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# Highly electrocatalytic ethylene production from CO<sub>2</sub> on nanodefective Cu nanosheets

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KEYWORDS:  $CO_2$  electroreduction • metallic copper • nanosheet • nanoscale defect • confinement

ABSTRACT: The electrochemical synthesis of chemicals from carbon dioxide, which is an easily available and renewable carbon resource, is of great importance. However, to achieve high product selectivity for desirable  $C_2$  products like ethylene is a big challenge. Here we design Cu nanosheets with nano-scaled defects (2-14 nm) for the electrochemical production of ethylene from carbon dioxide. A high ethylene Faradaic efficiency of 83.2% is achieved. It is proved that the nano-scaled defects can enrich the reaction intermediates and hydroxyl ions on the electrocatalyst, thus promoting C-C coupling for ethylene formation.

## INTRODUCTION

Ethylene  $(C_2H_4)$  is a building block of particular importance due to its high demand in chemical industry. Usually, ethylene is prepared from steam cracking of naphtha under harsh production conditions (800-900 °C). In recent years, the electrochemical synthesis of ethylene from carbon dioxide reduction reaction (CO<sub>2</sub>RR) has attracted increasing attention because it offers a mild and environmentally benign pathway for ethylene production.<sup>1,2</sup> Up to now, diverse kinds of strategies have been proposed for ethylene production from electrocatalytic CO<sub>2</sub>RR, including constructing Cu nanostructures,<sup>3,4</sup> controlling oxidation state,<sup>4-6</sup> using dopants,<sup>7,8</sup> alloying9,10 and molecule decoration.1,11-13 Among these methods, constructing nanostructures of metallic Cu (without any additive) for  $C_{2+}$  products is much promising, for the simple synthesis and easy-to-study structure-activity relationship of catalyst. Kanan and coworkers proposed the control of grain boundaries in a single electrocatalyst for CO<sub>2</sub>RR, which has been demonstrated to be an efficient pathway for CO<sub>2</sub> conversion.<sup>14-16</sup> In general, C1 products such as carbon monoxide (CO) and methane and  $C_{2+}$  species like ethane and ethanol are generated simultaneously with ethylene in electrochemical CO<sub>2</sub>RR. To date, the highest Faradaic efficiency (FE) of ethylene is 72%, which was achieved by the molecule decorated Cu electrocatalyst using a flow cell system.<sup>1</sup> It is urgent to further improve the ethylene selectivity in electrochemical CO<sub>2</sub>RR, promisingly through the development of electrocatalysts with desirable nanostructures.

Here we design the nano-defective Cu nanosheets as an electrocatalyst for ethylene synthesis from CO<sub>2</sub>RR. The nanoscaled defects are in size of 2-14 nm, which can be considered as a large collection of atomic defects. Such a nano-defective structure strengthens the adsorption, enrichment and confinement for reaction intermediates and hydroxyl ions on the electrocatalyst. The C-C coupling is thus promoted to produce ethylene efficiently. The maximum ethylene FE can reach 83.2%, which is the highest value among all the studied electrocatalysts to date. The mechanism for the high ethylene selectivity on the nano-defective Cu nanosheets was investigated by a series of experiments and calculations.

## **RESULTS AND DISCUSSION**

The nano-defective Cu nanosheets were prepared by an electrochemical reduction method<sup>17</sup> for the pre-formed CuO nanosheets in K<sub>2</sub>SO<sub>4</sub> electrolyte (see details in Methods). As characterized by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), the product has a morphology of nanosheets with a lateral size of 1 μm (Figure 1a). Atomic force microscopy (AFM) image reveals that the thickness of the nanosheet is  $\sim 23$  nm (Figure S1). It is clear that there are numerous pits on each nanosheet (Figure 1b), which is further proved by scanning electron microscopy (SEM, Figure S2). Enlarged HAADF-STEM image shows that the pits are 2~14 nm in size (Figure 1c). Figure 1d shows the HAADF-STEM image of one typical pit. The lattice fringes around the pit is 0.21 nm, which can be indexed to (111) plane of face-centered cubic Cu (Figure S3). Figure 1e is the magnified HAADF-STEM image of the square marked in ACS Paragon Plus Environment

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Figure 1d. It reveals a growing number of atomic defects from the edge to the center of the pit, which is further proved by the intensity profile along the line shown in Figure 1d and e (Figure 1f). Here the nanoscale pit on Cu nanosheet is named as nanodefect,<sup>18-20</sup> which can be considered as a collection of many atomic defects. Similar results were observed for Cu(200) plane around one nano-defect (Figure 1g-i). All the above results confirm the formation of nano-defective nanosheets instead of perforated nanosheet. The nano-defective Cu nanosheets were further characterized by powder X-ray diffraction (XRD), wideangle X-ray scattering two-dimensional map and energy dispersive spectroscopy (EDS). The results prove the formation of metallic Cu and the major exposed planes are Cu(111) and Cu(200) of face-centred cubic Cu (Figure S4), which are in accordance with the above HAADF-STEM results.

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For comparison, other two samples of Cu nanosheets with smooth surfaces and Cu nanoparticles were synthesized and characterized. As shown in Figure 1j and k, the Cu nanosheet has a smooth surface with lateral size of  $\sim 2 \mu m$  and thickness of  $\sim 20$  nm (Figure S5). The Cu nanoparticles have an average diameter of  $\sim 20$  nm (Figure 11). The nano-defective Cu nanosheets, Cu nanosheets with smooth surfaces and Cu nanoparticles are defined as *n*-CuNS, CuNS and CuNP, respectively.



**Figure 1.** Structural characterization of different catalysts. (a-e,g,h) HAADF-STEM images of *n*-CuNS. Inset in (c), size distribution of the nano-defects on *n*-CuNS. Insets in (d,g), the corresponding fast Fourier transform patterns. (e,h) The enlarged area in the square of (d,g). The cool color (dark spots) and warm color (bright spots) represent the highly defective area and the less defective area, respectively. (f,i) The corresponding intensity profile along the line as shown in (d,g) (top) and (e,h) (bottom). (j-k) TEM images of CuNS (j,k) and CuNP (l).

To further gain an insight into the chemical state and local structure of the as-synthesized sample, a series of spectroscopic

techniques were performed. X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) are commonly used technologies for monitoring the valence of Cu in Cu based materials.7,21,22 Cu 2p and Auger Cu LMM XPS spectra of n-CuNS and CuNS reveal that the Cu valence is zero (Figure 2a,b). The Cu K-edge X-ray absorption near-edge spectra (XANES) confirm that *n*-CuNS and CuNS are metallic Cu (Figure 2c). The extended Cu K-edge X-ray absorption fine structure (EXAFS) of the two samples present Cu-Cu coordinations at 2.23 Å, which is identical to that of Cu foil (Figure 2d). The above results suggest that the two catalysts keep the metallic state under X-ray exposure, which is consistent with the reported results.<sup>21,22</sup> By quantitative EXAFS curve fitting analysis, the coordination configuration of Cu atom for *n*-CuNS is confirmed to be 9.7, smaller than those of CuNS (10.9) and Cu foil (12.0) (Figure 2e,f, Figure S6 and Table S1), which is consistent with the abundant atomic defects confined in nano-defective *n*-CuNS (Figure 1d, g).



**Figure 2.** Spectroscopy characterization of different catalysts. (a,b) The Cu 2p (a) and Cu LMM (b) XPS spectra of *n*-CuNS (red) and CuNS (blue). (c,d) Cu K-edge XANES (c) and EXAFS (d) spectra of *n*-CuNS (red), CuNS (blue) and Cu foil (black). (e,f) EXAFS fitting curves in *R* space (e) and *q* space (f) of *n*-CuNS.

The electrochemical CO<sub>2</sub>RR on *n*-CuNS, CuNS and CuNP was conducted using a three electrode H-type cell in a CO<sub>2</sub> saturated 0.1 M K<sub>2</sub>SO<sub>4</sub> electrolyte.<sup>7</sup> The electrolysis products were analyzed by <sup>1</sup>H nuclear magnetic resonance (NMR) spectroscopy and gas chromatography. As catalyzed by *n*-CuNS, ethylene and H<sub>2</sub> in gas phase were detected and no liquid products were produced (Figure S7). It is obvious that *n*-CuNS catalyst presents much enhanced total current density (*j*) as compared with the two reference catalysts (Figure 3a). For example, the current density at -1.18 V versus a reversible

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hydrogen electrode (vs RHE) on *n*-CuNS is 6 and 1.6 times higher than those of CuNS and CuNP, respectively. The ethylene FE over *n*-CuNS maintains values of >60% in a wide potential range of -0.88 to -1.48 V (vs RHE), much higher than those of CuNS and CuNP (Figure 3b). A maximum ethylene FE of 83.2% can be achieved at -1.18 V (vs RHE), while those on CuNS and CuNP are 45.7% and 37.2% (Table S2), respectively. The partial current density of ethylene for *n*-CuNS reaches 66.5 mA cm<sup>-2</sup> at -1.48 V (vs RHE), whereas those of CuNS and CuNP are lower than 5 and 8.5 mA cm<sup>-2</sup>, respectively (Figure 3c). Interestingly, no CO was detected at applied potential range by n-CuNS, while the other two reference catalysts show considerable formation of competitive CO (4%-24%) (Figure S8). It indicates that CO, which is an intermediate for  $CO_2$ transformation to ethylene during CO<sub>2</sub>RR and is often produced along with ethylene,<sup>1,13</sup> is strongly confined on *n*-CuNS for efficient C-C coupling rather than desorbed to form gas CO on CuNS and CuNP. Figure 3d shows a summary for the FE of ethylene and H<sub>2</sub> at various applied potentials on *n*-CuNS.

17 The electrochemical double-layer capacitance measurements 18 were performed to estimate the electrochemical surface area 19 (ECSA). The ECSA for *n*-CuNS is roughly 10- and 4-fold those 20 of CuNS and CuNP, respectively (Figure S9 and Table S3). It 21 indicates that n-CuNS can afford much more accessible active 22 sites than the other two catalysts. To compare the intrinsic activity for CO2RR, the ECSA-normalized current densities of 23 different products were obtained. It reveals that the activity of 24 CO<sub>2</sub>RR to ethylene on *n*-CuNS is intrinsically higher than those 25 on CuNS and CuNP (Figure S10). The stability of n-CuNS was 26 examined at -1.18 V (vs RHE) for 14 h, which shows a stable 27 ethylene FE of ~80% with current density ~60 mA cm<sup>-2</sup> over 28 the span of stability test (Figure 3e). The slight increase of 29 ethylene FE at the beginning (~2 h) can be attributed to the 30 initial activation of the catalyst layer.<sup>22,23</sup> The *n*-CuNS after 14 31 h CO<sub>2</sub>RR test was characterized, which shows that the nano-32 defective nanosheet morphology can be well maintained 33 (Figure S11). As compared with all the reported heterogeneous electrocatalysts, the n-CuNS catalyst displays the highest 34 ethylene FE and total current density under comparable 35 conditions (Figure 3f, Table S4). 36



**Figure 3.** Electrochemical  $CO_2RR$  performance. (a,b) Total current density (a) and ethylene FE (b) at various applied potentials for different catalysts. (c) Ethylene partial current density at various applied potentials for different catalysts. (d) FE of the products at various applied potentials for *n*-CuNS. (e) Chrono-amperometry and FE results of *n*-CuNS at a potential of -1.18 V vs RHE. (f) Performance of *n*-CuNS catalysts ompared with those of other  $CO_2$  to ethylene electrocatalysts in H-type cell.

To reveal the mechanism of the high activity of *n*-CuNS, the CO<sub>2</sub>RR process over *n*-CuNS was traced by in situ XANES and EXAFS spectra. The results show that the catalyst keeps identical species of Cu<sup>0</sup> during electocatalysis. Thus the influence of the well-known oxidized and constantly evolved Cu species for promoting ethylene production<sup>4-8,24-27</sup> can be excluded (Figure 4a,b and Figure S12). Linear sweep voltammetry (LSV) curve of *n*-CuNS exhibits an intense peak at ca. -0.2 V (Figure 4c). It indicates the existence of a large amounts of atomic defects on n-CuNS,<sup>28,29</sup> which is favorable for promoting the adsorptions to CO and OH- that are crucial to ethylene formation.<sup>4,12,13</sup> In contrast, the CuNS shows a largely suppressed peak, which is consistent with its smooth surface. To further confirm this, LSV curves of n-CuNS in N2-saturated electrolyte and CO-saturated electrolyte were determined, respectively. It shows that the difference between the current densities in N2-saturated and CO-saturated electrolytes of n-CuNS is larger than that of CuNS (Figure 4d), suggesting easier adsorption of CO on n-CuNS catalyst.30 Moreover, in situ Raman spectra reveal that the signal of adsorbed CO on n-CuNS is much more pronounced than that on CuNS (Figure S13). It suggests the enhanced adsorption of CO on n-CuNS catalyst during CO<sub>2</sub>RR, which is consistent with LSV results.<sup>1,9</sup> Furthermore the OH- electrosorption (OH<sub>ads</sub>) on *n*-CuNS was determined, which is influenced by local pH effect (Figures S14, 15).<sup>31,32</sup> The results show that *n*-CuNS catalyst has much pronounced (100), (110) and (111)  $OH_{ads}$  features,<sup>33,34</sup> while CuNS only presents a weak (111)  $OH_{ads}$  peak (Figure 4e).

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Such a concentrated effect of CO and OH- components in nano-defects was further investigated by electrolysis using a controlled convective flow.<sup>35-38</sup> As shown in Figure 4f, the n-CuNS electrode exhibits a ~50% enhanced CO<sub>2</sub>RR activity to ethylene with the increased rotation speed of electrode from 0 to 2000 rpm, while the CuNS electrode shows a decline of ~6%. It means that the reaction intermediates and OH<sup>-</sup> are strongly confined in n-CuNS for producing ethylene even under vigorous rotation.<sup>35-38</sup> Meanwhile, the mass transport can be accelerated at higher rotation speed.35 Therefore, the CO<sub>2</sub>RR efficiency to ethylene on n-CuNS electrode is much improved with increasing rotation speed of electrode. For CuNS, the reaction intermediates are weakly confined on its smooth surface, which can be easily lost by the increased rotation speed of electrode.<sup>37</sup> As a result, a low selectivity of ethylene was obtained on CuNS electrode with increasing rotation speed of electrode.

Density functional theory (DFT) calculations were employed to study the CO dimerization on *n*-CuNS and CuNS catalysts, which is a rate-determining step to ethylene production.<sup>39,40</sup> It reveals that the introduced Cu defect facilitates the adsorptions to the key reaction intermediates (\*CO and \*OCCO) (Figure 4g) and OH<sup>-</sup> (Figure S16). With the adsorbed OH<sup>-</sup>, the defective Cu (111) surface decreases the energy barrier for 110 meV in \*CO+\*CO  $\rightarrow$  \*OCCO step than that of the non-defective Cu(111) surface without OH<sup>-</sup> (Figure 4h). The calculations provide molecular-level insights into the enhanced OH<sup>-</sup> and reaction intermediate adsorptions on defective Cu, which are concentrated in one nano-defect for synergistically facilitating the CO dimerization process (Figures S17-20).



**Figure 4.** Mechanism investigation. (a) In situ Cu K-edge XANES spectra. (b) In situ Cu K-edge EXAFS spectra. (c) LSV curves of *n*-CuNS and CuNS. (d) LSV curves obtained on *n*-CuNS and CuNS catalysts in N<sub>2</sub>-saturated and CO-saturated electrolytes. (e) Voltammograms of  $OH_{ads}$  peaks collected in a 0.1 M KOH batch cell. (f) Convective effect on CO<sub>2</sub>RR, FE and *j* for ethylene as a function of rotation rate. (g) Comparison of adsorption energy of key intermediates that affect selectivity on different facets. (h) Energy diagrams and geometries of CO dimerisation on OH-adsorbed and defective Cu(111) of *n*-CuNS (red) and non-defective

Cu(111) of CuNS (black). Red, grey, white and blue stand for oxygen, carbon, hydrogen and copper atoms, respectively.

### CONCLUSION

Here we demonstrate the efficient production of ethylene from electrochemical reduction of CO<sub>2</sub> on nano-defective Cu nanosheets. The ethylene FE can reach a high value of 83.2%, with current density of ~60 mA cm<sup>-2</sup>. Experimental and calculation results reveal that the nano-defects on Cu nanosheet create concentrated atomic defects that favor the adsorption. enrichment and confinement for the reaction intermediates and OH-, which synergistically promote the C-C coupling for ethylene formation. Compared with the usually adopted strategies of random atomic defects for catalyst design, the construction of nano-scaled defects is more active and selective for  $C_2$  hydrocarbon production, which have great potential for practical applications. This work not only paves a promising approach for selectively producing single multi-carbon product from CO<sub>2</sub> electroreduction, but also provides a new insight for catalyst design through creating nano-scaled local environment.

## **EXPERIMENTAL SECTION**

**Synthesis of** *n***-CuNS.** CuO nanosheets were synthesized in a high concentrated alkaline solution. 50 mM CuCl<sub>2</sub> aqueous solution was mixed with 3 M NaOH in distilled water. The solution was vigorously stirred and then transferred into a Teflon-lined autoclave, sealed and heated at 100 °C for 12 h. The system was allowed to cool to room temperature naturally and the resulting product was centrifuged, rinsed with distilled water and ethanol several times to remove any alkaline salt and then dried in a vacuum oven at 60 °C for 4 h. The derived *n*-CuNS nanocatalyst was prepared via in situ CO<sub>2</sub> electroreduction at -1.08 V (vs RHE) from the CuO nanosheet electrode after an initial electrolysis running for 60 min.

**Synthesis of CuNS.** The CuNS catalyst was prepared according to the reported literature with small modification.<sup>22</sup> (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, 100 mg) and l-ascorbic acid (200 mg) were mixed with 30 ml deionized water were stirred to form a homogeneous solution. Then CTAB (200 mg) and HMTA (200 mg) were added followed by 30 min of stirring. The mixture solution was sealed and heated from room temperature to 80 °C and kept at 80 °C for 3 h in an oil bath. The resulting products were centrifuged, rinsed with distilled water and ethanol several times and then dried in a vacuum oven at 60 °C for 4 h.

Synthesis of CuNP. (Cu(NO<sub>3</sub>)<sub>2</sub>· $3H_2O$ , 300 mg) mixed with 10 mL deionized water were stirred to form a homogeneous solution. Then NaBH<sub>4</sub> (150 mg) was added followed by 10 min of stirring. The resulting products were centrifuged, rinsed with distilled water and ethanol several times and then dried in a vacuum oven at 60 °C for 4 h.

**Characterization.** Powder X-ray diffraction pattern was performed on a Rigaku D/max-2500 diffractometer with Cu Ka radiation ( $\lambda = 1.5418$  Å) at 40 kV and 200 mA. The morphologies were characterized by SEM (HITACHI S-4800), TEM (JEOL-1011) operated at 100 kV and high-resolution TEM (HRTEM, JEOL-2100F) operated at 200 kV. The HAADF-STEM characterization was performed on a JEOL JEM-ARF200F TEM/STEM with a spherical aberration corrector. AFM image was obtained on a tapping-mode atomic force microscope (Nanoscope IIIa, Digital Instruments, Santa Barbara, CA), with a silicon cantilever probes. XPS was measured by VG Scientific ESCALab220i-XL spectrometer

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using Al Ka radiation with 500 µm X-ray spot. The base pressure was about  $3 \times 10^{-10}$  mbar in the analysis chamber. Raman spectrum was obtained on a laser confocal Raman spectroscopy (Labram-010, Horiba-JY) employing the Nd: YAG laser wavelength of 633 nm). Wide-angle X-ray scattering measurements were performed at Beamline 1W2A at Beijing Synchrotron Radiation Facility (BSRF). The XAFS experiment was carried out at Beamline 1W1B at BSRF. Data of XAFS were processed using the Athena and Artemis programs of thee IFEFFIT package based on FEFF 6. Prior to merging, the spectra were aligned to the first and largest peak in the smoothed first derivative of the absorption spectrum, normalized and background removed. Data were processed by k<sup>3</sup>-weighting and an R<sub>bkg</sub> value of 1.0. Merged data sets were aligned to the largest peak in the first derivative of the adsorption spectrum. Normalized  $\mu(E)$  data was obtained directly from the Athena program of the IFEFFIT package. The quantitative structural parameters were obtained using a leastsquares curve parameter fitting method by ARTEMIS module.

**Preparation of working electrode.** The glassy carbon working electrode was prepared according to the commonly adopted method.<sup>5,7</sup> The catalyst ink was prepared through ultrasonically dispersing 2 mg of the sample powder with 5  $\mu$ l Nafion solution (5%) in 100  $\mu$ l ethanol for 30 min. Then 10  $\mu$ l of the catalyst ink was drop-coated on the glass carbon electrode with diameter of 3 mm. The electrode was then dried slowly at room temperature to obtain the working electrode for the subsequent electrochemical tests.

Electrochemical measurements. Electrochemical measurements and product identification and quantification were similar to protocols described in our previous work.<sup>41,42</sup> Electrocatalytic measurements were performed in a gas-tight two-compartment H-type cell with three electrode system using an electrochemical station (Chi660E). Pt gauze and Ag/AgCl (3.5 M KCl) electrode were used as the counter electrode and reference electrode, respectively. The working and reference electrodes keep small spacing (~0.5 cm) to minimize uncompensated solution resistance. A 0.1 M solution of K<sub>2</sub>SO<sub>4</sub> dissolved in 18.2 MOcm deionized water was used as the electrolyte. Each compartment contains 20 ml electrolyte and the electrolyte in the working-electrode compartment was bubbled with  $N_2$  or  $CO_2$  for at least 30 min to form  $N_2$  or  $CO_2$ saturated solution and maintained this flow rate during measurements. The working and reference electrodes were placed in the cathode chamber, while the counter electrode was placed in the anode chamber, which was separated by a piece of Nafion 117 ionic exchange membrane to avoid the re-oxidation of CO<sub>2</sub>RR-generated products. The measurements were performed at constant IR-corrected potential. Electrode potentials were converted to RHE using the following equation,  $E_{\rm RHE} = E_{\rm Ag/AgCl} + 0.21 \text{ V} + 0.0591 \times \text{pH}.$ 

ECSA referred the CV results under the potential windows of 0.42 V~0.52 V (vs RHE). To compare with the literature,<sup>17</sup> the LSV measurements for defective peak were performed similarly in CO<sub>2</sub>-saturated 0.1 M KHCO<sub>3</sub> electrolyte. LSV curves in N<sub>2</sub>-saturated and CO-saturated 0.1 M KHCO<sub>3</sub> electrolytes were obtained to detect the CO adsorption according to the reported literature.<sup>18</sup>

**Product analysis.** For product identification and quantification of gas, 2 ml of collected gas was injected into a gas chromatograph (GC, HP 4890D) during the chronoamperometry measurements at each 15 min to analyse

the concentration of gas products. The gas chromatograph was equipped with FID and TCD detectors using helium as the internal standard. The amounts of gas products were calculated from the peak areas of gas chromatography with conversion factors for ethylene,  $H_2$  and CO based on calibration of standard samples at 1.013 bar and 300 K. The liquid product was analyzed by <sup>1</sup>H NMR on Bruker AVANCE AV III 400, in which the used electrolyte was mixed with D<sub>2</sub>O (deuterated water). After the quantification, the faradaic efficiencies (FE) toward each product were calculated as follows:

$$FE(\%) = \frac{Amount of product \times n \times F}{C} \times 100$$

where *n* is number of moles of electrons to participate in the faradaic reaction, *F* is the Faraday constant (96485 C mol<sup>-1</sup>), and *C* is the amount of charge passed through the working electrode.

**Rotating disk electrode measurements.** Rotating disk electrode measurements was controlled using a Pine Modulated Speed Rotator in a three-electrode electrochemical cell with an air-tight seal. The electrodes were polished and sonicated using a bath sonicator for 5 min prior to each experiment. Rotation rate dependent product determination were measured by conducting controlled potential electrolysis at -1.18 V (vs RHE) in CO<sub>2</sub>-saturated 0.1 M K<sub>2</sub>SO<sub>4</sub> electrolyte. For a given rotation rate, the formed gases were detected by GC after the generated gases were equilibrated in the headspace. The rotation rate was varied in the following order, 2000, 1000, 1500, 500 rpm.

**In-situ X-ray absorption spectroscopy.** The XAFS experiment was carried out at Beamline 1W1B at BSRF. A home-made plastic electrochemical cell was employed for in situ XAS measurement under the sensitive fluorescence model. The cell was filled with electrolyte saturated with CO<sub>2</sub>. Ag/AgCl and Pt gauze were used as reference electrode and counter electrode, respectively. The working electrode compartment had walls with a single square hole of 1.0 cm in edge length. A catalyst/thin carbon paper as the working electrode was in contact with a slip of copper tape and fixed with Kapton (polyimide) tape to the exterior of the wall of the cell, over the hole, catalyst layer facing inwards. During the measurement, the XAS data was collected at different time.

Computational details for calculations. Spin-polarized density functional theory calculations were performed using DMol<sup>3</sup> package with the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) exchangecorrelation functional. Three layers of 4x4 Cu(111) and Cu (100) surfaces which contain 48 Cu atoms was chosen as the catalysts, and the defective 4x4 Cu(111) and Cu(100) surfaces which contains 47 Cu atoms were comparatively studied. The density functional semicore pseudopotential (DSPP) was chosen to describe the Cu atoms. During the geometry optimization, the tolerances of energy and force were 2×10<sup>-5</sup> Ha and 0.004 Ha/Å, and the maximum displacement was  $5 \times 10^{-3}$  Å, respectively. The Monkhorst-Pack scheme k-point meshes were 2×2×1. The adjacent slabs were separated by a vacuum layer of 12 Å thickness along the z-direction, thus the real Cu surface can be created. The adsorption energy  $(E_{ads})$ of different adsorbates on both the non-defective and the defective Cu surfaces were calculated according to:

$$E_{ads} = E_{total} - (E_{surface} + E_{adsorbate})$$

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Page 6 of 8

where  $E_{ads}$  is the adsorption energy of various adsorbates which includes the mono or/and the coexisted OH<sup>-</sup>, CO and OCCO;  $E_{total}$  is the total energy for the adsorption state,  $E_{surface}$  is the energy of either the non-defective or the defective Cu surface,  $E_{adsorbate}$  is the energy of accumulated adsorbates.

The coupling energy barrier of OCCO was calculated using the equations formula:

 $E_{\text{OCCO coupling}} = E_{\text{OCCO}} - E_{2\text{CO}}$ 

## ASSOCIATED CONTENT

**Supporting Information**. This material is available free of charge via the Internet at http://pubs.acs.org. The Supporting Information including the additional SEM, TEM, EDS Mapping, AFM and HRTEM images, XRD patterns, XPS spectra, electrochemical performance of materials and simulation details.

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Notes

The authors declare no competing financial interests.

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