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Cu_3N Nanocubes for Selective Electrochemical Reduction of CO_2 to Ethylene

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Keywords: CO_2 reduction • copper(I) nitride • perovskite structure • nanocubes • ethylene formation

Abstract: Understanding Cu-catalyzed electrochemical CO_2 reduction reaction (CO_2RR) under ambient conditions is both fundamentally interesting and technologically important for selective CO_2RR to hydrocarbons. Current Cu-catalysts studied for the CO_2RR can show high activity, but tend to yield a mixture of different hydrocarbons, posing a serious challenge on using any of these catalysts for selective CO_2RR. Here, we report a new perovskite-type copper(I) nitride (Cu_3N) nanocube (NC) catalyst for selective CO_2RR. The 25 nm Cu_3N NCs show high CO_2RR selectivity and stability to ethylene (C_2H_4) at -1.6 V (vs reversible hydrogen electrode (RHE)) with the Faradaic efficiency of 60%, mass activity of 34 A/g and C_2H_4/CH_4 molar ratio > 2000. More detailed electrochemical, X-ray photon spectroscopy, and density functional theory calculation suggest that the high CO_2RR selectivity is likely a result of (100) Cu(I) stabilization by the Cu_3N structure, which favors CO-CHO coupling on the (100) Cu_3N surface, leading to selective formation of C_2H_4. Our study presents a good example of utilizing metal nitrides as highly efficient

nanocatalysts for selective CO_2RR to hydrocarbons that will be important for sustainable chemistry/energy applications.

Active and selective CO_2 reduction reaction (CO_2RR) is an essential step to recycle the over-produced CO_2 back to reusable forms of carbon and to build an energy-sustainable society.[1-3] Electrochemical CO_2RR can proceed under ambient conditions and has been studied extensively to understand catalysis fundamentals and to develop efficient catalysts for practical applications.[4-8] Among all nanostructured catalysts tested thus far, nanostructured Cu catalysts are unique to catalyze CO_2RR to hydrocarbons.[9-14] However, past studies also show that it is difficult to control Cu surface catalysis under ambient condition and the reaction often leads to the formation of a mixture of hydrocarbons, which makes the separation of a specific hydrocarbon product extremely challenging. Recently, a flow-cell design was used to convert CO_2 more selectively to hydrocarbons, especially to ethylene (C_2H_4) with the Faradaic efficiency (FE) reaching up to 70%.[15,16] However, this cell device does require corrosive alkaline electrolyte, such as 10 M KOH, to realize the desired conversion.

Here we introduce perovskite structured copper(I) nitride (Cu_3N) nanocubes (NCs) as a new catalyst for selective CO_2RR to ethylene (C_2H_4) under ambient condition.

Nanostructured transition metal nitrides have been studied for electrocatalytic reactions[17,18] but very limited number of metal nitrides were tested for CO_2RR. Ni_3N was studied for CO_2RR to CO.[19] Cu_3N nanowires prepared from nitridation of $Cu(OH)_2$ nanowires were converted to multi-grained Cu nanowires to show high CO_2RR selectivity to C_2 products[20] due likely to the semiconductivity of Cu_3N.[21] Different from these nitride catalysts, our Cu_3N NCs have a phase-pure anti-ReO_3 perovskite-type structure,[22] and in 0.1 M $KHCO_3$ electrolyte solution, they catalyze the CO_2RR to C_2H_4 with 60% Faradaic efficiency (FE) and 34 A/g Cu mass activity at -1.6 V vs RHE. More importantly, the NC catalyst suppresses the formation of CH_4 in the gas phase product with the C_2H_4/CH_4 molar ratio > 2000, the highest selectivity ever reported on Cu-based CO_2RR catalysis. Our Cu_3N NC structure is also stable in the CO_2RR condition, showing only 7% FE drop (from 60% to 53%) under continuous electrolysis for 20 h. The combined ease of synthesis and high CO_2RR catalytic selectivity and durability make the Cu_3N NCs a promising new catalyst for practical CO_2RR to C_2H_4, an important industry feedstock used to produce ethylene oxide, ethylene dichloride, ethylbenzene and polyethylene.

Cu_3N NCs were synthesized by modifying a published method.[23] 25 nm Cu_3N NCs were prepared by partially reducing $Cu(NO_3)_2{\cdot}3H_2O$ with octadecylamine/oleylamine (2.5g/2.5 mL, ~1/0.8 mass ratio, see Methods for details) at 240°C, while 20 nm, and 10 nm NCs were made at 250°C and 260℃, respectively. These synthetic results indicate that higher reaction temperature initiates faster nucleation, consuming more Cu-precursor in the nucleation stage and leading to the formation of smaller NCs. Another observation is that the formation of cubic Cu_3N requires the reaction temperature to be at 240°C or above. Low reaction temperatures took longer times for the Cu precursor to nucleate and the Cu_3N seeds obtained from this slow nucleation event may be defected, and it is difficult for the defected seeds to grow into NCs.[24] As a result, at 230°C, 20 nm sphere-like Cu_3N nanoparticles (NPs) were separated. Figure 1a-c show transmission electron microscopy (TEM) images of the as-synthesized Cu_3N NCs with the lateral dimension at 9.7 ± 0.4 nm, 20.0 ± 0.7 nm, and 25.0 ± 1.5 nm, and Figure S1 shows the TEM image of the 20 nm Cu_3N NPs. High resolution TEM (HRTEM) of a representative 25 nm Cu_3N NC (Figure 1d) shows clear lattice fringes with their inter-fringe distance at 0.38 nm, which is close to inter-planar distance of the (100) planes of the cubic Cu_3N P*m3m* structure. High-angle annular dark-field scanning TEM (HAADF-STEM) and STEM-electron energy loss spectroscopy (STEM-EELS) (Figure 1e) show that the Cu and N are uniformly distributed across the cubic structure. X-ray diffraction (XRD) of the 10, 20 and 25 nm Cu_3N NC powder further confirms that the NCs have the cubic P*m3m* structure (Figure 1f), which is an anti-ReO_3 perovskite structure.[22] These Cu_3N NCs are colloidally and chemically stable under ambient conditions as they showed neither aggregation nor obvious sign of surface oxidation two weeks after their hexane dispersion was exposed to air (Figure S2). Annealed at 200°C under Ar for 2 h, the Cu_3N NCs showed no structure change (Figure S3), but at 300℃ for 2 h, they were converted to Cu NPs (Figure S4), which was further confirmed by thermal gravimetric analysis (TGA) (Figure S5). As these Cu_3N NCs are stable under ambient conditions, they are a viable catalyst for studying CO_2RR.

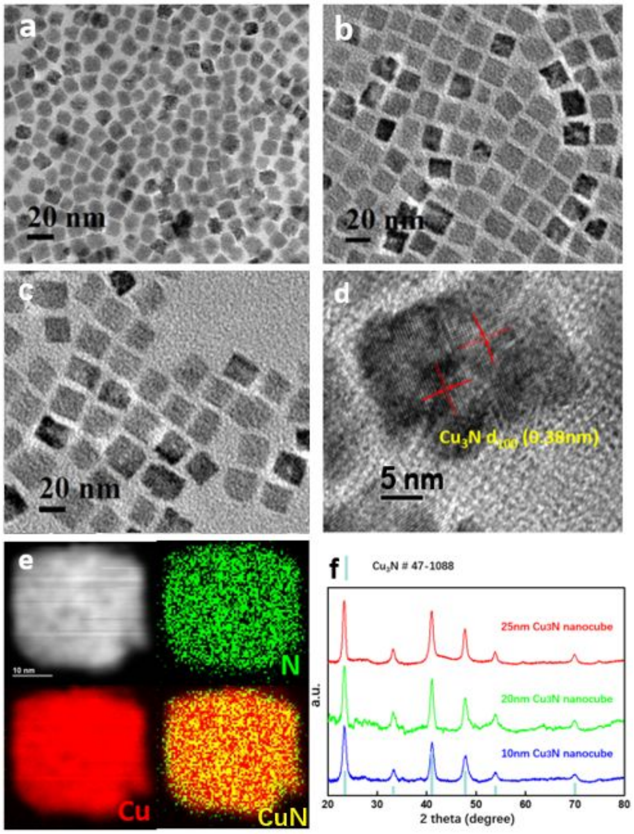

Figure 1. Characterizations of Cu_3N NCs. **a-c,** low resolution TEM images of the as-synthesized 10 nm (**a**), 20 nm (**b**) and 25 nm (**c**) Cu_3N NCs. **d,** high resolution TEM image of a representative 25 nm Cu_3N NC, showing lattice fringe along <100> direction. **e,** HAADF-STEM image of Cu_3N NC and the corresponding STEM-EELS elemental mapping of the NC. **f**, XRD patterns of 10 nm, 20 nm and 25 nm Cu_3N NCs, showing typical diffraction patterns that correspond to the perovskite-type P_{m3m} structure.

The Cu_3N NCs were deposited on Ketjen carbon (Figure S6) and painted on carbon paper (Toray TGP-H-060) for electrochemistry and electrocatalytic CO_2RR studies in 0.1 M $KHCO_3$ (see Methods for details). The cyclic voltammetry (CV) curve of the 25 nm Cu_3N NCs under Ar atmosphere shows no Cu redox peaks (Figure 2a), which is different from what is commonly observed from the Cu NP catalyst,[25] indicating that there is no measureable metallic Cu on the Cu_3N NC surface. Other Cu_3N NCs and Cu_3N NPs show similar CV behaviors (Figure S7). The increased current after -0.5 V is attributed to proton reduction (hydrogen evolution reaction (HER)). CV under CO_2 atmosphere is similar to that under Ar condition except the drop of current after -0.5 V (Figure 2a) due to the competition between CO_2RR and HER.[26]

With continuous CO_2 flow, electrochemical CO_2RR was tested under different potentials and the gas/liquid products were characterized by gas chromatography and ^{1}H NMR (see Methods for details). The reduction potential dependent FEs of C_2H_4 formed in the presence of different Cu_3N catalysts were listed in Figure 2b. The general trend is that the larger the NCs, the better the CO_2RR selectivity. Other smaller NCs are less effective and their peak FEs reach 45% (20 nm NCs) and 35% (10 nm NCs) at -1.4 V. The sphere 20 nm Cu_3N NP catalyst is least active with the FE of C_2H_4 being less than 10% in the reduction potential range tested. The 25 nm Cu_3N-catalyzed CO_2RR generates C_2H_4 (14% FE) at -0.8 V. At -1.6 V, the FE of C_2H_4 reaches the maximum 60% with the mass activity of 34 A/g and current density of 30 mA/cm^2 (Figure S8), and their overall CO_2RR results are summarized in Figure 2c. In addition to C_2H_4, the gas products obtained from various reduction potentials also contain H_2 (< 40% FE) from HER, and CO (<9% FE) (CO was undetectable at -1.6 V or beyond). The liquid phase products separated from the reaction contain only formate (<33% FE) and ethanol (< 5.7% FE) over the potential range we studied. The 25 nm Cu_3N-catalyzed CO_2RR is most selective at -1.6 V for generating C_2H_4 (60%) with remarkable current density (the ^{1}H NMR spectrum of the corresponding minor liquid products HCOOH and ethanol is shown in Figure S9.). We measured the capacitive behaviors of the Cu_3N NCs in a potential range from -0.05 to 0.05 V at different scanning rates, and obtained their double-layer capacitance of 4.34 mF/cm^2 (Figure S10), which is 150 times larger than the standard capacitance of smooth Cu electrode

(0.029 mF)[27], suggesting that high current density observed from the CO_2RR originates from the large electrochemical surface area of the NC-electrode.

We should note that compared with the common Cu metal catalyst, our Cu_3N catalyst show higher CO_2RR overpotentials due most likely to the decrease in electron conductivity of the Cu_3N structure. However, since 25 nm Cu_3N NCs are more active and selective than smaller Cu_3N NCs or Cu_3N NPs for the CO_2RR to C_2H_4, it is evident that Cu_3N NCs with larger fractions of (100) facets are especially selective to catalyze CO_2RR to C_2H_4. Another important feature of the Cu_3N NC catalysis is that the catalyst suppresses the formation of C_2H_6 and CH_4 (only <1% FE of C_2H_6 + CH_4 was detected), and show the highest C_2H_4/CH_4 ratio (> 2000) ever reported for the Cu-catalyzed CO_2RR.[28]

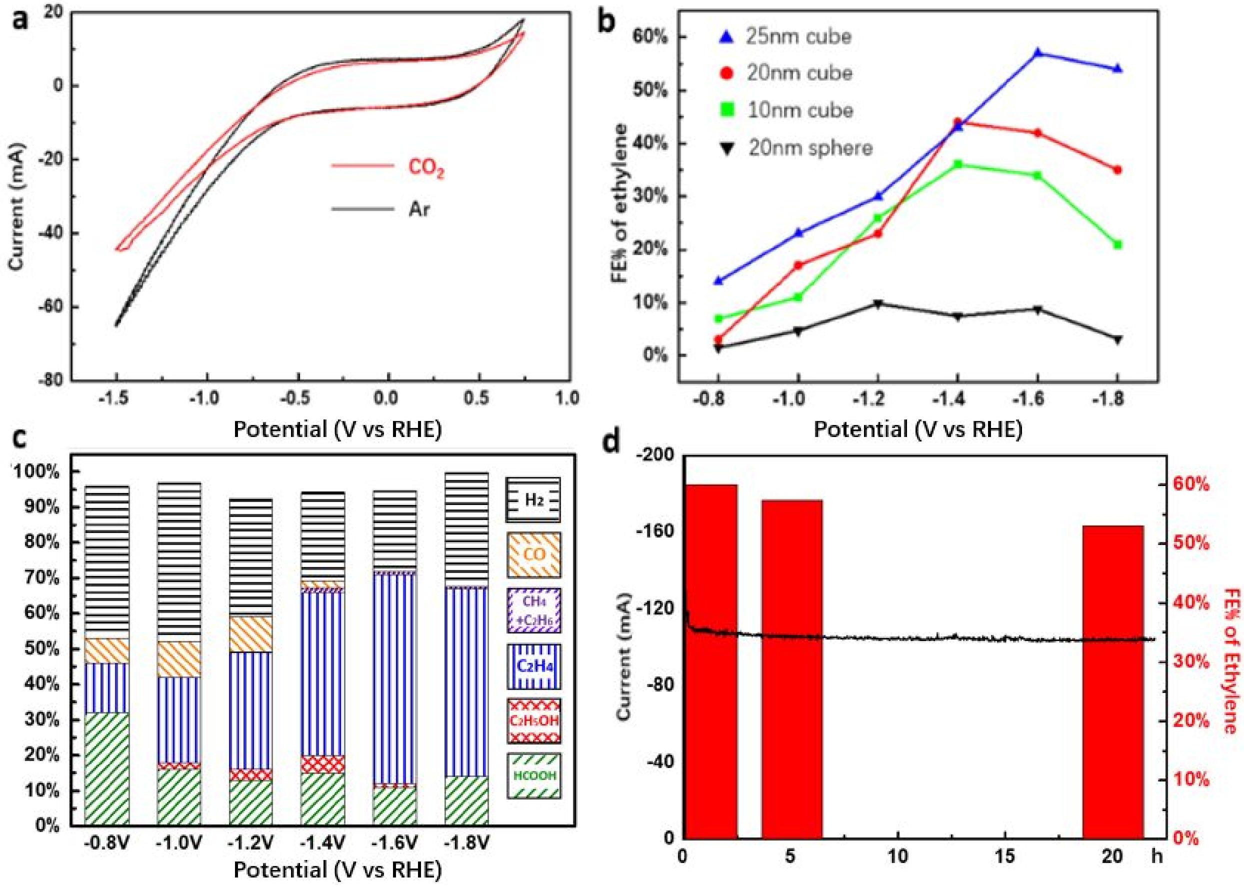

Figure 2. Cu_3N-catalyzed CO_2RR in 0.1 M $KHCO_3$ solution. **a**, CV curves of Cu_3N NCs under Ar (black) and CO_2 (red) atmosphere. **b,** Reduction potential dependent ethylene formation FE of CO_2RR catalyzed by different Cu_3N catalysts. **c,** Product distribution of CO_2RR catalyzed by 25 nm Cu_3N NC catalyst at different reduction potentials. **d,** Reduction current change (black) and ethylene formation FE (red) over time during the continuous CO_2RR catalyzed by 25 nm NCs at -1.6 V.

The stability of the Cu_3N-catalyzed CO_2RR was studied at -1.6 V (Figure 2d). The reduction current dropped from 135 mA in the first hour to 101 mA 20 h after the continued electrolysis. The C_2H_4 formation FE was at 60% in the first hour, and was stabilized at around 53%. TEM image of the Cu_3N NCs after the 20 h of electrolysis (Figure S11) shows that there is only small degree of NC aggregation, which supports why there is the 7% FE drop from 60% to 53% during the 20 h electrolysis at -1.6 V. Compared to Cu-based nanocatalysts, especially Cu NCs,[29-31] reported previously with very limited stability in the selected CO_2RR condition, our Cu_3N NCs show much enhanced stability, suggesting that N^{3-} stabilizes Cu^+ more efficiently in the perovskite-type Cu_3N structure.

To confirm that the high CO_2RR selectivity to C_2H_4 is from the Cu_3N (100), not from Cu (100), we prepared 29.3 ± 3.2 nm Cu NCs, denoted as 29 nm Cu NCs (Figure 3a)[32] and studied/compared their electrochemical CO_2RR with 25 nm Cu_3N NCs. As seen in Figure 3b, on Cu NCs, C_2H_4 is produced starting from -0.8 V, and the highest FE of C_2H_4 is about 15.4% at -1.4 V. As a comparison, the Cu_3N NCs show much higher CO_2RR selectivity to C_2H_4 in all reduction potentials from -0.8 V to -1.8 V. As both 29 nm Cu NCs and 25 nm Cu_3N NCs have similar sizes and cube morphology, the superior CO_2RR performance of Cu_3N NCs over Cu NCs suggests that the Cu-N units in the Cu_3N NC structure is essential for the NCs to achieve high CO_2RR selectivity towards C_2H_4.

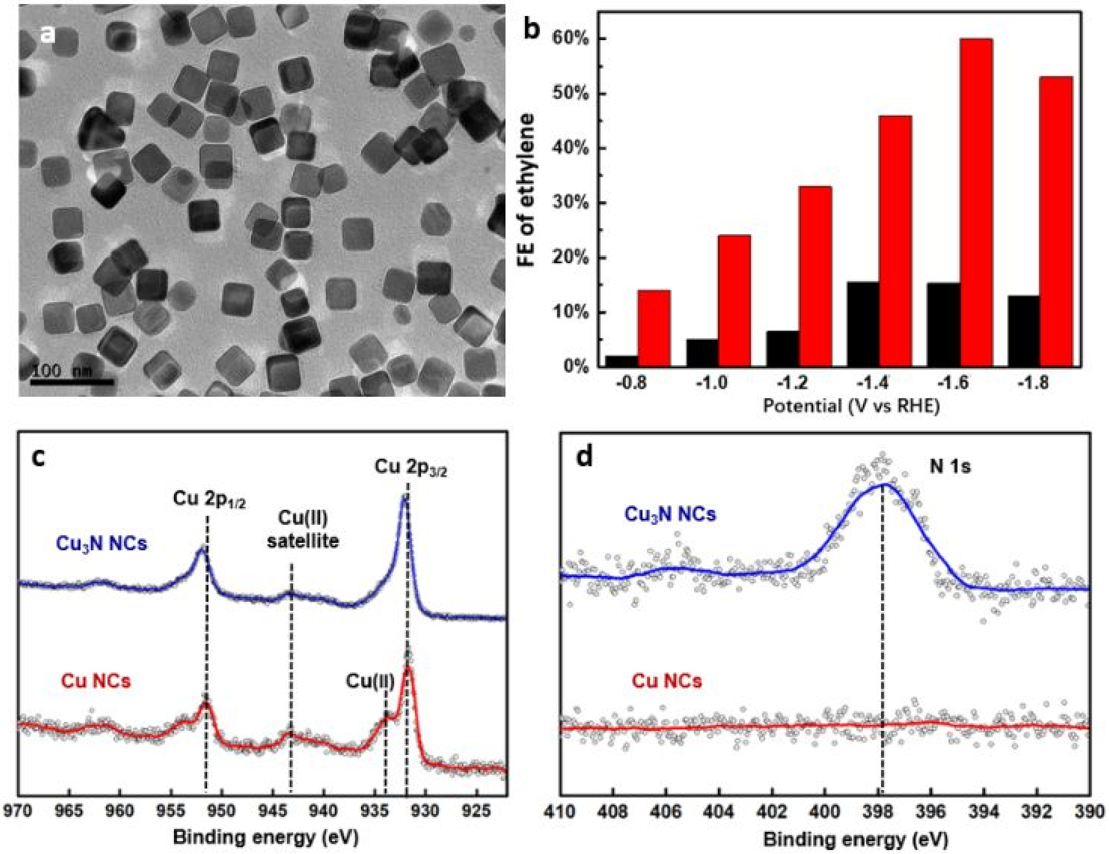

Figure 3. Catalytic performance and surface properties of Cu and Cu_3N catalysts. **a,** TEM image of as-synthesized 29 nm Cu NCs. **b,** Reduction potential-dependent FE of ethylene obtained from CO_2RR catalyzed by 25 nm Cu_3N NCs (red) and 29 nm Cu NCs (black). **c,** XPS of Cu and Cu_3N

NCs showing Cu 2p and Cu(II) peaks. Cu/Cu(I) peaks are too close to separate from the spectra. **d,** XPS of Cu and Cu_3N NCs showing N 1s binding energy.

To identify which Cu oxidation state, Cu(0) or Cu(I), on the Cu_3N surface dominates the CO_2RR selectivity, we studied surface Cu oxidation and reduction properties of both Cu and Cu_3N NCs using X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry (CV). The XPS of Cu NCs shows typical Cu 2p peaks at 932 and 952 eV, as well as two Cu(II) peaks at 934 and 944 eV (Figure 3c), but they are free from N 1s peak (Figure 3d), indicating that Cu NC surface has Cu, Cu(I) and Cu(II) components. Cu_3N NCs also show two Cu 2p peaks that slightly shift to higher energies, and a nearly invisible Cu(II) peak. This indicates that unlike Cu NCs, the Cu_3N NCs have Cu(I) enriched on their surfaces. N 1s peak is at around 398 eV (Figure 3d), close to the common value (~397 eV) observed from metal nitrides. CV of the Cu NCs in Ar-saturated 0.1 M $KHCO_3$ solution exhibit two reduction peaks at 0.35 V (Cu(II)/(Cu(I)) and -0.05 V (Cu(I)/Cu) (Figure S12), indicating that Cu NC surface after the oxidation scan is surrounded with Cu(II) and Cu(I). These two reduction peaks shift to more positive potentials under CO_2-saturated condition due likely to the CO_2 interaction with Cu(I)/Cu(II). Under the same CV scanning condition, Cu_3N NCs show no obvious reduction peaks (Figure 2a), indicating that on the Cu_3N surface, Cu^+ is better stabilized by N^{3-}, and Cu-N must show the desired synergistic effect on selective CO_2RR to C_2H_4.

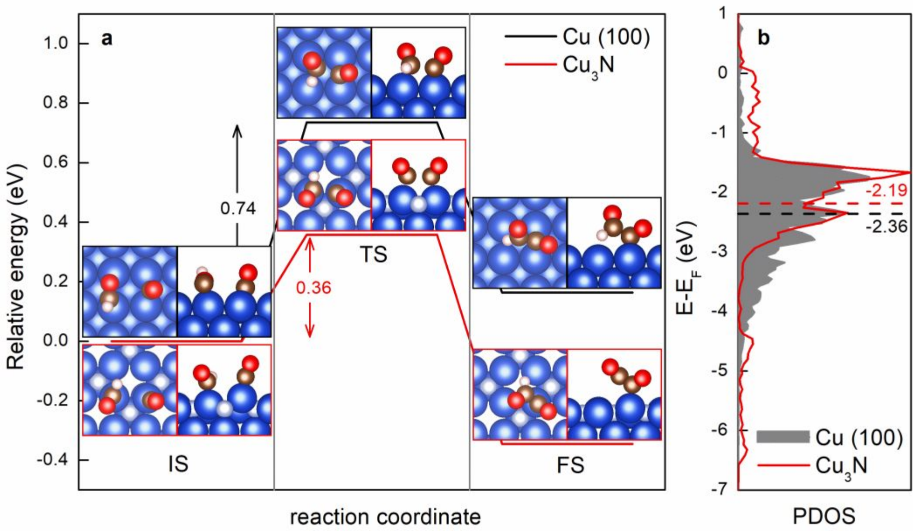

Figure 4. Relative free energy diagram and electronic density of states. **a,** Relative free energy diagram for the coupling between CHO_{ads} and CO_{ads} on Cu (100) and Cu_3N (100) surface, respectively. The optimized atomic geometries of the initial, transition, and final states are shown in the insets. Blue, blue grey, grey, red, and white spheres represent Cu, N, C, O, and H atoms,

respectively. **b,** The calculated density of states of the *d*-band on Cu (100) and Cu_3N (100) surface. The horizontal dashed lines indicate the *d*-band centers.

We performed density functional theory (DFT) calculations to elucidate why Cu_3N NCs are so selective for the CO_2RR to C_2H_4. As C-C coupling is essential for the formation of C_2 products, such as C_2H_4, we focus on the relevant C-C coupling reactions on the Cu_3N (100) surface. Previous work[33] has established that C-C bond can be formed on a Cu (100) surface via the coupling between two CO* molecules (to form $OCCO_{ads}$) or between CHO* and CO* (to form $OCCHO_{ads}$). Our calculations show that the CO-CO coupling is not favored on the Cu_3N (100) surface, while the CO-CHO coupling has the energy benefits, as shown in Figure 4a. The free energy barrier for the formation of $OCCHO_{ads}$ on the Cu_3N (100) surface is 0.36 eV, less than half of that on the Cu (100) surface (0.74 eV). From the atomic structures of the initial, transition, and final states of the CHO-CO coupling reaction (inset of Figure 4a), we can see that on the Cu (100) surface, CHO_{ads}, CO_{ads}, and $OCCHO_{ads}$ occupy the Cu bridge sites, while on the Cu_3N (100) surface, they are stabilized on the Cu(I) top sites due likely to the upshift of the Cu *d*-band center on the Cu_3N surface relative to the Cu (100) surface (Figure 4b), as well as the N^{3-} induced protonation of CO to CHO. The high energy barrier for the CO-CO coupling on the Cu_3N surface suggests that the CO-CO pathway leading to the formation of C_2 products is suppressed, leaving the OCCHO coupling a dominant pathway to C_2H_4.[34-36]

In this work, we report a new catalyst based on Cu_3N NCs for electrochemical CO_2RR. Among 10, 20, and 25 nm NCs studied, 25 nm Cu_3N NCs show highest activity and selectivity to convert CO_2 to C_2H_4 with FE reaching 60%. More importantly, at the C_2H_4 formation potential (-1.6 V), C_2H_4 is the dominant gas product with C_2H_4/CH_4 ratio being >2000, and liquid products contain mostly formate (<15% FE), which makes the separation of C_2H_4 from the CO_2RR practical. Our studies confirm that Cu(I) is stabilized by N in the Cu_3N structure and the stabilized Cu(I) is key for the (100) Cu(I) to show enhanced CO_2RR selectivity to C_2H_4. DFT calculations suggest that the stabilized (100) Cu(I) sites are energetically favored for OC-CHO (not CO-CO) coupling, inferring that the formation of $COCHO_{ads}$ is a dominant pathway in the Cu_3N-catalyzed CO_2RR to C_2H_4.

This Cu_3N-induced catalysis enhancement on selective CO_2RR may offer a new direction to develop highly efficient nanocatalysts for selective CO_2RR to C_2H_4 or other hydrocarbons.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website

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Notes

The authors declare no competing financial interest

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Notes

Any additional relevant notes should be placed here.

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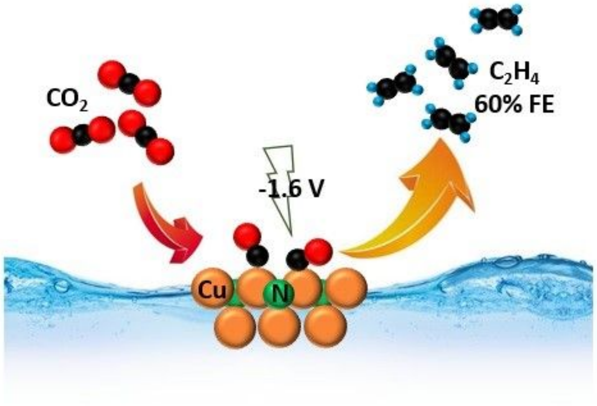
SYNOPSIS (Word Style “SN_Synopsis_TOC”).

The perovskite-type copper(I) nitride nanocube catalyst has stable (100) Cu(I)-N facets, favoring OC-CHO coupling for selective electrochemical reduction of CO_2 to ethylene.


CO_2
-1.6 V
C_2H_4
60% FE
Cu
N