Supporting Information for:

# Efficient Reduction of $CO_2$ to CO with High Current Density using in-situ or ex-situ Prepared Bi-based Materials

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## Experimental Methods

**Materials and Methods.** Reagents and solvents were purchased from Sigma Aldrich, Acros or Fisher. Bismuth(III) nitrate pentahydrate (99.999%) was purchased from Alfa Aesar; ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM]$BF_4$), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]$BF_4$), 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]$PF_6$), 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([BMIM]OTf), 1-butyl-3-methylimidazolium bromide ([BMIM]Br) and 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) were either purchased from Alfa Aesar or Sigma-Aldrich. Electrochemistry grade tetrabutylammonium hexafluorophosphate ($TBAPF_6$), potassium bromide, sodium chloride and hydrochloric acid (36.5–38.0 % in water) were purchased from Sigma-Aldrich. Carbon dioxide was purchased from Keen Compressed Gas Company.

**Electrochemical Measurements.** Electrochemistry was performed using either a CHI-620D potentiostat/galvanostat or a CHI-720D bipotentiostat. Cyclic and linear sweep voltammetry experiments were performed using a standard three-electrode configuration. The working electrode was either a bare glassy carbon disk electrode (GCE, 3.0 mm diameter CH Instruments), or a Bi-CMEC modified glassy carbon electrode. A piece of platinum gauze (Sigma 99.9%) was used as the counter electrode. All potentials were measured against a Ag/AgCl reference electrode (1.0 M KCl, CH Instruments) and converted to the SCE reference scale using $E_{SCE} = E_{Ag/AgCl} + 0.044$ V. Cyclic and linear sweep voltammograms were recorded at 100 mV/s with iR drop compensation.

**Ex-Situ Electrodeposition of Bi-CMEC.** A glassy carbon disk electrode (GCE, 3.0 mm diameter) or glassy carbon plate (1 cm × 3 cm) 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 20 mM bismuth(III) nitrate, 1.0 M hydrochloric acid and 0.5 M KBr. The GCE was preconditioned by cycling the applied potential (10 cycles) from 0 to –0.55 V vs. SCE at a sweep rate of 100 mV/sec 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 $Bi^{3+}$ solution at –0.21 V versus SCE until ~3 C/$cm^2$ of charge had been passed. The Bi-CMEC modified GCE was sequentially rinsed with 1 M hydrochloric acid, Millipore water, and acetonitrile prior to being dried under a gentle stream of nitrogen.

**In-Situ Electrodeposition of Bi-CMEC:** A glassy carbon disk electrode (GCE, 3.0 mm diameter) or glassy carbon plate (1 cm × 3 cm) 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 rinsed with acetonitrile and placed in a $CO_2$ saturated acetonitrile solution containing 1 mM [$Bi(OTf)_3$] and 300 mM [BMIM]OTf. A 1 cm × 2.5 cm piece of Pt mesh was used as the auxiliary electrode. Controlled potential

electrolysis (CPE) with stirring was initiated at –2.0 V with the reference electrode placed a few mm from the GCE surface, leading to the rapid formation of a dark coating on the electrode surface.

**Powder X-ray Diffraction.** Powder X-ray diffraction (PXRD) patterns were collected at room temperature using a Rigaku MiniFlex powder diffractometer housed within a nitrogen-filled glovebox. Samples for analysis were ground into a fine powder and PXRD data were collected using Cu K$\alpha$ radiation ($\lambda$ = 1.54056 Å). Data analysis was carried out using the JADE 6.5 software package.

**SEM and XPS Analysis of Bi-CMEC.** Scanning electron microscopy images and energy dispersive X-ray (EDX) spectra were acquired with a JEOL JSM 7400F Scanning Electron Microscope (SEM). X-ray photoelectron spectroscopy (XPS) was conducted using a PHI 5600 X-ray spectrometer. The X-rays used were non-monochromatic Al Kα X-ray (1486.7eV) with a power of 400 W. The operating pressure in the main chamber was less than1 × $10^{-8}$ torr.

Initial XPS survey scans were collected at a pass energy of 93.9 eV using a step size of 0.8 eV. High-resolution XPS spectra were collected at a pass energy of 23.5 eV using a step size of 0.2 eV. All atomic ratios ($\chi_i$) were calculated from the high-resolution spectra and were determined using the equation:

$$\chi_i = \frac{A_i/S_i}{\sum_i A_i/S_i}$$

where $A_i$ is the area calculated with a Shirley-type baseline, and $S_i$ is the relative sensitivity factor. Atomic ratios do not include hydrogen in XPS.

**$CO_2$ 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 S6. Both the anode and cathode compartments contained 20 mL of MeCN containing 300 mM of ionic liquid, and were sparged with MeCN saturated $CO_2$ for at least 30 min.

During electrolysis, the solution in the cathode compartment was stirred while a steady 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 (SRI Instruments, SRI-8610C). A GC acquisition was initiated every 11 minutes by placing the sampling loop in line with both a packed HeySep D column and a packed MoleSieve 5A 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 $\alpha$ and $\beta$ 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 = 273 K. Faradaic efficiencies for a given product were calculated by dividing these partial current densities by the total current density.

$^1$H and $^{19}$F NMR spectroscopy was performed on aliquots of the electrolyte solution at the completion of each electrolysis experiment to check for the formation of nonvolatile $CO_2$ reduction products and/or the decomposition of the electrolyte solution.

**Tafel Analysis.** The current density (*j*) versus overpotential ($\eta$) data was obtained via stepped-potential electrolysis experiments using a two-compartment cell with a Nafion membrane separating the anode and cathode compartments. Measurements were conducted under a steady flow of $CO_2$ (5.0 $cm^3$/min).

**Determination of $E°_{CO_2/CO}$ under Electrolysis Conditions.** The position of $E°_{CO_2/CO}$ is dependent on the proton donating ability of the electrolyte solution. In order to determine the standard potential for CO production under a given set of conditions, the strongest acid present must be considered. For conversion of $CO_2$ to CO in acetonitrile, the value of $E°_{CO_2/CO}$ can be approximated by the expression below.[1]

$$E°_{CO_2/CO} = 0.105 - \frac{RT \bullet \ln(10)}{F} pK_a(\mathrm{HA, MeCN})\ \mathrm{V} \qquad (\mathrm{versus\ SCE})$$

Under the electrolysis conditions employed in this work, deprotonation of the central imidazolium carbon of the [BMIM] ionic liquids is the most likely source of protons to

1. Costentin, C., Drouet, S., Robert, M. & Saveant, J. M. A local proton source enhances $CO_2$ electroreduction to CO by a molecular Fe catalyst. *Science*, **338**, 90–94 (2012).

drive the $2e^-/2H^+$ conversion of $CO_2$ to CO. The p$K_a$ value for deprotonation of these 1,3-dialkylimidazolium cations is approximately 32 in MeCN.[2]

Thus, for the present system:

$pK_a$([BMIM], MeCN) = 32, which leads to $E°_{CO_2/CO}$ = –1.78 V versus SCE

**Determination of Cathodic Half Reaction Energy Efficiency for Reduction of $CO_2$ to CO.** Determination of the cathodic half reaction energy efficiency ($\Phi_{CO}$) with which Bi-CMEC drives the reduction of carbon dioxide to a fuel such as CO, requires an estimation of the standard potential of the $CO_2$/CO redox couple ($E°_{CO_2/CO}$) and calculation of the overpotential ($\eta$) at which CPE is carried out. With these values in hand, the energy efficiency of electrocatalytic CO production by a given system can be

$$\Phi_{CO} = \frac{FE \times E°_{CO_2/CO}}{E}$$

calculated using the expression below,
in which FE represents the Faradaic efficiency for CO production, $E°_{CO_2/CO}$ represents the standard reduction potential for conversion of $CO_2$ to CO under the CPE conditions and $E$ is the applied potential.[3]


2. Magill, A. M., Cavell, K. J. & Yates, B. F. Basicity of nucleophilic carbenes in aqueous and nonaqueous solvents theoretical predictions. *J. Am. Chem. Soc.* **126**, 8717–8724 (2004).
3. Whipple, D. T. & Kenis, P. J. A. Prospects of $CO_2$ utilization via direct heterogeneous electrochemical reduction. *J. Phys. Chem. Lett.* **1**, 3451–3458 (2010).

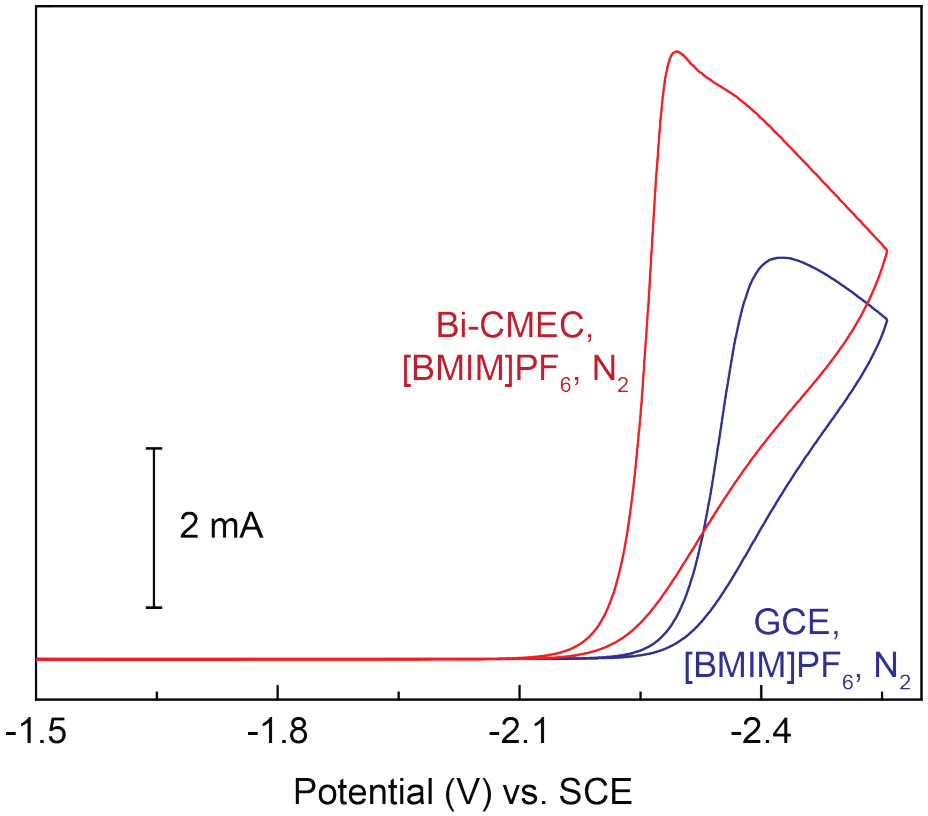


**Figure S1.** CVs recorded at either a Bi-CMEC modified or bare GCE in MeCN containing 300 mM [BMIM]$PF_6$ under $N_2$ at a scan rate of 0.1 V $s^{-1}$.

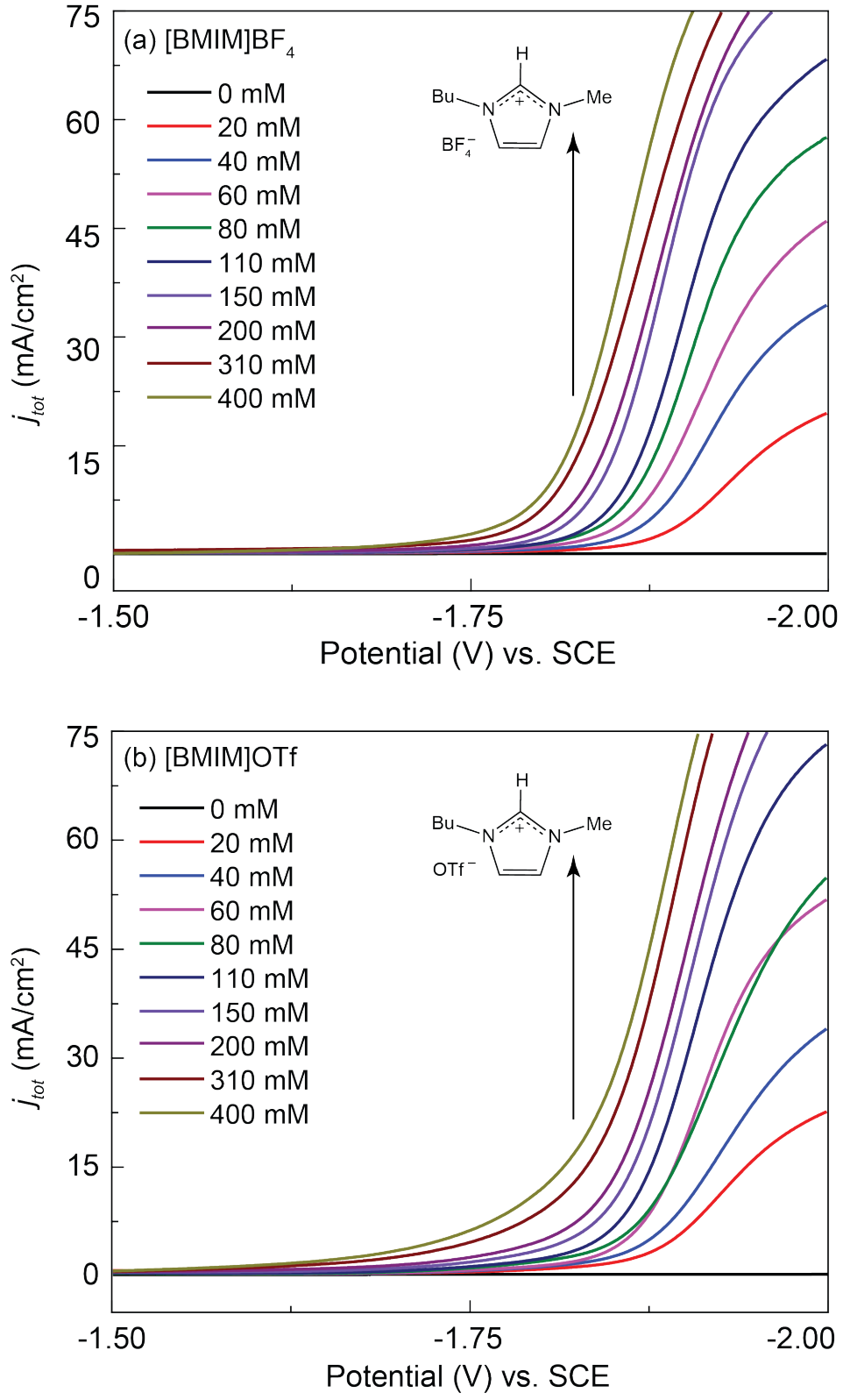


**Figure S2.** LSV traces recorded for a Bi-CMEC modified GCE in $CO_2$ saturated MeCN containing varying amounts of either (a) $[BMIM]BF_4$ or (b) [BMIM]OTf.

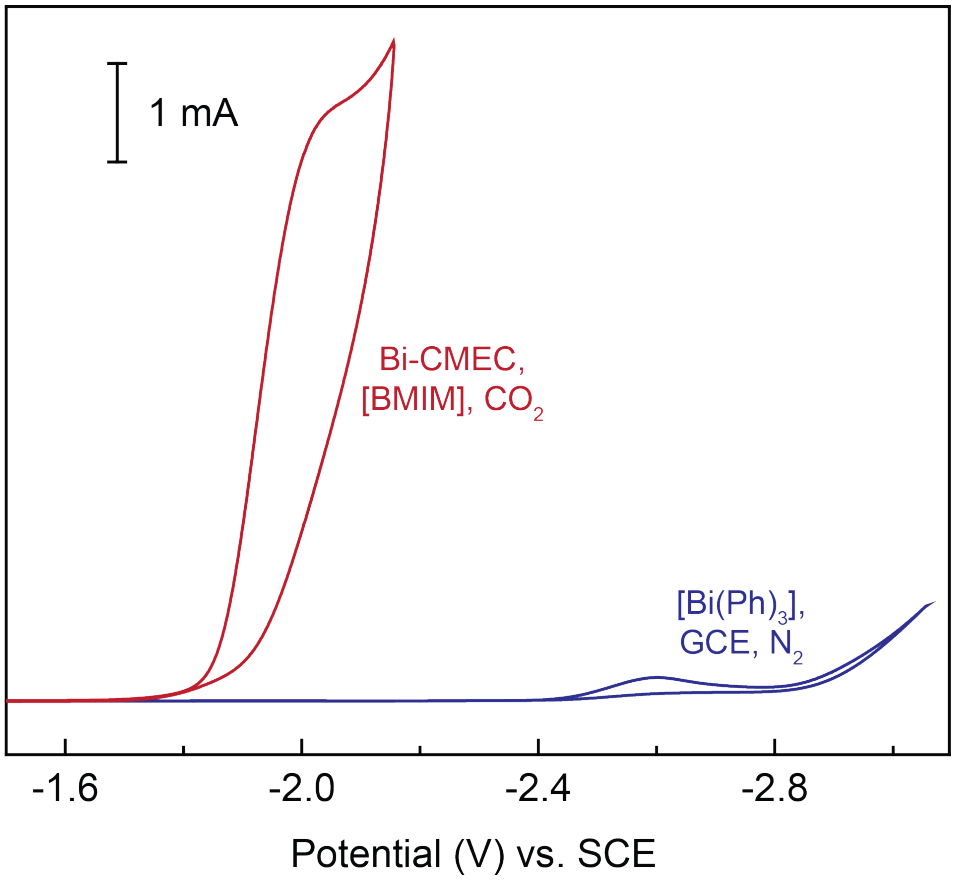


**Figure S3.** CVs recorded at a scan rate of 0.1 V $s^{-1}$. The red trace was recorded using a Bi-CMEC modified GCE in $CO_2$ saturated MeCN containing 300 mM [BMIM]OTf. The blue trace was recorded using a GCE in $N_2$ saturated MeCN containing 100 mM $TBAPF_6$ and 1 mM of $[Bi(Ph)_3]$.

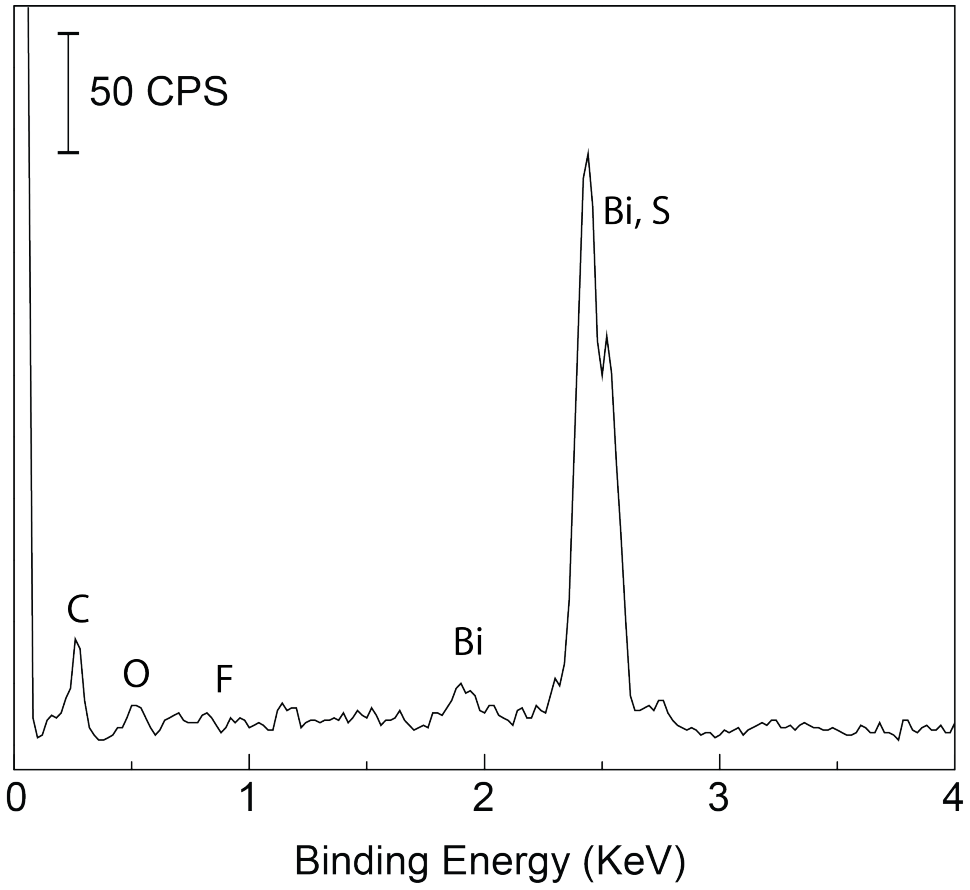


**Figure S4.** EDX spectrum recorded for in-situ prepared Bi-CMEC on glassy carbon.

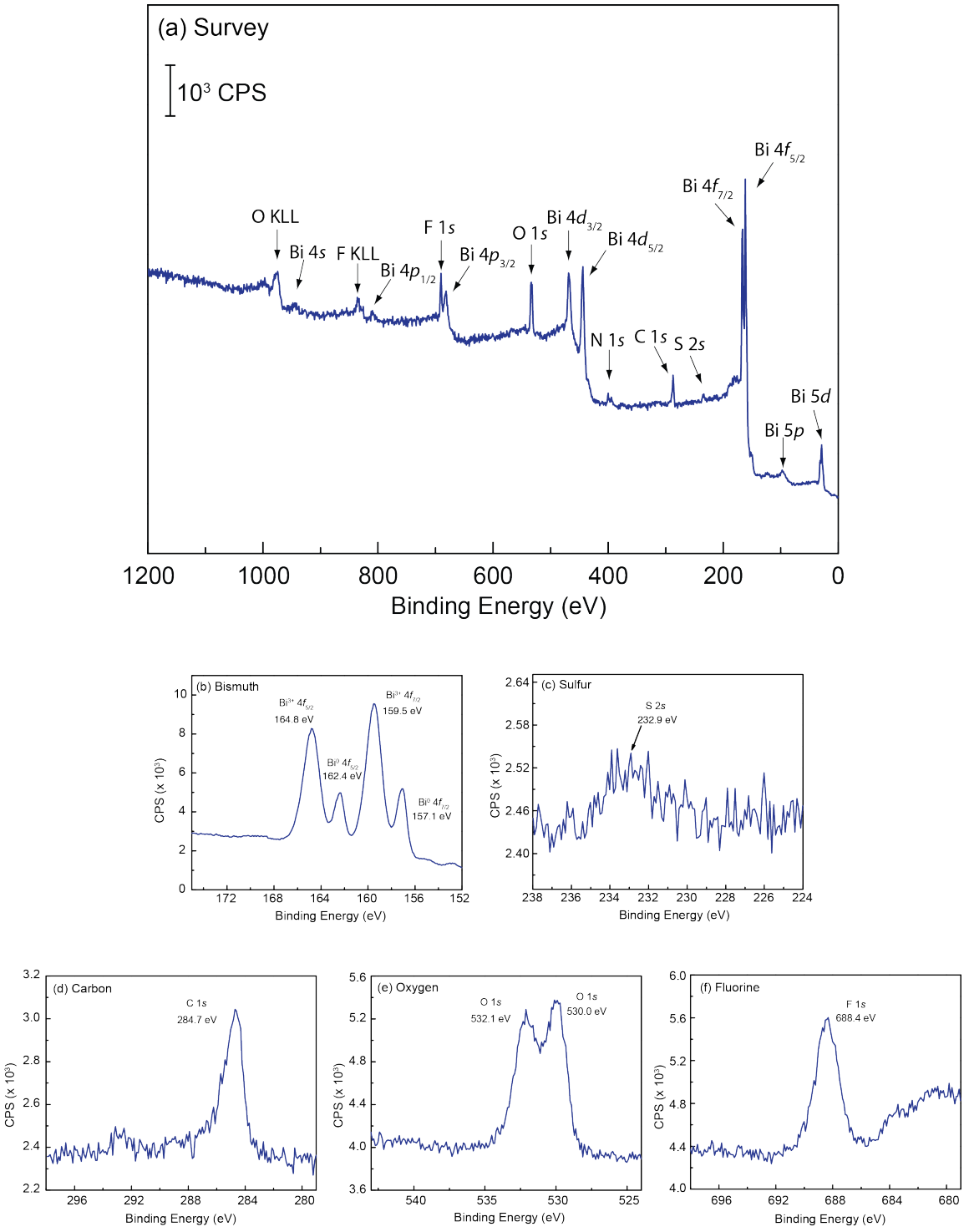


**Figure S5.** XPS spectra recorded for in-situ prepared Bi-CMEC on glassy carbon (a) survey scan, (b) high-resolution bismuth region, (c) high-resolution sulfur region, (d) high-resolution carbon region, (e) high-resolution oxygen region, and (f) high-resolution fluorine region.

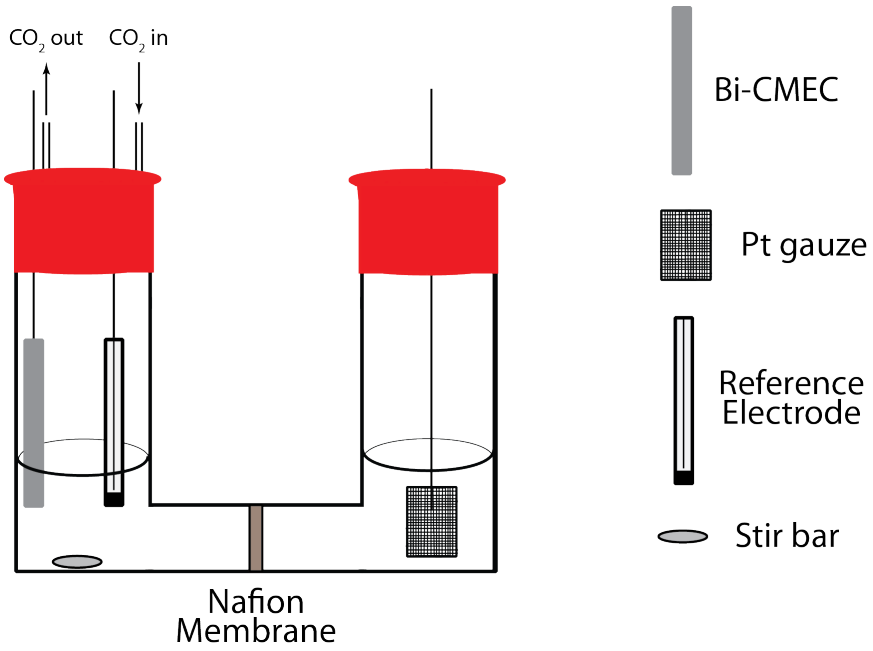


**Figure S6.** Schematic illustration of the two-compartment electrochemistry cell employed for $CO_2$ electrolysis experiments.