

## RESEARCH ARTICLE

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Cite this: *Inorg. Chem. Front.*, 2024, **11**, 4770

# Steady $\text{Cu}^+$ species *via* magnesium and boron co-modification for enhanced $\text{CO}_2$ electroreduction to $\text{C}_{2+}$ products: an *in situ* Raman spectroscopic study†

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The electrochemical carbon dioxide reduction reaction ( $\text{CO}_2\text{RR}$ ) to produce high-value multi-carbon ( $\text{C}_{2+}$ ) compounds holds significant practical importance in realizing carbon neutrality. Copper-based electrocatalysts are promising for  $\text{CO}_2$ -to- $\text{C}_{2+}$  conversion. However, the labile Cu valence at high current densities impedes  $\text{C}_{2+}$  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  $\text{C}_{2+}$  yield, with a Faraday efficiency ( $\text{FE}_{\text{C}_{2+}}$ ) of 79.59% at  $-1.57$  V vs. RHE (reversible hydrogen electrode). Additionally, the partial current density of  $\text{C}_{2+}$  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  $\text{FE}_{\text{C}_{2+}}$  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  $\text{Cu}^+$  at negative potentials compared to the amorphous phase. Further *in situ* Raman spectroscopy reveals that at increasingly negative potentials, the higher copper species ( $\text{Cu}^{2+}$ ) is inevitably reduced to the lower copper species ( $\text{Cu}^0/\text{Cu}^+$ ). However, the synergy of Mg and B prolongs the presence of  $\text{Cu}^+$  on the catalyst surface across a broad potential range, and  $\text{*CO}$  and  $\text{*CO}_2^-$  could still be recorded at quite negative reduction potentials. This suggests enhanced binding strength of  $\text{*CO}$  intermediates on the catalyst surface, promoting the C–C coupling process.

Received 2nd April 2024,  
Accepted 16th May 2024

DOI: 10.1039/d4qi00842a

rsc.li/frontiers-inorganic

## 1. Introduction

The electrocatalytic carbon dioxide reduction reaction ( $\text{CO}_2\text{RR}$ ) represents a pathway for producing high-value-added chemicals and fuels, offering a means to reduce global carbon dioxide ( $\text{CO}_2$ ) emissions and alleviate the shortage of non-renewable carbon resources.<sup>1–3</sup> The  $\text{CO}_2\text{RR}$  yields primarily hydrocarbons and oxygen-containing compounds. Among them, multi-carbon ( $\text{C}_{2+}$ ) products such as ethylene ( $\text{C}_2\text{H}_4$ ) and ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) have broader industrial applications and higher energy densities compared with  $\text{C}_1$  products like

carbon monoxide (CO) and methane ( $\text{CH}_4$ ), 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  $\text{CO}_2$  (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  $\text{CO}_2\text{RR}$ .<sup>7–9</sup> Addressing these issues requires the exploration and design of electrocatalysts with enhanced efficiency to facilitate  $\text{CO}_2$  conversion while minimizing product distribution variability during the  $\text{CO}_2\text{RR}$  process.

To date, copper-based materials, which have been found crucial for C–C coupling, remain the major electrocatalysts for efficiently converting  $\text{CO}_2$  to long-chain hydrocarbons and multi-carbon oxygenates.<sup>10–12</sup> Previous studies suggest that  $\text{Cu}^+$  species on Cu-based materials could enhance the selectivity of  $\text{C}_{2+}$  products.<sup>13,14</sup> However, under high-current electrolysis, particularly at the negative potentials required for  $\text{C}_{2+}$

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† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4qi00842a>

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-

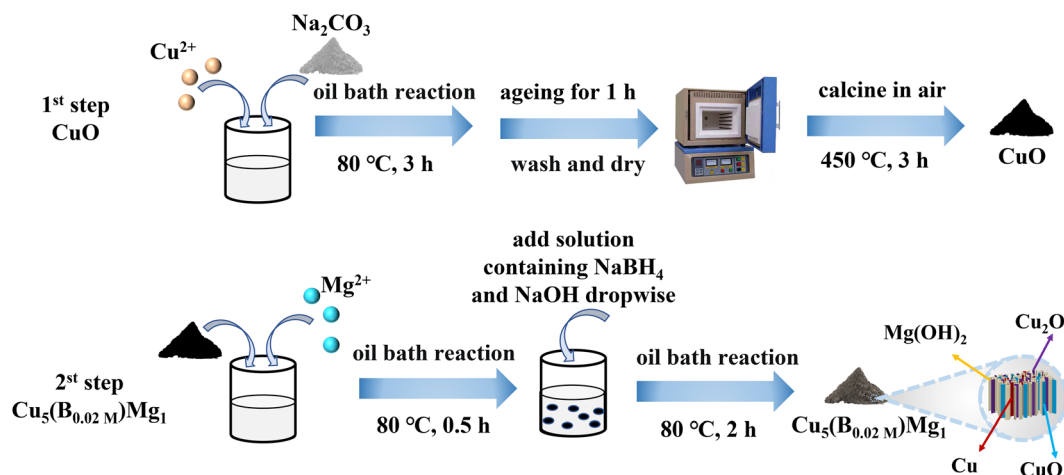


Fig. 1 Graphical scheme for the synthesis of the  $\text{Cu}_5(\text{B}_{0.02 \text{ M}})\text{Mg}_1$  catalyst.

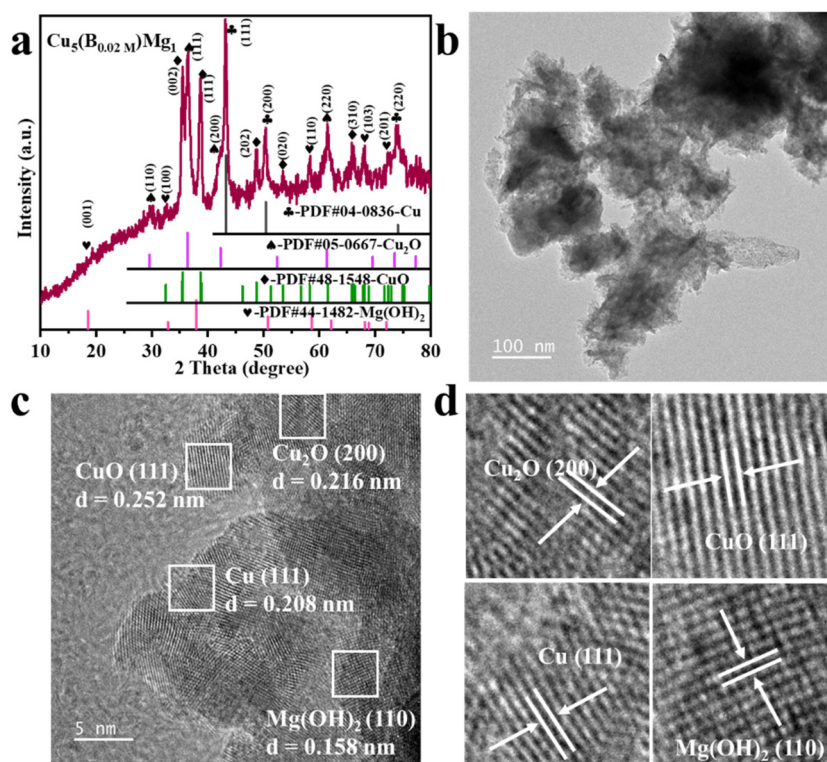


Fig. 2 (a) XRD, (b) TEM and (c) HRTEM characterization of the  $\text{Cu}_5(\text{B}_{0.02 \text{ M}})\text{Mg}_1$  catalyst. (d) is the enlarged view of (c).

lyst surface (Fig. S2c and d†). 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.† 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†). 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†). Conversely, the  $\text{Cu}_5\text{Mg}_1$  catalyst primarily exhibits the CuO (111) crystalline phase, along with some amorphous species (Fig. S9†). 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.<sup>†</sup>

## 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<sup>†</sup>). 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<sup>†</sup>).

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<sup>†</sup>). 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.<sup>†</sup> 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<sup>†</sup>). The results reveal that appropriate amounts of

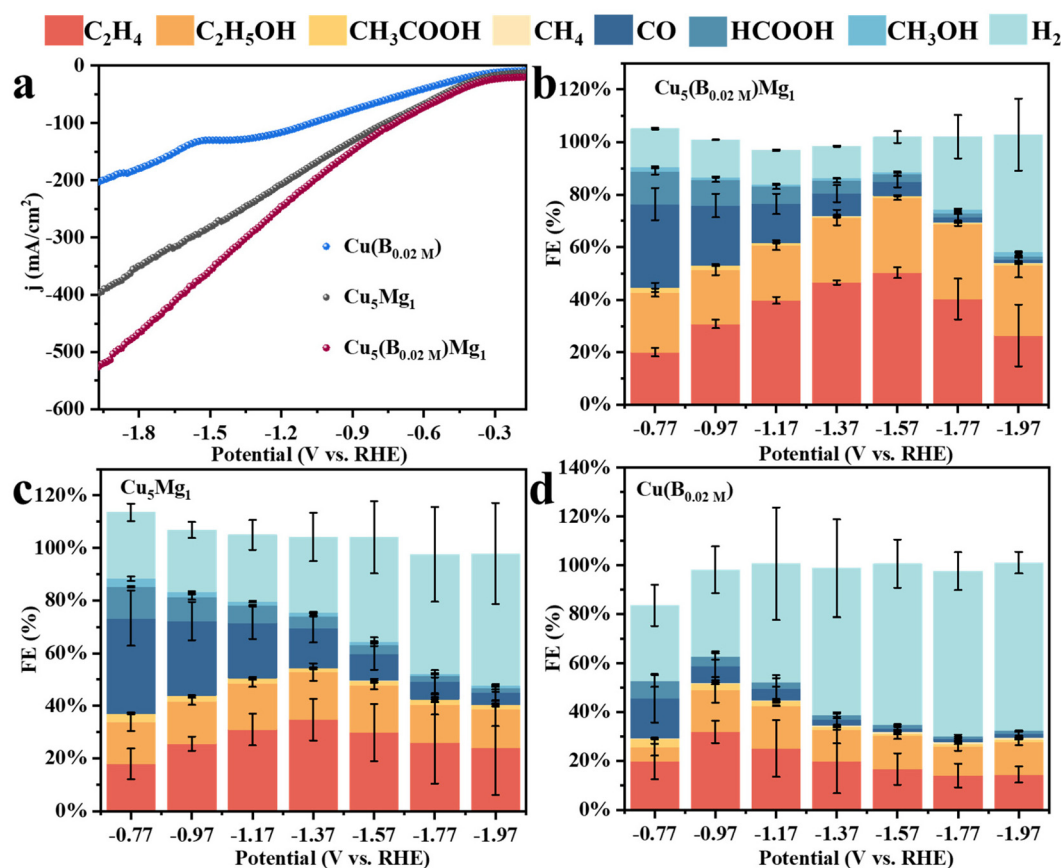


Fig. 4 (a) LSVs of  $\text{Cu}(\text{B}_{0.02}\text{M})$ ,  $\text{Cu}_5\text{Mg}_1$  and  $\text{Cu}_5(\text{B}_{0.02}\text{M})\text{Mg}_1$ . The Faraday efficiencies (FEs) of all products for different catalysts: (b)  $\text{Cu}_5(\text{B}_{0.02}\text{M})\text{Mg}_1$ , (c)  $\text{Cu}_5\text{Mg}_1$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



Fig. 5 Electrochemical  $\text{CO}_2\text{RR}$  performance of the  $\text{Cu}_5(\text{B}_{0.02} \text{ M})\text{Mg}_1$  catalyst: (a) FEs of  $\text{C}_{2+}$  ( $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{CH}_3\text{COOH}$ ) at different potentials and (b) partial current densities of  $\text{C}_{2+}$ .

$\text{NaBH}_4$  and  $\text{Mg}$  reactants during synthesis are conducive to enhanced  $\text{C}_{2+}$  selectivity, while excessive usage will reduce  $\text{C}_{2+}$  products. This could be because the selective promoting and blocking effects of these elements in  $\text{Cu}_5(\text{B}_{0.02} \text{ M})\text{Mg}_1$  reach a relatively balanced state for efficient  $\text{CO}_2\text{RR}$  catalysis (Table S4†).<sup>33</sup> Furthermore, we have compared the  $\text{CO}_2\text{RR}$  activities of  $\text{Cu}_5(\text{B}_{0.02} \text{ M})\text{Mg}_1$  with other different catalysts in previous literature, which shows that the synergy of  $\text{Mg}$  and  $\text{B}$  contributes to a competitive selectivity towards  $\text{C}_{2+}$  products (Table S6†).

The long-term catalytic performance of  $\text{Cu}_5(\text{B}_{0.02} \text{ M})\text{Mg}_1$  for the  $\text{CO}_2\text{RR}$  was measured through chronoamperometry at  $-1.57 \text{ V}$  (Fig. S14†). Within a 10 h period, the current density shows negligible attenuation, but the yield of  $\text{C}_2\text{H}_4$  gradually decreases over time. After the long-term  $\text{CO}_2\text{RR}$  measurement,  $\text{Cu}_5(\text{B}_{0.02} \text{ M})\text{Mg}_1$  was subjected to XRD characterization. The results indicate that the bulk of the catalyst post  $\text{CO}_2\text{RR}$  is primarily composed of  $\text{Cu}$  (PDF#04-0836),  $\text{Cu}_2\text{O}$  (PDF#05-0667) and  $\text{Mg}(\text{OH})_2$  (PDF#44-1482), with  $\text{CuO}$  completely reduced. Notably, the XRD peaks of  $\text{Mg}(\text{OH})_2$  diminish post  $\text{CO}_2\text{RR}$ , which we believe leads to the decline in the stability of  $\text{Cu}_5(\text{B}_{0.02} \text{ M})\text{Mg}_1$  (Fig. S15†). Besides, previous literature studies have suggested that the accumulation of impurities like  $\text{NO}_x$ ,  $\text{SO}_x$ , and carbon on the catalyst surface can also affect the active sites for the  $\text{CO}_2\text{RR}$ , 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  $\text{Cu}_5(\text{B}_{0.02} \text{ M})\text{Mg}_1$  catalyst surface (Fig. S16†). As depicted in Fig. S16a,† copper species, in the form of  $\text{Cu}^0$  and  $\text{Cu}^+$ , predominantly exist on the catalyst surface. The crystalline  $\text{Mg}(\text{OH})_2$  species nearly vanishes after the long-term  $\text{CO}_2\text{RR}$ , therefore contributing to the decline in the performance of the  $\text{Cu}_5(\text{B}_{0.02} \text{ M})\text{Mg}_1$  catalyst (Fig. S16b†). Additionally, XPS results show that the  $\text{B}$  element still exists on the catalyst (Fig. S16c†).

To study the enhanced  $\text{CO}_2\text{RR}$  performance of the  $\text{Cu}_5(\text{B}_{0.02} \text{ M})\text{Mg}_1$  catalyst, the electrochemically active surface areas of all the electrocatalysts were estimated by calculating their double layer capacitances ( $C_{\text{dl}}$ ) (Fig. S17 and S18†). Obviously, compared with  $\text{Cu}_5\text{Mg}_1$  ( $2.83 \text{ mF cm}^{-2}$ ),  $\text{Cu}_5(\text{B}_{0.1} \text{ M})$

$\text{Mg}_1$  ( $1.61 \text{ mF cm}^{-2}$ ),  $\text{Cu}(\text{B}_{0.02} \text{ M})$  ( $0.99 \text{ mF cm}^{-2}$ ),  $\text{Cu}_{10}(\text{B}_{0.02} \text{ M})\text{Mg}_1$  ( $2.20 \text{ mF cm}^{-2}$ ) and  $\text{Cu}_1(\text{B}_{0.02} \text{ M})\text{Mg}_1$  ( $1.19 \text{ mF cm}^{-2}$ ),  $\text{Cu}_5(\text{B}_{0.02} \text{ M})\text{Mg}_1$  ( $3.28 \text{ mF cm}^{-2}$ ) has the largest  $C_{\text{dl}}$  value, revealing that the  $\text{Cu}_5(\text{B}_{0.02} \text{ M})\text{Mg}_1$  catalyst can provide more active sites for the  $\text{CO}_2\text{RR}$ . Meanwhile, it is worth noting that the active surface area of  $\text{Cu}_5\text{Mg}_1$  is lower than that of  $\text{Cu}_5(\text{B}_{0.02} \text{ M})\text{Mg}_1$ , which may be due to the formation of amorphous  $\text{Mg}(\text{OH})_2$  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  $\text{Cu}_5\text{Mg}_1$ .<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  $\text{Mg}$  and  $\text{B}$  could accelerate the charge transfer process during the  $\text{CO}_2\text{RR}$ .

*In situ* Raman spectroscopy was further conducted to examine the effects of  $\text{B}$  and/or  $\text{Mg}$  on the valence of  $\text{Cu}$  ( $\text{Cu}^0$ ,  $\text{Cu}^+$  or  $\text{Cu}^{2+}$ ) as well as to probe probable intermediates during the  $\text{CO}_2\text{RR}$  (Fig. 6). Fig. 6a presents the *in situ* Raman spectra of the  $\text{Cu}_5(\text{B}_{0.02} \text{ M})\text{Mg}_1$  catalyst in  $1.0 \text{ M KOH}$  electrolyte (saturated with  $\text{CO}_2$ ) during the  $\text{CO}_2\text{RR}$ . At the open circuit voltage, three characteristic peaks are observed at around  $147$ ,  $522$  and  $626 \text{ cm}^{-1}$ , attributed to  $\text{Cu}_2\text{O}$ .<sup>55–57</sup> After applying a cathodic potential of  $-0.37 \text{ V}$ , a new Raman band appears at  $703 \text{ cm}^{-1}$  on the  $\text{Cu}_5(\text{B}_{0.02} \text{ M})\text{Mg}_1$  catalyst, corresponding to surface  $\delta\text{CO}_2^-$ , which represents the umbrella motion of oxygen atoms of the  $^*\text{CO}_2^-$  intermediate. Previous studies recognized  $^*\text{CO}_2^-$  as the initial intermediate just after  $\text{CO}_2$  activation.<sup>58</sup> At the same time, Raman peaks at  $290$  and  $374 \text{ cm}^{-1}$  are recorded, assigned to the frustrated rotation and tensile vibrations of  $\text{Cu-CO}$ , respectively.<sup>59–61</sup> Besides, the band at  $1071 \text{ cm}^{-1}$  corresponds to the symmetric  $\text{C-O}$  stretching band of  $\text{CO}_3^{2-}$  from the electrolyte.<sup>62,63</sup> It is worth noting that over the wide potential range of  $-0.37$  to  $-1.37 \text{ V}$ ,  $\text{Cu}_2\text{O}$  peaks at  $147$ ,  $522$  and  $626 \text{ cm}^{-1}$  consistently appear on the  $\text{Cu}_5(\text{B}_{0.02} \text{ M})\text{Mg}_1$  catalyst, indicating that the  $\text{CuO}$  species on the catalyst surface has been completely reduced, while  $\text{Cu}^+$  persists, probably being the reactive sites during the electrochemical  $\text{CO}_2\text{RR}$ . We propose that the robust stability of  $\text{Cu}_2\text{O}$  species over a wide potential window is attributed to the synergy of  $\text{B}$  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.

## Acknowledgements

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (21905118 and 12304020), the Natural Science Foundation of Jiangsu Province (BK20230909), and the Funding for Scientific Research Startup of Jiangsu University (18JDG033).

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