Supporting Information for:

Insights Into the Composition and Function of a Bismuth Based Catalyst for Reduction of CO_2 to CO

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Experimental Method

Materials and Methods. Reagents and solvents were purchased from Sigma Aldrich, Acros, TCI, Fisher, Alfa Aesar Strem, or Cambridge Isotopes Laboratories. Bismuth(III) trifluoromethanesulfonate ($Bi(OTf)_3$) was purchased from Aldrich. Ionic liquids 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([BMIM]OTf) ≥ 98% and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([EMIM]OTf) ≥ 98% were purchased from Sigma-Aldrich. Electrochemical grade tetrabutylammonium hexafluorophosphate ($TBAPF_6$), was purchased from TCI America and purified by recrystallization from ethanol. Carbon dioxide was purchased from Keen Compressed Gas Company. All other chemicals were used without further purification.

Physical Methods. ^1H, ^{13}C, and ^{19}F NMR were recorded at 25 °C on a Bruker 600 MHz spectrometer. High-resolution mass spectrometry analyses were performed by the Mass Spectrometry Laboratory in the Department of Chemistry and Biochemistry at the University of Delaware.

Electrodeposition of Bi-modified electrodes. A glassy carbon disk electrode (GCE, 3.0 mm diameter) or graphite plate (~1 cm × 1 cm × 0.1 cm; purchased from Ohio Carbon) was polished with a slurry of 0.05 micron alumina powder in Millipore water. Residual alumina was rinsed from the GCE surface with Millipore water, and the electrode was then sonicated in Millipore water for five minutes. The polished GCE was placed in an electrodeposition bath containing the respective 20 mM of $Bi(OTf)_3$ and 100 mM $TBAPF_6$ dissolved in N_2 saturated MeCN. The GCE was preconditioned by cycling the applied potential (2 cycles) from –0.25 to –1.95 V vs. SCE at a sweep rate of 100 mV/s and was then briskly agitated in the deposition solution to remove any exfoliated material from the GCE surface. Controlled potential electrolysis (CPE) was initiated using this conditioned GCE in the quiescent $Bi(OTf)_3$ solution at –1.25 V until approximately 3.0 C/cm^2 of charge was passed. The Bi-modified GCE was rinsed with MeCN prior to being dried under a gentle stream of nitrogen.

Electrochemical Measurements. Electrochemistry was performed using either a CHI-620D potentiostat/galvanostat or a CHI-720D bipotentiostat. Cyclic voltammetry was performed using a standard three-electrode configuration. The working electrode was a bismuth-modified glassy carbon disk electrode (GCE, 3.0 mm diameter CH Instruments), a piece of platinum gauze (Sigma 99.9%) was used as the counter electrode. All potentials were measured against a Ag/ reference electrode (1.0 M KCl, CH Instruments) and converted to the SCE reference scale using $E_{SCE} = E_{Ag/AgCl} + 0.044$ V. The supporting electrolyte employed for electrochemistry experiments in organic solution was 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) unless indicated otherwise. Cyclic voltammograms were recorded at 100 mV/s with iR drop compensation.

XAS and XPS Analysis. XAS data were recorded at the Bi L_{III}-edge (13814 eV) at beamline X19a at the National Synchrotron Light Source, Brookhaven National

Laboratory. A Si(111) double crystal monochromator was used and detuned by 30% to reject higher harmonics. The X-ray absorption was measured in transmission mode. Ion chambers for measuring I_o and I_t were filled with nitrogen and a 1:1 mixture of N_2 and Ar.

Bi-based films for XAS and XPS analysis were electrodeposited onto graphite plates by polarization of MeCN solutions containing 20 mM $Bi(OTf)_3$ and 0.1 M $TBAPF_6$ at –1.3 V versus SCE under an atmosphere of N_2. Following electrodeposition and prior to XAS analysis, the Bi-containing sample was scrapped off the working electrode under ambient conditions, ground to a fine powder, and spread on Kapton tape which was then folded to produce a uniform thickness and an absorbance (μ(x)) of ca. 0.2–0.6. XAS measurements were also recorded for reference samples of metallic Bi^0 powder and Bi_2O_3. The photon energy was referenced relative to the peak in the first derivative at the absorption edge of metallic Bi at 13419 eV.

The ATHENA program (available through the DEMETER software package, version 0.9.17) was used to reduce the XAS data.[1] Data reduction consisted of pre-edge subtraction, background determination, normalization and spectral averaging. The ARTEMIS program was used to fit the experimental data.

XPS spectra were acquired using a thermo fisher K-alpha+ spectrometer equipped with a monochrometer and a 128 channel CCD detector plate. The X-rays used were monochromatic Al Kα X-rays (1486.7eV) with a power of 72 W (12 kv, 6 mA). The X-ray spot size was elliptical in shape with a semi-major axis of roughly 400 μm. Initial XPS survey scans were collected at a pass energy of 50 eV using a step size of 1.0 eV. High-resolution XPS spectra were collected at a pass energy of 20 eV using a step size of 0.1 eV. Reported values for average atomic surface composition were taken by integration of the high-resolution spectra using the Scofield cross sections for the relative sensitivity factors. Atomic percentages determined by XPS do not include hydrogen.

Depth profiling of electrodeposited Bi films was performed using a MAGCIS™ dual beam ion source utilizing an Ar^+ monotomic ion beam operating in low current mode at an energy of 2 keV at an angle of 30°. Spectra were acquired before, in-between and after 33 etching cycles. The duration of each etching cycle was 25 seconds.

CO_2 Reduction Electrolysis and Headspace Analysis. Current densities were determined by performing electrolyses in a gas-tight two-compartment cell. A Nafion (NRE-212) membrane separated the anode and cathode compartments. A schematic illustration of this cell is shown in Figure S5. Both the anode and cathode compartments contained 100 mM BMIMOTf and 100 mM $TBAPF_6$ dissolved in 20 mL of solvent, and were sparged with CO_2 for at least 30 min.

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1. Ravel, B.; Newville, M., ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J Synchrotron Radiat* **2005,** *12*, 537-541.

During all CPE experiments, the cathode solution was stirred vigorously while a constant supply of CO_2 gas was delivered to the headspace of the cell at a rate of 5.0 cm^3/min. The cathode compartment was vented directly into the sampling loop of a gas chromatograph (GC) (SRI Instruments, SRI-8610C). A GC acquisition was initiated in 15 min increments by placing the sampling loop in line with both a packed HayeSep D column and a packed MoleSieve 13X column. Argon (Keen, 99.999%) was used as the GC carrier gas. The GC columns led directly to a thermal conductivity detector (TCD) to quantify hydrogen and a flame ionization detector (FID) equipped with a methanizer to quantify carbon monoxide. The partial current densities associated with production of CO and H_2 were calculated from the GC peak area as follows:

$$J_{CO} = \frac{Peak\ Area}{\alpha} \times Flow\ Rate \times \frac{2Fp_0}{RT} \times (Electrode\ Area)^{-1}$$

$$J_{H_2} = \frac{Peak\ Area}{\beta} \times Flow\ Rate \times \frac{2Fp_0}{RT} \times (Electrode\ Area)^{-1}$$

where α and β are the conversion factors based on calibration of the GC with standard samples of CO and H_2, respectively, F = 9.65 x 10^4 C mol^{-1}, p_0 = 1 atm, R = 82.1 mL atm K^{-1} mol^{-1}, and T = 298 K. Faradaic efficiencies for a given product were calculated by dividing these partial current densities by the total current density.

The same equipment and procedures were used to study CO_2 electrolysis by Bi-modified GCEs in neat ionic liquids, with one exception: instead of using a 2-compartment cell, a single-compartment cell was used, which housed the Bi-modified GCE working electrode the Pt mesh counter electrode, and the reference electrode (Ag wire). The one compartment cell contained 5 mL of the neat ionic liquid for these experiments.

Tafel Slope Analysis. Tafel plots were constructed using a Bi-modified GCE submersed in 10 mL of a CO_2-saturated solution (MeCN, DMSO, DMF or PC solvent) containing 100 mM $TBAPF_6$ and 100 mM [BMIM]OTf. A stir bar was used to agitate the solution throughout the experiment. Stepped potential electrolyses were conducted until the observed current response plateaued (~30 – 60 seconds). The final current for these experiments was then recorded, and the applied potential was plotted as a function of the log of the steady-state current.

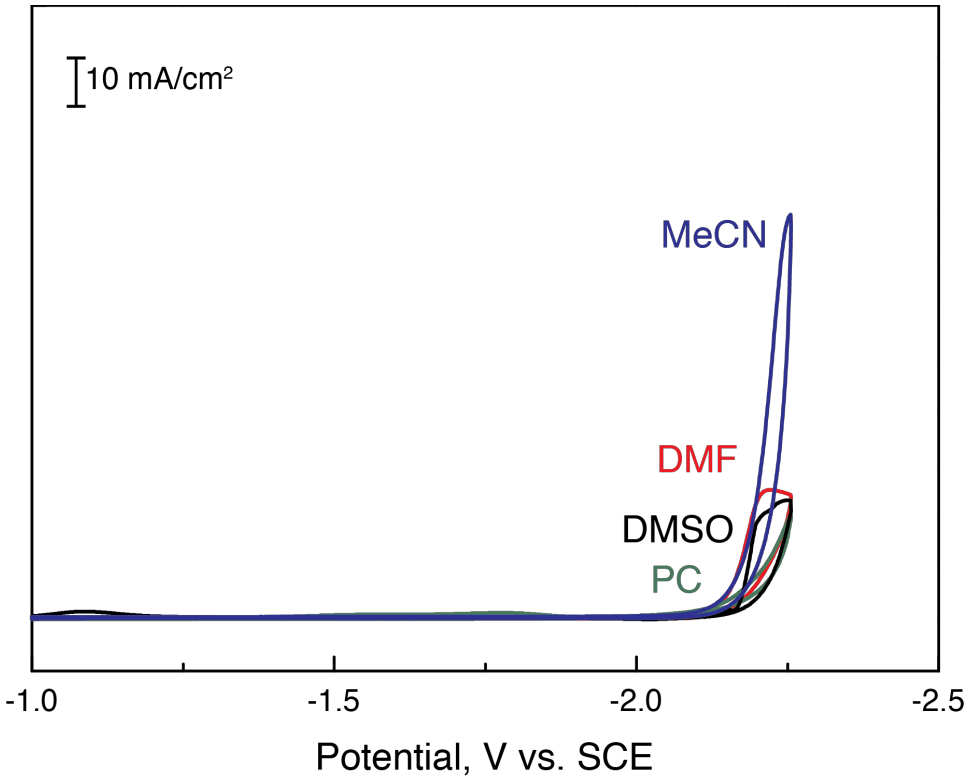

Figure S1. Cyclic voltammograms recorded for Bi-modified GCEs in either MeCN, DMSO, DMF or PC containing 100 mM $TBAPF_6$ and 100 mM [BMIM]OTf under 1 atm of N_2.

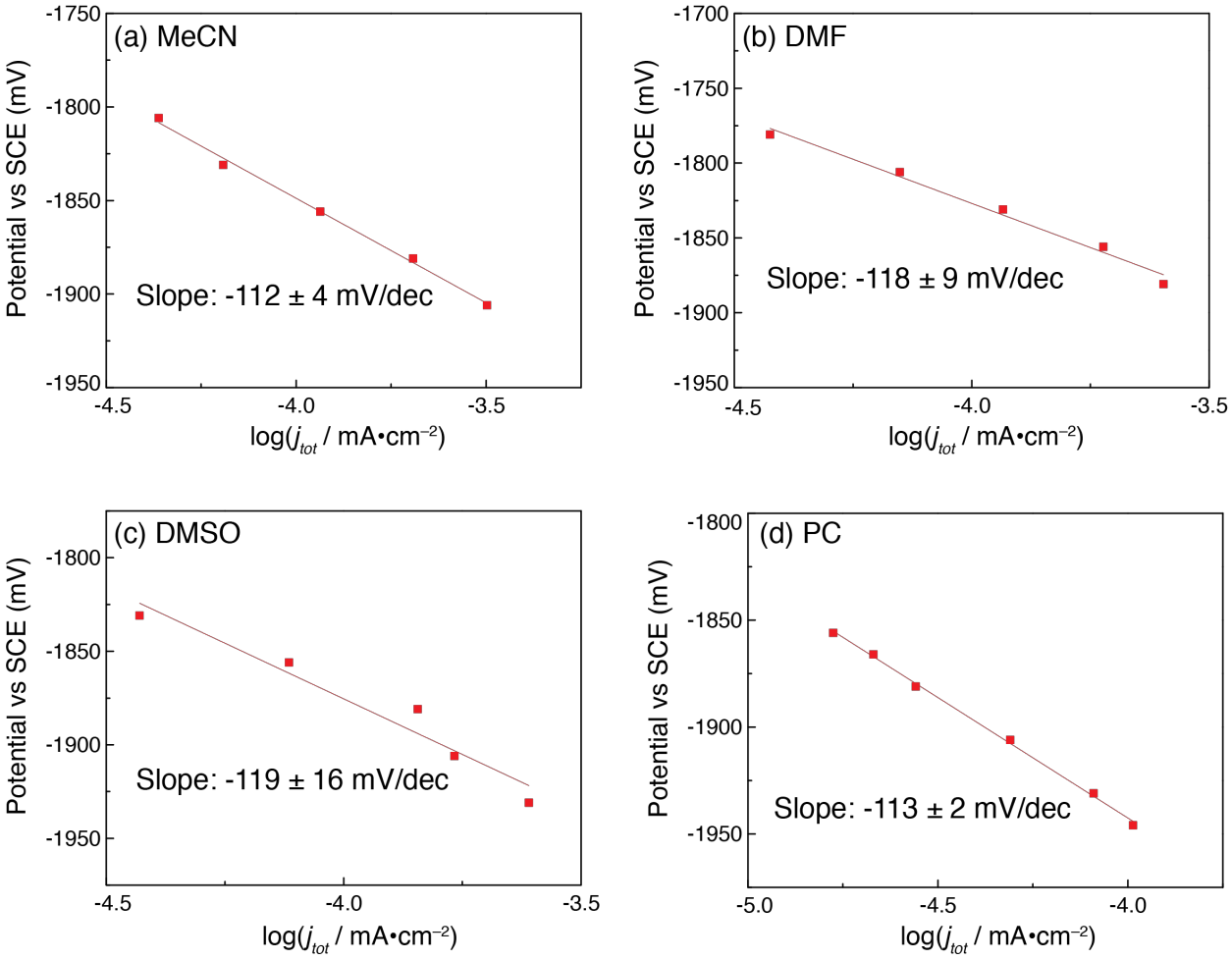

Figure S2. Tafel plots recorded for Bi-modified GCE in either CO_2 saturated (a) MeCN, (b) DMF, (c) DMSO, and (d) PC containing 100 mM $TBAPF_6$ and 100 mM [BMIM]OTf.

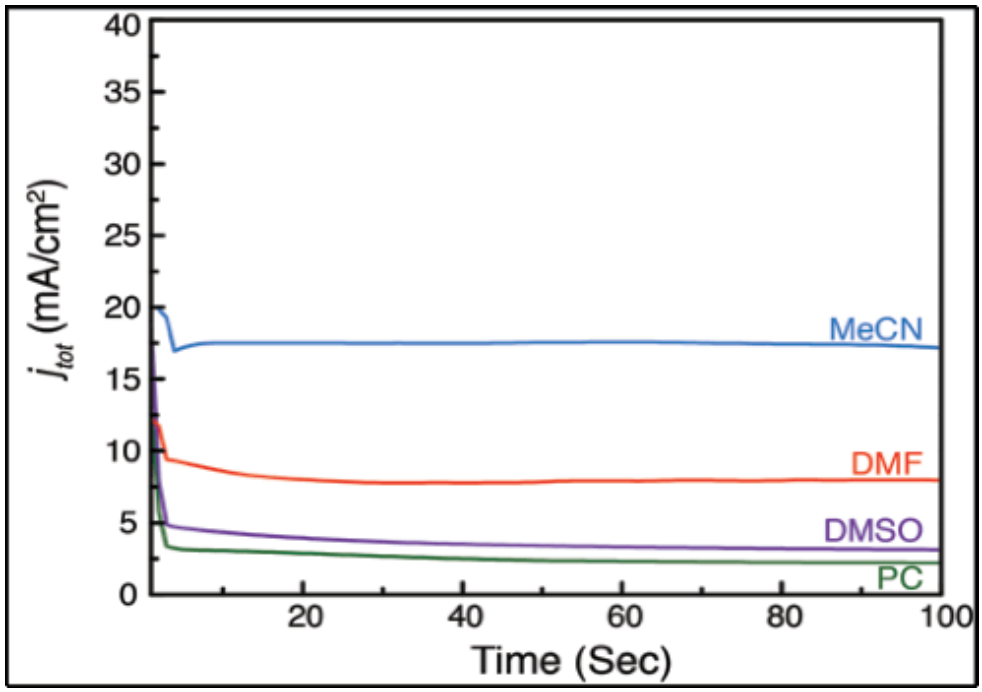

Figure S3. Chronoamperometric responses recorded for Bi-modified GCEs in either MeCN, DMSO, DMF or PC containing 100 mM $TBAPF_6$ and 100 mM [BMIM]OTf under 1 atm of CO_2 at an applied potential of E = –1.95 V versus SCE.

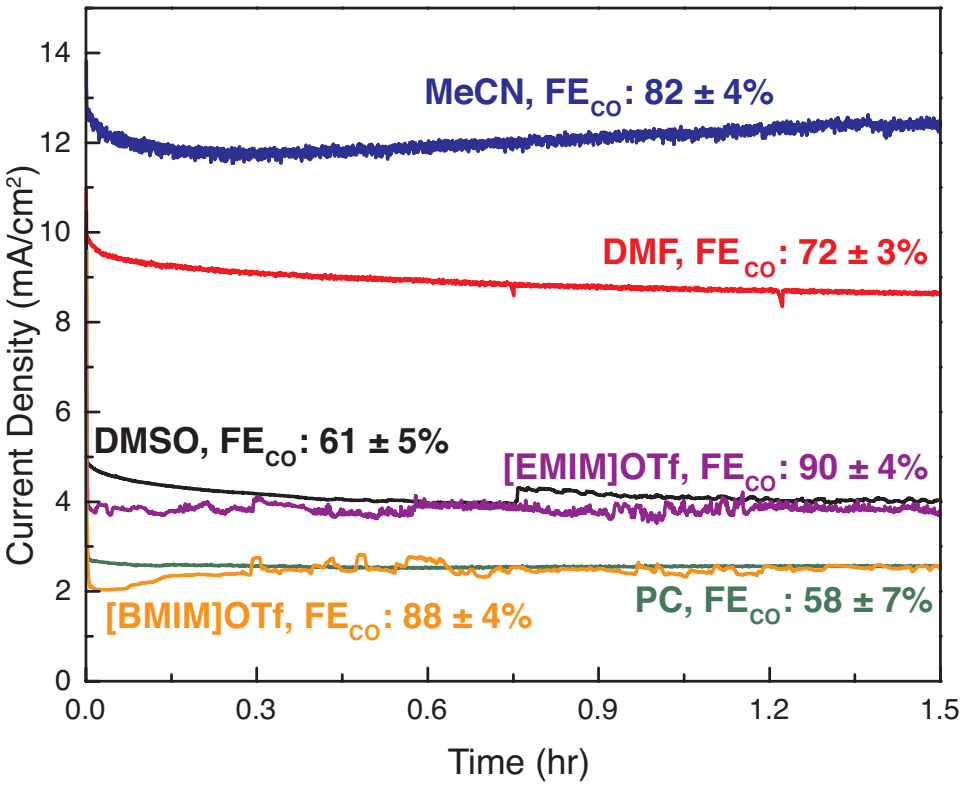

Figure S4. Current density profiles for Bi-modified GCEs in either MeCN (blue), DMSO (black), DMF (red) or PC (green) containing 100 mM $TBAPF_6$ and 100 mM [BMIM]OTf. Traces in purple and orange represent current density profiles recorded for CPE experiments conducted in neat EMIM[OTf] and [BMIM]OTf, respectively. All CPE traces were recorded under 1 atm of CO_2 at an applied potential of E = –1.95 V versus SCE.

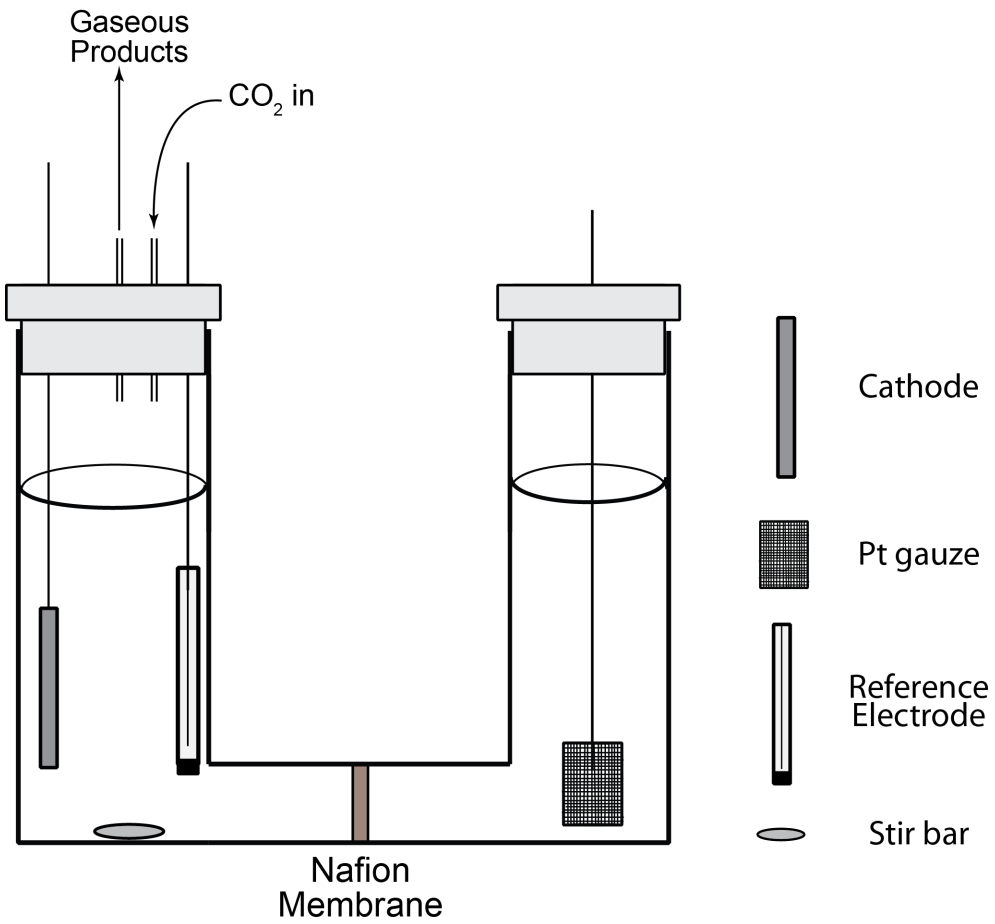

Figure S5. Schematic illustration of the two-compartment electrochemistry cell employed for CO_2 electrolysis experiments.