2+}}$  as high as 79.59%, demonstrating enormous potential for its scalable applications. This work not only provides a low-cost, simple and effective synthesis method for efficient electrocatalysts but also offers an in-depth understanding of the active sites and reaction intermediates during  $\text{CO}_2$ -to- $\text{C}_{2+}$  conversion. We believe that this will help inspire the rational design of future  $\text{CO}_2\text{RR}$  electrocatalysts.

### Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## References

- H. H. Wang, N. Wen, Y. Q. Wang, X. L. Jiao, Y. G. Xia and D. R. Chen, Boosting Electrochemical Reduction of CO<sub>2</sub> to Formate over Oxygen Vacancy Stabilized Copper-Tin Dual Single Atoms Catalysts, *Adv. Funct. Mater.*, 2023, **33**, 2303473.
- J. Y. Liu, P. S. Li, J. H. Bi, S. Q. Jia, Y. Wang, X. C. Kang, X. F. Sun, Q. G. Zhu and B. X. Han, Switching between C<sub>2+</sub> Products and CH<sub>4</sub> in CO<sub>2</sub> Electrolysis by Tuning the Composition and Structure of Rare-Earth/Copper Catalysts, *J. Am. Chem. Soc.*, 2023, **145**, 23037–23047.
- J. Yin, J. Jin, Z. Y. Yin, L. Zhu, X. Du, Y. Peng, P. Xi, C. H. Yan and S. H. Sun, The built-in electric field across FeN/Fe<sub>3</sub>N interface for efficient electrochemical reduction of CO<sub>2</sub> to CO, *Nat. Commun.*, 2023, **14**, 1724.
- P. S. Li, J. H. Bi, J. Y. Liu, Y. Wang, X. C. Kang, X. F. Sun, J. L. Zhang, Z. M. Liu, Q. G. Zhu and B. X. Han, p-d Orbital Hybridization Induced by p-Block Metal-Doped Cu Promotes the Formation of C<sub>2+</sub> Products in Ampere-Level CO<sub>2</sub> Electroreduction, *J. Am. Chem. Soc.*, 2023, **145**, 4675–4682.
- Z. Y. Zhang, H. Tian, L. Bian, S. Z. Liu, Y. Liu and Z. L. Wang, Cu-Zn-based alloy/oxide interfaces for enhanced electroreduction of CO<sub>2</sub> to C<sub>2+</sub> products, *J. Energy Chem.*, 2023, **83**, 90–97.
- R. Shi, J. Guo, X. Zhang, G. I. N. Waterhouse, Z. Han, Y. Zhao, L. Shang, C. Zhou, L. Jiang and T. Zhang, Efficient wettability-controlled electroreduction of CO<sub>2</sub> to CO at Au/C interfaces, *Nat. Commun.*, 2020, **11**, 3028.
- X. T. Wang, Z. Z. Wang, Y. Li, J. T. Wang and G. K. Zhang, Efficient photocatalytic CO<sub>2</sub> conversion over 2D/2D Ni-doped CsPbBr<sub>3</sub>/Bi<sub>3</sub>O<sub>4</sub>Br Z-scheme heterojunction: Critical role of Ni doping, boosted charge separation and mechanism study, *Appl. Catal., B*, 2022, **319**, 121895.
- J. Wu, Y. Huang, W. Ye and Y. Li, CO<sub>2</sub> Reduction: From the Electrochemical to Photochemical Approach, *Adv. Sci.*, 2017, **4**, 1700194.
- Z. Li, R. Wu, L. Zhao, P. Li, X. Wei, J. Wang, J. S. Chen and T. Zhang, Metal-support interactions in designing noble metal-based catalysts for electrochemical CO<sub>2</sub> reduction: Recent advances and future perspectives, *Nano Res.*, 2021, **14**, 3795–3809.
- Y. Yang, S. Louisia, S. M. Yu, J. B. Jin, I. Roh, C. B. Chen, M. V. F. Guzman, J. Feijóo, P. C. Chen, H. S. Wang, C. J. Pollock, X. Huang, Y. T. Shao, C. Wang, D. A. Muller, H. D. Abruña and P. D. Yang, Operando studies reveal active Cu nanograins for CO<sub>2</sub> electroreduction, *Nature*, 2023, **614**, 262–269.
- S. Y. Lee, J. M. Kim, G. Bak, E. C. Lee, D. Kim, S. Yoo, J. Kim, H. Yun and Y. J. Hwang, Probing Cation Effects on \*CO Intermediates from Electroreduction of CO<sub>2</sub> through Operando Raman Spectroscopy, *J. Am. Chem. Soc.*, 2023, **145**, 23068–23075.
- T. Ahmad, S. Liu, M. Sajid, K. Li, M. Ali, L. Liu and W. Chen, Electrochemical CO<sub>2</sub> reduction to C<sub>2+</sub> products using Cu-based electrocatalysts: A review, *Nano Res. Energy*, 2022, **1**, e9120021.
- C. Liu, M. M. Wang, J. Y. Ye, L. B. Liu, L. G. Li, Y. H. Li and X. Q. Huang, Highly Selective CO<sub>2</sub> Electroreduction to C<sub>2+</sub> Products over Cu<sub>2</sub>O-Decorated 2D Metal–Organic Frameworks with Rich Heterogeneous Interfaces, *Nano Lett.*, 2023, **23**, 1474–1480.
- P. De Luna, R. Quintero-Bermudez, C. T. Dinh, M. B. Ross, O. S. Bushuyev, P. Todorović, T. Regier, S. O. Kelley, P. D. Yang and E. H. Sargent, Catalyst electro-redeposition controls morphology and oxidation state for selective carbon dioxide reduction, *Nat. Catal.*, 2018, **1**, 103–110.
- L. C. Ding, N. N. Zhu, Y. Hu, Z. Chen, P. Song, T. Sheng, Z. C. Wu and Y. J. Xiong, Over 70% Faradaic Efficiency for CO<sub>2</sub> Electroreduction to Ethanol Enabled by Potassium Dopant-Tuned Interaction between Copper Sites and Intermediates, *Angew. Chem., Int. Ed.*, 2022, **61**, e202209268.
- C. Peng, G. Luo, J. B. Zhang, M. H. Chen, Z. Q. Wang, T. K. Sham, L. J. Zhang, Y. F. Li and G. F. Zheng, Double sulfur vacancies by lithium tuning enhance CO<sub>2</sub> electroreduction to n-propanol, *Nat. Catal.*, 2021, **12**, 1580.
- Y. R. Lin, D. U. Lee, S. Q. Tan, D. M. Koshy, T. Y. Lin, L. Wang, D. Corral, J. E. Avilés Acosta, J. A. Z. Zeledon, V. A. Beck, S. E. Baker, E. B. Duoss, C. Hahn and T. F. Jaramillo, Vapor-Fed Electrolyzers for Carbon Dioxide Reduction Using Tandem Electrocatalysts: Cuprous Oxide Coupled with Nickel-Coordinated Nitrogen-Doped Carbon, *Adv. Funct. Mater.*, 2022, **32**, 2113252.
- X. P. Qin, S. Q. Zhu, F. Xiao, L. L. Zhang and M. H. Shao, Active Sites on Heterogeneous Single-Iron-Atom Electrocatalysts in CO<sub>2</sub> Reduction Reaction, *ACS Energy Lett.*, 2019, **4**, 1778–1783.
- Y. J. Shi, Y. J. Wang, J. Y. Yu, Y. K. Chen, C. Q. Fang, D. Jiang, Q. H. Zhang, L. Gu, X. W. Yu, X. Li, H. Liu and W. J. Zhou, Superscalar Phase Boundaries Derived Multiple Active Sites in SnO<sub>2</sub>/Cu<sub>6</sub>Sn<sub>5</sub>/CuO for Tandem Electroreduction of CO<sub>2</sub> to Formic Acid, *Adv. Energy Mater.*, 2023, **13**, 2203506.
- P. T. Wang, M. Qiao, Q. Shao, Y. C. Pi, X. Zhu, Y. F. Li and X. Q. Huang, Phase and structure engineering of copper tin heterostructures for efficient electrochemical carbon dioxide reduction, *Nat. Catal.*, 2018, **9**, 4933.
- D. G. Park, J. W. Choi, H. J. Chun, H. S. Jang, H. B. Lee, W. H. Choi, B. C. Moon, K. H. Kim, M. G. Kim, K. M. Choi, B. C. Han and J. K. Kang, Increasing CO Binding Energy and Defects by Preserving Cu Oxidation State via O<sub>2</sub>-Plasma-Assisted N Doping on CuO Enables High C<sub>2+</sub>

- Selectivity and Long-Term Stability in Electrochemical CO<sub>2</sub> Reduction, *ACS Catal.*, 2023, **13**, 9222–9233.
- 22 G. Park, H. Kim, G. H. Han, J. Ha, J. Y. Seo, M. J. Kang, M. G. Seo, Y. H. Choi, S. Y. Kim and S. H. Ahn, The effect of Cu oxidation states on C<sub>2</sub>H<sub>4</sub> production from electrochemical CO<sub>2</sub> conversion, *J. CO<sub>2</sub> Util.*, 2023, **75**, 102569.
- 23 R. B. Sun, C. Wei, Z. X. Huang, S. W. Niu, X. Han, C. Chen, H. R. Wang, J. Song, J. D. Yi, G. Wu, D. W. Rao, X. S. Zheng, Y. Wu, G. M. Wang and X. Hong, Cu<sub>2+1</sub>O/CuO<sub>x</sub> heterostructures promote the electrosynthesis of C<sub>2+</sub> products from CO<sub>2</sub>, *Nano Res.*, 2022, **16**, 4698–4705.
- 24 H. H. Yang, S. Y. Li and Q. Xu, Efficient strategies for promoting the electrochemical reduction of CO<sub>2</sub> to C<sub>2+</sub> products over Cu-based catalysts, *Chin. J. Catal.*, 2023, **48**, 32–65.
- 25 J. Wang, J. J. Liu, Y. Q. Song, S. B. Geng, Z. H. Peng, J. L. Yu, F. Liu, Y. H. Wang, S. B. Xi, Z. J. Zhang and Z. X. Fan, Simultaneous Defect and Size Control of Metal–Organic Framework Nanostructures for Highly Efficient Carbon Dioxide Electroreduction to Multicarbon Products, *ACS Mater. Lett.*, 2023, **5**, 2121–2130.
- 26 J. W. Su, D. H. Pan, Y. Dong, Y. Y. Zhang, Y. L. Tang, J. Sun, L. J. Zhang, Z. Q. Tian and L. Chen, Ultrafine Fe<sub>2</sub>C Iron Carbide Nanoclusters Trapped in Topological Carbon Defects for Efficient Electroreduction of Carbon Dioxide, *Adv. Energy Mater.*, 2023, **13**, 2204391.
- 27 R. G. Cai, M. Z. Sun, F. Yang, M. Ju, Y. P. Chen, M. D. Gu, B. L. Huang and S. H. Yang, Engineering Cu(I)/Cu(0) interfaces for efficient ethanol production from CO<sub>2</sub> electroreduction, *Chem*, 2023, **10**, 1–23.
- 28 Y. P. Zang, T. F. Liu, P. F. Wei, H. F. Li, Q. Wang, G. X. Wang and X. H. Bao, Selective CO<sub>2</sub> Electroreduction to Ethanol over a Carbon-Coated CuO<sub>x</sub> Catalyst, *Angew. Chem., Int. Ed.*, 2022, **61**, e202209629.
- 29 C. F. Wen, M. Zhou, P. F. Liu, Y. W. Liu, X. F. Wu, F. X. Mao, S. Dai, B. B. Xu, X. L. Wang, Z. Jiang, P. Hu, S. Yang, H. F. Wang and H. G. Yang, Highly Ethylene-Selective Electrocatalytic CO<sub>2</sub> Reduction Enabled by Isolated Cu–S Motifs in Metal–Organic Framework Based Precatalysts, *Angew. Chem., Int. Ed.*, 2021, **61**, e202111700.
- 30 Y. Yao, Y. Zhou, X. Liu, Y. Li, D. Wang, X. Chi, X. Wang, R. Zhao, H. Zhang, Y. Sun, Z.-Y. Yang, Y. Wei and Y.-M. Yan, Restraining lattice oxygen of Cu<sub>2</sub>O by enhanced Cu–O hybridization for selective and stable production of ethylene with CO<sub>2</sub> electroreduction, *J. Mater. Chem. A*, 2022, **10**, 20914–20923.
- 31 S. Sinha and J. J. Jiang, Main group elements in electrochemical hydrogen evolution and carbon dioxide reduction, *Chem. Commun.*, 2023, **59**, 11767–11779.
- 32 C. Peng, J. Ma, G. Luo, S. Yan, J. Zhang, Y. Chen, N. Chen, Z. Wang, W. Wei, T. K. Sham, Y. Zheng, M. Kuang and G. Zheng, (111) Facet-oriented Cu<sub>2</sub>Mg Intermetallic Compound with Cu<sub>3</sub>-Mg Sites for CO<sub>2</sub> Electroreduction to Ethanol with Industrial Current Density, *Angew. Chem., Int. Ed. Engl.*, 2024, e202316907.
- 33 M. C. Xie, Y. Shen, W. C. Ma, D. Y. Wei, B. Zhang, Z. H. Wang, Y. H. Wang, Q. H. Zhang, S. J. Xie, C. Wang and Y. Wang, Fast Screening for Copper–Based Bimetallic Electrocatalysts: Efficient Electrocatalytic Reduction of CO<sub>2</sub> to C<sub>2+</sub> Products on Magnesium-Modified Copper, *Angew. Chem., Int. Ed.*, 2022, **61**, e202213423.
- 34 J. Fan, X. Zhang, M. Han, X. Xiang, C. Guo, Y. Lin, N. Shi, D. Xu, Y. Lai and J. Bao, Amorphous Ni–Fe–Mo Oxides Coupled with Crystalline Metallic Domains for Enhanced Electrocatalytic Oxygen Evolution by Promoted Lattice–Oxygen Participation, *Small*, 2023, **20**, 2303927.
- 35 Y. Z. Li, Z. B. Wang, C. Li, F. Qi, P. W. Yan, Y. P. Wang, M. F. He, Z. L. Chen, Q. Wang, Y. Wang, H. Zheng, A. Ikhlaq, J. Kumirska, E. Maria Siedlecka and O. Ismailova, Reducing agents enhanced prometone degradation by CuBi<sub>2</sub>O<sub>4</sub>/peroxymonosulfate: Development of interfacial electron transport and circulation of Cu<sup>+</sup>/Cu<sup>2+</sup>, *Chem. Eng. J.*, 2023, **470**, 144387.
- 36 Z. P. Ma, T. Wan, D. Zhang, J. A. Yuwono, C. Tsounis, J. Jiang, Y. H. Chou, X. Y. Lu, P. V. Kumar, Y. H. Ng, D. Chu, C. Y. Toe, Z. J. Han and R. Amal, Atomically Dispersed Cu Catalysts on Sulfide-Derived Defective Ag Nanowires for Electrochemical CO<sub>2</sub> Reduction, *ACS Nano*, 2023, **17**, 2387–2398.
- 37 Z. Q. Zhang, J. L. Liang, W. Zhang, M. Zhou, X. L. Zhu, Z. Y. Liu, Y. Li, Z. Q. Guan, C. S. Lee, P. K. Wong, H. M. Li and Z. F. Jiang, Modified-pollen confined hybrid system: A promising union for visible-light-driven photocatalytic antibiotic degradation, *Appl. Catal., B*, 2023, **330**, 122621.
- 38 X. L. Zhou, J. Q. Shan, L. Chen, B. Y. Xia, T. Ling, J. J. Duan, Y. Jiao, Y. Zheng and S. Z. Qiao, Stabilizing Cu<sup>2+</sup> Ions by Solid Solutions to Promote CO<sub>2</sub> Electroreduction to Methane, *J. Am. Chem. Soc.*, 2022, **144**, 2079–2084.
- 39 D. X. Tan, J. L. Zhang, L. Yao, X. N. Tan, X. Y. Cheng, Q. Wan, B. X. Han, L. R. Zheng and J. Zhang, Multi-shelled CuO microboxes for carbon dioxide reduction to ethylene, *Nano Res.*, 2020, **13**, 768–774.
- 40 V. Okatenko, A. Loiudice, M. A. Newton, D. C. Stoian, A. Blokhina, A. N. Chen, K. Rossi and R. Buonsanti, Alloying as a Strategy to Boost the Stability of Copper Nanocatalysts during the Electrochemical CO<sub>2</sub> Reduction Reaction, *J. Am. Chem. Soc.*, 2023, **145**, 5370–5383.
- 41 P. T. Wang, H. Yang, C. Tang, Y. Wu, Y. Zheng, T. Cheng, K. Davey, X. Q. Huang and S. Z. Qiao, Boosting electrocatalytic CO<sub>2</sub>-to-ethanol production via asymmetric C–C coupling, *Nat. Catal.*, 2022, **13**, 3754.
- 42 W. Lai, L. H. Ge, H. Yang, Y. L. Deng, H. M. Li, B. Ouyang, L. Xu and J. Bao, Reprogramming the redox states of nickel via interface engineering and heteroatom doping to boost overall water splitting, *J. Mater. Chem. A*, 2022, **10**, 10525–10539.
- 43 J. H. Jang, S. Q. Zhu, E. P. Delmo, T. H. Li, Q. L. Zhao, Y. N. Wang, L. L. Zhang, H. W. Huang, J. J. Ge and M. H. Shao, Facile design of oxide-derived Cu nanosheet electrocatalyst for CO<sub>2</sub> reduction reaction, *EcoMat*, 2023, **5**, e12334.
- 44 Y. Zhang, Z. B. Si, H. H. Du, Y. L. Deng, Q. K. Zhang, Z. L. Wang, Q. Yu and H. Xu, Selective CO<sub>2</sub> Reduction to

- Ethylene Over a Wide Potential Window by Copper Nanowires with High Density of Defects, *Inorg. Chem.*, 2022, **61**, 20666–20673.
- 45 X.-J. Cui, Y.-Q. Qiu, H.-Q. Wang and C.-G. Liu, Direct coupling of two inert CO<sub>2</sub> molecules to form a C–C bond on the Cu<sup>0</sup> atomic interfaces of the nitrogen-doped graphene-supported Cu<sub>4</sub> cluster, *Inorg. Chem. Front.*, 2024, **11**, 85–97.
- 46 G. M. Tomboc, S. Choi, T. Kwon, Y. J. Hwang and K. Lee, Potential Link between Cu Surface and Selective CO<sub>2</sub> Electroreduction: Perspective on Future Electrocatalyst Designs, *Adv. Mater.*, 2020, **32**, e1908398.
- 47 Z. Li, Z. Liu, S. Li, Y. Pei, D. Li, J. Mao, R. Zhou, C. Qiu, Y. Lu and B. Zhang, Modulating the localized electronic distribution of Cu species during reconstruction for enhanced electrochemical CO<sub>2</sub> reduction to C<sub>2+</sub> products, *J. Mater. Chem. A*, 2024, DOI: [10.1039/d4ta01184h](https://doi.org/10.1039/d4ta01184h).
- 48 S. J. Han, L. L. Mao, T. Wu and H. Z. Wang, Homogeneous polyethersulfone hybrid membranes prepared with in-situ synthesized magnesium hydroxide nanoparticles by phase inversion method, *J. Membr. Sci.*, 2016, **516**, 47–55.
- 49 H. Zhang, D. Y. Zhang, M. Y. Guo, Z. Huang, X. Wang, C. Q. Gao, F. Gao, M. Terrones and Y. Q. Wang, Combustion Activation Induced Solid–State Synthesis for N, B Co–Doped Carbon/Zinc Borate Anode with a Boosting of Sodium Storage Performance, *Adv. Sci.*, 2023, **10**, 2207751.
- 50 H. Q. Peng, X. Ming, K. Pang, Y. R. Chen, J. Zhou, Z. Xu, Y. J. Liu and C. Gao, Highly electrically conductive graphene papers via catalytic graphitization, *Nano Res.*, 2022, **15**, 4902–4908.
- 51 J. Leverett, J. A. Yuwono, P. Kumar, T. Tran-Phu, J. Qu, J. Cairney, X. Wang, A. N. Simonov, R. K. Hocking, B. Johannessen, L. Dai, R. Daiyan and R. Amal, Impurity Tolerance of Unsaturated Ni–N–C Active Sites for Practical Electrochemical CO<sub>2</sub> Reduction, *ACS Energy Lett.*, 2022, **7**, 920–928.
- 52 S. Van Daele, L. Hintjens, S. Hoekx, B. Bohlen, S. Neukermans, N. Daems, J. Hereijgers and T. Breugelmans, How flue gas impurities affect the electrochemical reduction of CO<sub>2</sub> to CO and formate, *Appl. Catal., B*, 2024, **341**, 123345.
- 53 W. Lai, Y. Qiao, Y. Wang and H. Huang, Stability Issues in Electrochemical CO<sub>2</sub> Reduction: Recent Advances in Fundamental Understanding and Design Strategies, *Adv. Mater.*, 2023, **35**, e2306288.
- 54 G. X. Zhang, X. L. Zheng, X. M. Cui, J. Wang, J. H. Liu, J. F. Chen and Q. Xu, Doping of Vanadium into Bismuth Oxide Nanoparticles for Electrocatalytic CO<sub>2</sub> Reduction, *ACS Appl. Nano Mater.*, 2022, **5**, 15465–15472.
- 55 D. Ren, Y. L. Deng, A. D. Handoko, C. S. Chen, S. Malkhandi and B. S. Yeo, Selective Electrochemical Reduction of Carbon Dioxide to Ethylene and Ethanol on Copper(I) Oxide Catalysts, *ACS Catal.*, 2015, **5**, 2814–2821.
- 56 S. J. Mu, H. L. Lu, Q. B. Wu, L. Li, R. I. Zhao, C. Long and C. H. Cui, Hydroxyl radicals dominate reoxidation of oxide-derived Cu in electrochemical CO<sub>2</sub> reduction, *Nat. Commun.*, 2022, **13**, 3694.
- 57 H. T. Du, L. X. Liu, P. Li, Q. H. Min, S. J. Guo and W. L. Zhu, Enriching Reaction Intermediates in Multishell Structured Copper Catalysts for Boosted Propanol Electroreduction from Carbon Monoxide, *ACS Nano*, 2023, **17**, 8663–8670.
- 58 Y. Zhao, X. G. Zhang, N. Bodappa, W. M. Yang, Q. Liang, P. M. Radjenovica, Y. H. Wang, Y. J. Zhang, J. C. Dong, Z. Q. Tian and J. F. Li, Elucidating electrochemical CO<sub>2</sub> reduction reaction processes on Cu(*hkl*) single-crystal surfaces by in situ Raman spectroscopy, *Energy Environ. Sci.*, 2022, **15**, 3968–3977.
- 59 Y. L. Deng, Y. Huang, D. Ren, A. D. Handoko, Z. W. Seh, P. Hirunsit and B. S. Yeo, On the Role of Sulfur for the Selective Electrochemical Reduction of CO<sub>2</sub> to Formate on CuS<sub>x</sub> Catalysts, *ACS Appl. Mater. Interfaces*, 2018, **10**, 28572–28581.
- 60 D. Ren, J. H. Fong and B. S. Yeo, The effects of currents and potentials on the selectivities of copper toward carbon dioxide electroreduction, *Nat. Commun.*, 2018, **9**, 925.
- 61 Z. Yang, D. G. Ji, Z. Li, Z. D. He, Y. Hu, J. Yin, Y. H. Hou, P. X. Xi and C. H. Yan, CeO<sub>2</sub>/Cu Nanoplates Electroreduce CO<sub>2</sub> to Ethanol with Stabilized Cu<sup>+</sup> Species, *Small*, 2023, **19**, 2303099.
- 62 X. P. Yan, M. L. Zhang, Y. Z. Chen, Y. H. Wu, R. Z. Wu, Q. Wan, C. X. Liu, T. T. Zheng, R. J. Feng, J. Zhang, C. J. Chen, C. Xia, Q. G. Zhu, X. F. Sun, Q. L. Qian and B. X. Han, Synergy of Cu/C<sub>3</sub>N<sub>4</sub> Interface and Cu Nanoparticles Dual Catalytic Regions in Electrolysis of CO to Acetic Acid, *Angew. Chem., Int. Ed.*, 2023, **62**, e202301507.
- 63 R. Amirbeigiarab, J. Tian, A. Herzog, C. R. Qiu, A. Bergmann, B. R. Cuenya and O. M. Magnussen, Atomic-scale surface restructuring of copper electrodes under CO<sub>2</sub> electroreduction conditions, *Nat. Catal.*, 2023, **6**, 837–846.
- 64 H. Zhang, Y. Qiao, Y. Wang, Y. Zheng and H. Huang, In situ oxidative etching-enabled synthesis of hollow Cu<sub>2</sub>O nanocrystals for efficient CO<sub>2</sub>RR into C<sub>2+</sub> products, *Sustainable Energy Fuels*, 2022, **6**, 4860–4865.
- 65 M. Fang, M. Wang, Z. Wang, Z. Zhang, H. Zhou, L. Dai, Y. Zhu and L. Jiang, Hydrophobic, Ultrastable Cu<sup>δ+</sup> for Robust CO<sub>2</sub> Electroreduction to C<sub>2</sub> Products at Ampere-Current Levels, *J. Am. Chem. Soc.*, 2023, **145**, 11323–11332.
- 66 Y. Zhou, Y. Yao, R. Zhao, X. Wang, Z. Fu, D. Wang, H. Wang, L. Zhao, W. Ni, Z. Yang and Y. M. Yan, Stabilization of Cu<sup>+</sup> via Strong Electronic Interaction for Selective and Stable CO<sub>2</sub> Electroreduction, *Angew. Chem., Int. Ed.*, 2022, **61**, e202205832.
- 67 H. Cheng, S. Jia, J. Jiao, X. Chen, T. Deng, C. Xue, M. Dong, J. Zeng, C. Chen, H. Wu, M. He and B. Han, Stabilization of Cu<sup>+</sup> sites by amorphous Al<sub>2</sub>O<sub>3</sub> to enhance electrochemical CO<sub>2</sub> reduction to C<sub>2+</sub> products, *Green Chem.*, 2024, **26**, 2599–2604.
- 68 P. Wang, S. Meng, B. Zhang, M. He, P. Li, C. Yang, G. Li and Z. Li, Sub-1 nm Cu<sub>2</sub>O Nanosheets for the Electrochemical CO<sub>2</sub> Reduction and Valence State-Activity Relationship, *J. Am. Chem. Soc.*, 2023, **145**, 26133–26143.