

Supporting Information

for

Cathodic Electrodeposition of Polymer Networks as Ultrathin Films on 3-D Micro-Architected Electrodes

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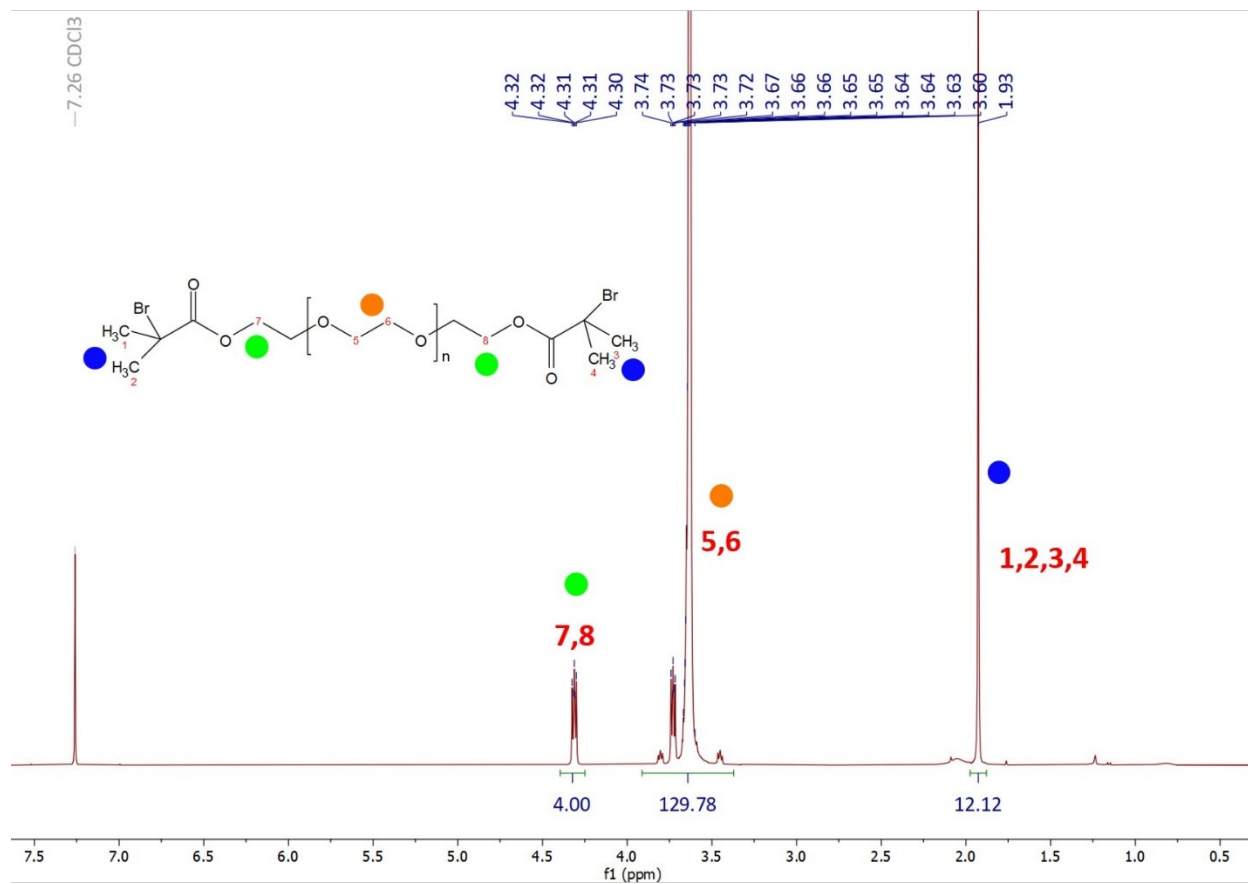


Figure S1. ¹H-NMR spectrum (400 MHz, in CDCl₃) of synthesized poly(ethylene glycol)-bis(2-bromoisobutyrate) (PEG-2bib). Colored dots and numbers label the protons associated with the respective peaks.

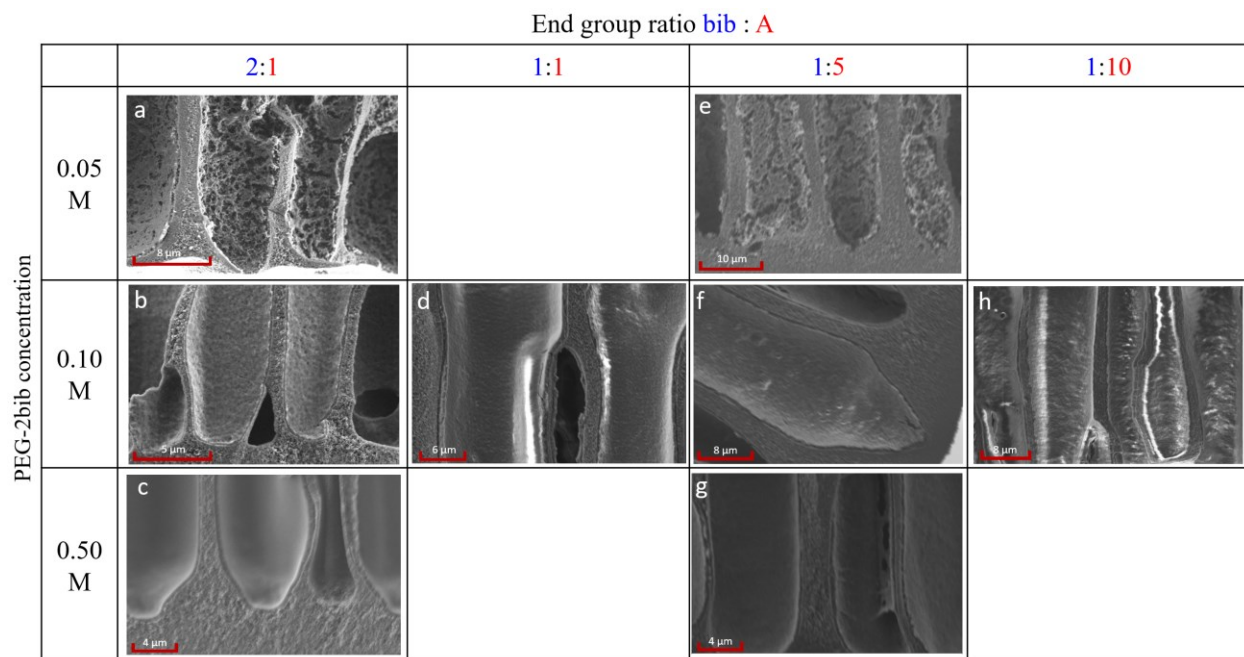


Figure S2. Cross-sectional SEM images of $(\text{PEG-2bib})_x-(4\text{A})_y$ films electrodeposited from different PEG-2bib concentration and bib:A end-group ratios.

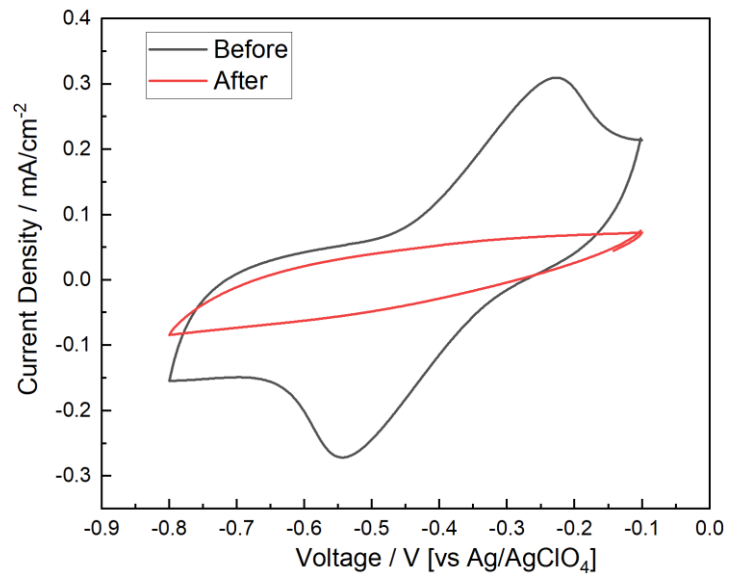


Figure S3. Cyclic voltammograms of decamethyl ferrocene (DmFc) before and after electropolymerization of 4A on a 3D carbon electrode at -2.75 V vs. Ag/AgClO₄ (0.1 M).

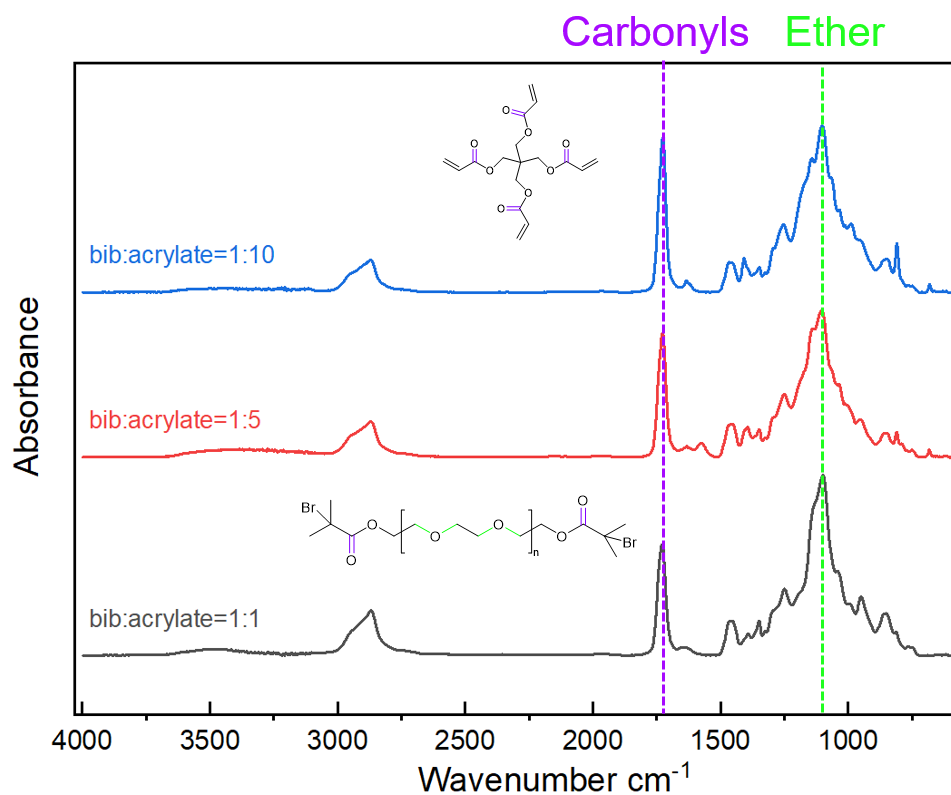


Figure S4: ATR-FT-IR spectra of polymer films electrodeposited at different end group ratios.

Table S1: Absorbance of the carbonyl group (1730 cm^{-1}) and ether group (1100 cm^{-1}), and their ratio in EPoN-derived films obtained from various end-group ratios.

End Group Ratio	C=O 1730 cm^{-1}	C-O-C 1100 cm^{-1}	Absorbance Ratio (Ether/Carbonyls)
1:10	0.26	0.28	1.08
1:5	0.21	0.25	1.19
1:1	0.19	0.30	1.58

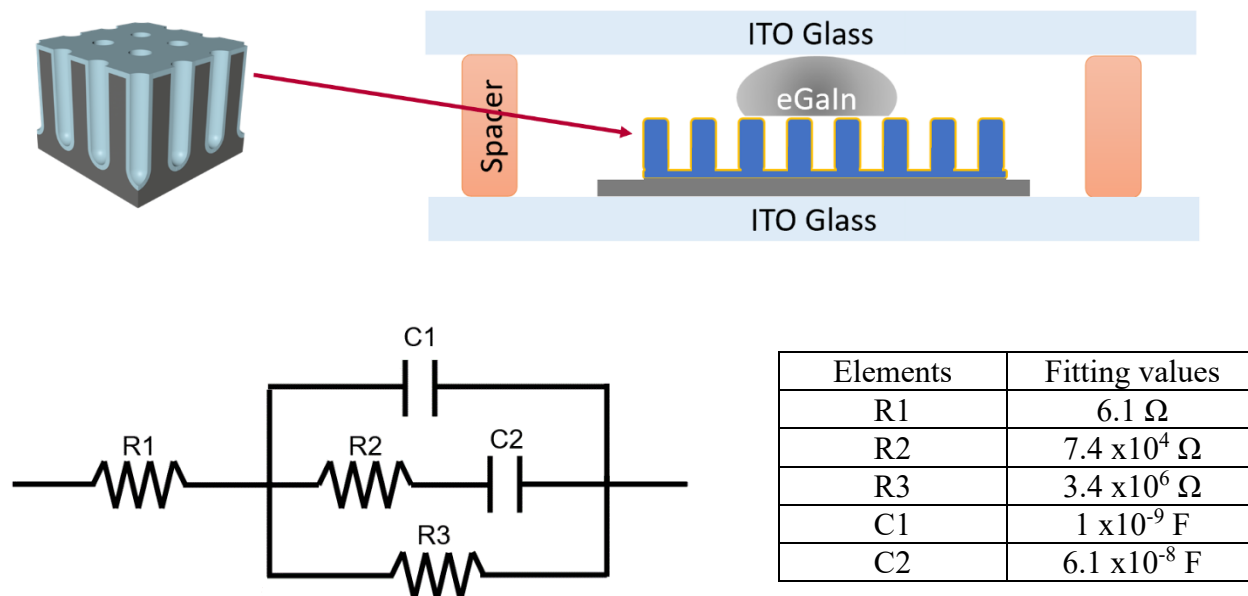


Figure S5. Schematic illustration of the setup for EIS measurement (top) and equivalent circuit model (bottom) used to fit the EIS spectrum of a (PEG-2bib)_x-(4A)_y-coated 3-D carbon in contact with a liquid eutectic indium-gallium (eGaIn) counter electrode. The table summarizes the obtained fitting parameters: R1 = system resistance, R2 = ionic resistance, R3 = electronic resistance, C1 = plate capacitance, C2 = double layer capacitance.

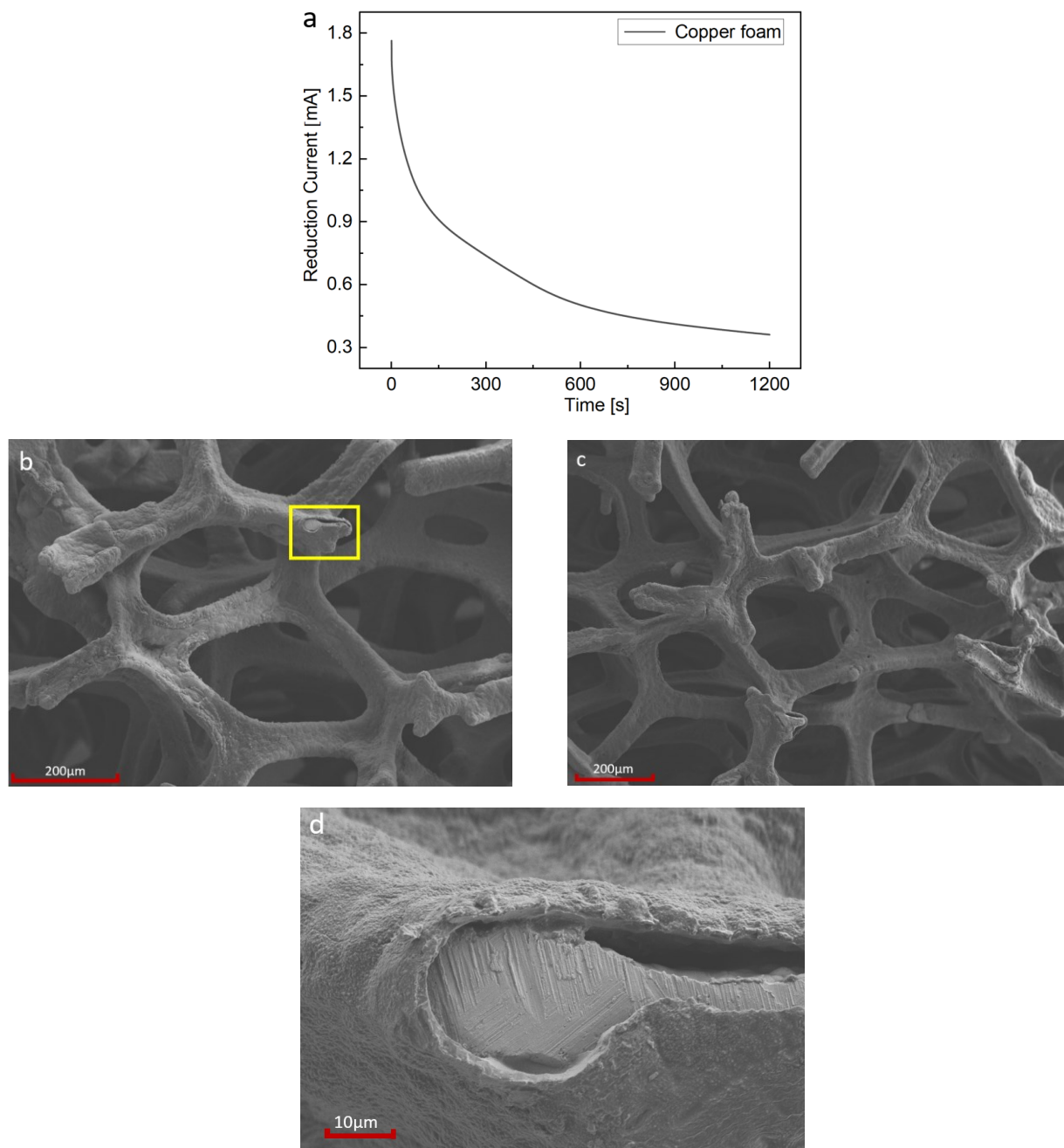


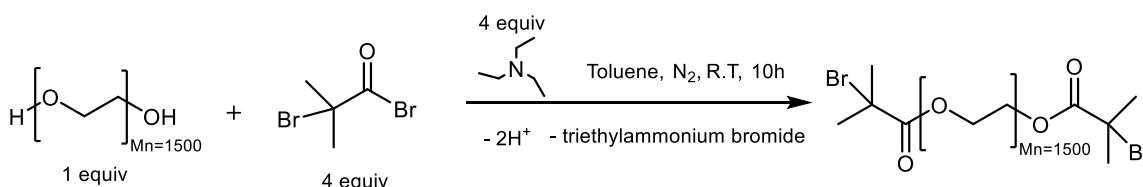
Figure S6. (a) Chronoamperometry of the potentiostatic electrodeposition of PEG-2bib with 4A on copper foam. (b, c, d) SEM images of the copper foam coated with electrodeposited $(\text{PEG-2bib})_x-(4\text{A})_y$. (d) shows a cross-sectional SEM image at higher magnification of the area labeled by a yellow rectangle in (b).

Experimental:

2.1. Materials

The platinum wire (diam. 0.25 mm, 99.9% trace metals basis) for the counter electrode and the chemicals decamethylferrocene (“DmFc”, 97%), eutectic indium-gallium (“eGaIn”, gallium 75.5%, indium 24.5%), pentaerythritol tetraacrylate, silver perchlorate (anhydrous), α -bromoisobutyryl bromide, triethylamine, dimethyl formamide (“DMF”, degassed with three freeze-pump-thaw cycles before use), and toluene were purchased from Sigma Aldrich and used as received. Acetonitrile (anhydrous), tetraethylammonium p-toluenesulfonate, and poly(ethylene glycol) ($M_w = 1500$ g/mol, hydroxy terminated) were purchased from Fisher Scientific. The silver wire for the reference electrode was purchased from Gamry Instruments.

2.2 Synthesis and Purification of poly(ethylene glycol) bis(2-bromoisobutyrate)



Poly(ethylene glycol) ($M_w = 1500$ g/mol, 15 g, 10 mmol) was added to a 500 mL one-neck flask equipped with magnetic stir bar and transferred to a nitrogen glove box. Anhydrous toluene (300 mL) was added into the flask and the mixture was left to stir for 5 mins. Subsequently, triethylamine (4 eq.) was added to the solution through a rubber septum via a syringe and the mixture was placed in an ice bath outside the glovebox. α -bromoisobutyryl bromide (4 eq.) was added dropwise via the syringe through the septum. Upon complete addition, the mixture was left to stir at 0 °C for 30 minutes and then at ambient temperature for 10 hours. The resulting mixture was filtered to remove the triethyl ammonium bromide and precipitated in hexane. The solid white product was separated from the hexane by centrifugation and redissolved in chloroform (50 mL). The solution was washed three times with deionized water and a saturated solution of NaCl. The organic phase was precipitated twice in cold hexane to yield a light yellow solid (14.9 g, 79% yield).

2.3 3-D Carbon Electrode Fabrication

Porous 3-D carbon electrodes were prepared using the non-solvent induced phase inversion of a PAN solution (84 wt% in DMSO, 10.5 wt% PAN, 5.5 wt% water) that was cast at on a DMSO-swollen organogel and subsequently immersed in DI-water. After drying the porous 3D polymer was cross-linked at 250 °C in air and subsequently carbonized at 750 °C for 1 hour (See Ref. 4 of the manuscript for details). A stainless steel substrate was attached to the dense side of the 3-D carbon electrode with an aqueous mixture of carbon black and PVA as the glue.

2.4 Electrochemical Experiments

All electrochemical experiments were performed on a Gamry Reference 600+ potentiostat. A platinum wire served as the counter electrode and the reference electrode was Ag/Ag⁺ (silver wire in 0.1 M silver perchlorate solution with 0.1 M tetraethylammonium p-toluenesulfonate electrolyte in DMF separated by a Gamry glass frit from the deposition solution). All potentials are measured and displayed vs. this Ag/AgClO₄ (0.1 M) reference electrode. The solvent DMF is degassed with three freeze-pump-thaw cycles before use. The concentration of the supporting electrolyte tetraethylammonium p-toluenesulfonate was 1 M for the deposition solution. For electrodeposition on a 50 nm-gold coated glass substrate, a cylindrical glass cell was clamped to the substrate together with an O-ring (DuPont Kalrez®), confining the deposition area to a circle of 15 mm in diameter. The deposition on 3-D carbon electrodes was carried out in same configuration using the stainless steel-attached 3-D carbon on top of the gold substrate. The optimized electrodeposition solution contained PEG-2bib at a concentration of 0.5 M and molar ratio between bib and acrylate at 2-to-1. Vacuum was used to help infiltrate the porous 3-D carbon electrode with the deposition solution. The deposition cells for both 3-D carbon and planar gold electrode were filled with 1 mL of deposition solution. All resulting coated electrodes were cleaned with acetonitrile and dried at room temperature in an ambient atmosphere.

2.5 Li-salt infusion into (PEG-2bib)_x-(4A)_y thin films

To introduce ions into the EPoN-derived thin films, lithium salt was infused from solution. The films swell well in DMF. Thus, lithium bis(trifluoromethane)sulfonimide (LiTFSI) was dissolved in DMF and the solution completely imbibed into the film. A controlled amount of LiTFSI was introduced into the film by applying 1 μL of LiTFSI solution to the top of the film. The swollen films were dried at room temperature in ambient atmosphere to obtain Li-infused (PEG-2bib)_x-(4A)_y thin film.

2.6 Film Characterization

Scanning electron microscopy (SEM) of the films was performed on a Zeiss Supra 55 field-emission SEM with an electron beam accelerating voltage of 3 kV using a secondary electron detector. Attenuated total reflectance-fourier transform infrared (ATR-FTIR) Spectroscopy was performed on a Bruker FT-IR Microscope. Two-electrode electrochemical impedance spectroscopy (EIS) measurements were performed on a Gamry Reference 600+ potentiostat using a eutectic gallium indium drop sandwiched between the coated 3D carbon (working electrode) and a bare ITO-coated glass slide (counter and reference electrode) separated by a 1 mm silicone rubber spacer resulting in a contact area of approximately 3.1 mm². EIS measurements were taken around the open circuit potential with a signal amplitude of 100 mV over the frequency range of [0.05 Hz, 5 MHz].