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Supporting Information

Fundamental Nanoscale Surface Strategies for Robustly Controlling Heterogeneous Nucleation of Calcium Carbonate

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Experimental Section

1. Deposition of Polymer Coatings

1.1 Initiated Chemical Vapor Deposition (iCVD) of Poly(1,3,5-Trivinyl-1,3,5-Trimethyl cyclotrisiloxane) (PV_3D_3)

PV_3D_3 thin films were performed on Cu/Ni alloy foils (Cu70/Ni30, Goodfellow) in a custom-built cylindrical iCVD reactor described previously.[1] 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane (V_3D_3, Gelest) monomer and *tert*-butyl peroxide (TBPO, 98%, Sigma-Aldrich) initiator were both used as received. The Cu/Ni substrates were loaded into the reactor chamber and pumped down overnight. During the deposition, TBPO vapor was delivered at room temperature with a flow rate of 0.6 sccm using a range adjustable mass flow controller (MKS M100B). V_3D_3 monomer was heated to 70 °C, and delivered at a flow rate of 0.9 sccm through a metering bellows sealed valve (Swagelok). The temperature of the resistive heating filaments (Chromalloy O, Goodfellow) was kept at 250±3 °C during the iCVD processes, while the temperature of the sample stage was controlled at 30 °C by a circulating chiller (Thermo Neslab RTE-7). The chamber pressure was set to 200 mTorr by an exhaust throttle valve (MKS Instruments) during the deposition. An interferometer equipped with a 633 nm HeNe laser (JDSU) was used to monitor the film growth on Si wafers in real time. The growth rate of PV_3D_3 is 0.5~0.6 nm/min.

1.2 iCVD of Poly(1,3,5,7-Tetravinyl-1,3,5,7-Tetramethylcyclotetrasiloxane) (PV_4D_4)

PV_4D_4 thin films were deposited in a similar procedure as PV_3D_3. 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (V_4D_4, Gelest) monomer was used as received. TBPO was delivered at room temperature at 0.6 sccm, while V_4D_4 was heated to 80 °C and delivered at 0.3 sccm. The chamber pressure was set to 200 mTorr. The temperature of the sample stage was controlled at 45 °C. The heating filaments were kept at 250±3 °C during the iCVD processes for PV_4D_4. The growth rate of PV_4D_4 is 1.2~1.3 nm/min.

1.3 iCVD of Poly(Divinylbenzene) (PDVB)

PDVB thin films were deposited using a procedure reported previously.[2] Divinylbenzene (DVB, 80%, Sigma-Aldrich) monomer was used as received. TBPO was delivered at room temperature at 0.6 sccm, while DVB monomer was heated to 65 °C and delivered at 2.0 sccm using a heated mass flow controller (MKS 1152C). The chamber pressure was set to 200 mTorr. The temperature of the sample stage was controlled at 35 °C. The heating filaments were kept at 250±3 °C during the iCVD processes for PDVB. The growth rate of PDVB is ca. 1.6 nm/min.

1.4 iCVD of Poly(1H,1H,2H,2H-Perfluorodecyl Acrylate) (PPFDA)

PPFDA thin films were deposited using a procedure similar to a previous report.[3] 1H,1H,2H,2H-perfluorodecyl acrylate (PFDA, 97%, Sigma-Aldrich) monomer was used as received. During the deposition, TBPO vapor was delivered at room temperature with a flow rate of 0.85 sccm. PFDA monomer was heated to 70 °C and delivered at a flow rate of 0.13 sccm through a metering bellows sealed valve. The chamber pressure was set to 30 mTorr. The temperature of the sample stage was controlled at 30 °C, while the heating filaments were kept at 270±3 °C during the iCVD process for PPFDA. The growth rate of PPFDA is ca. 0.9 nm/min.

2. Materials Characterization

Film thicknesses were analyzed using a variable angle ellipsometer (J.A. Woollam M-2000). Spectroscopic data collected at 65^o, 70^o and 75^o incident angles were fit to a Cauchy-Urbach model using WVASE32 software. Surface morphology and roughness of iCVD polymer films and Cu/Ni foils were characterized using a Veeco Dimension 3100 atomic force microscope in tapping mode. Fourier transform infrared spectroscopy (Thermo Scientific Nicolet iS50) was used to analyze the polymer composition. Contact angles for iCVD polymer films were measured using a Ramé-Hart Model 500 goniometer with an automatic dispensing system. SEM and EDX mapping images were obtained using a JEOL 6700F field-emission Scanning Electron Microscope. GIXRD was measured using a Rigaku SmartLab diffractometer. Quartz crystal microbalance with dissipation (QCMD, Biolin Scientific QSense Analyzer) was employed to measure the heterogeneous nucleation of $CaCO_3$ on iCVD polymer surfaces. Mixed aqueous solution of 2 mM $NaHCO_3$ and 10 mM $CaCl_2$ was used to flow through an iCVD coated QCMD crystal in a liquid cell (Biolin Scientific). The supersaturation of the aqueous solution for the nucleation measurements using QCMD is below the critical supersaturation for homogeneous nucleation of ACC, aragonite, vaterite and calcite,[4] and is similar to the lowest concentration used in previous study for heterogeneous nucleation of $CaCO_3$.[5]

3. Corrosion Measurments

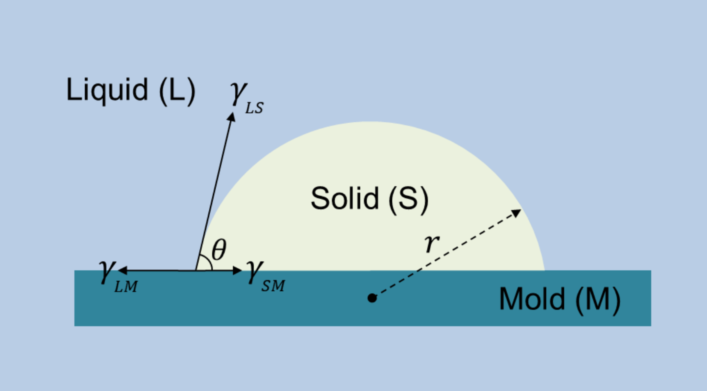
Electrochemical corrosion tests were performed in a 3.5 wt% NaCl aqueous solution with 1 cm^2 of sample surface exposed to the electrolyte. A custom-made three electrodes cell was used in these tests together with Pt counter electrode, Ag/AgCl reference electrode and the working electrode of uncoated and iCVD-coated Cu/Ni foils. The cell was purged with N_2 for 5 min. before each measurement. Bio-Logic VMP3 potentiostat was employed to obtain the potentiodynamic polarization curves. Corrosion current was extracted from the linear sweep voltammetry curves via Tafel analysis in EC-Lab® Software. Corrosion rate (CR) was calculated using the following equation:

$$\mathrm{CR} = \mathrm{K}\frac{i_{corr}}{\rho}EW \tag{S1}$$

Where K is the constant defining the units for the corrosion rate (K = 3.27×10^{-3} mm·g·μA^{-1}·cm^{-1}·yr^{-1}), i_{corr} is the corrosion current density (in units of μA·cm^{-2}), ρ is the density and equals to 8.94 g·cm^{-3} for Cu/Ni (Ni 30%) (ASTM G1−03 (2017)), EW is the equivalent weight and equals to 30.98 for Cu/Ni (Ni 30%) (ASTM G102 − 89 (2015)).

4. Adhesion Measurements and Nucleation Energy Calculation

Adhesion measurement was performed on a molecular force probe (MFP, Asylum Research MFP-3D). $CaCO_3$ single crystals were purchased from MTI Corporation and used as received. Si MFP tips (AC240TS) were coated with iCVD PV_3D_3, PV_4D_4, PDVB and PPFDA for adhesion force measurements on $CaCO_3$ single crystals. Film thickness is ca. 50 nm for PV_3D_3, PV_4D_4, and PPFDA, and ca. 200 nm for PDVB, respectively. 40 μL of CaCO3 saturated aqueous solution was added on to the top surface of the $CaCO_3$ single crystal mounted on the sample stage. Uncoated and iCVD-coated MFP tips were controlled to approach, contact and detach from the $CaCO_3$ surface in the aqueous environment.



Scheme S1. Schematic of heterogeneous nucleation on flat surface

Work of adhetion (W_{ad}) was calculated from measured adhesion force (F_{ad}) using Johnson-Kendall-Roberts (JKR) Model, assuming hemispherical tip geometry with radius of R for the iCVD-coated tips.

$$W_{ad} = \frac{F_{ad}}{1.5\pi R} \tag{S2}$$

Based on the W_{ad}, the contact angle θ of $CaCO_3$ on iCVD polymers was estimated using Young-Dupré Equation

$$W_{ad} = \gamma_{LS}\,(1 + \cos\theta) \tag{S3}$$

where γ_{LS} (in units of J/m^2) is the interfacial energy between H_2O and $CaCO_3$. The reported value for water on calcite surface is 83 mN/m.[6]

Heterogeneous nucleation on flat surfaces can be described using a simplified model with a spherical nuclei cap formed on a flat mold (Scheme S1). The corresponding energy barrier ΔG^*_{Het} is given by

$$\Delta G^*_{Het} = \Delta G^*_{Hom} \cdot g(m) \tag{S4}$$

where ΔG^*_{Hom} is the energy barrier for homogenous nucleation, the geometric factor *g(m)* is defined as a function of *m* ($m = \cos\theta$)

$$g(m) = \frac{1}{4}(1-m)^2(2+m) \tag{S5}$$

Induction time (τ) is inversely proportional to nucleation rate (J), assuming neglected crystal growth during the nucleation delay[7]

$$\tau \propto \frac{1}{J} \tag{S6}$$

where J is correlated with the nucleation energy barrier through Equation S7

$$J = A\,\exp(-\frac{\Delta G^*_{Het}}{k_B T}) \tag{S7}$$

where A is a kinetic parameter, k_B is the Boltzmann constant, T is the temperature (in units of K).[8] Combining Equations S6 and S7

$$\frac{1}{\tau} = A'\,\exp(-\frac{\Delta G^*_{Het}}{k_B T}) \qquad (A' \equiv \frac{A}{\tau \cdot J}) \tag{S8}$$

Taking natural log of Equation S7 gives

$$-\ln\frac{1}{\tau} = \varphi \cdot \frac{\Delta G^*_{Het}}{\Delta G^*_{Hom}} - \ln A' \quad (\varphi \equiv \frac{\Delta G^*_{Hom}}{k_B T}) \tag{S8}$$

where A' and φ are both constant for $CaCO_3$ nucleation at given temperature.

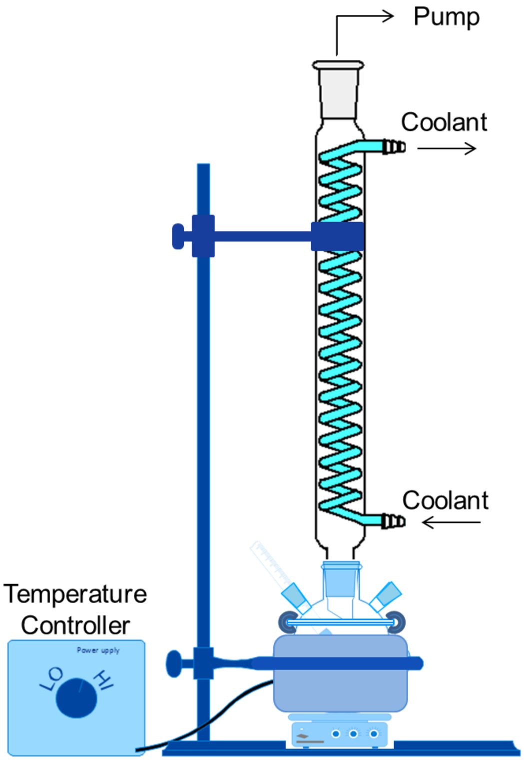
5. Simulated MSF Scaling Tests

The anti-scaling performance of iCVD polymer coatings was evaluated by exposing the iCVD-coated Cu/Ni (Cu70/Ni30, Goodfellow) surfaces to 1L of heated aqueous solution of 2 mM $NaHCO_3$ and 10 mM $CaCl_2$ in a cylindrial glass vessle (Scheme S2). All the samples were taped with Kapton tape on the back side so that only the top surface is exposed to the solution. The samples were also vertically aligned and taped to the wall of the glass vessel. The boiling temperature of the aqueous solution was controled from 50 to 110 °C by varying the pressure inside the apparatus. After 2 h, the samples were taken out, washed with deionized water to remove $CaCl_2$ and $CaCO_3$ formed homogenously form the solution, characterized using optical microscope and GIXRD, and finally digested with 10 mL of 0.1% v/v HNO_3 solution for ICP-OES.

The total Ca surface density can be calculated from the following equation:

$$Total\ Ca\ Surface\ Density = \frac{C_{Ca,ICP} \cdot V}{A} \tag{S6}$$

where $C_{Ca,ICP}$ is the concentration (mg/L) measured from ICP, V is the total volume of 0.1% HNO_3 solution used to dissolve $CaCO_3$ (10mL), and A is the area of the sample (in units of cm^2) determined using ImageJ image processing software.



Scheme S2. Schematic of the experimental apparatus used for the simulated MSF scaling tests.

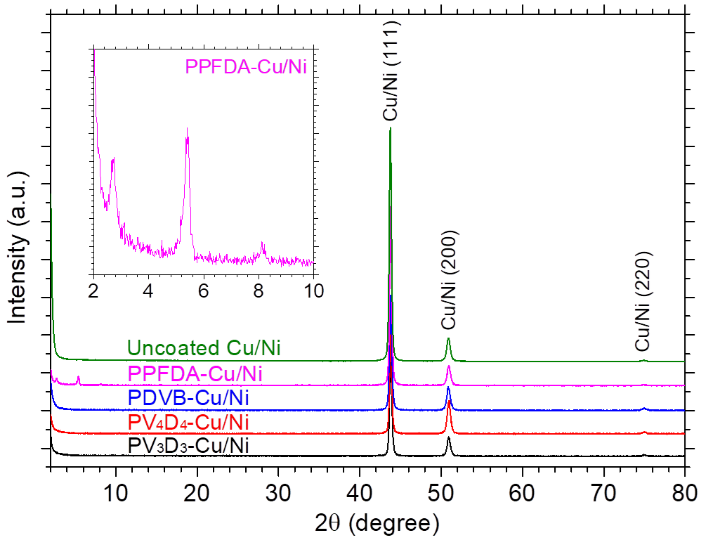


Figure S1. Grazing incidence X-ray diffraction (GIXRD) patterns for uncoated Cu/Ni foil and Cu/Ni coated with different iCVD polymers. Inset represents the diffraction peaks for iCVD PPFDA at low 2θ angles.

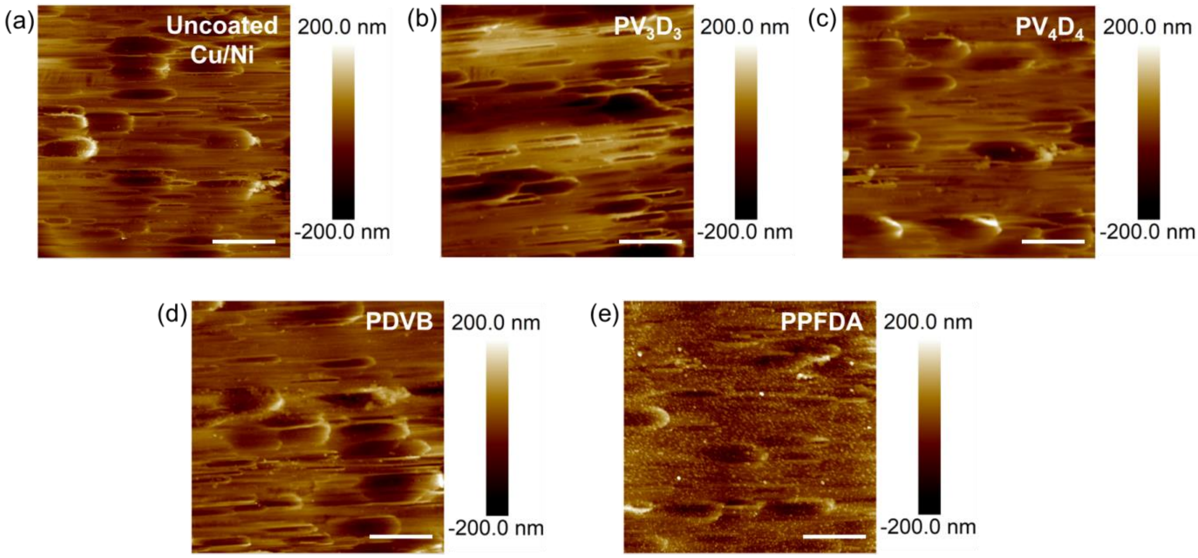


Figure S2. Atomic force microscopy (AFM) images for uncoated Cu/Ni foil and Cu/Ni coated with iCVD PV_3D_3, PV_4D_4, PDVB and PPFDA, respectively (Scale bars represent 10μm).

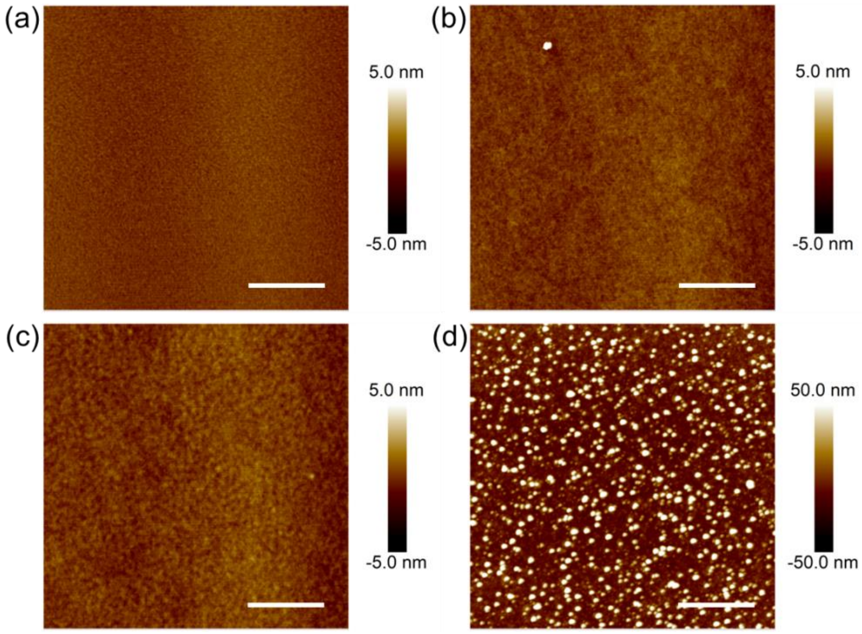


Figure S3. AFM images for Si wafers coated with (a) iCVD PV_3D_3, (b) PV_4D_4, (c) PDVB and (d) PPFDA, respectively (Scale bars represent 5 μm).

Table S1. Surface Roughness (nm) of Si and Cu/Ni substrates coated with and without iCVD polymer films

	No Film	PV_3D_3	PV_4D_4	PDVB	PPFDA
Si Substrate	0.15 ±0.03	0.27 ±0.06	0.49 ±0.09	0.48 ±0.03	15.8 ±1.5
Cu/Ni Substrate	37.8 ± 11.0	40.3 ±21.3	32.9 ±3.0	36.7 ±5.8	35.6 ±6.6

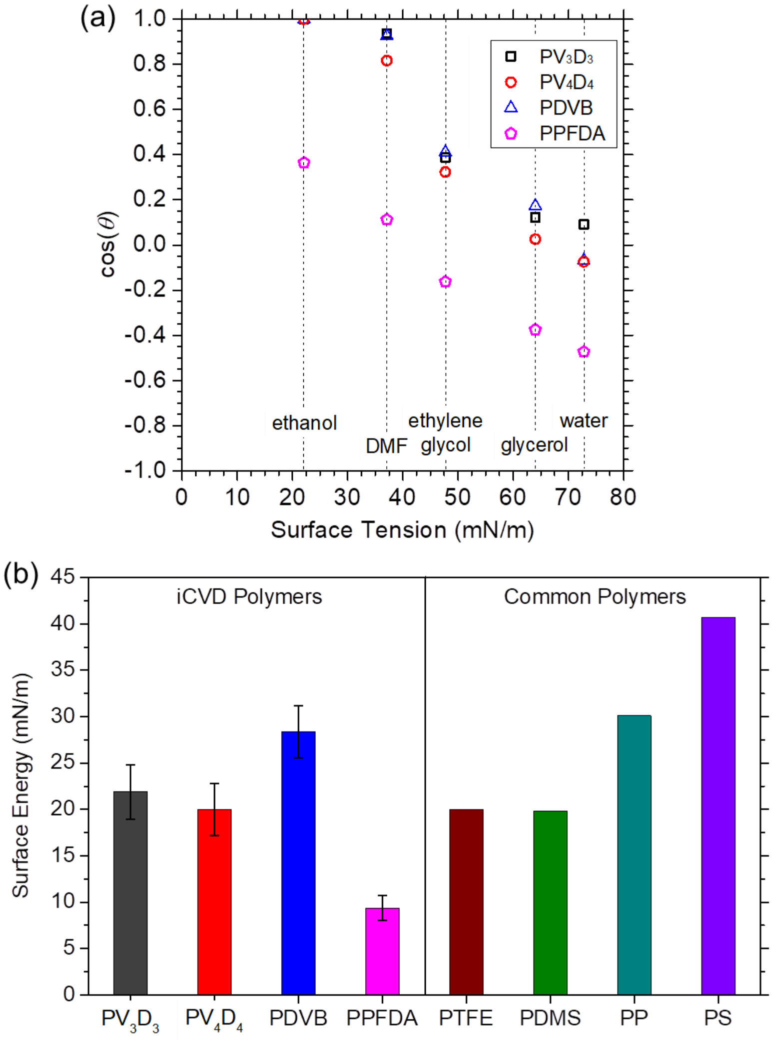


Figure S4. (a) Contact angles of liquids with different known surface tension on iCVD polymer surfaces. (b) Calculated surface energy for iCVD polymers and reported surface energy values for common commercial polymers.

Table S2. Comparison of adhesion with calcite

Contact Material	F_{ad} (nN)	Tip Radius (nm)	W_{ad} Calculated (mN/m)	Test Medium	Ref.
Cu	11.4	24.3	99.3	$CaCO_3$ saturated aq.	[9]
SiO_2 coated Cu	6.18	23.2	56.5	$CaCO_3$ saturated aq.	[9]
Silane coupled Cu	29.2	23.3	266	$CaCO_3$ saturated aq.	[9]
Glass	6.22	26.3	50.2	$CaCO_3$ saturated aq.	[9]
Si_3N_4	1.9	35	11.5	Water	[12]
PV_3D_3	5.75	50	24	$CaCO_3$ saturated aq.	This work
PV_4D_4	4.05	50	17	$CaCO_3$ saturated aq.	This work
PDVB	18.6	200	19.7	$CaCO_3$ saturated aq.	This work
PPFDA	1.21	50	5.1	$CaCO_3$ saturated aq.	This work

Table S3. Polar and dispersive components of the surface energy for iCVD polymers

	PV_3D_3	PV_4D_4	PDVB	PPFDA
Polar Component (mN/m)	12.02	4.39	1.91	0.50
Dispersive Component (mN/m)	9.87	15.57	26.49	8.86
Surface Energy (mN/m)	21.89	19.96	28.4	9.36
Polarity	0.55	0.22	0.067	0.053

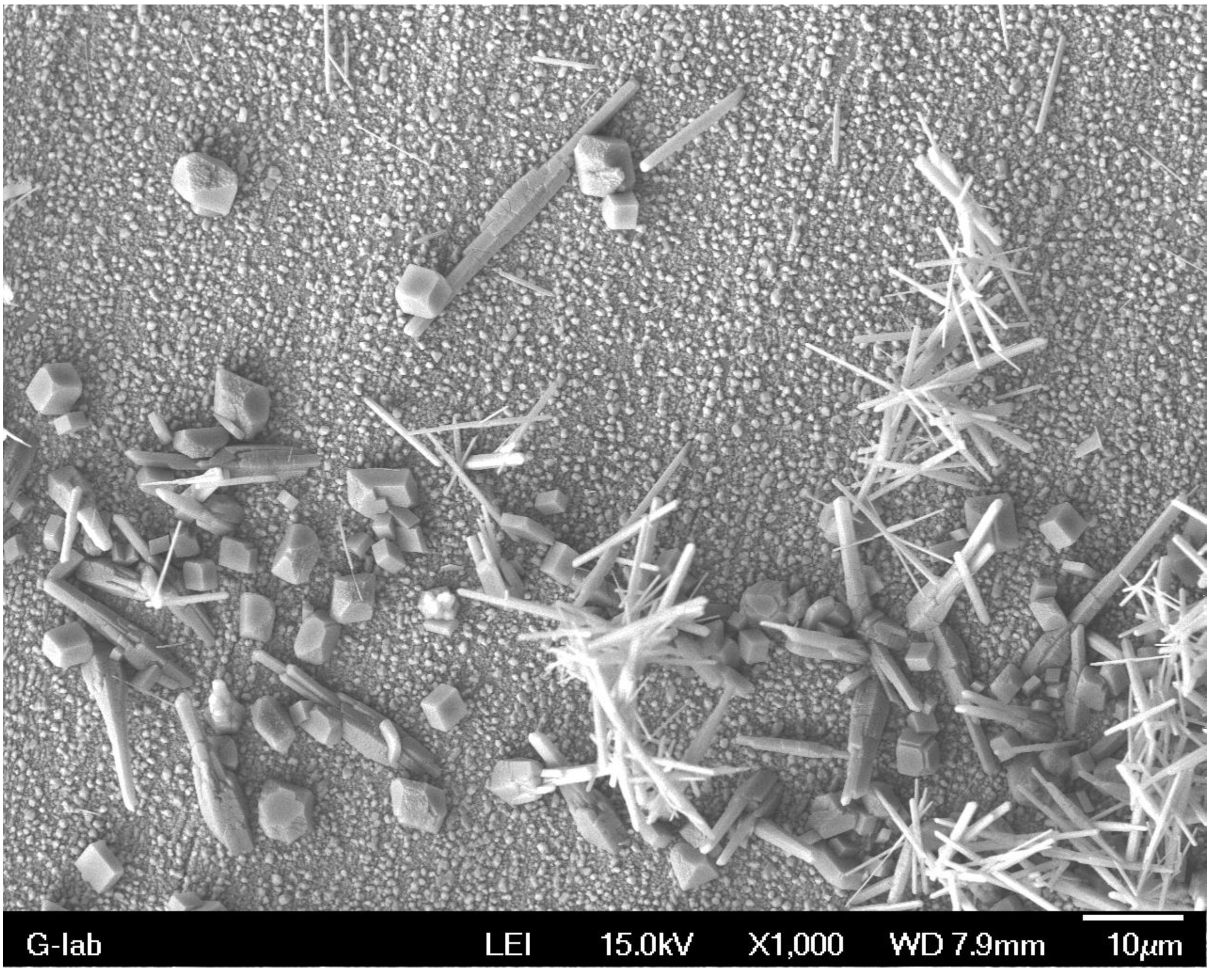


Figure S5. SEM image for uncoated and iCVD coated Cu/Ni foil surfaces after $CaCO_3$ scaling tests at 110 °C.

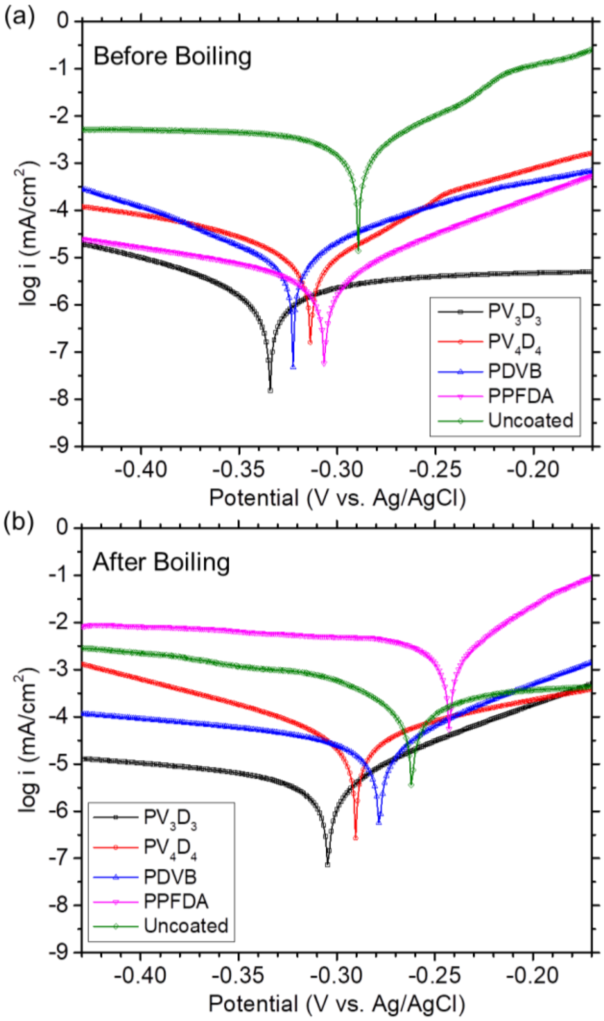


Figure S6. Tafel plots for uncoated and iCVD coated Cu/Ni foils before and after exposure to boiling water for 2 h.

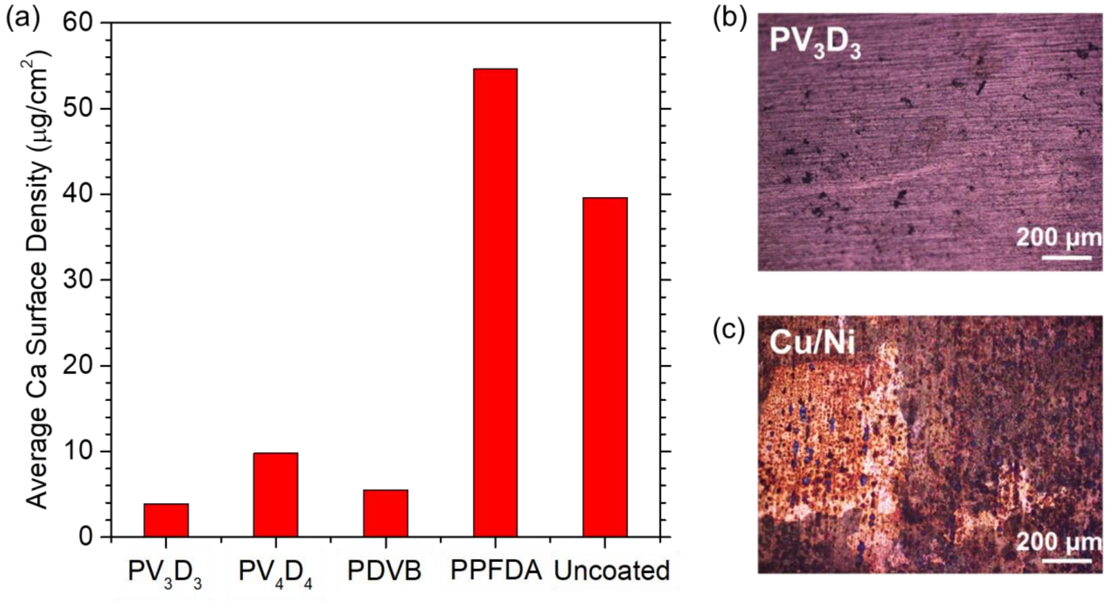


Figure S7. (a) Calcium surface density for uncoated and iCVD-coated Cu/Ni after simulated MSF tests for 72 h. (b-c) Optical micrographs for (b) iCVD PV_3D_3 coated Cu/Ni after 72 h test, and (c) uncoated Cu/Ni after 72 h tests.

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