

## RESEARCH ARTICLE

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# 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  $\text{Cu}/\text{Cu}_2\text{O}/\text{CuO}/\text{Mg}(\text{OH})_2$  *via* the co-addition of Mg and B during the preparation (referred to as  $\text{Cu}_5(\text{B}_{0.02}\text{M})\text{Mg}_1$ ). The  $\text{Cu}_5(\text{B}_{0.02}\text{M})\text{Mg}_1$  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  $\text{Cu}_5(\text{B}_{0.02}\text{M})\text{Mg}_1$  catalyst is  $-317.03\text{ mA cm}^{-2}$ , 2.7 and 3.5 times higher than those catalysts lacking B ( $\text{Cu}_5\text{Mg}_1$  catalyst) or Mg ( $\text{Cu}(\text{B}_{0.02}\text{M})$  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  $\text{Cu}_5(\text{B}_{0.02}\text{M})\text{Mg}_1$  catalyst. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and high-resolution transmission electron microscopy (HRTEM) characterization studies indicate the  $\text{NaBH}_4$  reactant could promote the formation of crystalline  $\text{Mg}(\text{OH})_2$  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.

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## 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  $750\text{ kJ mol}^{-1}$ ). 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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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-

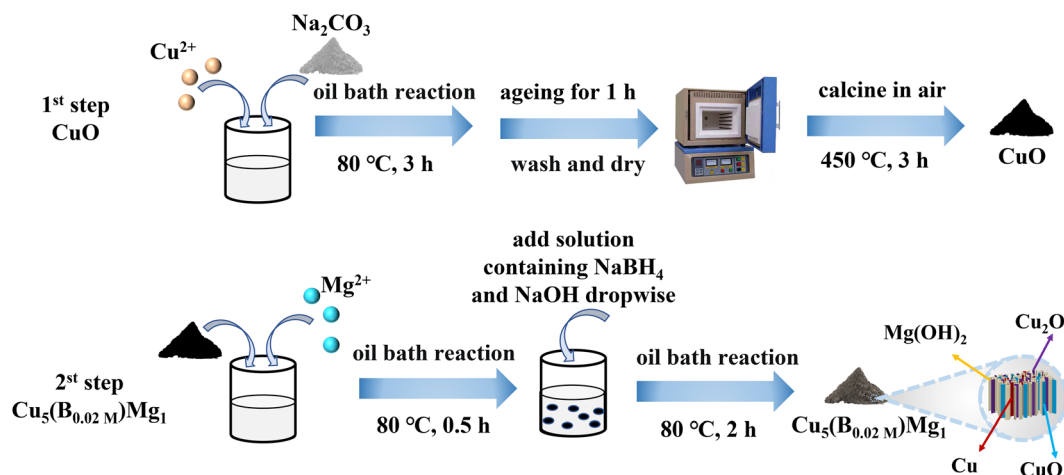


Fig. 1 Graphical scheme for the synthesis of the  $\text{Cu}_5(\text{B}_{0.02 \text{ M}})\text{Mg}_1$  catalyst.

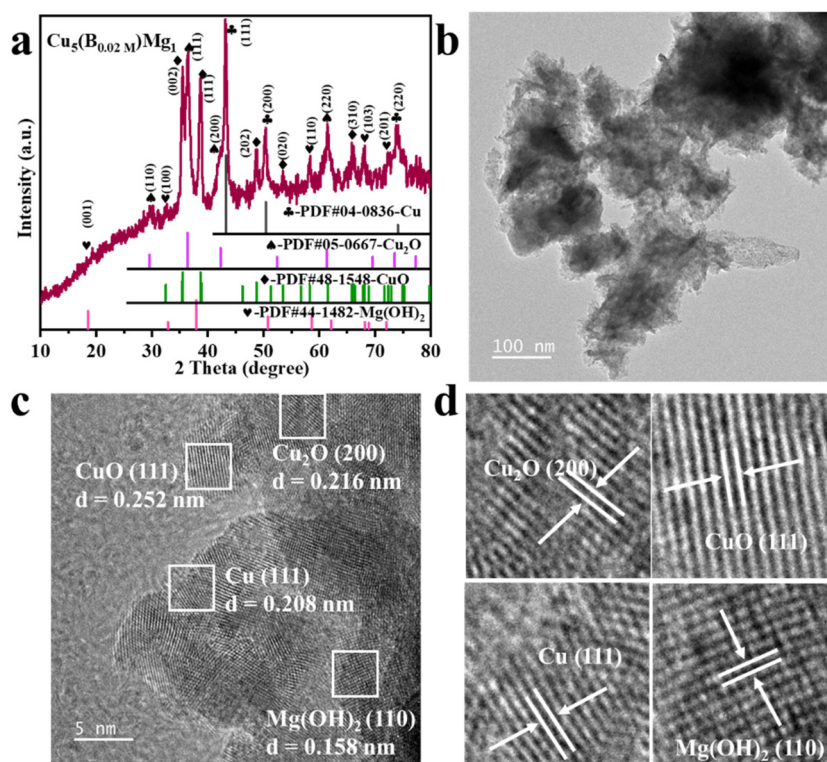


Fig. 2 (a) XRD, (b) TEM and (c) HRTEM characterization of the  $\text{Cu}_5(\text{B}_{0.02 \text{ M}})\text{Mg}_1$  catalyst. (d) is the enlarged view of (c).

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

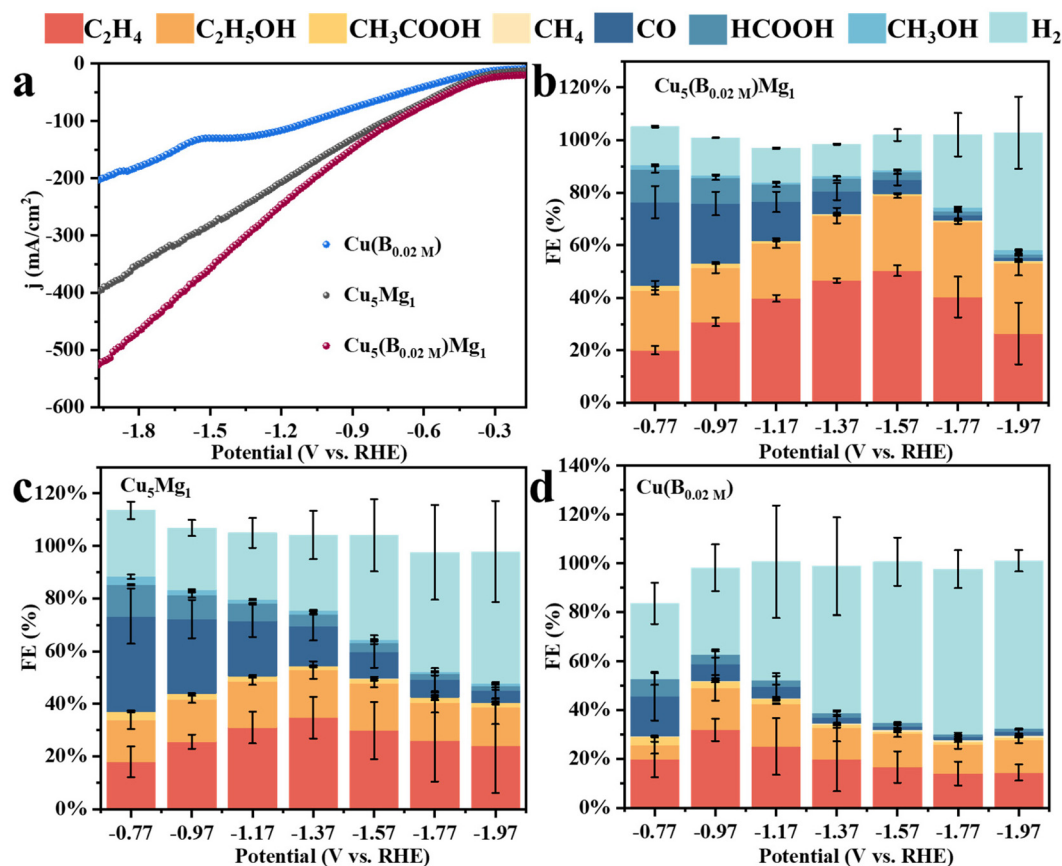


Fig. 4 (a) LSVs of  $\text{Cu}(\text{B}_{0.02}\text{M})$ ,  $\text{Cu}_5\text{Mg}_1$  and  $\text{Cu}_5(\text{B}_{0.02}\text{M})\text{Mg}_1$ . The Faraday efficiencies (FEs) of all products for different catalysts: (b)  $\text{Cu}_5(\text{B}_{0.02}\text{M})\text{Mg}_1$ , (c)  $\text{Cu}_5\text{Mg}_1$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

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