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Steady Cu⁺ species *via* magnesium and boron co-modification for enhanced CO₂ electroreduction to C₂₊ products: an *in situ* Raman spectroscopic study[†]

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The electrochemical carbon dioxide reduction reaction (CO2RR) to produce high-value multi-carbon (C2+) compounds holds significant practical importance in realizing carbon neutrality. Copper-based electrocatalysts are promising for CO₂-to-C₂₊ conversion. However, the labile Cu valence at high current densities impedes C2+ product generation. Here, we present an electrocatalyst derived from CuO, featuring a heterostructure of Cu/Cu₂O/CuO/Mg(OH)₂ via the co-addition of Mg and B during the preparation (referred to as $Cu_5(B_{0.02\ M})Mg_1$). The $Cu_5(B_{0.02\ M})Mg_1$ shows an impressive C_{2+} yield, with a Faraday efficiency (FE_{C2},) of 79.59% at -1.57 V vs. RHE (reversible hydrogen electrode). Additionally, the partial current density of C_{2+} on the $Cu_5(B_{0.02\ M})Mg_1$ catalyst is $-317.03\ mA\ cm^{-2}$, 2.7 and 3.5 times higher than those catalysts lacking B (Cu₅Mg₁ catalyst) or Mg (Cu(B_{0.02 M}) catalyst), respectively. Over a wide potential range of 600 mV between -1.17 and -1.77 V vs. RHE, the overall FE_{C2+} surpasses 60% on the Cu₅(B_{0.02 M}) Mq₁ catalyst. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and high-resolution transmission electron microscopy (HRTEM) characterization studies indicate the NaBH₄ reactant could promote the formation of crystalline Mg(OH)₂ in the catalyst structure, which is found to better stabilize Cu⁺ at negative potentials compared to the amorphous phase. Further in situ Raman spectroscopy reveals that at increasingly negative potentials, the higher copper species (Cu²⁺) is inevitably reduced to the lower copper species (Cu⁰/Cu⁺). However, the synergy of Mg and B prolongs the presence of Cu⁺ on the catalyst surface across a broad potential range, and $^{*}CO$ and $^{*}CO_{2}^{-}$ 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_2RR) represents a pathway for producing high-value-added chemicals and fuels, offering a means to reduce global carbon dioxide (CO_2) emissions and alleviate the shortage of nonrenewable carbon resources. The CO_2RR yields primarily hydrocarbons and oxygen-containing compounds. Among them, multi-carbon (C_{2+}) products such as ethylene (C_2H_4) and ethanol (C_2H_5OH) have broader industrial applications and higher energy densities compared with C_1 products like

carbon monoxide (CO) and methane (CH₄), thus commanding a higher economic value per unit mass. $^{4-6}$ 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 CO₂ (about 750 kJ mol⁻¹). Furthermore, the multistep proton-coupling process contributes to the poor selectivity and yield of target products during the CO₂RR. $^{7-9}$ Addressing these issues requires the exploration and design of electrocatalysts with enhanced efficiency to facilitate CO₂ conversion while minimizing product distribution variability during the CO₂RR process.

To date, copper-based materials, which have been found crucial for C–C coupling, remain the major electrocatalysts for efficiently converting CO_2 to long-chain hydrocarbons and multi-carbon oxygenates. Previous studies suggest that Cu^+ species on Cu-based materials could enhance the selectivity of C_{2^+} products. However, under high-current electrolysis, particularly at the negative potentials required for C_{2^+}

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product formation, the catalyst structure becomes unstable, and Cu⁺ is readily reduced to Cu⁰ during the CO₂RR. Consequently, prolonging the lifetime of Cu⁺ at reduction potentials is a current research focus. To preserve Cu⁺ during the CO₂RR so as to enhance C₂₊ formation, essential steps involve generating Cu⁺ sites and optimizing intermediate adsorption. Researchers have developed several strategies for this purpose, including doping modification, 15,16 addition of different metallic elements, 17,18 heterogeneous interface engineering, 19,20 oxidation state regulation, 21-23 control, 21,24-26 etc. Until now, nonmetallic elements such as B, C, F, and S have been reported to effectively regulate the electronic structure and stabilize Cu⁺ in Cu lattices, facilitating the reduction of CO2 to C2+ products at large current densities. 27-29 For example, Yao et al. devised a B-Cu₂O 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 Cu₂O, thereby stabilizing Cu⁺ species on the B-Cu₂O surface. This was believed to strengthen Cu-O bonds, significantly enhancing C-C coupling and facilitating the formation of C₂₊ products.³⁰ Alkaline-earth metals such as Mg, Ba and Ca were found to not only maintain Cu⁺ on catalyst surfaces, but also enhance the adsorption of intermediates at active centers, thereby influencing the reaction kinetics of the CO₂RR process.³¹ For instance, Peng et al. synthesized a nano-Cu₂Mg intermetallic catalyst predominantly oriented along the (111) crystal face on a carbon black substrate (denoted as Cu₂Mg(111)). In situ Raman spectroscopy and DFT calculations confirmed that the $Cu_3^{\delta-}$ -Mg^{$\delta+$} active sites in Cu_2 Mg(111) enhanced the coverage of *CO on the catalyst surface, lowered the energy barrier for *CO-CO coupling, and stabilized the *CHCHOH intermediates to promote ethanol production. 32 In addition, Xie et al. engineered a Mg-modified CuxO nanoparticle catalyst targeting the C₂H₄ product. In situ XRD, in situ Raman spectroscopy and DFT calculations demonstrated that the amorphous Mg(OH)₂ species stabilized Cu⁺ species, promoting the presence of vital high *CO intermediates for C2+ products.³³ However, challenges still exist regarding these Cubased materials specially designed for C2+ products. Under current modification measures, Cu⁺ has a relatively short lifetime and could only exist within a narrow potential window, significantly limiting its effectiveness during the CO₂RR. 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 Cu⁺ has not been thoroughly studied.

Based on the above considerations, we have designed a B-Cu/Cu₂O/CuO/Mg(OH)₂ catalyst through a simple two-step protocol involving calcination and wet chemical reduction, aiming to enhance C2+ products at high current densities across wide potential ranges. The target catalyst is referred to as Cu₅(B_{0.02 M})Mg₁, named according to the content of the elements during its preparation. X-ray diffraction (XRD), highresolution transmission electron microscopy (HRTEM) and ex

situ X-ray photoelectron spectroscopy (XPS) reveal that the addition of NaBH₄ during catalyst synthesis could promote the formation of crystalline Mg(OH)2 in the catalyst structure, which we suggest would better stabilize Cu⁺ compared to the amorphous Mg(OH)2 phase. Further in situ Raman investigation confirms that Cu⁺ on the Cu₅(B_{0.02 M})Mg₁ catalyst could persist across a much broader potential window compared to those catalysts lacking crystalline Mg(OH)2 or B. Additionally, the *CO intermediate, a significant precursor of C₂₊ products, is recorded on the Cu₅(B_{0.02 M})Mg₁ surface even at rather negative potentials during the CO₂RR. Benefiting from the stabilized Cu⁺, Cu₅(B_{0.02 M})Mg₁ shows high selectivity towards C₂₊ 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 Mg(OH)2 in Cu⁺ stabilization and provides a comprehensive understanding of the role of Cu⁺ in the efficient CO₂RR towards C₂₊ products.

2. Results and discussion

Morphological and structural characterization of the 2.1 catalysts

The typical fabrication process of Cu₅(B_{0.02 M})Mg₁ is depicted in Fig. 1, with detailed synthesis described in the ESI.† The XRD pattern indicates diffraction peaks of Cu, Cu₂O, CuO and Mg(OH)₂ in the Cu₅(B_{0.02 M})Mg₁ catalyst (Fig. 2a). The characteristic peaks at 42.3°, 50.4°, and 74.1° correspond to the (111), (200) and (220) planes of Cu (PDF#04-0836), respectively. Additionally, four peaks at 29.5°, 36.4°, 42.3° and 61.3° correspond to the (110), (111), (200) and (220) planes of Cu₂O (PDF#05-0667), respectively. Peaks at 35.4°, 39.7°, 48.7°, 53.5° and 66.4° are attributed to the (002), (111), (202), (020) and (310) planes of CuO (PDF#48-1548), respectively. Furthermore, peaks at 18.5°, 32.9°, 58.6° and 68.2° align well with the (001), (100), (110) and (103) planes of Mg (OH)2 (PDF#44-1482), respectively. The XRD pattern demonstrates that the Cu₅(B_{0.02 M})Mg₁ catalyst mainly comprises Cu, Cu₂O, CuO and Mg(OH)₂ crystal phases. On the other hand, XRD patterns of the corresponding reference Cu₅Mg₁, $Cu_5(B_{0.1 M})Mg_1$, $Cu(B_{0.02 M})$, $Cu_{10}(B_{0.02 M})Mg_1$ and $Cu_1(B_{0.02 M})Mg_1$ _M)Mg₁ catalysts are provided in Fig. S1.† The $Cu_5(B_{0.1 \text{ M}})Mg_1$, $Cu_{10}(B_{0.02 \text{ M}})Mg_1$ and $Cu_1(B_{0.02 \text{ M}})Mg_1$ catalysts also consist of Cu, Cu₂O, CuO and Mg(OH)₂. The Cu(B_{0.02 M}) catalyst comprises three phases: Cu, Cu₂O and CuO. Notably, for the Cu₅Mg₁ catalyst (lacking the NaBH₄ reactant during its preparation), XRD only reveals the existence of CuO (PDF#48-1548), while the Mg(OH)₂ (PDF#44-1482) crystalline phases are absent. We propose that this results from the generation of amorphous Mg(OH)2 rather than crystalline Mg(OH)2 when the reducing agent NaBH₄ is absent (Fig. S1a†).³⁴

Scanning electron microscopy (SEM) and TEM reveal that the as-prepared Cu₅(B_{0.02 M})Mg₁ 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-

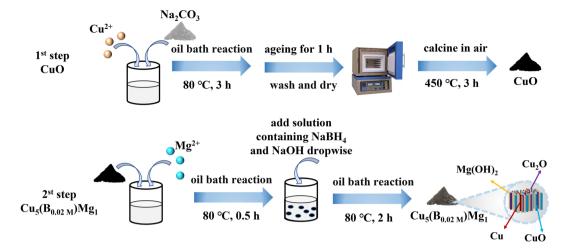


Fig. 1 Graphical scheme for the synthesis of the Cu₅(B_{0.02 M})Mg₁ catalyst.

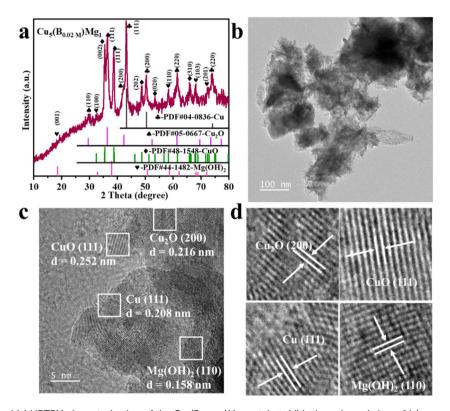


Fig. 2 (a) XRD, (b) TEM and (c) HRTEM characterization of the $Cu_5(B_{0.02 \text{ M}})Mg_1$ catalyst. (d) is the enlarged view of (c).

lyst surface (Fig. S2c and d†). SEM and EDS characterization studies were performed on the Cu₅Mg₁, Cu₅(B_{0.1 M})Mg₁, Cu (B_{0.02 M}), Cu₁₀(B_{0.02 M})Mg₁ and Cu₁(B_{0.02 M})Mg₁ 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 (Cu₂O (200)), 0.252 (CuO (111)) and 0.158 nm $(Mg(OH)_2 (110))$ in the $Cu_5(B_{0.02 M})Mg_1$ catalyst, consistent with its XRD result (Fig. 2c and d). TEM and HRTEM were also conducted on Cu(B_{0.02 M}) and Cu₅Mg₁ to explore the effect of Mg and B on the structure of the catalyst (Fig. S8 and S9†). For the Cu(B_{0.02 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), Cu₂O (111), and CuO (111) lattices (Fig. S8†). Conversely, the Cu₅Mg₁ 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 Cu₅Mg₁ arises from some Mg-based amorphous

species formed due to the absence of the NaBH₄ 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). ^{35,36} The peaks at 933.98 and 953.78 eV are attributed to the Cu2+ of CuO in Cu₅Mg₁ (Fig. 3a and Table S1†), ³⁷⁻³⁹ indicating that in the absence of NaBH4 reducing agent, the Cu species in the catalyst mainly exists in the form of Cu2+. Notably, upon NaBH₄ addition, the Cu²⁺ bands of Cu₅(B_{0.02} M)Mg₁ and Cu₅(B_{0.1 M})Mg₁ catalysts shift to higher electron binding energies by 0.55 and 0.64 eV, respectively, and at the same time Cu⁰/Cu⁺ is produced. Additionally, with increasing NaBH₄ content, the Cu⁰/Cu⁺ electron binding energies decrease from 932.43/952.23 eV $(Cu_5(B_{0.02} _{M})Mg_1)$ to 932.17/951.97 eV $(Cu_5(B_{0.1\ M})Mg_1)$ (Fig. 3a and Table S1†). $^{40-42}$ These results demonstrate that the NaBH4 content is a key factor affecting the electronic structure of Cu centers. To further differentiate between Cu⁰ and Cu⁺, Cu LMM Auger electron spectroscopy analysis was performed on Cu₅(B_{0.02 M})Mg₁ and Cu₅(B_{0.1 M}) Mg₁ catalysts (Fig. S10†). The two peaks at around 568.00 and 569.75 eV correspond to Cu⁰ and Cu⁺, 43,44 respectively, confirming the co-existence of Cu⁰ and Cu⁺ species on these two catalysts. According to previous studies, Cu⁰ and Cu⁺ played different roles during the CO₂RR. Cu⁰ contributed to activating CO₂ molecules. 45 At the initial stage of the reaction, CO₂ tended to be above the Cu^0 zone. After CO_2 activation, $Cu^{\delta+}$ (0 $< \delta \le 1$) was proposed to stabilize CO₂ molecules, which can promote the dimerization process between *CO intermediates and enhance the subsequent C-C coupling. 46,47 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 Cu²⁺ shifts to a higher electron binding energy, while the Cu⁰/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 NaBH₄, the Mg(OH)₂ species persists on the catalysts, as indicated by its characteristic peak at ~1303.60 eV.⁴⁸ Taking the XPS and the above XRD/TEM results into comprehensive consideration, it is suggested that the NaBH4 reactant plays a significant role in tuning the crystalline state of the Mg(OH)₂ species. In the absence of NaBH₄, Mg(OH)₂ exists in an amorphous phase, while with NaBH₄ addition, Mg(OH)₂ exists as crystals. We propose that the existing form of Mg(OH)2 could be a critical influencing factor on the CO₂RR performance of the catalyst. Nonetheless, the high-resolution B 1s spectra of $Cu_5(B_{0.02 \text{ M}})$ Mg_1 and $Cu_5(B_{0.1 M})Mg_1$ show two peaks at 191.92 and 191.81 eV, belonging to B-O (Fig. 3d). 49,50 Additionally, the contents

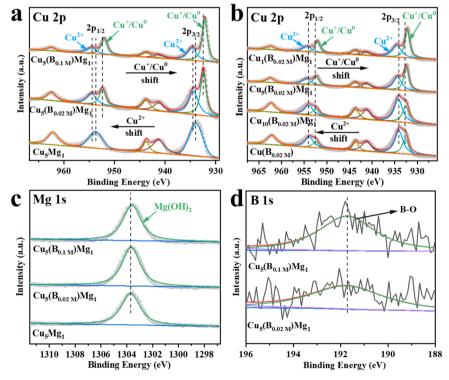


Fig. 3 XPS spectra of Cu 2p in (a) Cu_5Mg_1 , $Cu_5(B_{0.02\ M})Mg_1$, $Cu_5(B_{0.1\ M})Mg_1$ (varying the NaBH₄ feeding amount while keeping the Cu/Mg ratio at 5:1) and (b) $Cu(B_{0.02\ M})$, $Cu_{10}(B_{0.02\ M})Mg_1$, $Cu_5(B_{0.02\ M})Mg_1$ and $Cu_1(B_{0.02\ M})Mg_1$ (varying the ratio of Cu/Mg while keeping the NaBH₄ feeding amount the same at 0.02 M). (c) XPS spectra of Mg 1s in Cu_5Mg_1 , $Cu_5(B_{0.02\ M})Mg_1$, and $Cu_5(B_{0.1\ M})Mg_1$. (d) The corresponding B 1s XPS spectra of $Cu_5(B_{0.02\ M})Mg_1$ and $Cu_5(B_{0.1\ M})Mg_1$ catalysts.

of Cu, Mg and B elements on the Cu₅(B_{0.02 M})Mg₁ catalyst surface were determined via XPS analysis, as provided in Table S3.†

2.2 Electrochemical CO₂RR performance in a flow cell

Research Article

The CO_2RR performances of $Cu_5(B_{0.02\ M})Mg_1$, $Cu_5(B_{0.1\ M})Mg_1$, Cu_5Mg_1 , $Cu_{10}(B_{0.02 \text{ M}})Mg_1$, $Cu_1(B_{0.02 \text{ M}})Mg_1$ and $Cu(B_{0.02 \text{ M}})$ catalysts were evaluated in 1.0 M KOH electrolyte saturated with CO_2 at potentials ranging from -0.77 to -1.97 V. Typical gaseous products (C₂H₄, CH₄, CO, and H₂) and liquid products (CH₃CH₂OH, CH₃COOH, CH₃OH, and HCOOH) were analyzed (Fig. S11 and S12†). Among these different materials, Cu₅(B_{0.02} $_{\rm M}$)Mg₁ (Cu: Mg = 5:1, NaBH₄ = 0.02 M) shows excellent selectivity towards C₂₊ 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 CO₂RR conditions (Fig. 4a). It is found that the Cu₅(B_{0.02 M})Mg₁ catalyst exhibits a significantly higher current density as compared to the Cu₅Mg₁ and Cu(B_{0.02 M}) catalysts, suggesting a potentially better CO2RR 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, Cu₅(B_{0.02} M)Mg₁ shows the highest C₂₊

product selectivity (Fig. 4b). Notably, the FE_{C2} for the Cu₅(B_{0.02} _M)Mg₁ catalyst remains >60% across a wide potential range of 600 mV (from −1.17 to −1.77 V), significantly outperforming Cu_5Mg_1 and $Cu(B_{0.02 \text{ M}})$ (Fig. 4b-d). It should be noted that the Cu₅(B_{0.02 M})Mg₁ catalyst also shows a low FE for H₂ (FE_{H₂}) 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 FE_{Co.} of 79.59% at -1.57 V is recorded for $Cu_5(B_{0.02 \text{ M}})Mg_1$ (FE_{C₂H₄} = 50.31%, $FE_{C,H,OH}$ = 28.58%, with a small amount of CH₃COOH), significantly higher than those of Cu_5Mg_1 (FE_{C₂₊} = 49.53%) and $Cu(B_{0.02 \text{ M}})$ catalysts (FE_{C₂₄} = 31.21%) (Fig. 5a and Table S4†). Furthermore, Cu₅(B_{0.02 M})Mg₁ shows prominently enhanced partial current densities for C_{2+} products $(j_{C_{2+}})$. As depicted in Fig. 5b, $j_{C_{3}}$ of $Cu_5(B_{0.02 \text{ M}})Mg_1$ (-317.03 mA cm⁻²) is 2.7 and 3.5 times higher than those of Cu_5Mg_1 (-116.74 mA cm⁻²) and $Cu(B_{0.02 \text{ M}})$ (-91.09 mA cm⁻²) at the same working potential of −1.57 V, suggesting the synergistic promotion of C₂₊ formation on Cu surfaces by Mg and B. In addition, $j_{C_{2+}}$ of Cu₅(B_{0.02 M}) Mg₁, Cu₅Mg₁ and Cu(B_{0.02 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 CO2RR activities of the catalysts (Fig. S13†). The results reveal that appropriate amounts of

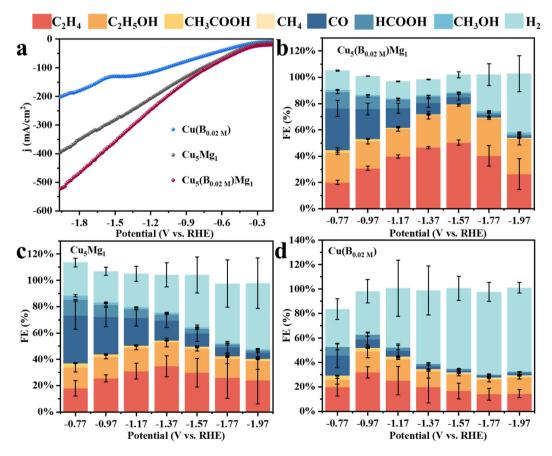


Fig. 4 (a) LSVs of Cu(B_{0.02 M}), Cu₅Mg₁ and Cu₅(B_{0.02 M})Mg₁. The Faraday efficiencies (FEs) of all products for different catalysts: (b) Cu₅(B_{0.02 M})Mg₁. (c) Cu_5Mg_1 , and (d) $Cu(B_{0.02 \text{ M}})$.

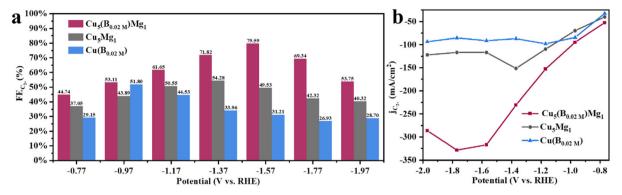


Fig. 5 Electrochemical CO₂RR performance of the Cu₅(B_{0,02 M})Mg₁ catalyst: (a) FEs of C₂₊ (C₂H₄, C₂H₅OH and CH₃COOH) at different potentials and (b) partial current densities of C2+.

NaBH4 and Mg reactants during synthesis are conducive to enhanced C₂₊ selectivity, while excessive usage will reduce C₂₊ products. This could be because the selective promoting and blocking effects of these elements in Cu₅(B_{0.02 M})Mg₁ reach a relatively balanced state for efficient CO2RR catalysis (Table S4†).33 Furthermore, we have compared the CO2RR activities of Cu₅(B_{0.02 M})Mg₁ with other different catalysts in previous literature, which shows that the synergy of Mg and B contributes to a competitive selectivity towards C2+ products

The long-term catalytic performance of Cu₅(B_{0.02 M})Mg₁ for the CO2RR 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 C2H4 gradually decreases over time. After the long-term CO₂RR measurement, Cu₅(B_{0.02 M})Mg₁ was subjected to XRD characterization. The results indicate that the bulk of the catalyst post CO₂RR is primarily composed of Cu (PDF#04-0836), Cu₂O (PDF#05-0667) and Mg(OH)₂ (PDF#44-1482), with CuO completely reduced. Notably, the XRD peaks of Mg(OH)₂ diminish post CO₂RR, which we believe leads to the decline in the stability of Cu₅(B_{0.02 M})Mg₁ (Fig. S15†). Besides, previous literature studies have suggested that the accumulation of impurities like NO_x, SO_x, and carbon on the catalyst surface can also affect the active sites for the CO2RR, thereby resulting in a gradual decrease in performance. 51-53 In addition to XRD, XPS characterization was employed to analyze the elemental distribution on the Cu₅(B_{0.02 M})Mg₁ catalyst surface (Fig. S16†). As depicted in Fig. S16a,† copper species, in the form of Cu⁰ and Cu⁺, predominantly exist on the catalyst surface. The crystalline Mg (OH)₂ species nearly vanishes after the long-term CO₂RR, therefore contributing to the decline in the performance of the Cu₅(B_{0.02 M})Mg₁ catalyst (Fig. S16b†). Additionally, XPS results show that the B element still exists on the catalyst (Fig. S16c†).

To study the enhanced CO₂RR performance of the Cu₅(B_{0.02 M})Mg₁ catalyst, the electrochemically active surface areas of all the electrocatalysts were estimated by calculating their double layer capacitances ($C_{\rm dl}$) (Fig. S17 and S18†). Obviously, compared with Cu₅Mg₁ (2.83 mF cm⁻²), Cu₅(B_{0.1 M})

 Mg_1 (1.61 mF cm⁻²), $Cu(B_{0.02 \text{ M}})$ (0.99 mF cm⁻²), $Cu_{10}(B_{0.02 \text{ M}})$ Mg_1 (2.20 mF cm⁻²) and $Cu_1(B_{0.02 \text{ M}})Mg_1$ (1.19 mF cm⁻²), $Cu_5(B_{0.02 \text{ M}})Mg_1$ (3.28 mF cm⁻²) has the largest C_{dl} value, revealing that the Cu₅(B_{0.02 M})Mg₁ catalyst can provide more active sites for the CO₂RR. Meanwhile, it is worth noting that the active surface area of Cu₅Mg₁ is lower than that of Cu₅(B_{0.02 M}) Mg1, which may be due to the formation of amorphous Mg (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 Cu₅Mg₁.⁵⁴ 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 CO2RR.

In situ Raman spectroscopy was further conducted to examine the effects of B and/or Mg on the valence of Cu (Cu⁰, Cu⁺ or Cu²⁺) as well as to probe probable intermediates during the CO₂RR (Fig. 6). Fig. 6a presents the in situ Raman spectra of the Cu₅(B_{0.02 M})Mg₁ catalyst in 1.0 M KOH electrolyte (saturated with CO₂) during the CO₂RR. At the open circuit voltage, three characteristic peaks are observed at around 147, 522 and 626 cm⁻¹, attributed to Cu₂O.⁵⁵⁻⁵⁷ After applying a cathodic potential of -0.37 V, a new Raman band appears at 703 cm⁻¹ on the Cu₅(B_{0.02 M})Mg₁ catalyst, corresponding to surface δCO_2^- , which represents the umbrella motion of oxygen atoms of the *CO²⁻ intermediate. Previous studies recognized *CO₂as the initial intermediate just after CO₂ activation.⁵⁸ At the same time, Raman peaks at 290 and 374 cm⁻¹ are recorded, assigned to the frustrated rotation and tensile vibrations of Cu-CO, respectively. 59-61 Besides, the band at 1071 cm⁻¹ corresponds to the symmetric C-O stretching band of CO₃²⁻ from the electrolyte. 62,63 It is worth noting that over the wide potential range of -0.37 to -1.37 V, Cu₂O peaks at 147, 522 and 626 cm⁻¹ consistently appear on the Cu₅(B_{0.02 M})Mg₁ catalyst, indicating that the CuO species on the catalyst surface has been completely reduced, while Cu⁺ persists, probably being the reactive sites during the electrochemical CO2RR. We propose that the robust stability of Cu₂O species over a wide potential window is attributed to the synergy of B and crystal-

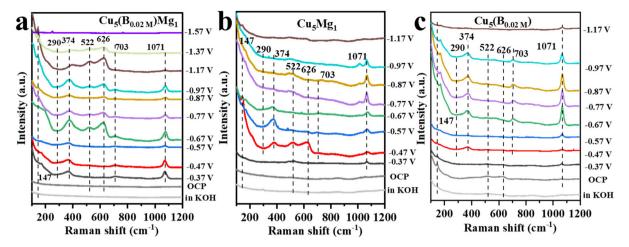


Fig. 6 The in situ Raman spectra of (a) Cu₅(B_{0.02 M})Mq₁, (b) Cu₅Mq₁ and (c) Cu(B_{0.02 M}) catalysts at various potentials in 1.0 M KOH electrolyte during CO2RR catalysis.

line Mg(OH)₂. According to previous literature, the Cu⁺ on the catalyst surface is crucial for the formation of multi-carbon products. 64-67 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 Cu₅Mg₁ and Cu(B_{0.02 M}) are also recorded under the same conditions as Cu₅(B_{0.02 M})Mg₁ to explore the influences of Mg and B on the Cu catalysts, as shown in Fig. 6b and c. In contrast to the Cu₅(B_{0.02 M})Mg₁ catalyst, Cu₂O peaks vanish at only -0.87 V and -0.97 V for Cu₅Mg₁ and Cu(B_{0.02 M}) catalysts, respectively. In addition, unlike the Cu₅(B_{0.02 M})Mg₁ catalyst which displays characteristic bands of *CO and *CO2 at -0.37 V, neither Cu₅Mg₁ nor the Cu(B_{0.02 M}) catalyst shows these bands until -0.47 V. Hence, it is evident that compared to the Cu_5Mg_1 and $\text{Cu}(B_{0.02~\text{M}})$ catalysts, the collaborative effect of Mg and B, which induces the formation of crystalline Mg(OH)2 species in the catalyst structure, facilitates the early formation of *CO₂⁻ and *CO intermediates during the CO₂RR.

A previous study by Yang et al. utilized cerium as a selfsacrificing agent to stabilize Cu⁺ in their catalyst, taking advantage of the easy redox properties of Ce³⁺/Ce⁴⁺. Their in situ Raman and Fourier transform infrared spectroscopy results demonstrated that the stabilized Cu⁺ components promoted C-C coupling under the CO₂RR. DFT calculations further revealed that strong *CO adsorption and low C-C coupling energy were conducive to the formation of C₂H₅OH.⁶¹ Wang et al. prepared an ultra-thin 2D Cu2O nanosheet (Cu2O-NS) catalyst with abundant oxygen vacancies. In situ Raman spectroscopy and DFT calculations supported that Cu₂O-NS prevented the reduction of surface Cu oxides, thereby stabilizing Cu⁺ and enhancing the conversion of CO₂ to C₂₊.⁶⁸ Similarly, in our work, Cu⁺ stabilization is achieved through the introduction of appropriate Mg and B into Cu materials. We found that the addition of the NaBH4 reactant can tune the amorphous or crystalline phases of Mg(OH)₂. Crystallized Mg(OH)₂ is crucial for prolonging the lifetime of Cu⁺ during the CO₂RR and facilitating the activation of CO2 on the Cu surface to

generate key *CO intermediates for C-C coupling. Consequently, this enhances the selectivity towards C2+ 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 Mg(OH)2 and B. XRD, TEM, and XPS analyses indicate that the addition of the NaBH4 reactant can induce the formation of crystalline Mg (OH)2, which is proposed to enhance the conversion of CO2 to C_{2+} during the CO_2RR compared to amorphous $Mg(OH)_2$. In support of this, in situ Raman spectroscopy reveals that the synergy of crystalline Mg(OH)₂ and B can stabilize Cu⁺ at rather cathodic potentials during the CO₂RR process, effectively producing and preserving the *CO intermediates, therefore greatly enhancing the *CO-CO coupling. As a result, the FEC, surpasses 60% on the Cu₅(B_{0.02 M})Mg₁ 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 $FE_{C_{2+}}$ 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 CO2-to-C2+ conversion. We believe that this will help inspire the rational design of future CO2RR 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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