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## Hydroxylation boosted low-overpotential CO<sub>2</sub> reduction to ethylene for a Cu/PTFE electrode†

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**We present a Cu/PTFE electrode for the CO<sub>2</sub> reduction reaction with a high coverage of \*OH which facilitates both the activation of CO<sub>2</sub> and the C–C coupling, leading to a faradaic efficiency for ethylene exceeding 50% at an exceptionally low potential of –246 mV vs. RHE, with the maximum FE<sub>C<sub>2</sub>H<sub>4</sub></sub> reaching 60.3%.**

The escalating global levels of CO<sub>2</sub> and the excessive consumption of fossil fuels present major obstacles to sustainable development.<sup>1–3</sup> The CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR), powered by renewable energy, emerges as a viable solution for CO<sub>2</sub> conversion while generating high-value chemicals under ambient conditions. Among various products of the electrochemical CO<sub>2</sub>RR, multi-carbon compounds, especially ethylene, have garnered significant attention due to their versatility in industry.<sup>4–6</sup> Cu is the only single-metal catalyst capable of reducing CO<sub>2</sub> to diverse multi-carbon compounds, owing to the appropriate adsorption energy for \*CO and \*H species.<sup>7,8</sup> Cu-based catalysts are thus extensively employed in the CO<sub>2</sub>RR to produce ethylene; however, there are still challenges including high overpotentials,<sup>9,10</sup> limited ethylene selectivity,<sup>11,12</sup> and competing hydrogen evolution reactions.<sup>13,14</sup>

Among Cu-based catalysts, Cu(OH)<sub>2</sub> exhibits notable selectivity towards the production of ethylene in the CO<sub>2</sub>RR, attributed to the high \*OH coverage on the Cu surface derived from Cu(OH)<sub>2</sub> during the CO<sub>2</sub>RR process.<sup>15,16</sup> The presence of \*OH promotes the adsorption of CO at an atop site (\*CO<sub>atop</sub>) on Cu rather than at a bridge site (\*CO<sub>bridge</sub>)<sup>17</sup> and impacts the work function of the Cu surface,<sup>18</sup> which facilitates the C–C coupling to generate C<sub>2+</sub> products. Many efforts have been made to further enhance the ethylene selectivity of Cu(OH)<sub>2</sub> catalysts,

including morphology and facet engineering,<sup>19,20</sup> tuning surface \*OH amounts and particle size<sup>15,18</sup> and microenvironment control.<sup>21</sup> Polytetrafluoroethylene (PTFE) has been used to suppress the hydrogen evolution side reaction by enhancing the local hydrophobic environment of the catalyst and augmenting the solid–liquid–gas interfaces, which effectively enhances the selectivity for C<sub>2</sub>H<sub>4</sub>.<sup>14,21</sup> In addition to the selectivity, the overpotential for the CO<sub>2</sub>RR stands as a pivotal merit for evaluating electrocatalytic performance. For most CO<sub>2</sub>RR catalysts, the overpotentials required for achieving high selectivity (over 50%) of ethylene typically exceed 500 mV.<sup>10,22,23</sup> These high overpotentials are commonly attributed to the significant energy barriers associated with the first step of CO<sub>2</sub> activation and the step of carbon–carbon coupling. Achieving both high ethylene selectivity and low overpotentials remains a significant challenge in the realm of CO<sub>2</sub>RR.

In this study, to enhance the active sites and catalytic ability, an ion sputtering method was employed to deposit nano-sized Cu catalysts onto the PTFE membrane, to obtain a uniformly dispersed Cu/PTFE electrode with good hydrophobicity and sufficient mechanical strength (Fig. S1 and S2, ESI†). Furthermore, to modulate the surface \*OH, Cu particles were sputtered under dry and moist Ar atmospheres, denoted as D\_Cu and M\_Cu, respectively. The moist atmosphere was achieved by introducing water molecules through the addition of a hygroscopic polylactide (PLA) material into the vacuum chamber of the ion sputtering coater, which facilitated the formation of Cu(OH)<sub>2</sub> (Fig. 1a and Fig. S3, ESI†). Experimental results demonstrated that our M\_Cu catalyst exhibited high selectivity and low overpotential for the generation of ethylene, with a faradaic efficiency for ethylene (FE<sub>C<sub>2</sub>H<sub>4</sub></sub>) of 55.1% at a low potential of –246 mV vs. reversible hydrogen electrode (RHE), and the highest FE<sub>C<sub>2</sub>H<sub>4</sub></sub> reached 60.3%. This superior electrochemical performance was attributed to the abundant coverage of \*OH on the surface of the nano-sized Cu catalyst. Density functional theory (DFT) simulations revealed that the presence of \*OH on the Cu catalyst surface lowers both the barriers of CO<sub>2</sub> activation and C–C coupling, thereby efficiently decreasing the overpotential and enhancing the selectivity for ethylene.

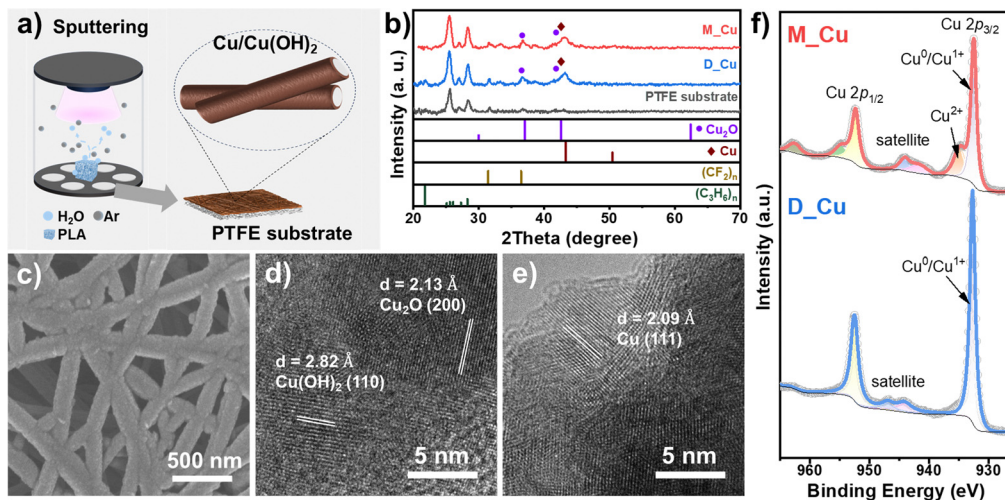
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**Fig. 1** (a) Schematic illustration of the method for the deposition of Cu/Cu(OH)<sub>2</sub> catalysts onto a polytetrafluoroethylene (PTFE) substrate via ion sputtering in a moist Ar atmosphere. (b) Grazing incidence X-ray diffraction (GI-XRD) patterns of M<sub>-</sub>Cu, D<sub>-</sub>Cu and the PTFE substrate (with (CF<sub>2</sub>)<sub>n</sub> (JCPDS#54-1594), (C<sub>3</sub>H<sub>6</sub>)<sub>n</sub> (JCPDS#54-1936), Cu<sub>2</sub>O (JCPDS#34-1354) and Cu (JCPDS#04-0836) as references). (c) Field-emission scanning electron microscopy (FESEM) image of M<sub>-</sub>Cu. (d) and (e) High-resolution transmission electron microscopy (HRTEM) of M<sub>-</sub>Cu. (f) X-ray photoelectron spectroscopy (XPS) of M<sub>-</sub>Cu and D<sub>-</sub>Cu.

The morphology of the as-prepared Cu-sputtered PTFE electrodes was characterized using field-emission scanning electron microscopy (FESEM). The ion-sputtered Cu species were coated uniformly on PTFE fibers while maintaining the porous structure, which facilitated the gas diffusion of CO<sub>2</sub> from the back to the Cu front (Fig. 1c and Fig. S4 and S5, ESI<sup>†</sup>). The crystalline phase of the Cu catalysts was identified using grazing incidence X-ray diffraction (GI-XRD) (Fig. 1b). Apart from the characteristic peaks of (CF<sub>2</sub>)<sub>n</sub> and (C<sub>3</sub>H<sub>6</sub>)<sub>n</sub> from the polypropylene-supported PTFE membrane, M<sub>-</sub>Cu and D<sub>-</sub>Cu showed diffraction patterns matching with Cu<sub>2</sub>O and metallic Cu. We assume that the formation of Cu<sub>2</sub>O is due to the rapid oxidation of Cu nanoparticles upon exposure to air. From the high-resolution transmission electron microscopy (HRTEM) image in Fig. S6 (ESI<sup>†</sup>), the lattice fringes of 0.208 and 0.213 nm of D<sub>-</sub>Cu match well with the Cu (111) and Cu<sub>2</sub>O (200), indicating the coexistence of Cu and Cu<sub>2</sub>O, consistent with the XRD analysis. For M<sub>-</sub>Cu (Fig. 1d and e), lattice fringes with interplanar spacings of 0.209, 0.213, and 0.282 nm were observed, aligning with the Cu (111), Cu<sub>2</sub>O (200), and (110) lattice planes of Cu(OH)<sub>2</sub>, respectively. We assume that the formation of Cu(OH)<sub>2</sub> was facilitated by the introduction of H<sub>2</sub>O molecules during the sputtering process. Elemental mapping conducted to assess the distribution of Cu along individual PTFE fibers (Fig. S7, ESI<sup>†</sup>) demonstrated the co-localization of Cu, O, C, and F in both M<sub>-</sub>Cu and D<sub>-</sub>Cu, signifying the uniform coating of sputter-deposited Cu onto the PTFE fibers. The presence of O is attributed to the oxidation of Cu in ambient air.

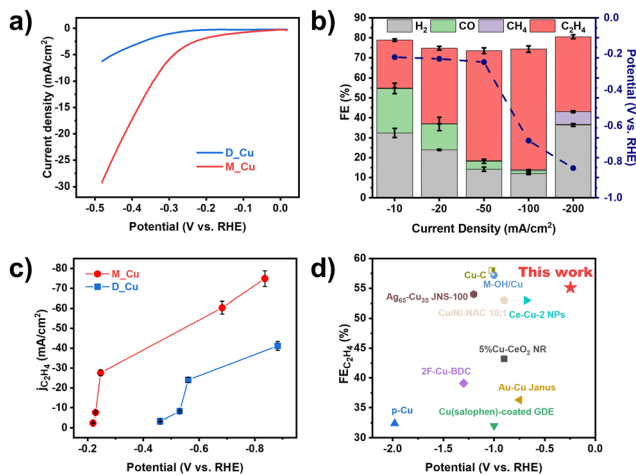
X-ray photoelectron spectroscopy (XPS) analysis was used to further investigate the chemical states of the surface Cu species (Fig. 1f). D<sub>-</sub>Cu showed a distinct Cu 2p<sub>3/2</sub> peak at 932.6 eV and a weak satellite feature, corresponding to Cu<sup>0</sup>/Cu<sup>1+</sup>. It is difficult to distinguish the oxidation states of Cu<sup>0</sup> and Cu<sup>1+</sup> using the Cu 2p<sub>3/2</sub> peak since the binding energies of the two species are too close.

For M<sub>-</sub>Cu, apart from the spark Cu<sup>0</sup>/Cu<sup>1+</sup> peak, a shoulder at a higher binding energy (934.7 eV) was clearly observed, which can be attributed to Cu(OH)<sub>2</sub>.<sup>15</sup> In addition, the Cu 2p<sub>3/2</sub> XPS of M<sub>-</sub>Cu showed more pronounced satellite features at a lower binding energy compared to D<sub>-</sub>Cu, supporting the presence of Cu<sup>2+</sup> species. The Cu LMM Auger spectrum (Fig. S8, ESI<sup>†</sup>) showed a peak at 570.0 eV for D<sub>-</sub>Cu and at 570.4 eV for M<sub>-</sub>Cu, corresponding to Cu<sub>2</sub>O and Cu(OH)<sub>2</sub>, respectively.<sup>15</sup> The presence of Cu(OH)<sub>2</sub> on M<sub>-</sub>Cu was also corroborated by the OH vibrational peaks in the infrared spectra (Fig. S9, ESI<sup>†</sup>).<sup>24</sup>

Owing to their porous structure and the electrically conductive Cu coating, the Cu/PTFE electrodes were directly used as gas diffusion electrodes for CO<sub>2</sub>RR measurements. As shown in Fig. 2a, the linear sweep voltammetry (LSV) curves of M<sub>-</sub>Cu exhibited a larger current density and a lower onset potential than those of D<sub>-</sub>Cu, implying higher catalytic activity of M<sub>-</sub>Cu. In addition, M<sub>-</sub>Cu showed a lower charge transfer resistance and Tafel slope (Fig. S10, ESI<sup>†</sup>) than D<sub>-</sub>Cu, indicating faster reaction kinetics. The faradaic efficiencies for each gaseous product of M<sub>-</sub>Cu and D<sub>-</sub>Cu at different current densities from -10 to -200 mA cm<sup>-2</sup>, along with the corresponding potentials, are depicted in Fig. 2b and Fig. S11, S12 (ESI<sup>†</sup>). The FE<sub>C<sub>2</sub>H<sub>4</sub></sub> of M<sub>-</sub>Cu (Fig. 2b) reached up to 60.34% at a current density of -100 mA cm<sup>2</sup> and achieved long-term stability for 12 h (Fig. S13, ESI<sup>†</sup>). In contrast, the optimal FE<sub>C<sub>2</sub>H<sub>4</sub></sub> of D<sub>-</sub>Cu was only 48%. It is worth noting that both M<sub>-</sub>Cu and D<sub>-</sub>Cu exhibited better CO<sub>2</sub>RR performance in comparison to commercial copper nanoparticles (Cu NPs; Fig. S14a, ESI<sup>†</sup>) and copper sputtered carbon paper (Fig. S14b, ESI<sup>†</sup>), demonstrating the advantage of our ion-sputtered Cu/PTFE electrodes with smaller particle size and more solid-liquid-gas three-phase interfaces.

Furthermore, M<sub>-</sub>Cu exhibits an exceptionally low overpotential, *ca.* -0.2 V, for catalyzing CO<sub>2</sub>RR-ethylene conversion, indicating the prompt activation of CO<sub>2</sub> to CO and subsequent

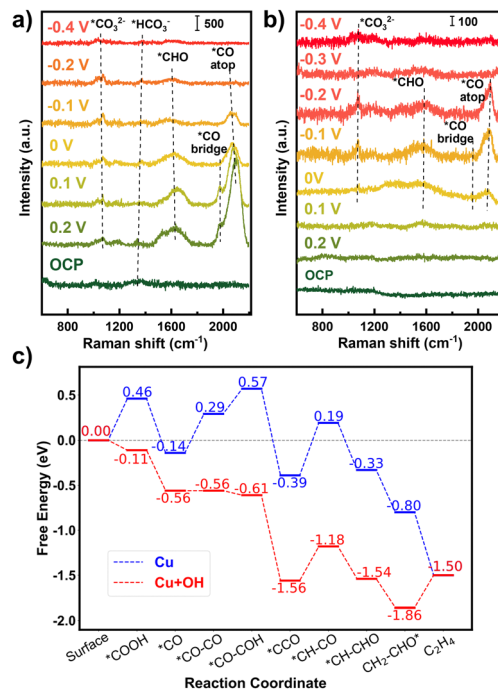




**Fig. 2** (a) Linear-sweep voltammetry (LSV) curves of M\_Cu and D\_Cu. (b) Faradaic efficiency for each CO<sub>2</sub>RR gaseous product of M\_Cu at different current densities and the corresponding potentials. (c) Partial current density of C<sub>2</sub>H<sub>4</sub> of M\_Cu and D\_Cu at different applied potentials. (d) Comparison of the faradaic efficiency for C<sub>2</sub>H<sub>4</sub> (FE<sub>C<sub>2</sub>H<sub>4</sub></sub>) and the corresponding potentials with documented CO<sub>2</sub>RR electrocatalysts.

coupling to ethylene. Notably, the FE<sub>C<sub>2</sub>H<sub>4</sub></sub> of M\_Cu surpassed 50% when the potential reached  $-249$  mV (Fig. 2b and Fig. S15, ESI<sup>†</sup>), demonstrating excellent performance in terms of overpotential and ethylene selectivity compared to recently reported advanced studies (Fig. 2d).<sup>25–34</sup> In addition, Fig. 2c compares the potential-dependent ethylene partial current density of the catalysts. M\_Cu exhibited nearly double the partial current density of D\_Cu and a steeper slope across the tested potential range. These findings suggest the key function of Cu–OH species in activating CO<sub>2</sub>RR-to-ethylene at lower potentials.

In order to identify the reaction intermediates on the surface of Cu catalysts during the CO<sub>2</sub>RR, *in situ* Raman spectroscopy was carried out under applied potentials from open circuit potential (OCP) to  $-0.4$  V. M\_Cu and D\_Cu were prepared on Au electrodes instead of PTFE membranes to enhance the Raman signals. The Raman spectrum of M\_Cu (Fig. 3a) showed distinct peaks at Raman shifts of 1610, 1976, and 2075 cm<sup>-1</sup> upon reaching 0.2 V. These peaks are assigned to \*CHO, \*CO<sub>bridge</sub>, and \*CO<sub>atop</sub>, respectively. The intensity of these peaks gradually reduced as the applied potential decreased from 0.1 V to  $-0.1$  V, and diminished at  $-0.2$  V, suggesting a faster CO<sub>2</sub>RR process at lower potentials, where the intermediate products were rapidly consumed. The peak intensity of \*CO<sub>atop</sub> is much higher than that of \*CO<sub>bridge</sub>, indicating preferential adsorption of CO at the atop site of Cu for M\_Cu, which is beneficial for carbon–carbon coupling.<sup>17</sup> In addition, two weak peaks were observed at 1060 and 1355 cm<sup>-1</sup>, corresponding to \*CO<sub>3</sub><sup>2-</sup> and \*HCO<sub>3</sub><sup>-</sup> species from the electrolyte, respectively. The *in situ* Raman spectra of D\_Cu (Fig. 3b) showed three peaks at 1080, 1545, 1960, and 2070 cm<sup>-1</sup> at 0 V, attributed to \*CO<sub>3</sub><sup>2-</sup>, \*CHO, \*CO<sub>bridge</sub> and \*CO<sub>atop</sub> species, respectively. Comparing the Raman spectra of M\_Cu and D\_Cu, it is evident that M\_Cu exhibited significant intermediate product peaks at a higher potential (0.2 V). This observation



**Fig. 3** *In situ* Raman spectra of (a) M\_Cu and (b) D\_Cu. (c) DFT calculated free energy diagram of the CO<sub>2</sub>RR path for C<sub>2</sub>H<sub>4</sub> on the Cu(111) surface with and without hydroxylation.

correlates with the electrochemical results that M\_Cu displayed a lower onset potential during the CO<sub>2</sub>RR (Fig. 2b). Additionally, M\_Cu exhibited a much higher peak intensity for the intermediate products compared to D\_Cu (Fig. S16, ESI<sup>†</sup>), implying higher reaction activity. Control experiments conducted on bare Au electrodes did not show observable Raman signals (Fig. S17, ESI<sup>†</sup>).

After the CO<sub>2</sub>RR experiments, M\_Cu and D\_Cu were characterized using SEM. The morphology of post-reaction D\_Cu was similar to its pristine structure (Fig. S18a, ESI<sup>†</sup>). Surprisingly, the post-reaction M\_Cu (Fig. S18b, ESI<sup>†</sup>) showed needle-like structures, suggesting substantial restructuring of the Cu catalyst during the reaction induced by Cu–OH. In Fig. S19a (ESI<sup>†</sup>), XPS of post-reaction M\_Cu exhibited a decrease in the area of the Cu<sup>2+</sup> peak, indicating partial reduction of Cu(OH)<sub>2</sub> to Cu during the CO<sub>2</sub>RR. After Ar etching (approximately 4 nm depth), as shown in Fig. S19b (ESI<sup>†</sup>), the disappearance of the Cu<sup>2+</sup> peak confirmed the presence of Cu(OH)<sub>2</sub> mainly at the surface (Fig. S19a, ESI<sup>†</sup>). The XPS peaks for post-reaction D\_Cu are in accordance with those in the pre-reaction state (Fig. S20a and b, ESI<sup>†</sup>), suggesting minimal changes in the catalyst.

To understand the promotional mechanism of the OH species on Cu for the CO<sub>2</sub>RR, we calculated the CO<sub>2</sub>RR reaction path for C<sub>2</sub>H<sub>4</sub> on the Cu(111) surface employing density functional theory (DFT). The potential energy surfaces with and without hydroxylation were compared, as shown in Fig. 3c. The corresponding structures of the intermediates are listed in Fig. S21 (ESI<sup>†</sup>). For the first CO<sub>2</sub> activation step, the intermediate \*COOH on the clean Cu surface has a relatively higher energy (0.46 eV), while an additional OH group brings its energy below



zero. This result is consistent with the *in situ* Raman spectroscopy results in Fig. 3a and b, where CO was observed much earlier (lower voltage needed) for M\_Cu catalyst. After hydroxylation, the energy of \*CO–CO coupling decreases from 0.43 eV to nearly 0 eV. This demonstrates a good agreement with the experimental observation that M\_Cu exhibited a lower overpotential and a higher faradaic efficiency of ethylene compared to D\_Cu. Furthermore, the rate-determining step (\*CO–COH to \*CCO) for the Cu–OH structure showed a lower energy barrier of 0.38 eV than that of bare Cu (0.58 eV), which is consistent with the low CO<sub>2</sub>RR overpotential of M\_Cu.

In summary, we present an efficient CO<sub>2</sub>RR electrode, which is obtained by uniform dispersion of nano-sized copper particles onto a PTFE substrate using ion sputtering. The hydrophobic PTFE effectively inhibited the H<sub>2</sub> evolution and enhanced the solid–liquid–gas interfaces. Particularly, the surface \*OH on the electrode was elegantly modulated by sputtering in a moist Ar atmosphere. The prepared M\_Cu with increased surface \*OH coverage achieved a FE<sub>C<sub>2</sub>H<sub>4</sub></sub> over 50% at an exceptionally low potential of –246 mV, with an optimal ethylene faradaic efficiency of 60.3%. Through *in situ* Raman spectroscopy and DFT calculations, it has been revealed that the surface \*OH species facilitate both the activation of CO<sub>2</sub> and the C–C coupling steps. This work demonstrates a novel strategy for the modification of Cu-based catalysts for a low-potential CO<sub>2</sub>RR to ethylene with high activity and selectivity. We believe our findings deepen the comprehension of CO<sub>2</sub> electroreduction mechanisms and contribute valuable insights for the efficient design of catalysts.

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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## Data availability

The data supporting this article have been included as part of the ESI.†

## Conflicts of interest

There are no conflicts to declare.

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