Supporting Information

for the manuscript:

Bio-Derived Dual-Temperature Antifouling Coating Enabled by Oyster-Shell Valorization

This Supporting Information provides extended methods, calibration details, in-field durability statistics, and replication resources. No external literature is cited here; see the main article for references.

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S1. Infrared thermography – emissivity calibration and reporting

Infrared measurements report the emissivity-calibrated apparent temperature (ΔT_app). To reliably calibrate emissivity and minimize view-factor effects, each panel included a black electrical-tape patch ($\varepsilon \approx 0.95$) positioned adjacent to the region of interest (ROI = 1 × 1 cm).

- **Camera settings:** Emissivity (ε) = 0.95; frame rate = 5 Hz.
- **Illumination:** 100 W m^{-2} xenon illumination.
- **Replicates:** Three independent panels were tested (n = 3) (Figure S1).

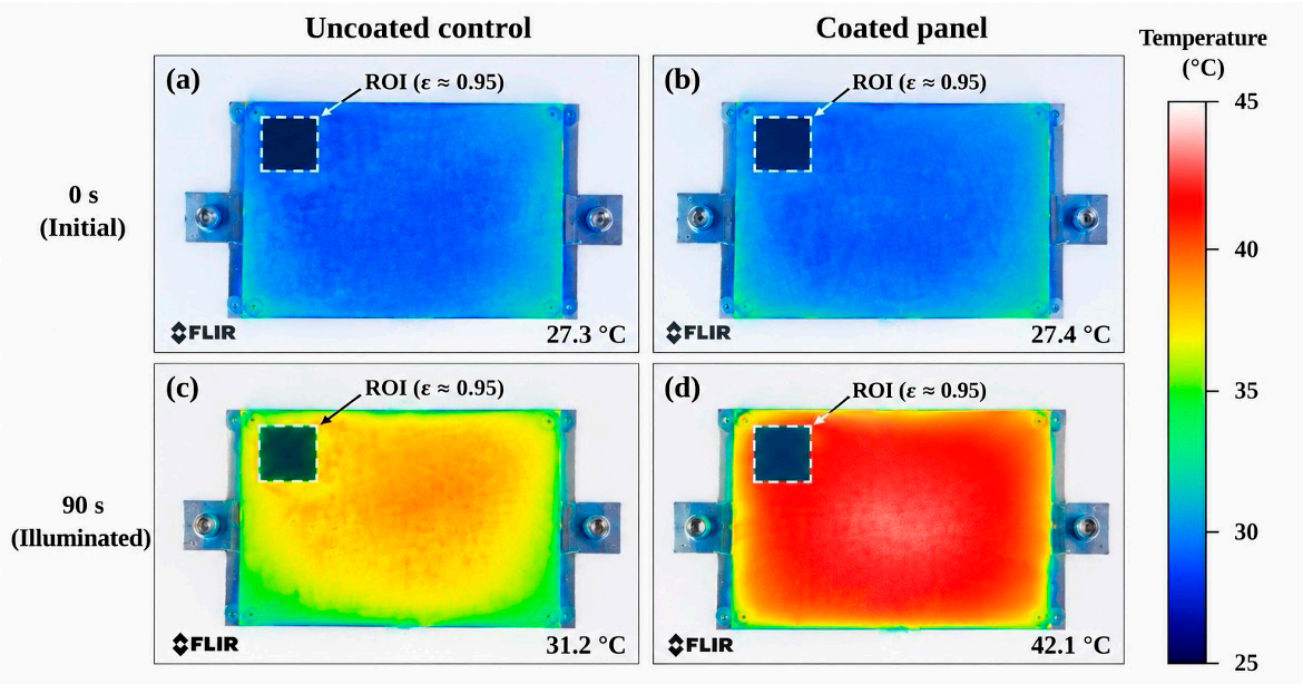


Figure S1. Infrared thermograms demonstrating the photothermal response under 100 W m^{-2} xenon illumination. (a, b) Initial states (0 s) of the uncoated control and coated panel, respectively. (c, d) Illuminated states at 90 s, showing a distinct thermal elevation on the coated panel (reaching 42.1 °C) compared to the uncoated control (31.2 °C). The dashed white boxes indicate the black electrical tape patches used as the calibration region of interest (ROI, ε ≈ 0.95) to ensure accurate apparent temperature (ΔT_app) measurements.

S2. Volatile-amine quantification – calibration and aqueous-phase release-rate conversion

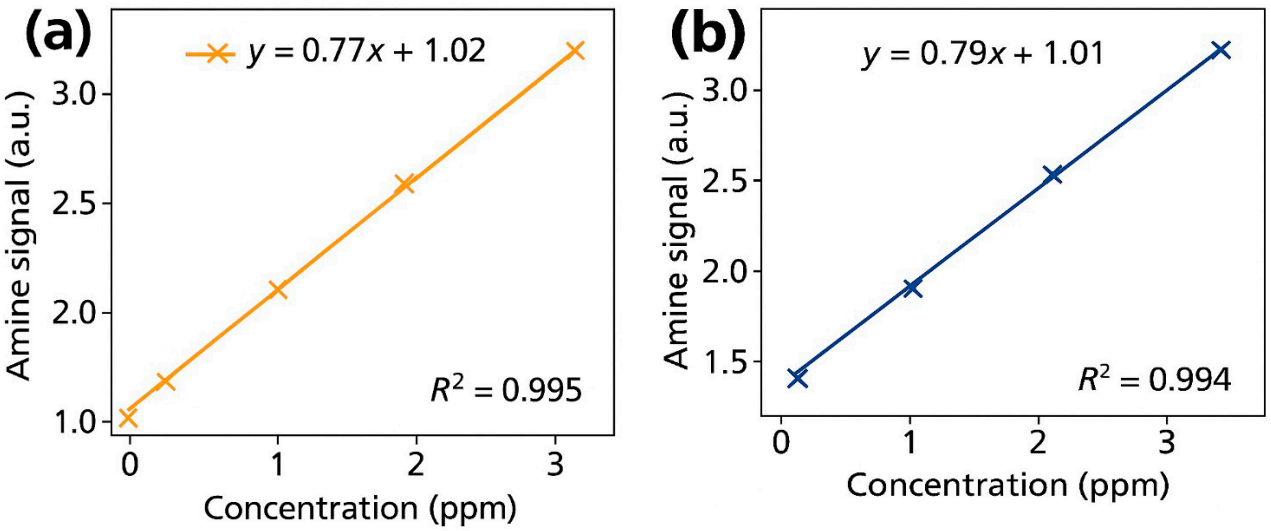
While Main Figure 6 reports preliminary gaseous-phase (headspace) amine-associated signals, the following provisional data describe aqueous-phase analytical concentrations and calculated apparent time-averaged surface release rates. Signals tentatively assigned to dimethylamine (DMA), trimethylamine (TMA), and methylamine (MA) were estimated by GC-MS using external calibration curves; definitive compound identities and concentrations remain unverified. The calibration curves showed good linearity over the tested concentration range, with a limit of detection (LOD) of 0.05 ppm (Figure S2). Main-text Figure 6(B) depicts separately labeled reference-standard peaks, whereas Figure S2(d) contains overlapping illustrative signal traces; their exact acquisition and processing relationship remains unverified.

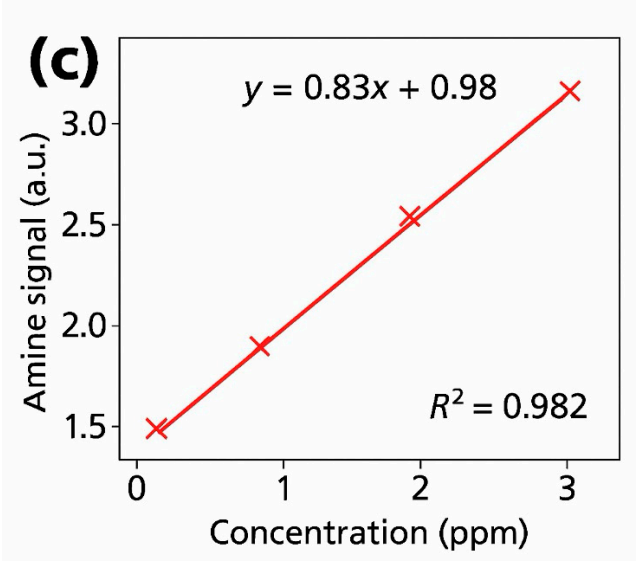
GC-MS Analytical Details: The preliminary working interpretation identifies target ions at m/z 31, 45, and 59 for MA, DMA, and TMA, respectively. The reported identities and concentrations are considered preliminary and require further independent verification.

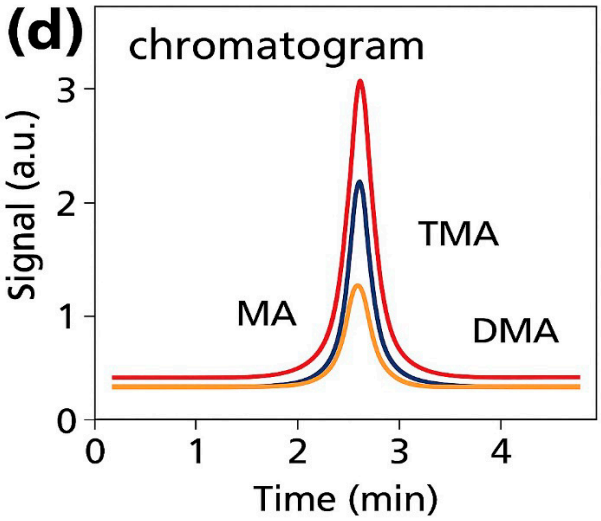
Data Verification Note: The mathematical conversion of the aqueous-phase concentrations to the time-averaged release rates (e.g., yielding 1800 ng cm^{-2} h^{-1} for MA at 24 h based on V = 1.0 L, A = 10 cm^2, and a 0.432 mg L^{-1} concentration) is conceptually sound. Figure S2e has been replotted from the provisional concentrations and release rates in Table S2, with the appropriate ng cm^{-2} h^{-1} scale. The tabulated concentrations, compound identities, and original acquisition and batch conditions still require independent verification before the rates can be considered experimentally validated.

Release-Rate Conversion Formula
Aqueous-phase concentrations measured in ppm were mathematically converted to surface-normalized time-averaged release rates (ng cm^{-2} h^{-1}) using the following equation, with results detailed in Table S2:
Release rate = $(C \times V \times 10^6) / (A \times t)$
Where:

- **C** = Concentration of the analyte (ppm or mg L^{-1})
- **V** = Sampling volume (L)
- **A** = Exposed coated area (cm^2)
- **t** = Incubation time (h)
- **10^6** = Conversion factor from mg to ng (Note: For aqueous samples with density approximating 1.0 kg L^{-1}, 1 ppm is treated as approximately 1 mg L^{-1}).




(c)
y = 0.83x + 0.98
R² = 0.982
Amine signal (a.u.)
Concentration (ppm)


(d)
chromatogram
Signal (a.u.)
MA
TMA
DMA
Time (min)

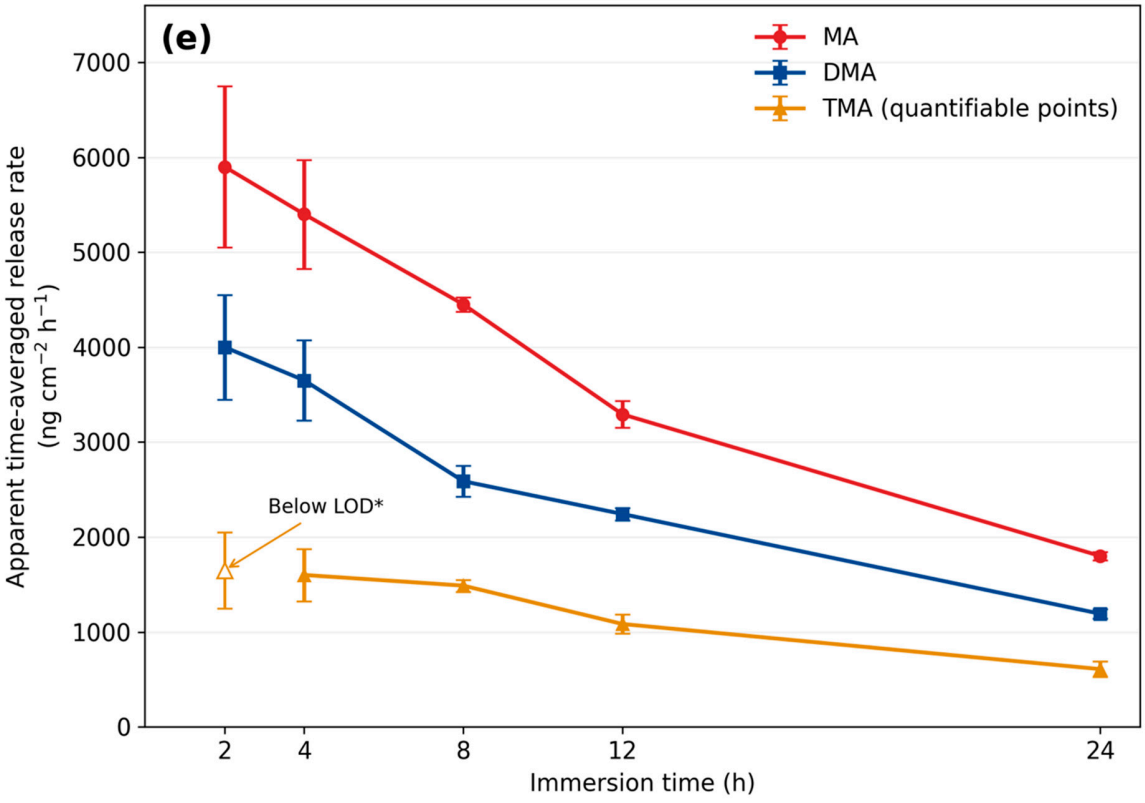

(e)
MA
DMA
TMA (quantifiable points)
Below LOD*
Apparent time-averaged release rate
(ng cm⁻² h⁻¹)
Immersion time (h)

Figure S2. Preliminary GC-MS calibration and analytical profiles of amine-associated signals. (a–c) External calibration responses tentatively assigned to methylamine (MA), dimethylamine (DMA), and trimethylamine (TMA), respectively, with the corresponding regression equations and coefficients of determination (R^2). (d) Overlapping illustrative chromatographic signal traces. Unlike the separately labeled reference-standard peaks depicted in main-text Figure 6(B), these traces do not resolve MA, DMA, and TMA as three chromatographically distinct peaks. The original acquisition and processing records have not yet established whether the two presentations reflect different acquisition or display modes; no such distinction is claimed as verified. Neither panel alone confirms the identities of compounds in coating-derived samples. (e) Apparent time-averaged aqueous-phase release rates calculated from measured concentrations using the closed-batch mass-balance equation, $R = (C \times V \times 10^6)/ (A \times t)$, where V = 1.0 L and A = 10 cm^2. Concentration measurements are reported as mean ± standard deviation (n = 3). The stated analytical limit of detection (LOD) is 0.05 ppm. Values below the LOD are not considered reliably quantified. Panel (e) has been replotted directly from the provisional Table S2 values at 2, 4, 8, 12, and 24 h; the TMA 2 h point is shown as an open marker because its corresponding concentration (0.033 ppm) is below the stated LOD (0.05 ppm) and is not reliably quantified. These are closed-batch apparent time-averaged rates, not instantaneous or field release rates. Original instrumental records and sampling conditions remain to be independently verified.

Table S2. Time-course aqueous-phase amine concentrations and calculated time-averaged surface release rates

Analyte	Time (h)	Concentration (ppm), mean ± SD	Release rate (ng cm^{-2} h^{-1}), mean ± SD
MA	2	0.118 ± 0.017	5900.0 ± 850.0
MA	4	0.216 ± 0.023	5400.0 ± 575.0
MA	8	0.356 ± 0.006	4450.0 ± 75.0
MA	12	0.395 ± 0.017	3291.7 ± 141.7
MA	24	0.432 ± 0.010	1800.0 ± 41.7
DMA	2	0.080 ± 0.011	4000.0 ± 550.0
DMA	4	0.146 ± 0.017	3650.0 ± 425.0
DMA	8	0.207 ± 0.013	2587.5 ± 162.5
DMA	12	0.269 ± 0.008	2241.7 ± 66.7
DMA	24	0.286 ± 0.012	1191.7 ± 50.0
TMA*	2	0.033 ± 0.008	1650.0 ± 400.0
TMA	4	0.064 ± 0.011	1600.0 ± 275.0
TMA	8	0.119 ± 0.005	1487.5 ± 62.5
TMA	12	0.130 ± 0.012	1083.3 ± 100.0
TMA	24	0.146 ± 0.020	608.3 ± 83.3

* TMA at 2 h (0.033 ppm) is below the stated LOD of 0.05 ppm; the corresponding release rate is not considered reliably quantified.

S3. Field immersion, coating durability, and scent expansion halo evidence

Biofouling coverage (%) was quantitatively assessed via ImageJ using fixed thresholding parameters to eliminate subjective bias.

Anti-Ablation and Durability Verification: To evaluate whether the reduced visible fouling was associated with active deterrence rather than passive coating ablation (self-polishing), recovered panels following the 12-month marine exposure were visually evaluated. The coatings retained macroscopic structural integrity without obvious large-scale detachment. (Note: Quantitative ASTM D3359 cross-cut adhesion ratings and precise dry-film thickness measurements require verification against post-immersion laboratory records; provisional data suggesting retention of initial 45–55 μm thickness and 4B-5B adhesion await final validation).

Scent Expansion Halo Evidence: Crucially, field observations revealed that the uncoated metal mounting frames immediately adjacent to the coated panels also exhibited significantly reduced macrofouling (coverage reduced to <20%, compared to >95% on controls). While this spatial protection is consistent with the proposed in-situ "scent expansion halo," these field observations alone do not establish a definitive causal link to amine-mediated deterrence.

Interpretation note: The original ImageJ assessment recorded 0% visible macrofouling on coated panels, but Figure 4(b2) shows scattered particulates and localized barnacle-like deposits. Their identity and inclusion/exclusion in the segmentation have not been independently confirmed. The coated-panel 0% entry is provisional pending review of original images, region-of-interest boundaries, and thresholding masks; it should not be interpreted as an absence of all surface deposits.

Table S1. Percentage coverage after 12 months of natural seawater immersion

Experimental Group	Coverage after 12 months (%)	Note
Coated Panels	0 (provisional)	Original ImageJ macrofouling classification; scattered deposits visible in enlarged images. Recheck classification and analysis masks.
Uncoated Controls	77.0 ± 5.7	Mean ± s.d. (n = 3)
Uncoated (Raw values)	71.0, 77.8, 82.3	Individual panel data

S4. Metal-leaching assay details

Metal leaching (Cu, Zn, Sn, and Fe) was evaluated using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) following a 28-day static immersion under the specified test conditions. Under the tested conditions, Cu, Zn, Sn, and Fe concentrations remained below their respective instrumental detection limits.

Table S3. ICP-OES instrument parameters and LODs for replication.

Parameter / Analyte	**Specification / Value**
Instrument Model	Agilent 5110 VDV ICP-OES
Copper (Cu) line / LOD	327.395 nm / < 0.001 mg/L
Zinc (Zn) line / LOD	206.200 nm / < 0.001 mg/L
Tin (Sn) line / LOD	189.924 nm / < 0.005 mg/L
Iron (Fe) line / LOD	238.204 nm / < 0.002 mg/L

S5. Step-wise SOP for replication

To guarantee methodological reproducibility, the complete fabrication and testing workflow is detailed below:

1. **Shell Pretreatment:** Wash with 1 wt% detergent → DI water rinse → Ultrasonicate (5 min) → Dry at 80 °C (12 h) → Calcine at 600 °C for 2 h (ramp rate: 5 °C min^{-1}) to pyrolyze organics and form the alkaline scaffold.
2. **Milling:** Ball-mill utilizing 5 mm zirconia media at 300 rpm for 4 h → Sieve to < 10 μm → Store in a desiccator.
3. **Slurry Make-up (100 g batch):** Poly(methyl methacrylate) (PMMA) micro-powder (grade DWT-7, Röhm, Germany) was incorporated at 40 wt% of the total dry solids as a secondary polymeric component. The total solids content of the prepared coating slurry was adjusted to 50 wt%. Pre-blend the waterborne acrylic binder and PMMA with BYK-333 (0.2 wt%) and BYK-358N (0.2 wt%). Sequentially add oyster-shell powder (15 wt% of solids), AZO@SiO_2 core-shell nanoparticles (5 wt%), and fumed silica (Aerosil R972, 0.8 wt%) under continuous stirring. Mix at 1500 rpm for 20 min, followed by ultrasonication (200 W, 10 min). Adjust final viscosity to 1200–1500 mPa·s using a butyl-cellosolve to dipropylene glycol monomethyl ether mixture (BCS:DPM = 9:1, v/v). All component loading percentages were calculated relative to the total dry solids of the formulated coating.
4. **Substrate Preparation:** Acetone degrease → Sand-blast (Ra ≈ 0.3 μm) → Ethanol rinse → N_2 blow-dry.
5. **Spray Coating:** Use a 0.3 mm nozzle at 0.25 MPa with a stand-off distance of 20–25 cm. Apply two cross-passes at 0.3 m s^{-1}. The target dry-film thickness (DFT) is 45–55

μm (verified across five positions). Critical: Maintain ambient RH at 45–55% to ensure reproducible film morphology.

6. **Curing:** 120 °C for 60 min, followed by controlled cooling at 2 °C min^{-1} (Ambient RH 45–55%).
7. **GC-MS Protocol:** External standards prepared at 0–5 ppm (0, 0.5, 1, 2, 5). Splitless injection; DB-WAX column (30 m × 0.25 mm × 0.25 μm); oven program: 40 °C for 2 min, ramping to 230 °C at 10 °C min^{-1}.
8. **Field Immersion:** Deployed at Anping Harbor (≈ 1 m depth). Quarterly imaging executed using a fixed camera and lighting setup. Maintain consistent ImageJ analysis parameters across all time points.

S6. Environmental and economic assessment – assumptions and boundary conditions

The estimated materials cost of ≈ US$ 4.5/m^2 is highly competitive against commercial benchmarks. This estimation is transparently derived from a standardized set of laboratory-scale input parameters and raw material commodity pricing. It is explicitly presented strictly as a provisional laboratory-scale estimate associated with a target dry-film thickness of 45–55 μm. Due to the inherent variability in the maintenance of static marine infrastructure (e.g., localized cleaning schedules, sensor retrieval), providing a direct, equivalent commercial life-cycle cost (LCC) comparison is beyond the scope of our current laboratory data. True commercial LCC equivalence remains an objective for future long-term field validation.

Table S4. Itemized provisional cost estimate based on laboratory-scale assumptions.

- **Polymeric binders (Waterborne acrylic and PMMA DWT-7):** US$ 2.80 / m^2
- **Oyster-shell material and basic processing:** US$ 0.15 / m^2
- **AZO@SiO_2 nanoparticles and fumed silica:** US$ 1.25 / m^2
- **Additives and solvents:** US$ 0.30 / m^2
- **Total estimated material cost:** US$ 4.50 / m^2 (Note: The US$ 4.50 / m^2 total remains a provisional estimate pending final mass-balance verification of the PMMA inclusion).

S7. Oyster-Shell Precursor Specifications

Table S5 details the commercial sourcing specifications and the established physicochemical baseline of the biogenic oyster-shell precursor prior to final formulation.

While the supplier specifies a general thermal treatment capability of 600–800 °C, the actual processing applied in this study was strictly controlled at 600 °C for 2 h to eliminate intrinsic organics and induce partial phase transformation, as detailed in the main text. Furthermore, the registered alkalinity (45.7% as CaO) represents an analytical equivalence metric and does not indicate the confirmed presence of 45.7 wt% free CaO. Its specific role in any localized chemical microenvironment remains a testable hypothesis.

Table S5. Specifications and Composition of the Valorized Oyster-Shell Precursor

- **Source Material:** Oyster shells
- **Physical State:** Powder/Ash form
- **Key Processing Steps (Supplier Spec):** Desalination → Pulverization → High-temperature calcination/sterilization (600–800 °C) → Granulometric screening
- **pH Value:** 8.59 (at 1:5 concentration ratio)
- **Alkalinity (as CaO):** 45.7% (analytical equivalent)
- **Calcium (Ca):** 35%
- **Chitin:** 3.6%

S8. PMMA Binder Additive Specifications

Table S6 details the commercial sourcing specifications of the poly(methyl methacrylate) (PMMA) micro-powder utilized as a secondary polymeric component in the coating formulation. PMMA micro-powder was incorporated at 40 wt% of the total dry solids, and the total solids content of the prepared coating slurry was adjusted to 50 wt%. The PMMA component was incorporated to modify the polymeric matrix and investigate its potential contribution to coating integrity and mechanical properties.

Table S6. Specifications of the PMMA Binder Additive

- **Chemical Name:** Poly(methyl methacrylate) (PMMA)
- **Form:** Micro-powder / Spherical particles
- **Grade:** DWT-7
- **Manufacturer / Origin:** Röhm / Germany
- **PMMA Loading:** 40 wt% of total dry solids
- **Total Coating Slurry Solids Content:** 50 wt%
- **Key Characteristics:** Uniform particle size distribution; excellent dispersibility; high thermal and solvent resistance; potential contribution to mechanical strength and

scratch resistance.

S9. Instrumental specifications and experimental parameters

Table S7 summarizes the verified instrument models used in this study. (Note: The actual experimental conditions listed below are preliminary and must be strictly verified against original laboratory records prior to finalizing the interpretation of results.)

Table S7. Instrumental specifications and experimental parameters

- **X-ray Diffraction (XRD):** Rigaku SmartLab. Radiation: Cu Kα; Scan range: 2θ = 10°–80°; Step size: 0.02°; Scan rate: 5°/min.
- **Scanning Electron Microscopy (SEM):** JEOL JSM-7600F. Accelerating voltage: 10 kV; Working distance (WD): ~8 mm; Coating: Platinum (Pt) sputtering.
- **Energy-Dispersive X-ray Spectroscopy (EDS):** Apollo X-SDD Det. Accelerating voltage: 15 kV; Mapping mode: Area scan; Live time: > 60 s.
- **Transmission Electron Microscopy (TEM):** FEI Tecnai G2 F20. Accelerating voltage: 200 kV; Sample grid: Carbon-coated Cu grid; Particle count for statistics: n = 100.
- **Fourier Transform Infrared Spectroscopy (FT-IR):** Thermo Scientific Nicolet iS50. Mode: Attenuated Total Reflectance (ATR); Spectral range: 400–4000 cm^{-1}; Resolution: 4 cm^{-1}; Number of scans: 32 per sample.
- **Water Contact Angle (WCA):** Ossila Contact Angle Goniometer. Test liquid: Deionized water; Dispensed volume: 3 μL; Measurements per sample: 5 independent locations; Temperature: 25 ± 1 °C; Fitting model: Young-Laplace method.