Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Copolymer Templated Nitrogen-Enriched Nanocarbon Films as Highly Active Electrocatalysts for Oxygen Reduction

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EXPERIMENTAL SECTION

Materials. Acrylonitrile (AN), *n*-butyl acrylate (BA), methyl 2-bromopropionate (MBP), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA), 2,2′-bipyridyl (bpy), CuBr, CuCl, $CuBr_2$, anisole, dimethylformamide (DMF), dimethylsulfoxide (DMSO), tetrahydrofuran (THF), N-methyl-2-pyrrolidone (NMP), ethanol, methanol, and Nafion®117 solution (5 wt %), polyacrylonitrile homopolymer (M_w = 150,000) were all obtained from Sigma-Aldrich. 20 wt% platinum on Vulcan carbon black was purchased from E-TEK. CuCl and CuBr were purified by stirring in glacial acetic acid followed by washing with ether and dried overnight under vacuum. Monomers were passed through a basic alumina column prior to use. All other chemicals were used as received.

Preparation of Bulk Copolymer-Templated Nitrogen-Enriched Nanocarbon (CTNCs). The block copolymer and homopolymer precursors were synthesized *via* atom transfer radical polymerization as reported previously.[1] The polymer samples were stabilized at 280 °C for 1 h under air flow (150 mL/min) with a heating rate of 1 °C/min, purged with nitrogen gas for one hour during cooling, and then pyrolyzed at 600 ~ 900 °C for 0.5 h under nitrogen gas flow (150 mL/min) with a heating rate of 10 °C/min. 1 mg of CTNC was dispersed in 1 mL solvent mixture of Nafion (5%) and ethanol (v/v = 1/9) by sonication. 20 μL of the solution was drop-casted on the glassy carbon (GC) electrode surface and dried in air. Pt/C based electrocatalysts were prepared using similar procedure.

Preparation of Binder-Free CTNC Films. Detachable GC disk insert (5 mm diameter, 4 mm thick, Pine AFED050P040GC) was carefully polished with 3 μm, 1 μm, and 0.25 μm diamond successively to obtain mirror-like surface. Then the electrode was washed with double distilled water and acetone and finally dried in air. The insert was then treated under UV to remove organic residues. The DMF solution of as-made block copolymer (BCP) (10 mg/mL) were drop-cast onto the GC insert using a microliter syringe pump and dried first at ambient condition followed by a 160 °C thermal annealing under vacuum. CNTC thickness was varied by varying the total volume of BCP solution used in the deposition of precursor film on GC electrode. The catalyst loadings, in such prepared CTNC films were estimated based on the mass of the deposited BCP under the assumption that the thin-film pyrolysis proceeded with the same yield as in the bulk.

Electrochemical Characterization. All of the voltammograms were recorded at 25 °C with a Gamry Reference 600 potentiostat. Measurements were carried out at a scan rate of 10 mV/s in N_2-saturated or O_2-saturated 0.1 M KOH aqueous solution. The as-prepared GC insert assembled onto the rotating electrode set-up (Pine E5TQ Series) was used as a working electrode and a platinum mesh as the counter electrode. Potentials were recorded versus Ag/AgCl reference electrode and converted to reversible hydrogen electrode (RHE) by E (RHE) = E (Ag/AgCl) + 0.965 V in 0.1 M KOH aqueous solution.[2]

Details of Calculating the Koutecky - Levich Plots

Kinetic parameters of oxygen reduction reaction (ORR) were analyzed on the basis of the Koutecky - Levich equations[2]:

$$\frac{1}{j}=\frac{1}{j_\mathrm{L}}+\frac{1}{j_\mathrm{K}}=\frac{1}{B\omega^{1/2}}+\frac{1}{j_\mathrm{K}} \qquad \text{(eq. S1)}$$

$$B=0.62n_\mathrm{e}FC_0D_0^{2/3}v^{-1/6} \qquad \text{(eq. S2)}$$

$$j_\mathrm{K}=n_\mathrm{e}FkC_0 \qquad \text{(eq. S3)}$$

where j (mA/cm^2) is the measured current density, j_K and j_L (mA/cm^2) are the kinetic- and diffusion-limiting current densities, ω is the angular velocity of the rotating disk ($\omega = 2\pi N$, where N is the linear rotating speed in rpm), n_e is the overall number of electrons transferred in ORR, F is the Faraday constant (97485 C/mol), C_0 is the bulk concentration of O_2 (1.2×10^{-3} mol/L), D_0 is diffusion coefficient of O_2 (1.9×10^{-5} cm^2 s^{-1}), v is the kinematic viscosity of the electrolyte (0.01 cm^2 s^{-1}), and k is the electron transfer rate constant, respectively. According to the Equations S1 to S3, the number of electrons transferred (n_e) and the kinetic-limiting current j_K can be obtained from the slope and intercept of the Koutecky–Levich plots ($1/j$ versus $\omega^{-1/2}$), respectively.

Content determination: X-ray photoelectron spectroscopy (XPS) measurements were performed with a Kratos Axis Ultra spectrometer under the pressure of 10^{-8} torr. The monochromatic X-ray source was Al Kα (1486.6 eV) and the power was 208 W (14 kV, 20 mA). The voltage step size was 0.5 eV for surveys and 0.1 eV for high resolution. The dwell time at every step was 150 ms for surveys, 600 ms for O and C, and 2000 ms for N high resolution. Quantification was performed by applying the appropriate relative sensitivity factors (RSFs, C 1*s* = 0.297, O 1*s* = 0.703, N 1*s* = 0.491) after subtracting Shirley-type background. The deconvolution into component peaks in high resolution peaks were carried out using 7:3 product of Gaussian-Lorentzian. Binding energy was corrected with reference to C 1*s* at 285.0 eV. The content of copper was also determined using an inductively coupled plasma mass spectrometer (ICP-MS) by Analytical Consulting Services (ACS) Labs in Houston, TX.

Nitrogen sorption analysis of CTNC Powder: The pore structure of carbon sample was assessed from the N_2 isotherm curve measured by a gas adsorption analyzer (NOVA2000 series, Quantachrome Instruments). Prior to the adsorption experiments, all samples were degassed at 300 °C for 3 h to eliminate the surface contaminants (water or oils). The standard analysis of nitrogen sorption isotherms recorded for all samples studied provided the Brunauer-Emmett-Teller (BET) surface area, S_{BET}, evaluated in the range of relative pressure between 0.04-0.2. For the carbonized material, calculation of volume fractions of carbon and pores was based on the total pore volume per gram (V_{tot}) obtained from nitrogen adsorption analysis. V_{total} was calculated as 0.67 cm^3/g based on the amount adsorbed at a relative pressure of 0.99. Conversion of this value to volume fractions of carbon and pores still required the knowledge of density of carbon matrix. This was estimated using the known relationship between the density of carbon materials as a function of the H/C ratio.[3] Using this relationship and the H/C ratio (~0.20) obtained for the bulk CTNC from elemental analysis, the carbon matrix density was estimated to be equal to ~1.75 g/cm^3. From the V_{tot} and carbon matrix density, the volume fractions of pore and carbon was, ϕ_{pore}= 0.539, ϕ_{carbon} = 0.461. Therefore, the density of CTNC can be calculated.

Atomic Force Microscopy (AFM):

Tapping mode-atomic force microscopy (TM-AFM) measurements were taken using a Veeco Metrology Group Digital Instruments Dimension V with NanoScope V controller and NanoScope 7 software. A Veeco TESPA cantilever with a spring constant of 20–80 N/m and resonance frequency of 320–375 kHz was used. Filtered height images were generated by 7th order 2D polynomial flattening, followed by a “soft edge” bandpass filter (2 nm to 50 nm). Image skeletons were computed by digital thinning of non-overlapping 500 nm x 500 nm sub-panels of each filtered height image (using the procedure above), binarized by thresholding at the mean height. To obtain the measure of domain connectivity on the surface, connected clusters in the skeletonized images were detected using morphological processing tools and then sorted by size. All digital image processing was performed with custom scripts written in MATLAB R2013a (The MathWorks Inc., Natic, MA) and *Mathematica* 9 (Wolfram Research, Champaign, IL).

Table S1. Characterization of bulk CTNCs synthesized under different pyrolysis conditions.

Entry	S_{BET} (m^2/g)	N/C (%)	Carbonization Yield (%)
CTNC-600	461	16.9	25.9
CTNC-700	491	13.5	23.6
CTNC-800	485	9.1	21.6
CTNC-900	509	6.1	20.5

SUPPORTING INFORMATION FIGURES

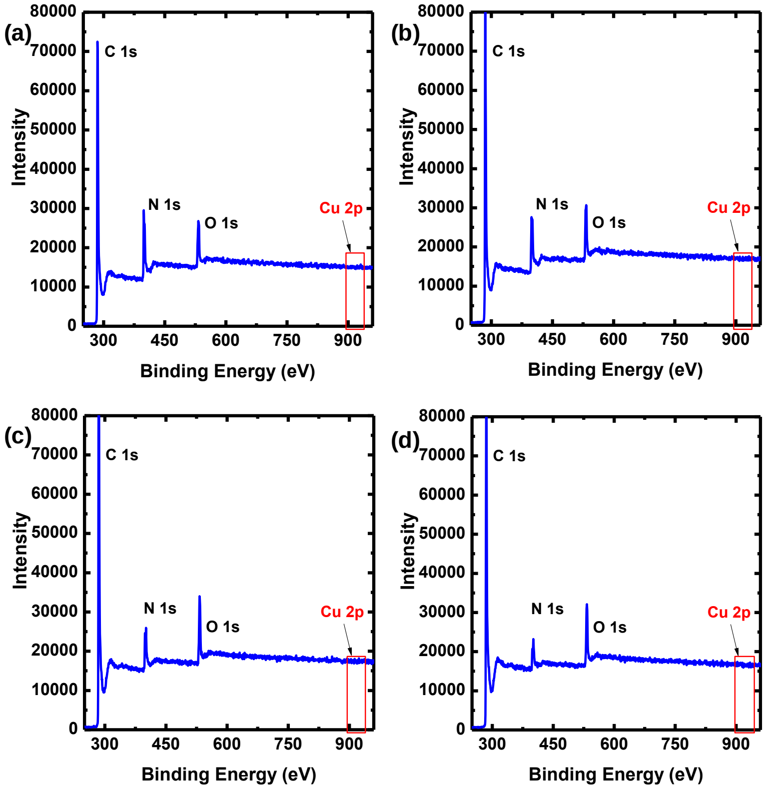

Figure S1. XPS survey spectra of CTNCs. (a) CTNC-600; (b) CTNC-700; (c) CTNC-800; (d) CTNC-900.

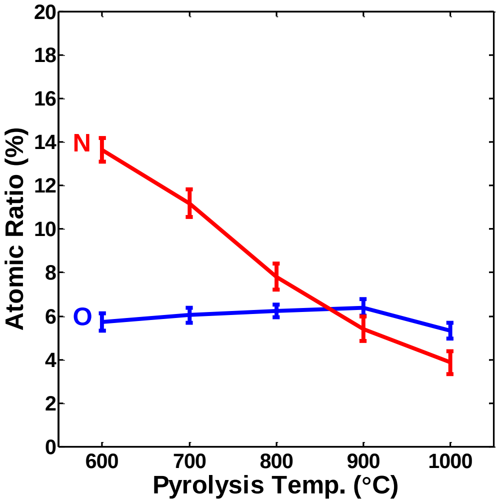

Figure S2. N% and O% against differing pyrolysis temperatures, measured by XPS.

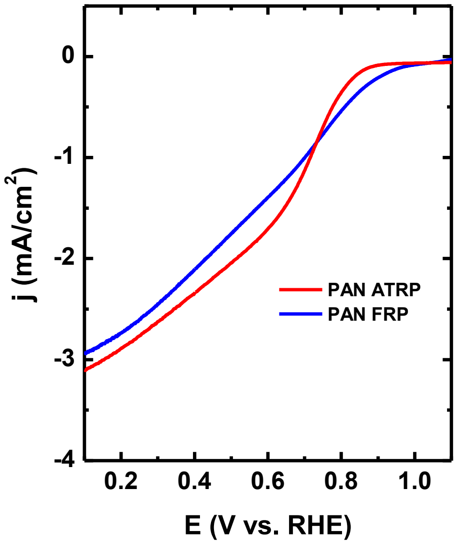

Figure S3. Polarization curves of carbon films pyrolyzed from PAN homopolymer at rotating speed of 1400 rpm.

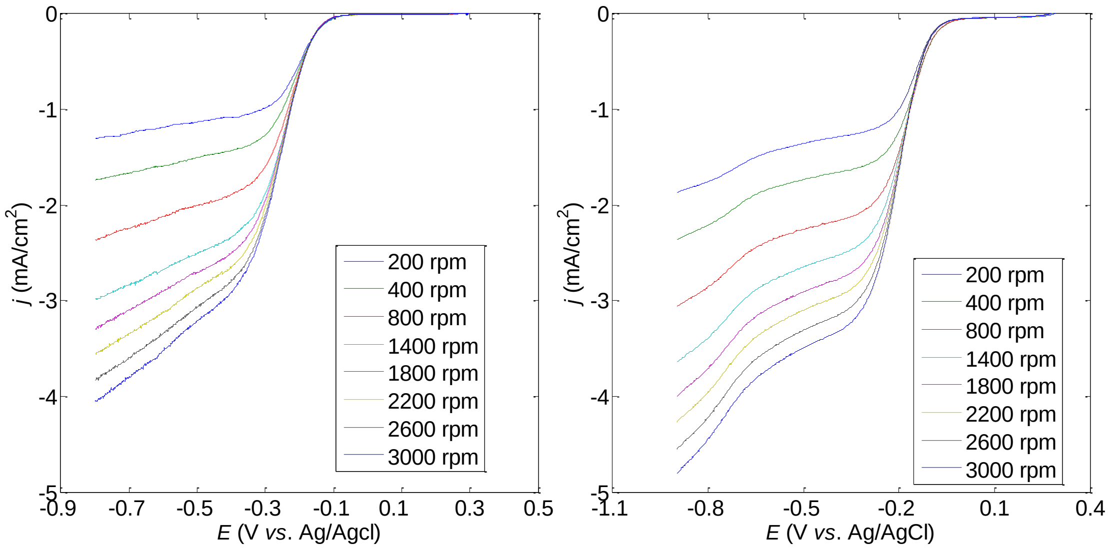

Figure S4a. Polarization curves of CTNC-700 film at different rotating speeds. Catalyst Loading: ***left***: 12 μg/cm^2; ***right***: 42 μg/cm^2.

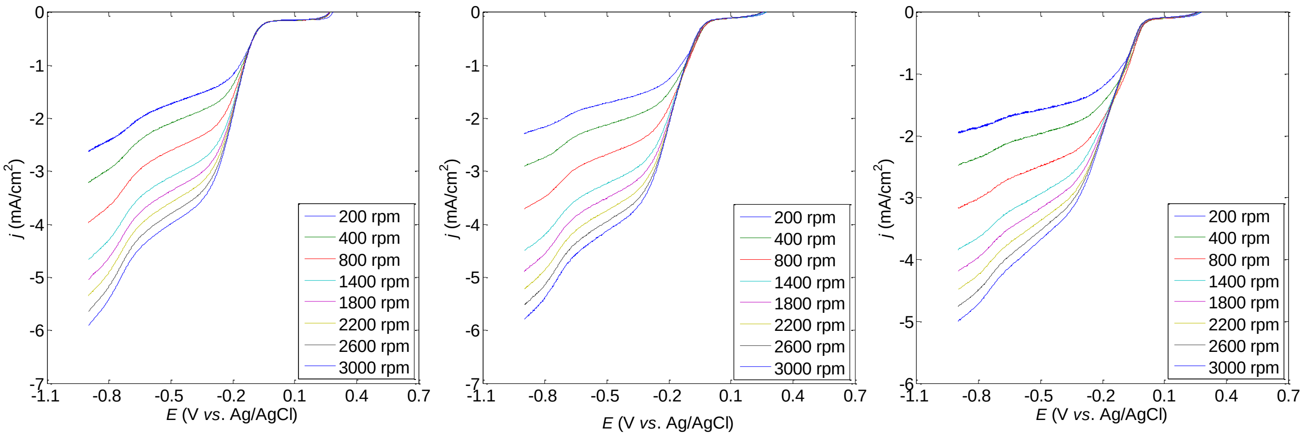

Figure S4b. Polarization curves of CTNC film at different rotating speeds. ***left***: CTNC-600; ***middle*****:** CTNC-800; ***right*****:** CTNC-900.

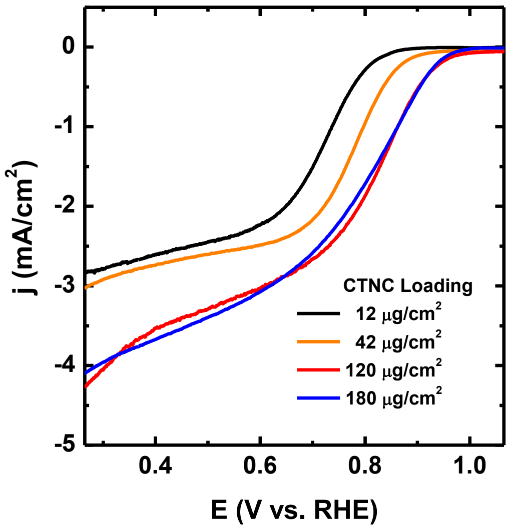

Figure S5. Polarization curves of CTNC-700 film with different catalyst loadings at rotating speed of 1400 rpm.

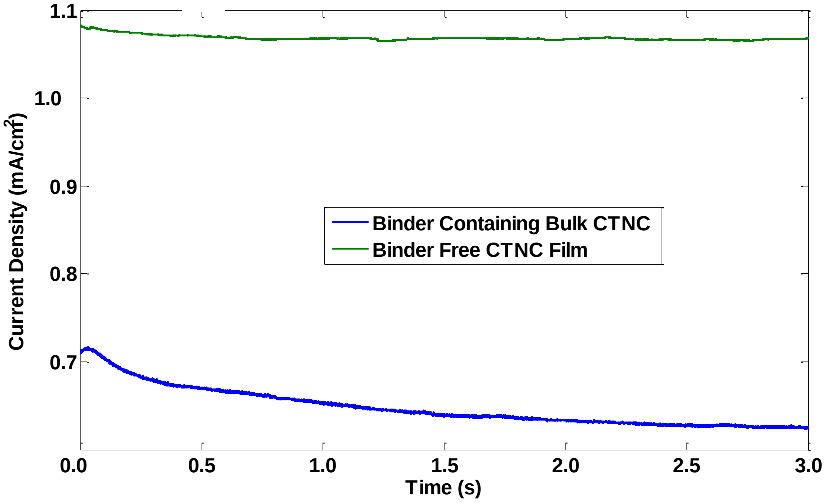

Figure S6. Current density-time chronoamperometric response of CTNC-700 at 0.865 V *vs*. RHE (rotating speed = 1400 rpm).

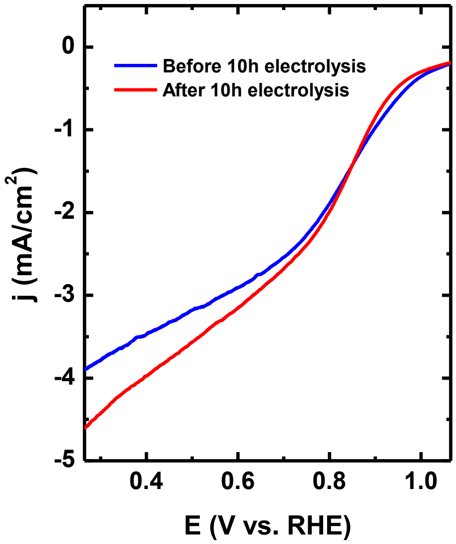

Figure S7. Comparison of polarization curves of CTNC before and after chronoamperometric experiments.

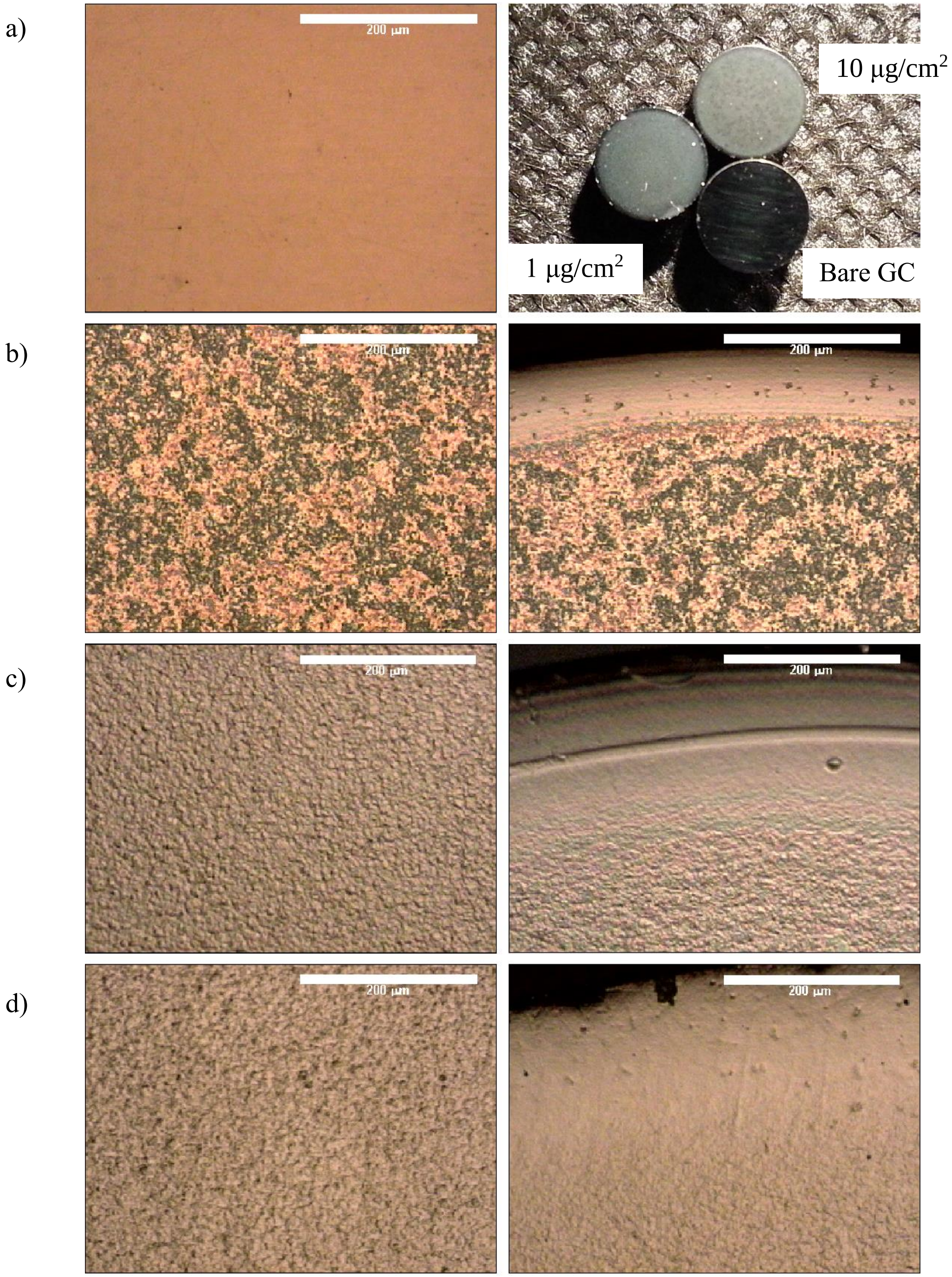

Figure S8. Optical microscopy images of electrodes used in electrochemical experiments demonstrating the continuity of all CTNC films. a) bare glassy carbon (***left***) and low magnification image of entire bare and catalyst coated GC electrodes; Images of the middle of the films (***left***) and edges of the films (***right***) for (b) 12 µg/cm^2, (c) 32 µg/cm^2, and (d) 120 µg/cm^2.

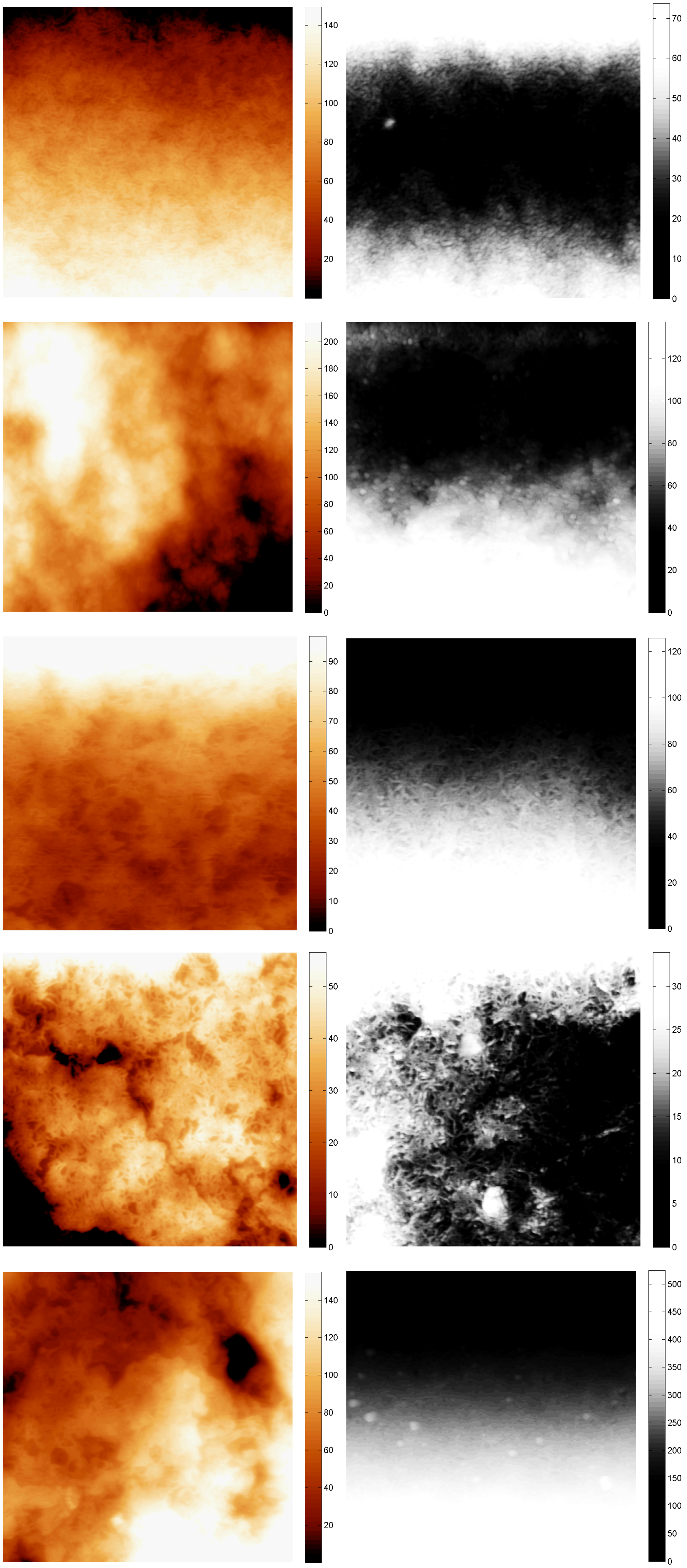

Figure S9. Unprocessed tapping mode AFM height images of films images of BCP films (***left column***) and resultant CTNC-700 films (***right column***) of different thickness. Film thicknesses correspond to CTNC catalyst loadings of 12 μg/cm^2, 42 μg/cm^2, 120 μg/cm^2, 150 μg/cm^2, and 180 μg/cm^2, and increase from top to bottom. Size of each image: 2000 nm × 2000 nm. Vertical color bars show color coding of height in nm.

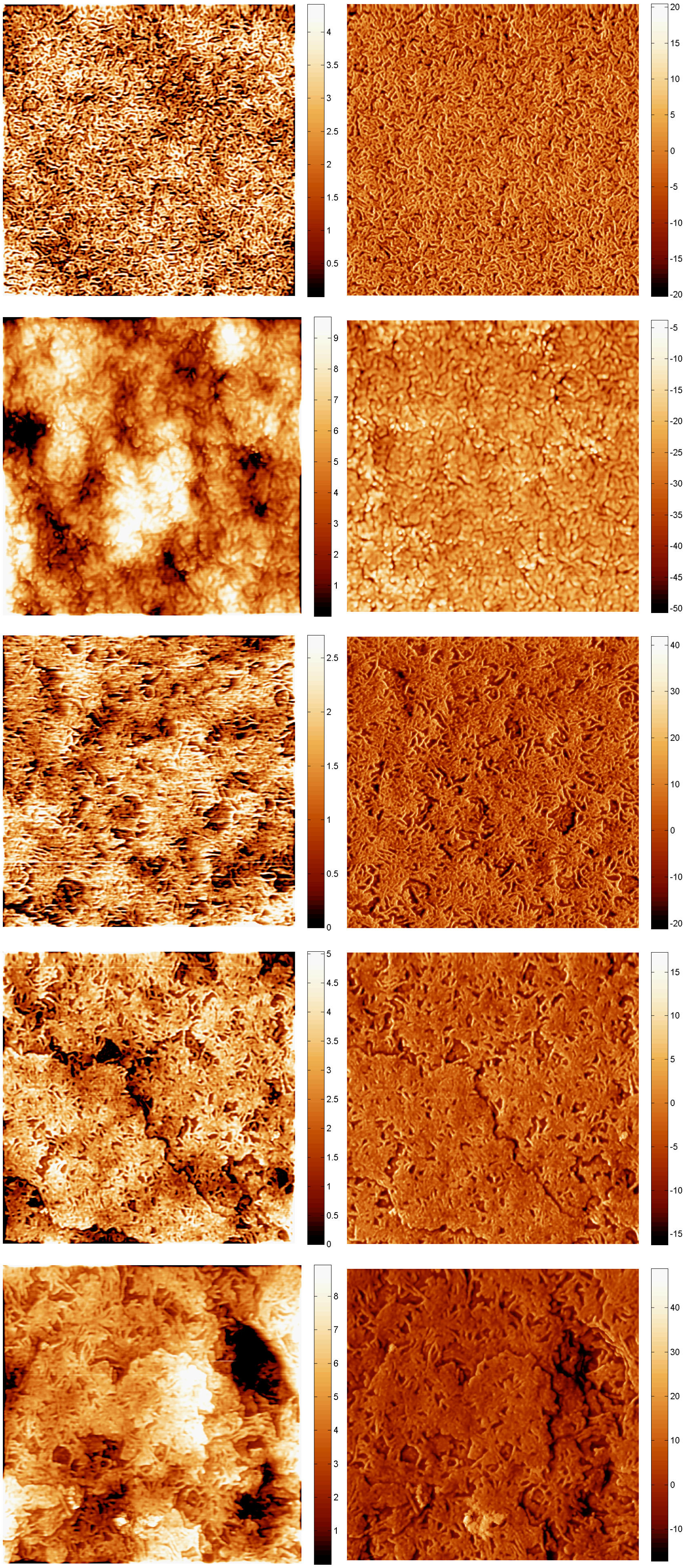

Figure S10. Tapping mode AFM images of BCP films of different thickness solution-deposited onto glassy carbon electrodes. Film thicknesses correspond to resultant CTNC catalyst loadings of 12 μg/cm^2, 42 μg/cm^2, 120 μg/cm^2, 150 μg/cm^2, and 180 μg/cm^2, and increase from top to bottom. ***Left column***: flattened high-pass filtered images; ***right column***: phase images. Size of each image: 2000 nm × 2000 nm. Vertical color bars show color coding of height in nm and phase shift in degrees.

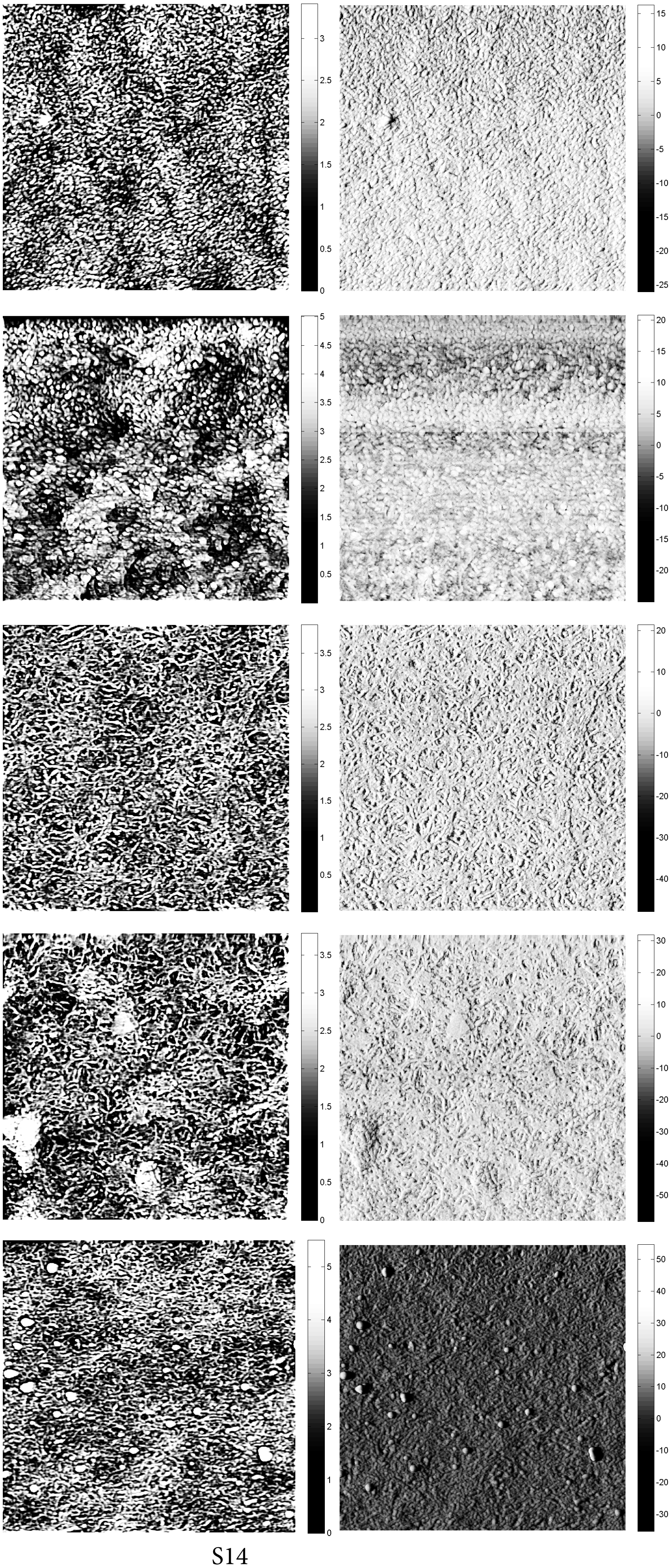

Figure S11. Tapping mode AFM images of CTNC films pyrolyzed from block copolymer precursor of different thickness solution-deposited onto glassy carbon electrodes. Film thicknesses correspond to resultant CTNC catalyst loadings of 12 μg/cm², 42 μg/cm², 120 μg/cm², 150 μg/cm², and 180 μg/cm², and increase from top to bottom. ***Left column***: flattened high-pass filtered images; ***right column***: phase images. Size of each image: 2000 nm × 2000 nm. Vertical color bars show color coding of height in nm and phase shift in degrees.

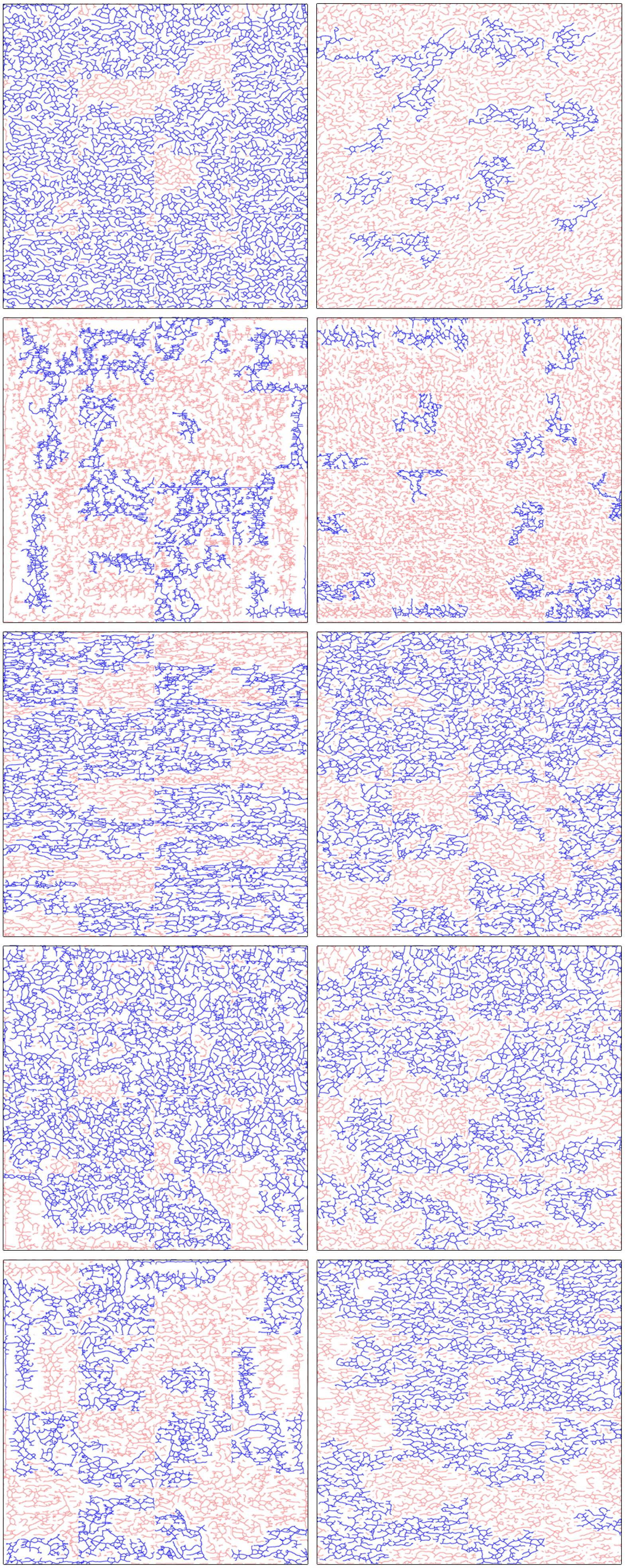

Figure S12. Digital skeletons of tapping mode AFM images of BCP films (***left column***) and resultant CTNC-700 films (***right column***) of different thickness. Film thicknesses correspond to resultant CTNC catalyst loadings of 12 μg/cm², 42 μg/cm², 120 μg/cm², 150 μg/cm², and 180 μg/cm², and increase from top to bottom. Size of each image: 2000 nm × 2000 nm. Image skeletons were computed by digital thinning of non-overlapping 500 nm × 500 nm sub-panels of each image, and the largest connected cluster within each sub-panel was colored blue. All remaining clusters were colored red. For each 2000 nm × 2000 nm image the mean and standard deviation of the size of the largest cluster (in pixels) were calculated as the mean and standard deviations of the sizes of the largest clusters within each sub-panel. Bar plots of such calculated means are shown in Figure 3d of the main manuscript.

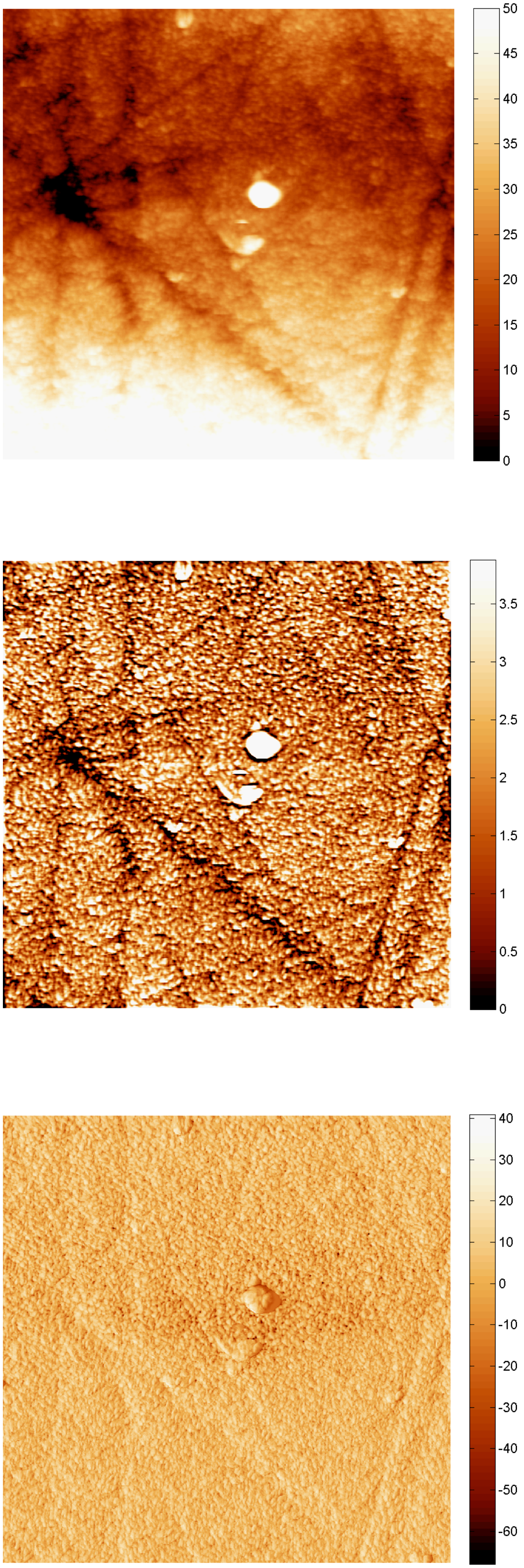

Figure S13. Tapping mode AFM images of uncoated glassy carbon electrode. ***Top***: unprocessed height image; ***Middle***: flattened high-pass filtered image; ***Bottom***: phase image. Size of each image: 2000 nm × 2000 nm. Vertical color bars show color coding of height in nm and phase shift in degrees.

References

1 Zhong, M.; Kim, E. K.; McGann, J. P.; Chun, S.-E.; Whitacre, J. F.; Jaroniec, M.; Matyjaszewski, K.; Kowalewski, T. *J. Am. Chem. Soc.* **2012**, *134*, 14846-14857.
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3 Kinoshita, K. *Carbon : electrochemical and physicochemical properties*; Wiley: New York, 1988.