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Self-Standing Superhydrophobic Thin Films Using Soft Lithography and Initiated Chemical Vapor Deposition (iCVD) Techniques

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Abstract

Conventional superhydrophobic coatings face severe constraints from solvent entrapment, poor conformality, and rigid substrate dependency. Here, we report an eco-friendly, solvent-free method to synthesize freestanding superhydrophobic thin films by combining sacrificial polyvinyl alcohol (PVA) soft lithography with initiated Chemical Vapor Deposition (iCVD). Micro-rough sacrificial templates replicated from P600/P1000 sandpapers were conformally coated in a single step with a PFDA-EHA-AA copolymer. AFM confirmed precise thermal control over secondary nanoscale roughness, tuning RMS roughness from 14.06 nm($T_f = 215°C$) to 31.78 nm($T_f = 250°C$). Following pure-water dissolution of the PVA template, the resulting flexible, substrate-free films exhibited robust Cassie–Baxter hydrophobicity without chemical residues, offering a versatile platform for flexible electronics and advanced functional interfaces.

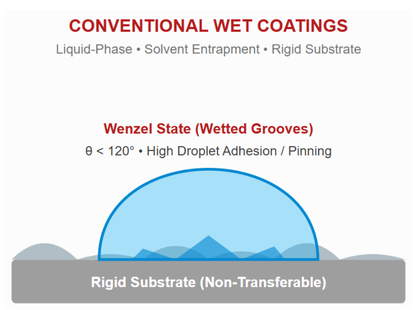
Introduction

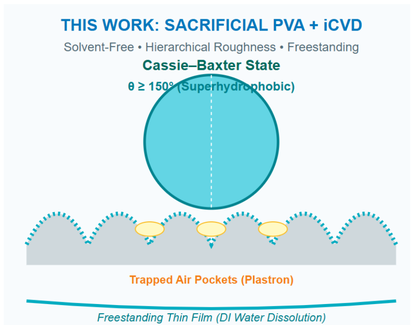
Advanced functional interfaces with extreme water repellency, anti-icing, and corrosion resistance are increasingly required in flexible electronics, wearable biosensors, and smart self-cleaning textiles.

Achieving sustainable superhydrophobicity requires a precise combination of hierarchical micro/nano-roughness and low surface energy chemistry to entrap stable air pockets (Cassie–Baxter state).

Utilizes biodegradable, water-soluble Polyvinyl Alcohol (PVA) to replicate commercial sandpaper textures (P600 / P1000) via soft lithography, providing a robust micro-scale scaffold.

Gas-phase copolymerization of PFDA, EHA, and AA yields pinhole-free, highly conformal fluoropolymer layers without damaging underlying organic templates.
Complete dissolution of the PVA template in benign DI water delivers freestanding, highly flexible superhydrophobic thin films without using toxic organic solvents.





Experimental

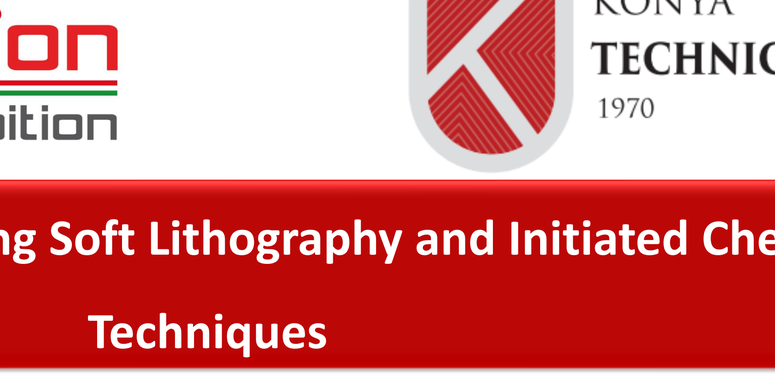


Figure 1. Step-by-step fabrication process of ultra-thin polymer films via sacrificial PVA templating and initiated chemical vapor deposition (iCVD).

Sacrificial Template Fabrication
Soft lithography replication of micro-textures from P600 and P1000 sandpapers onto water-soluble Polyvinyl Alcohol (PVA).

Conformal iCVD Polymeric Growth
Single-step vapor-phase copolymerization of PFDA, EHA, and acrylic acid (AA) monomers.
Precise thermal control over filament (T_f) and substrate (T_{sub}) temperatures.

Eco-Friendly Substrate Release
Total dissolution of the sacrificial PVA template in pure DI water at room temperature.
Yields a chemical-residue-free, self-standing ultra-thin film.

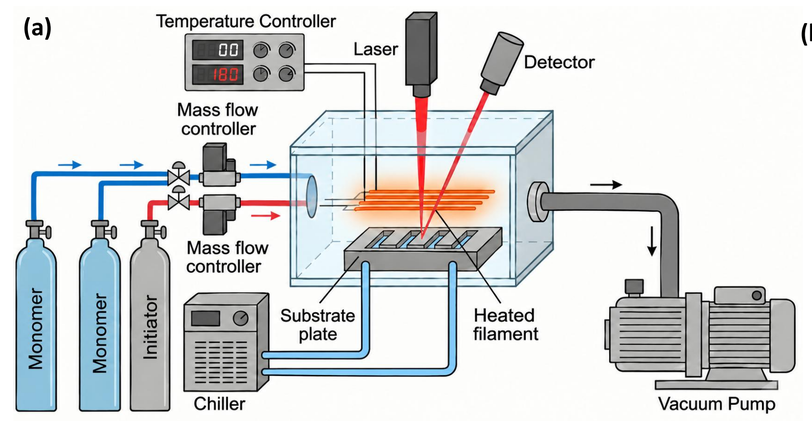


Fig. 2. (a) Schematic representation of vacuum system used for vapor deposition processes, **(b)** Chemicals Used.

Results and Discussion

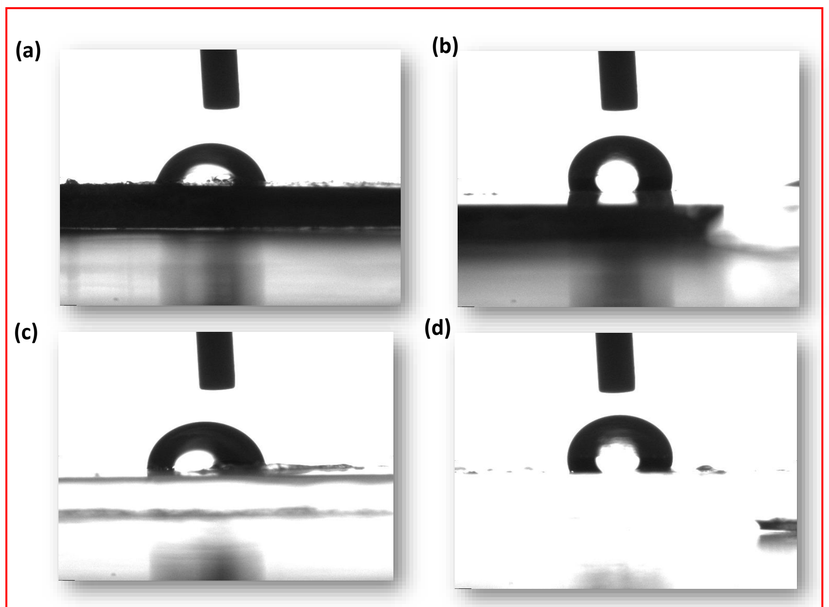


Figure 3. Static water contact angle profiles demonstrating the influence of template grit size and monomer deposition sequence: (a) P600 / PFDA / EHA-AA (81.6°), (b) P600 / EHA-AA / PFDA (107.1°), (c) P1000 / PFDA / EHA-AA (93.2°), and (d) P1000 / EHA-AA / PFDA (111.5°).

Impact of Deposition Sequence (Surface Chemistry Control):

Modulating the monomer deposition order directly governs surface wettability: placing the fluorinated PFDA as the capping top layer substantially increases hydrophobicity up to 111.5° due to the orientation of low-surface-energy perfluoroalkyl chains.
Conversely, capping with EHA-AA exposes hydrophilic acrylic acid domains, dropping the contact angle to 81.6°(P600) and 93.2°(P1000).

Micro-Scale Template Effect (P600 vs P1000):

The P1000-derived films consistently outperformed P600 across all architectures (107.1° → 111.5° for top-PFDA), indicating that denser micro-asperities reduce the liquid-solid contact area.

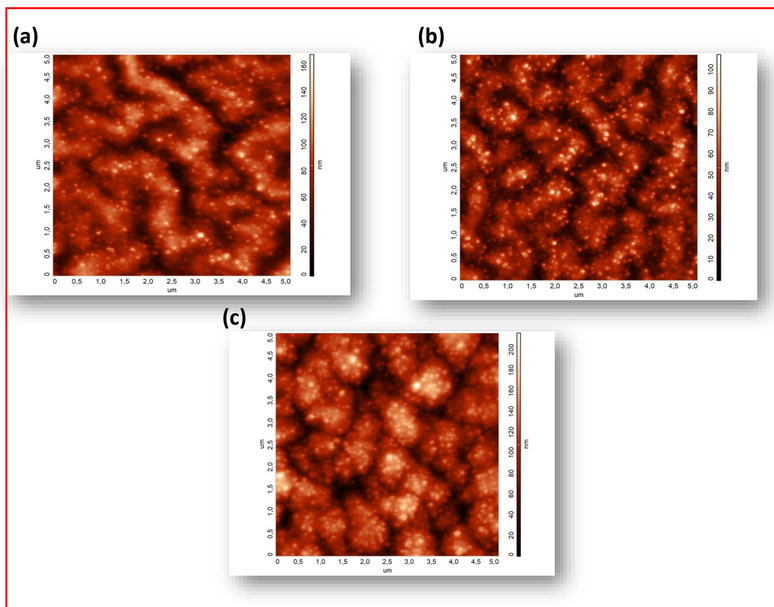


Figure 4. 5x5 μm^2 AFM height topographies of iCVD thin films at constant T_{sub} = 20°C under varying filament temperatures: (a) T_f = 180°C, (b) T_f = 215 °C(RMS = 14.06 nm), and (c) T_f = 250°C(RMS = 31.78 nm).

Nanotopography Evolution via AFM (5x5 μm^2 **Scan Area):**

(a) $T_f = 180°C$/ $T_{sub} = 20°C$**:** Initial radical generation leading to early-stage polymer nucleation along micro-grooves (Z-range: 0–160 nm).

(b) $T_f = 215°C$/ $T_{sub} = 20°C$**:** Optimal steady-state growth regime displaying the highest spatial uniformity, narrowest height distribution (Z-range: 0–100 nm), and an RMS roughness of 14.06 nm.

(c) $T_f = 250°C$/ $T_{sub} = 20°C$**:** High thermal decomposition regime triggering cluster coalescence, deep domain boundaries (Z-range: 0–200 nm), and pronounced nano-roughness reaching an RMS of 31.78 nm.

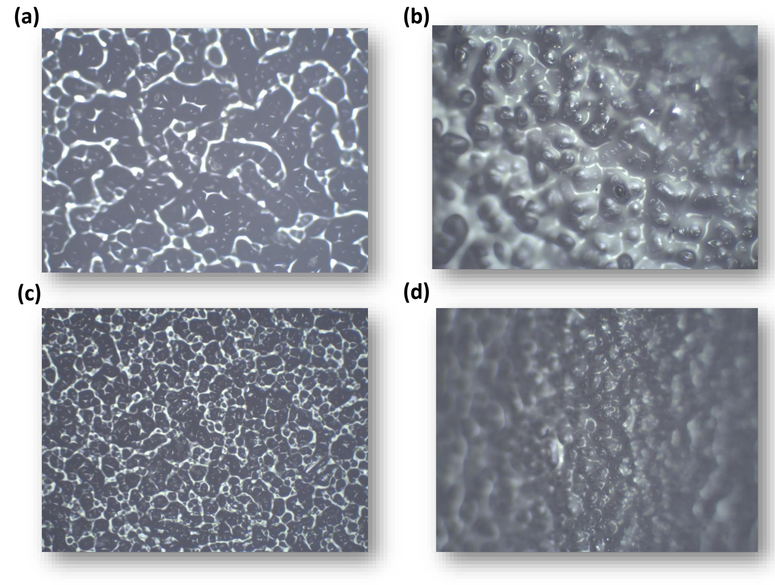


Figure 5. 10x optical microscopy micrographs of sandpaper templates and their corresponding sacrificial PVA replicas: (a) P600 sandpaper template, (b) cured PVA replica from P600, (c) P1000 sandpaper template, and (d) cured PVA replica from P1000.

Soft-Lithography Pattern Transfer (10x Optical Microscopy):

Template Morphology Comparison: The commercial P600 sandpaper template (a) exhibits a broader, coarse abrasive grain network, whereas the P1000 template (c) reveals a significantly denser and finer micro-domain distribution.

Replication Fidelity: The water-soluble sacrificial PVA films cast on both templates (b, d) demonstrate exceptional inverse replication of the micro-grooves and cavities without structural collapse or air void entrapment.

Conclusion

Sacrificial PVA soft lithography integrated with single-step iCVD copolymerization successfully enabled the synthesis of transferable, freestanding superhydrophobic polymer thin films without organic solvent residues. Sandpaper replication accurately established the micro-scale foundation, while iCVD thermal kinetics provided precise control over the secondary nanoscale roughness, systematically tuning RMS roughness from 14.06 nm to 31.78 nm via filament temperature. Surface wettability was strongly governed by both the deposition sequence and template texture, where capping the top layer with low-surface-energy PFDA on P1000 micro-domains elevated water contact angles up to 111.5° prior to hierarchical Cassie–Baxter transition. These findings demonstrate that benign DI water dissolution of PVA templates combined with conformal vapor deposition provides a versatile, green platform to manufacture substrate-free, flexible superhydrophobic structure for wearable electronics, smart textiles, and self-cleaning devices.

References

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Acknowledgement

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