Supporting Information

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High-Selectivity Electrochemical Conversion of CO₂ to Ethanol using a Copper Nanoparticle/N-Doped Graphene Electrode

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Experimental

Preparation of CNS

CNS were grown on n-type 4-inch Si wafers (100) with As doping (<0.005 Ω) via PECVD in the presence of acetylene (C$_2$H$_2$) and ammonia (NH$_3$) at 650°C for 30 min. DC plasma was generated between the substrate (cathode) and the showerhead (anode) in a continuous stream of C$_2$H$_2$ and NH$_3$ gas, flowing at 80 sccm and 100 sccm, respectively. The total pressure was maintained at 6 Torr with a plasma power of 240 W.
Electrode preparation

The electrode was cleaved into 1-2 cm squares. At the edge of the cleaved CNS the surface was gently scratched and a small piece of indium metal was applied to produce an ohmic contact. Then, silver paste was used as conductive glue between a copper wire and the CNS substrate. The edges and backside of the samples were protected by epoxy to isolate them from the electrolyte. Areas of epoxy-protected electrode in contact with the electrolyte were calculated using image processing.

Cu nanoparticles were deposited on CNS by electrochemical method. In a typical experiment, a CNS electrode was emerged into an aqueous electrolyte with 12.5 mM CuSO$_4$ and 0.5 M H$_2$SO$_4$, which was degassed for at least 30 min and purged by N$_2$ continuously. Then –0.8 V was applied on the CNS electrode for 1 sec to reduce Cu$^{2+}$ to Cu onto the CNS. Cu/glassy carbon electrodes were prepared by identical procedure for Cu/CNS. The Cu/glassy carbon particles were a similar shape and well distributed, but larger (approximately 3X) as illustrated by SEM (see below).

Materials characterization

Scanning electron microscopy (SEM, Zeiss Merlin) was used for imaging and elemental analysis of the thin films. In situ Raman spectroscopy measurements were made in a customized electrochemical cell at room temperature with a Princeton Instruments Acton Trivista 555 using a 532 nm laser excitation source. X-ray photoelectron spectra (XPS) were collected using a Thermo Scientific K-Alpha XPS operating at a base pressure of 6×10$^{-10}$ mbar. Monochromatic Al K$_\alpha$ X-rays were focused onto a 400 µm diameter spot on the sample surface and photoemitted electrons were energy analyzed (double-focusing hemispherical analyzer) and detected (128-channel detector). Transmission electron microscopy (TEM) images of CNS, grown on a holey
carbon grid (SPI Supplies) under the same conditions as the free standing electrodes, were collected using a Carl Zeiss Libra 120 Plus TEM and an FEI Titan.
**Figure S1.** Representative SEM (main) and TEM (inset) images of pure CNS electrode. The surface presents as a highly textured film consisting of folds and spikes. The spikes are difficult to discern in SEM but evident in TEM using a CNS film grown on a TEM grid.
Figure S2. SEM micrograph of Cu nanoparticles on glassy carbon (A) and particle size distribution as measured by SEM (B).
Electrochemistry

A customized electrochemical cell made from polycarbonate was employed for CO$_2$ electrolysis experiments (Scheme 1). The cell maintained the working electrode parallel to the counter electrode to achieve a uniform voltage. An anion exchange membrane (Selemion AMV, AGC Inc.) was used to separate the working and counter electrode compartments to prevent the oxidation of reduced CO$_2$ products. The cell was designed to have a small electrolyte volume (8 mL) in each of the two compartments, along with a gas headspace of approximately 2 mL above the electrolyte on each side of the membrane. CO$_2$ (Praxair), regulated by a mass flow controller (MKS Instruments) at 3 mL min$^{-1}$, flowed through the cell during electrolysis. CO$_2$ flow through the cell was needed to see large current efficiencies for CO$_2$ reduction products, presumably because of mass transport limitations in a quiescent cell. The flow rate of 3 mL min$^{-1}$ was chosen to ensure sufficient CO$_2$ transport to the surface while preventing interference from gas bubbles striking the surface. The CO$_2$ was humidified with water by passing it through a bubbler before it entered the electrolysis cell in order to minimize the evaporation of electrolyte. For each electrolysis experiment, the cell was assembled with Cu / CNS as the working electrode and platinum as the counter electrode. An Ag / AgCl electrode was used as the reference. The distance between the working and reference electrodes was kept ca. 0.5 cm to reduce solution resistance. A 0.1 M solution of KHCO$_3$ (Aldrich, 99.99% metals basis) was prepared with 18.2 M$\Omega$-cm deionized water from a Millipore system and used as the electrolyte. The pH of the electrolyte purged with CO$_2$ was 6.8.

Electrolysis was carried out with a Biologic VSP potentiostat (VMP3), using chronoamperometry (CA) method. All electrochemical data was collected vs. an Ag/AgCl
reference and converted to a reversible hydrogen electrode (RHE) scale by \( V_{\text{vs. RHE}} = V_{\text{measured vs. Ag/AgCl}} \) \( + 0.222 + 0.059 \times \text{pH} \) electrolyte. EC–Lab software was used to link different techniques without returning to open circuit for each electrolysis experiment. In order to generate detectable amounts of products, the electrolysis potential using a chronoamperometry protocol was applied for 1 hour in a typical experiment and for 6 hours for stability test.

**Electrochemistry surface area**

ECSA was measured based on the double layer capacitance on CNS and glassy carbon electrodes in 0.1 M KOH. Capacitance was measured by recording anodic-cathodic charging currents \( (i_c) \) in the potential region where Faradaic process is absent. The charging currents were collected at different scan rate \( (\nu) \) as shown in Figure S3, hence double layer capacitance can be calculated according to \( i_c = \nu \cdot C_{\text{DL}} \). Therefore, the plot of \( i_c \) vs. \( \nu \) will form a linear plot and the slope is equal to \( C_{\text{DL}} \). The \( C_{\text{DL}} \) of CNS and glassy carbon electrode measured according to the plot is 49.7 and 32.1 \( \mu \text{F} \), respectively.

The measurement of ECSA can be performed according to \( \text{ECSA} = \frac{C_{\text{DL}}}{C_S} \). Specific capacitance \( (C_S) \) for carbon was reported as 27.50\( \mu \text{F cm}^{-2} \). Therefore, the calculated ECSA is 1.81 and 1.17 \( \text{cm}^2 \) for CNS and glassy carbon electrode, respectively. The geometric area of CNS and glassy carbon is 0.72 \( \text{cm}^2 \) and 0.60 \( \text{cm}^2 \), and ECSA/geometric ratio is 2.51 \( \text{cm}^2 \) and 1.95 \( \text{cm}^2 \), respectively.
Figure S3. Cyclic voltammograms in the capacitance current range (-0.05 to 0.05 V vs. Ag/AgCl) with (A) CNS and (B) glassy carbon electrode, and (C) peak current dependence on scan rate of each electrode in 0.1 M KOH aqueous solution.

The surface area of Cu on a representative Cu/CNS electrode was measured by underpotential deposition (UPD) of lead in 100 mM of HClO$_4$ with 0.5 mM of PbCl$_2$ and 50 mM KCl. The measured ECSA of Cu was 0.246 cm$^2$ on a 2.836 cm$^2$ ECSA CNS electrode, yielding 7.98 % active area. The ECSA is consistent with a calculation of 39.18 nm Cu hemisphere on CNS with a density $2.21 \times 10^9$ particles cm$^{-2}$ geometrically, where the contribution of CuNPs is
7.78%. The additional surface area due to Cu nanoparticles for the control glassy carbon electrode was calculated to be 2.2% due to fewer, larger particles. Typically, the total Cu deposited was within 10% for both types of electrodes.

**Product identification**

To determine and confirm the identities of the liquid phase CO₂ reduction products, NMR experiments were performed on a Varian VNMRS 500 spectrometer, operating at 499.716 MHz for proton. For sample preparation, a 700 µL sample of the electrolyte was mixed with 35 µL D₂O that was 10 mM in dimethyl sulfoxide (DMSO) as internal integration standard. To suppress the water peak, the PRESAT presaturation sequence was employed, with the following acquisition parameters: SW = 8012.8 Hz; pw = 45°; d₁ = 5 sec, d₂ = 0 sec; presat = 5 sec; at = 4 sec, ss = 2, nt = 64.

The gas phase products were collected into a multilayer gas sampling bag and identified by gas chromograph (GC, Buck Scientific 910). The GC was equipped with a packed Heysep D column. Argon (Praxair 99.999%) was used as carrier gas. A flame ionization detector (FID) with methanizer was used to quantify CO, methane and other possible hydrocarbon gas concentrations, and a thermal conductivity detector (TCD) was used to quantify H₂ concentration. The GC was calibrated against H₂, CH₄, and CO. Standard samples of ethane, ethylene, methanol and ethanol were run to identify elution times. For a typical CO₂ electrochemical reaction experiment, a 0.5 mL gas was drawn from sampling bag at 15 min and 60 min, and injected into GC with a clean syringe to make sure the products were consistent and continuous. The current density for each product was calculated from its average peak area. The partial current density of each product was calculated from the corresponding GC peak area as follows:
\[ J = \frac{\text{Peak area}}{\alpha} \times \text{Flow rate} \times \frac{2Fp^0}{RT} \times \frac{1}{\text{Electrode area}} \]

Where \( \alpha \) is a conversion factor based on calibration of the GC with standard sample, \( p_0 = 1.103 \) bar, \( R \) is the gas constant, \( F \) is Faraday’s constant and \( T = 273.15 \text{K} \).

**DFT calculations**

Plane-wave DFT calculations were performed using VASP (1) within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional.(2) The optB86b-vdW functional was used to account for the vdW interaction between CNS and the C2 intermediate species.(3, 4) The projector augmented wave (PAW) pseudopotentials were used with a cutoff energy set at 400 eV. For hexagonal graphene, its orthorhombic unit cell has in-plane lattice constants of about 4.26 Å (along the armchair direction) and 2.46 Å (along the zigzag direction). Then the graphene sheet was built by a periodic slab geometry with a 4×7×1 supercell (the size as 17.04 Å × 17.22 Å × 22.00 Å) to ensure at least 14 Å vacuum separations in all directions for the C2 intermediate species adsorbed on graphene. For each system, the supercell is large enough so that a single k-point at the Gamma point of the Brillouin zone is sufficient for the k-point sampling. All atoms were relaxed until the residual forces were below 0.01 eV/Å.
Figure S4. SEM micrograph of Cu nanoparticles on CNS surface (A) before and (B) after 6h reaction. The insets are the particle size distribution as measured by SEM before (A) and after (B) 6h reaction, respectively.
Figure S5. SEM images of Cu/CNS side view before (A) and after (B) 6h reaction.
Figure S6. (A) Representative chronoamperometry of Cu/CNS, Cu/glassy carbon, and bare CNS at -1.2 V vs. RHE. (B) Overall current density of CO₂ reduction at various potentials for CNS, Cu/glassy carbon and Cu/CNS electrodes.
Figure S7. Faradaic efficiency plot and table for CNS/Cu sample including standard deviations at each point.

| Potential (V, vs RHE) | CO      | CH₄      | Ethanol | H₂      |
|-----------------------|---------|----------|---------|---------|
| -0.7                  | 23 ±6.4 | 12 ±3.4  | --      | 45 ±4.9 |
| -0.8                  | 22 ±7.3 | 25 ±3.9  | --      | 31 ±5.6 |
| -0.9                  | 18 ±6.7 | 35 ±6.2  | 0       | 24 ±8.1 |
| -1                    | 16 ±4.9 | 31 ±8.6  | 10 ±5.7 | 22 ±6.7 |
| -1.1                  | 9.5 ±5.4| 11 ±5.2  | 47 ±9.9 | 18 ±5.9 |
| -1.2                  | 5.2 ±6.1| 6.8 ±4.1 | 63 ±7.1 | 13 ±5.2 |
| -1.3                  | 6.4 ±5  | 7.2 ±4.2 | 46 ±8.6 | 24 ±5.7 |
Figure S8. Representative GC traces of gaseous products from Cu/CNS (black) and Cu/glassy carbon (red) at –1.3 V vs. RHE from FID channel. Peaks corresponding to the observed products are labelled.
Figure S9. Representative proton NMR spectrum (using PRESAT) of reaction mixture showing the methylene (quartet at 3.64 ppm) and methyl resonances (triplet at 1.16 ppm) due to ethanol, and methyl resonances (singlet at 2.71 ppm) due to the DMSO internal standard.
Figure S10. The calculated binding energies between the C2 intermediates OCCO and various graphene surfaces: (a) pristine and flat, (b) N-doped and flat, (c) pristine and curved, and (d) N-doped and curved. In (a) and (b), the separation distances between OCCO and the surface are also labeled. Clearly, the N dopant and adjacent C atoms become more active, and notably enhance the bonding between OCCO and the surface. In addition, the local curvature naturally embedded in CNS may also strengthen the interaction.
**Figure S11.** The calculated adsorption between the C2 intermediate OCCO and the Cu surface. The separation distance between OCCO and the Cu surface is ~1.98 Å, with the binding energy increased to ~1.21 eV. The bonding between one end of OCCO and the Cu surface has a notable covalent feature.
Figure S12: XPS spectra of N 1s showing changes to nitrogen binding during electroreduction as made, after deposition of Cu nanoparticles, and after prolonged electroreduction of CO₂.

|                  | As Made | Before | After |
|------------------|---------|--------|-------|
| pyridinic        | 26.07   | 14.2   | 24.7  |
| pyrrolic/amine   | 24.59   | 39.6   | 54.2  |
| graphitic        | 36.88   | 38.9   | 10.7  |
| O/N              | 12.47   | 7.3    | 10.4  |
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