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Authors
Ebaid, Mohamed
Jiang, Kun
Zhang, Zemin
et al.

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Production of C$_2$/C$_3$ Oxygenates from Planar Copper Nitride-Derived Mesoporous Copper via Electrochemical Reduction of CO$_2$

Mohamed Ebaid$^\dagger$, Kun Jiang$^{\dagger,\S,\¥,\*}$, Zemin Zhang$^\dagger$, Walter S. Drisdell$^{\dagger,\S}$, Alexis T. Bell$^{\dagger,\S,\*}$, and Jason K. Cooper$^{\dagger,\S,\*}$

$^\dagger$Joint Center for Artificial Photosynthesis, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA
$^\S$Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA
$^\¥$Department of Chemical and Biomolecular Engineering, University of California, Berkeley, California 94720, USA
$^\*$School of Mechanical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

$\dagger$Contributed equally

*E-mail: jkcooper@lbl.gov and alexbell@berkeley.edu
ABSTRACT

Electrochemical reduction of CO$_2$ provides an opportunity to produce fuels and chemicals in a carbon-neutral manner, assuming that CO$_2$ can be captured from the atmosphere. To do so, requires efficient, selective, and stable catalysts. In this study, we report a highly mesoporous metallic Cu catalyst prepared by electrochemical reduction of thermally nitrided Cu foil. Under aqueous saturated CO$_2$ reduction conditions, the Cu$_3$N-derived Cu electrocatalyst produces virtually no CH$_4$, very little CO, and exhibits a Faradaic efficiency of 68% to C$_{2+}$ products (C$_2$H$_4$, C$_2$H$_5$OH, and C$_3$H$_7$OH) at a current density of ~18.5 mA cm$^{-2}$ and a cathode potential of -1.0 V vs. the reversible hydrogen electrode (RHE). Under these conditions, the catalyst produces more oxygenated products than hydrocarbons. We show that surface roughness is a good descriptor of catalytic performance. The roughest surface reached 98% CO utilization efficiency for C$_{2+}$ product formation from CO$_2$ reduction and the ratio of oxygenated to hydrocarbon products correlates with the degree of surface roughness. These effects of surface roughness are attributed to the high population of under-coordinated sites as well as a high pH environment within the mesopores and adjacent to the surface of the catalyst.
INTRODUCTION

Anthropogenic emissions of greenhouse gases are responsible for the increase in global mean temperature, which is threatening the Earth’s ecosystem and its inhabitants. Therefore, there is a strong interest in exploring strategies for using atmospheric CO₂ as a renewable source of carbon to produce transportation fuels and chemicals. A possible route towards achieving this goal is electrochemical reduction of CO₂. Successful development of this concept into a technology requires the discovery and development of energy-efficient, stable, and selective catalysts for producing hydrocarbons and alcohols. Though various transition metals, metal alloys, and chalcogenides have been reported to promote the electrochemical CO₂ reduction reaction (CO₂RR), Cu remains the only electrocatalyst capable of generating multi-carbon products from CO₂/CO with high Faradaic efficiency (FE).

Different strategies have been explored to improve the selectivity towards multi-carbon products on Cu. Roughening Cu surfaces by the in-situ reduction of Cu₂O or Cu₃N during CO₂ reduction has been found to be the most efficient way to achieve a high selectivity C₂⁺ products in aqueous electrolytes. Such modified Cu surfaces have been reported to generate catalytically active sites by the creation of intrinsic defects such as grain boundaries, stepped sites, and other surface defects, which can bind CO and other intermediates strongly and promote C-C bond formation. Other factors such as local pH, temporal intermediates trapping by nano-/meso-cavities and cation-induced electric fields have also been found to enhance the formation of multi-carbon products. The relatively low selectivity to products involving more than two carbon atoms, in particular C₃ products (allyl alcohol and n-propanol), also remains an issue for virtually all Cu-based catalysts. Although surface roughening has contributed to the selective formation of multi-carbon products on Cu, there remains a need for novel ways to produce Cu surfaces with a more controlled roughness in order
to clearly investigate the structure-activity relationship of CO$_2$RR performances.

Herein we report a novel method to produce highly roughened mesoporous Cu catalyst that significantly differs from the single crystalline Cu electrodes produced by Bridgeman method$^{10}$ or metal ion battery cycling$^{11}$ as well as the electrochemically deposited Cu$_2$O oriented films on Cu substrates$^{15}$. This mesoporous Cu catalyst delivers state-of-the-art performance for aqueous CO$_2$RR. At -1.0 V vs. the reversible hydrogen electrode (RHE), the Faradaic efficiency to multi-carbon products (C$_{2+}$) exceeds 68%, and ~35% of this amount is in the form of C$_{2+}$ oxygenates of which ~10% is n-propanol (C$_3$). Only 1.1% CO and no detectable methane are formed at a current density of ~18.5 mA.cm$^{-2}$. Uniform Cu$_3$N films are produced by thermal nitriding of Cu foil at atmospheric pressure in a stream of NH$_3$/O$_2$. These materials are characterized in-situ by X-ray diffraction (XRD) and ex-situ by high-resolution scanning transmission electron microscopy (HR-STEM), X-ray absorption spectroscopy (XAS), and X-ray photoelectron spectroscopy (XPS). Under CO$_2$RR conditions, the Cu$_3$N precursor is reduced to a highly porous metallic Cu structure, exhibiting an electrochemical surface roughness > 17 compared to an electro-polished Cu foil. The outstanding CO$_2$RR performance of such Cu$_3$N-derived Cu is attributed to a high population of under-coordinated Cu sites as well as an increase in surface pH from local reaction environment.

EXPERIMENTAL SECTION

**Cu$_3$N CVD fabrication.** Polycrystalline Cu foils (Alfa Aesar; 0.1 mm thick, Puratronic, 99.999% metals basis) were first rinsed with Milli-Q water, dried with nitrogen, and then electrochemically polished in phosphoric acid (85% in water) by applying +2.1 V versus a graphite rod for 5 min. For the synthesis of the Cu$_3$N layer, the pre-cleaned Cu foil was loaded into a horizontal quartz tube reactor and heated by a two-zone Mellen furnace equipped with clamshell heating elements. Quartz tube and gas lines were
carefully evacuated prior to the introduction of the reactive gases. The Cu foil was then annealed at 550 °C in an NH₃/O₂ mixture for a period of 15 to 60 min at atmospheric pressure. The flows of NH₃ and O₂ were introduced through calibrated mass flow controllers in order to achieve a total flow rate of 75 sccm, with a nominal concentration of 2 vol% O₂. The annealed Cu foils were slowly cooled down to room temperature under the same gas environment before they were taken out of the reactor.

**Physical characterization.** *In-situ* XRD diffraction patterns were obtained using a Rigaku Smartlab X-ray diffractometer equipped with a ReactorX attachment; a corrosion resistant high-temperature reactor, and a HyPix-3000 high-energy-resolution 2D multidimensional semiconductor detector. The incident X-ray beam was filtered using a double-crystal high-resolution PB-Ge (220)x2 monochromator. The surface morphology was visualized using SEM (Quanta FEG 250, FEI). The microstructures were investigated by cross-sectional HAADF-STEM using a probe-corrected FEI Titan Themis 300 S/TEM with ChemiSTEM technology operated at 300 kV. TEM sample preparation was performed using the standard lift-out procedure with an FEI Scios Dual-Beam focused ion beam (FIB)-SEM system. EDS analysis was performed at 300kv using a Super-X EDS system. The surface compositions were investigated using XPS acquired by a Kratos Axis Ultra spectrometer using an Al Kα source (hv = 1486.69 eV) operated at 225 W and a hemispherical electron energy analyzer. XPS binding energies were calibrated using adventitious alkyl carbon signals by shifting the C 1s peak to 284.8 eV. The XAS data were acquired at beamline 9-3 (BL9-3) at Stanford Synchrotron Radiation Lightsource (SSRL), SLAC National Accelerator Laboratory. The SPEAR3 storage ring operated at 500 mA and 3.0 GeV. BL9-3 is equipped with a rhodium-coated vertical collimating mirror upstream of the Si(220) monochromator and an additional downstream rhodium-coated bent-cylindrical focusing mirror. Harmonic rejection was accomplished by setting the cut-off angle of the mirrors to an appropriate energy. Incident and transmitted X-rays were monitored using gas ionization chambers and X-ray
absorption was measured as the primary fluorescence excitation spectrum using an array of 100-element Ge detector.

**Electrochemical measurements.** All electrochemical experiments were conducted in a gas-tight electrochemical cell machined from polyether ether ketone (PEEK). A graphite rod (99.995%, Sigma Aldrich) was used as the counter electrode, placed parallel to the working electrode and separated by an anion conducting membrane (Selenium AMV AGC Inc.). Gas dispersion frits were incorporated into both electrode chambers to provide ample electrolyte mixing. The exposed geometric surface area of each electrode was 1 cm² and the electrolyte volume of each electrode chamber was 1.8 cm³. A leak-free Ag/AgCl electrode (Innovative Instruments Inc.) was used as the reference electrode, all potentials were measured against Ag/AgCl and then converted to the RHE scale using the relationship $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 \text{ V} + 0.0591 \times \text{pH}$, where pH values of electrolytes were determined by an Orion Dual Star Benchtop Meter (Thermo Scientific). A 0.05 M $\text{M}_2\text{CO}_3$ (99.995%, Sigma Aldrich) solution prepared using Milli-Q water was used as the electrolyte. Metallic impurities in the as-prepared electrolyte were removed before electrolysis by chelating the solution with Chelex 100 (Na form, Sigma Aldrich). Both electrode chambers were sparged with CO$_2$ (99.999%, Praxair Inc.) at a rate of 20 sccm for 40 min prior to and throughout CO$_2$ electrolysis. Prior to CO$_2$RR measurements, a pre-reduction step was carried out for 90 min chronoamperometry at -0.6 V in CO$_2$-saturated 0.1 M CsHCO$_3$. Electrochemistry was performed with a Biologic VSP-300 potentiostat. Potentiostatic electrochemical impedance spectroscopy (PEIS) and current interrupt (CI) methods were used to determine the uncompensated resistance ($R_u$) of the electrochemical cell. The potentiostat compensated for 85% of $R_u$ in situ. The roughness factors of Cu foil electrodes were determined relative to the electrochemically polished one, by taking the ratio of their double layer capacitances measured after 1-h electrolysis.
**CO\textsubscript{2}RR products quantification.** The effluent from the electrochemical cell was analyzed using an Agilent 7890B gas chromatograph (GC) equipped with a pulsed-discharge helium ionization detector (PDHID). He (99.9999%, Praxair Inc.) was used as the carrier gas. The constituents of the gaseous sample were separated using a Hayesep-Q capillary column (Agilent) connected in series with a packed ShinCarbon ST column (Restek Co.). The signal response of the PDHID was calibrated by analyzing a series of NIST-traceable standard gas mixtures (Airgas Inc.). The partial current density for a given gas product was calculated as \( j_i = x_i \times v \times \frac{n_i F p_0}{RT} \times \frac{1}{\text{electrode area}} \), where \( x_i \) is the volume fraction of certain product determined by online GC, \( v \) is the flow rate, \( n_i \) is the number of electrons required to form product \( i \), \( p_0 = 101.3 \text{ kPa} \), \( F \) is the Faradaic constant and \( R \) is the gas constant. The corresponding FE at each potential is calculated using the relationship \( \text{FE} = \frac{j_i}{i_{\text{total}}} \times 100\% \). The electrolyte from cathodic chamber was collected after electrolysis and analyzed using a Thermo Scientific UltiMate 3000 liquid chromatography (HPLC) equipped with a refractive index detector (RID). The electrolyte samples were stored in a refrigerated autosampler at 10 °C before analysis to minimize the evaporation of volatile products. The liquid-phase products contained in a 20 µL aliquot were separated using two Aminex HPX 87-H columns (Bio-Rad Inc.) connected in series and a 1 mM sulfuric acid eluent (99.999%, Sigma Aldrich). The column oven was maintained at 60 °C for the duration of the analysis. The signal response of the RID was calibrated by analyzing standard solutions of each product at a concentration of 1, 10, and 50 mM.

**RESULTS AND DISCUSSION**

Cu\textsubscript{3}N was prepared by thermal annealing of an electropolished Cu foil at atmospheric pressure in a NH\textsubscript{3}/O\textsubscript{2} mixture for 15 to 60 min at a temperature of 550°C which resulted in formation of a film of Cu\textsubscript{3}N on the surface of the
Cu foil. The growth of Cu$_3$N proceeds from top to bottom. It starts with the formation of a surface copper oxide that serves to activate the dehydrogenation of NH$_3$ producing water and copper nitride.\textsuperscript{26, 27,28, 29} After thermal nitriding, the resulting film has a green color and is confirmed by XRD to be Cu$_3$N, which has an anti-ReO$_3$ (anti-perovskite) cubic structure built up of eight corner-sharing NCu$_6$ octahedra (Figure 1A).

The relatively smooth surface of the electropolished Cu foil was significantly roughened as a result of the formation of Cu$_3$N, as revealed by scanning electron microscopy (SEM) (Figure 1B and 1C). This can be attributed to the crystallographic transformation of the Cu crystal lattice to accommodate the nitrogen atoms.\textsuperscript{30} The Cu molar density is 0.141 and 0.09 mol cm$^{-3}$ for Cu and Cu$_3$N, respectively. As such, a volumetric expansion of the Cu atomic density by a factor of 1.6 is necessary to accommodate the inclusion of the N atoms into the crystal. Considering the process temperature is well below the melting point of either material, the resulting film is significantly roughening by the transformation from Cu to Cu$_3$N. The degree of surface roughness was controlled by adjusting the nitriding time (Supporting Information, Figure S1); increasing the nitriding time increased the surface roughness.

To gain further insight into the mechanism of Cu$_3$N formation, the evolution of crystalline phase was monitored as a function of time and temperature by \textit{in-situ} out-of-plane XRD using a temperature-controlled reactor (ReactorX, Rigaku-Smartlab). This leak-tight reactor enables real-time XRD measurements while keeping the sample at well-controlled temperature and in a well-controlled atmosphere. To reproduce the same conditions as those in the nitridation furnace, the same flow rates of NH$_3$ and O$_2$ but diluted by Ar (to reduce the NH$_3$ concentration to acceptable levels for the ReactorX) were fed to the XRD reactor through calibrated mass flow controllers. The Cu foil was heated to and maintained at 550°C for 1 h, after which it was slowly cooled down to room temperature under the same gas composition (Supporting Information, Figure S2). As shown in Figure 1D, the
formation of Cu$_3$N begins during heating at 400°C and is characterized by the appearance of diffraction peaks centered at 23.27° and 47.18°. These features are assigned to the (100) and (200) crystallographic planes of Cu$_3$N, respectively. The Cu$_3$N formed exhibits a preferential orientation around (100)-planes with weak contributions from (111) and (210). The underlying Cu crystal exhibits a temperature-dependent lattice constant due to thermal expansion (Supporting Information, Figure S3).\textsuperscript{30} The crystalline quality of the Cu$_3$N was found to depend critically on the cooling rate. Rapid cooling led to poor Cu$_3$N crystallinity. These observations indicate that Cu$_3$N can be grown by activating NH$_3$ at a temperature as low as 400°C, a temperature that is much lower than that reported for similar growth techniques using nitrogen-based gas phase precursors.\textsuperscript{27, 31} The mechanism of Cu$_3$N formation and growth by this technique will be discussed in a separate study.
**Figure 1.** *In-situ* growth and surface morphology of Cu$_3$N. (A) Cu$_3$N primitive unit cell structure (space group Pm-3m) with a lattice parameter of 3.81Å. Opposite to perovskites, N anion is located in Cu$_3$N at the octahedron center, whereas six Cu cations form a regular octahedron. Tilted-view SEM surface morphology of (B) electro-polished Cu foil and (C) Cu$_3$N (30 min annealing). Insets, micrographs of the Cu foil before (B) and after (C) the thermal annealing. (D) Temperature-dependent crystalline phase evolutions obtained by *in-situ* XRD.

To determine the differences in the elemental composition and the oxidation state of Cu before and after the Cu-to-Cu$_3$N transformation, the electronic structure of the Cu$_3$N was investigated by X-ray absorption near-edge structure (XANES) at the Cu K-edge. As shown in Figure 2A, the XANES spectrum of Cu$_3$N is distinct from that of metallic Cu due to the incorporation
of N atoms. The pre-edge peak of Cu$_3$N appears at 8983 eV, which is a slightly higher than the binding energy for metallic Cu. This difference is a consequence of the difference in the oxidation states of the Cu ions in Cu$_3$N and metallic Cu. The Cu K-edge XANES spectrum of the Cu$_3$N was also compared with the spectra collected for Cu$_2$O, CuO, and Cu(OH)$_2$ (Supporting Information, Figure S4). The absorption edge of the Cu$_3$N is located between those of the metallic Cu and the CuO, indicating that the oxidation state of copper ions in Cu$_3$N to be 1+, consistent with expectations.$^{32-34}$ The assignment of the 1+ oxidation state is also supported by XPS (Figure S5) which demonstrates no satellite peaks in the Cu 2p spectrum of the as-prepared Cu$_3$N.

The local coordination environment of Cu atoms in Cu$_3$N was also probed by extended X-ray absorption fine structure (EXAFS) at the Cu K-edge (Figure 2B). The coordination structure of Cu in Cu$_3$N is observed to have a strong peak due backscattering from atoms in the first coordination shell at a radial distance of 1.5 Å, in good agreement with the expected first shell scatting path of 1.45 Å. A second smaller peak at 2.1 Å was also observed. Since the expected second shell of Cu$_3$N is at 2.35 Å, this feature is more likely related to underlying metallic copper.$^{32, 35-37}$ The combined XAS and EXAFS results demonstrates the successful incorporation of N atoms into Cu to form Cu$_3$N.
Figure 2. Fine structure and electronic states of Cu$_3$N. (A) Cu K-edge XANES spectra of the phase-pure Cu$_3$N compared to the Cu foil. Inset, a magnified view for the absorption edge shift. (B) Local coordination structure of the phase-pure Cu$_3$N and the Cu foil.

The nanostructure for the 30-min nitried Cu$_3$N film was characterized by cross-sectional high-angle annular dark-field (HAADF)-STEM. A relatively uniform layer of Cu$_3$N was observed with a thickness of approximately 600 nm (Figure 3A). The formation of Cu$_3$N was accompanied by the appearance of a number of micro-voids at the interface between Cu$_3$N film and Cu foil bulk region (Supporting Information, Figure S6). The formation of these voids could be attributed to strain related defects formed during the growth of Cu$_3$N by the insertion of nitrogen atoms into the Cu lattice. They can also be due to oxygen impurities in the Cu foil such as native oxygen or due to the formation of surface oxide layers during thermal annealing which tend to form micro-voids at elevated temperatures. 38, 39 Both the high-resolution
transmission electron microscopy (HR-TEM) (Figure 3B) and the selective area electron diffraction (SAED) pattern (Figure 3C) are indicative of highly ordered cubic crystalline structure of phase-pure Cu$_3$N and the absence of any metallic Cu or Cu oxide phases within the Cu$_3$N layer. Elemental mapping by energy-dispersive X-ray spectroscopy (EDS) (Figure 3D) demonstrates that nitrogen is uniformly distributed within the Cu$_3$N film with a distinct termination at the Cu$_3$N/Cu foil interface (Supporting Information, Figure S7).

Prior to the electrochemical CO$_2$RR measurements, as-prepared Cu$_3$N was pre-treated by electrochemical reduction at -0.6 V vs. RHE in 0.1 M CO$_2$-saturated CsHCO$_3$ electrolyte for 90 min in the same manner as that done for oxide-derived Cu.$^{10,11,15}$ Figure S8 shows the pre-treatment current of the 30-min annealed Cu$_3$N. During the first 8 min a current transient was observed which amounted to 1.2 C equating to 4.15 μmol Cu$_3$N reduced; over the entire 90 min, 8.13 C or 28.1 μmol equivalent of Cu$_3$N was passed. Given the layer thickness (~600 nm) and the geometric area of the electrode, only 1.8 μmol of Cu$_3$N was expected. These observations indicate that the pre-treatment was sufficient to convert the Cu$_3$N layer to metallic Cu. After electrochemical pre-treatment, cross-section imaging shows the uniform Cu$_3$N layer is converted into a highly porous interconnected network (Figure 3E and Figure S9). Both HR-TEM (Figure 3F) and the SAED pattern (Figure 3G) demonstrate that Cu$_3$N is converted back to metallic Cu during the pre-treatment. The SAED shows a cubic pattern with 0.18 nm d-spacing, corresponding to exposed Cu (200) square lattice. This finding is in good agreement with out-of-plane XRD (Figure 3J), which showed a strong diffraction peak centered at 50.8° corresponding to metallic Cu (200). The formation of (200)-oriented Cu after the electrochemical reduction can be attributed to the lower work function and higher surface energy of the (200) facet than those for the (111) facet, which can lead to a higher etching rate in this direction.$^{40,41}$ Furthermore, the exposure of Cu (200) planes was reported to promote the evolution of C$_2$ products such as ethylene and suppress the formation of methane.$^{10,11}$ Moreover, no nitrogen signal was
detected by EDS mapping (Figure 3H), selective area EDS (Figure 3I), or XPS (Figure S5), further supporting the complete transformation of Cu₃N into metallic Cu during the pre-treatment step. An oxygen signal was evident in the EDS spectrum of the reduced Cu₃N sample (Figure 3I), which is most likely related to sample transfer and air exposure of the sample.

The formation of the highly porous metallic Cu film during the pre-treatment electrochemical reduction of Cu₃N is the result of removal of nitrogen from the lattice. As discussed, the molar densities of Cu atoms in Cu₃N and Cu is 0.141 and 0.090 mol cm⁻³, respectively. Densification of the Cu atoms by a factor of 1.6 through removal of nitrogen produces a highly porous structure, which we attribute to film strain-induced void formation. The electrochemical reduction done at room temperature may be responsible for maintaining a high degree of porosity in the layer during its transformation. Further roughening might be possible by lowering the temperature with an ice bath or in non-aqueous electrolytes but confirmation of this hypothesis will require further investigations. We also note that CuP₁₀ would have a densification factor of 19.6 potentially providing access to even greater volume contraction and further roughening.
Figure 3. Microstructure and elemental composition of Cu$_3$N-derived Cu. (A) Cross-sectional HAADF-STEM view of the 30-min annealed Cu$_3$N layer. (B) Atomic-scale HR-TEM of the as-prepared Cu$_3$N layer (scale bar is 5 nm). (C) SAED pattern of the as-prepared Cu$_3$N layer. (D) STEM-EDS maps of as-prepared Cu$_3$N. (E) Cross-sectional HAADF-STEM view of the Cu$_3$N layer after 90 min electrochemical reduction. (F) Atomic-scale HR-TEM of the reduced Cu$_3$N layer (scale bar is 5 nm). (G) SAED pattern of the reduced Cu$_3$N layer. (H) STEM-EDS maps of the reduced Cu$_3$N layer. (I) Selective area EDS of the Cu$_3$N layer before and after the electrochemical reduction compared to the electrochemically polished Cu foil. (J) Out-of-plane XRD of the same samples shown in (I).

The CO$_2$ reduction activity of 30-min annealed Cu$_3$N-derived Cu was evaluated by chronoamperometric electrolysis in CO$_2$-saturated 0.1 M CsHCO$_3$ electrolyte.$^{42, 43}$ CsHCO$_3$ was selected because Cs$^+$ has the smallest hydrated cation radius compared to other alkali metal cations, which lead to a higher concentration of cations at the cathode and a larger surface charge density. This latter creates a stronger double layer field, which, in turn, enhances the adsorption of CO$_2$ and stabilizes the formation of OCCO, an
intermediate in the formation of C₂ products. Figure 4A shows the steady-state current densities averaged over 1-h electrolysis at each potential, with the H₂, C₁, C₂, and C₃ product distributions plotted in Figure 4B. A portion of missing FE observed at -0.6 V, probably arisen from the reduction current of Cu₂O formed during electrolyte switch after the pre-reduction step. The potential-dependence of each product is plotted in Figure 4C. The H₂ FE gradually decreases as the potential is reduced from -0.6 to -0.9 V vs. RHE, then increases slightly again when the potential reaches -1.0 V vs. RHE due to mass-transport limited current of dissolved CO₂. Formate is another dominant product at low overpotentials. The FE for formate reaches a maximum FE of 35.2% at -0.7 V and then decreases with decreasing potential. Notably, no CH₄ was observed throughout the investigated potential region. The FE for CO, a vital intermediate for multi-carbon products, decreases monotonically from -0.6 V vs. RHE (FE = 21.3%) to -1.0 V vs. RHE (FE = 1.1%), whereas the FEs for C₂ (ethylene and ethanol) and C₃ products (allyl alcohol and n-propanol) increase correspondingly. C₂H₄ evolution starts at -0.7 V vs. RHE and the generation of oxygenates, involving >2e, starts at ~ -0.8 V, for which the overall C₂⁺ FE gradually increases with decreasing applied potential. At -1.0V, this nitride-derived Cu electrode delivers a geometric current density of ~18.5 mA cm⁻² (see also Figure S10 of partial current densities for each product at different applied potentials), reaching a maximum C₂⁺ FE above 68% of which ~35% is due to oxygenates. Taking H₂ and C₂H₄ as representative CO₂RR products, we find that the FEs for these products remains stable with prolonged electrolysis (Figure S11). To the best of our knowledge, this is one of the most selective catalyst for producing multi-carbon products reported to date (Supporting Information, Table S1). We have recently proposed that the Cu surface roughness factor (RF) is a good descriptor for selectivity to multi-carbon product formed via the CO₂RR over Cu. Higher surface roughness increases the exposure of under-coordinated Cu surface sites that strongly bind adsorbed CO, thereby
promoting the reduction of adsorbed CO rather than its desorption, and creating square sites next to steps that stabilize intermediates (e.g., OC-CO, OC-CHO) involved in the formation of C₂ products (C₂H₄ and C₂H₅OH).²¹,⁵⁴

Figure 4. Electrocatalytic CO₂RR performance of electrochemical reduced Cu₃N catalyst within 0.1 M CO₂-saturated CsHCO₃ electrolyte. (A) steady-state current density averaged from 1-h electrolysis, together with potential-dependence of (B) Faradaic efficiencies for H₂, C₁, C₂, and C₃ products, and (C) detailed distribution of major CO₂RR products for a 30-min thermal annealed Cu₃N electrode (RF = 17.67).

The electrochemical surface area (ECSA), representative of the RF, of Cu₃N-derived Cu after 1-h CO₂RR electrolysis was determined by referencing to the double-layer capacitance of electro-polished Cu foil (RF = 1.00).
surface RF of Cu₃N-derived Cu was altered by varying the thermal annealing time (see Figure S12). For 15-, 30-, and 60-min annealed samples the RF was 16.78, 17.67 and 19.78, respectively. The ratio of C_{2+}/C_{1} products increased with increasing RF from 1.00 to 17.67 then leveled off to 19.78, as shown in Figure 5A. The CO₂ consumption rate is ca. ~ 30.45 nmol s⁻¹ cm⁻² on the most roughened Cu surface. This rate is close to the CO₂ mass transport limitation over a planar electrode in aqueous solution⁴³ suggesting a balance between RF and C_{2+} efficiency due to limitations of adsorbed CO availability for further C-C bond formation.

To compare the role of RF on the multi-carbon products selectivity in CO₂RR further, we examined roughened Cu foil electrodes produced by Ar⁺ plasma bombardment for which the RF ranged from 1.42 to 3.64. Figure 5B shows the roughness dependence of the ratio of C_{2+} to overall CO₂ reduction products. Both Cu₃N-derived Cu catalysts and Ar⁺ ion-roughened Cu foils follow a clear trend in RF; the C_{2+} selectivity increases with increasing Cu surface roughness independent of how the surfaces is roughened. This observation reinforces our earlier interpretation that controlled RF is of critical importance for improving CO₂RR efficiencies and selectivity. Increasing under-coordinated Cu sites improves multi-carbon product efficiency by binding adsorbed CO more strongly as compared to low-index Cu facets (e.g., Cu(111) and Cu(100)). Furthermore, an increased concentration of surface sites which having strong binding of CO also suppress the competitive adsorption of H (Figure S13), thus leading to an increased oxygenate/hydrocarbon ratio (Figure 5C). We also note that the high density of nanoscale-voids in the porous structure of the electrodes is expected to lead to an increase in the local pH at the electrode-electrolyte interface and, in turn, on the C_{2+}/C_{1} selectivity. Hori et al. has reported that high local pH can largely suppress CH₄ generation.¹⁹ We also note that the high density of nanoscale-voids in the electrode porous structure is expected to increase the local pH at the electrode-electrolyte interface and, in turn, suppressing methane generation with an increase on the C_{2+}/C_{1+} selectivity.
**Figure 5.** Surface Roughness dependence of CO$_2$RR products distribution. (A) Faradaic efficiency ratio of C$_2^+$ products versus C$_1$ products generated on Cu$_3$N-derived catalysts, with electro-polished Cu foil as reference (RF = 1.0), as a function of the surface roughness measured at a cathode potential of -1.0 V vs RHE. (B) C$_2^+$ products selectivity and (C) Faradaic efficiency ratio of oxygenate versus hydrocarbon products illustrated for physically roughened Cu foils obtained by Ar-plasma pretreatment and Cu$_3$N-derived Cu electrodes prepared with different annealing times; all measurements were made at a cathode potential of - 1 V vs RHE, within 0.1 M CO$_2$-saturated CsHCO$_3$.

**CONCLUSIONS**

In conclusion, we have developed an efficient Cu$_3$N-derived Cu catalyst that exhibits an exceptionally high Faradaic efficiency to C$_2^+$ products for CO$_2$ reduction in an aqueous solution of CsHCO$_3$ (0.1 M). The Cu$_3$N was formed by annealing a Cu-foil at temperatures as low as 400 °C in a mixture of NH$_3$/O$_2$. The active catalyst is produced by 90 min of electrochemical reduction of the Cu$_3$N covered Cu-foil in 0.1 M CO$_2$-saturated CsHCO$_3$ electrolyte. Analysis shows that all of the nitrogen in the as-prepared Cu$_3$N was eliminated leaving behind a mesoporous Cu structure that has ~ 17 times the roughness of the electro-polished Cu foil. The resulting Cu catalysts exhibits a Faradaic efficiency to C$_2^+$ products exceeding 68%, of which ~35% is C$_2^+$ oxygenates, when operated at a cathode potential of -1.0 V vs. RHE and a current density
of ~18.5 mA.cm$^{-2}$. The results of the present study extend those we reported recently for Cu roughened by Ar$^+$ bombardment in an Ar plasma and by oxidation in an O$_2$ plasma. In both cases, the Cu surface was roughened by up to a factor of four relative that of the starting electro-polished Cu surface. The performance of these catalysts demonstrated to be independent of the method of roughening and the active catalyst in all cases is metallic Cu. As illustrated in Fig. 5B, the ratio of C$_2$+/($C_1$+$C_2$+$C_3$) products increases monotonically with increasing roughness.

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Supporting Information:

Surface morphology as a function of annealing time, XRD analysis, XAS, XPS, FIB/SEM, TEM/EDS, CA of the electrochemical reduction of Cu$_3$N into metallic Cu, HR-TEM of Cu$_3$N before and after the electrochemical reduction, partial current densities of C-products, CO$_2$ reduction stability, ECSA on Cu$_3$N samples with varied annealing time, surface roughness impact on the H$_2$ Faradaic efficiency, and CO$_2$RR performance summary