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COMMUNICATION

Mussel-Inspired, Perfluorinated Polydopamine for Self-Cleaning Coating on Various Substrates

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We designed a perfluorinated dopamine derivative, which, upon oxidative polymerization, formed a structurally rough film of extremely low surface energy on various substrates. The static water contact angles larger than 150° and the low water sliding angles less than 7° confirmed the formation of superhydrophobic, self-cleaning surfaces.

A nearly sphere-shaped water droplet on lotus leaves, carrying dusts or contaminants, rolls off easily even at a slightly tilted angle of the leaves (<10°) and cleans the leaf surface.¹ Inspired by this outstanding water repellency of lotus leaves, the fabrication of lotus leaf-mimetic surfaces—superhydrophobic ones, defined to have a static water contact angle greater than 150°—has received a great deal of interest because of the potential applications in various areas, such as self-cleaning surfaces, antifouling or non-sticky surfaces, or water/oil separation.² In nature, the superhydrophobicity of lotus leaves is made realized by their hierarchical structures, composed of micropapillae with nanometer-sized particulates, which are covered with hydrophobic waxes. Therefore, it is crucial to tailor both roughness (i.e., structural heterogeneity) and surface energy (i.e., coatings or materials) in the fabrication of self-cleaning, superhydrophobic surfaces.

During the last decade, there have been innumerable reports on the fabrication of superhydrophobic surfaces. The reported methods can be classified as two main categories. The most widely adopted approach is the two-step, fabrication-coating process: a rough surface structure is fabricated, followed by coating with a material of low surface energy. Rough micro/nanostructures have been generated by various methods including lithographic approaches, bioinspired silicification, layer-by-layer deposition, colloidal assembly, anodization, laser fabrication, and deposition of hierarchically structured particles.³ The other approach is to directly make the micro/nanosurface structures of hydrophobic materials. The replica molding (or templation), involving the fabrication of a template with desired micro/nanofeatures and the replication of the features, is one of the most popular methods. In addition, the plasma treatment of hydrophobic polymers, such as polyethylene terephthalate (PET) and polytetrafluoroethylene (PTFE), has been used for the direct preparation of rough surface structures of low surface energy.⁴ Although successful, these two approaches are

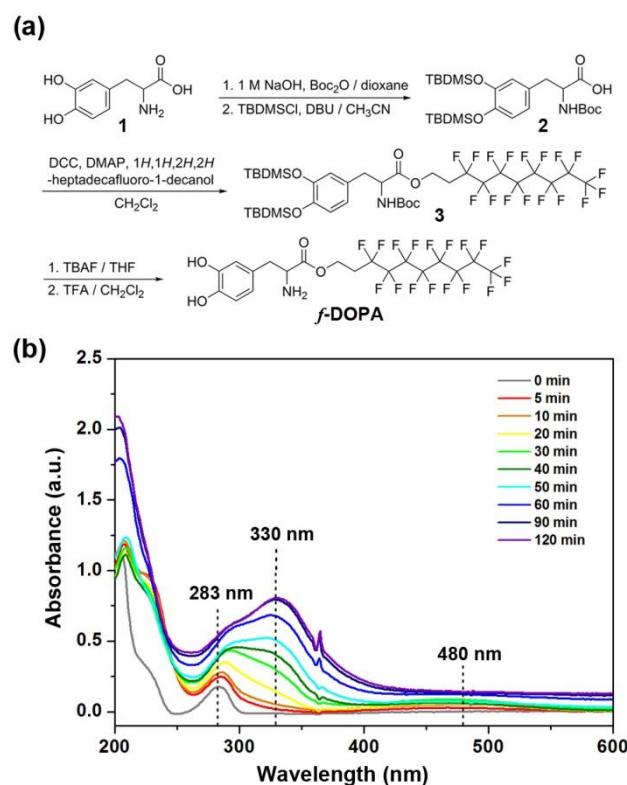


Fig. 1 (a) Synthesis of 1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl 2-amino-3-(3,4-dihydroxyphenyl)propanoate, *f*-DOPA. (b) UV-Vis spectra of the acetonitrile solution of *f*-DOPA during the NaIO₄-mediated oxidation. The data at 0 min indicates the absorbance from the solution containing only *f*-DOPA.

strictly material-dependent or require cumbersome two-step processes. It would be much beneficial in the generation of superhydrophobic surfaces to develop a method that generates rough hydrophobic structures on any substrates in one-step process, substrate-independent superhydrophobic coating. A substrate-independent coating was developed with inspiration from mussels in nature. The mussel, a marine organism, secretes adhesive proteins and sticks to many different types of surfaces.⁵ The 1,2-

dihydroxybenzene (catechol) and amine groups of 3-(3,4-dihydroxyphenyl)-L-alanine (L-DOPA) in the adhesive proteins were reported to be critical in the extraordinary adhesion capability of the mussel.⁶ 2-(3,4-dihydroxyphenyl)ethylamine (dopamine) has widely been used for functional coatings of various organic/inorganic substrates, electrodes, and even living cells.⁶⁻⁸ For example, we coated a superhydrophobic anodized aluminum oxide (AAO) surface with relatively hydrophilic polydopamine, a polymerized form of dopamine, to reverse the water wettability to hydrophilicity as well as showing universal coating characteristics of polydopamine.⁹ Recently, the dopamine motif was utilized for the nanostructured coating onto glass, polyester fiber, and carbon nanotubes.¹⁰ In this work, we designed a perfluorinated DOPA (*f*-DOPA) and successfully achieved a substrate-independent, superhydrophobic coating that did not require any fabrication steps. The *in situ* superhydrophobic, self-cleaning coating was applied to various substrates, such as gold, glass, polydimethylsiloxane (PDMS), PET, vanadium foil (V foil), zinc foil (Zn foil), and titanium dioxide (TiO₂). The manipulation of the water flow was also made possible by this coating approach.

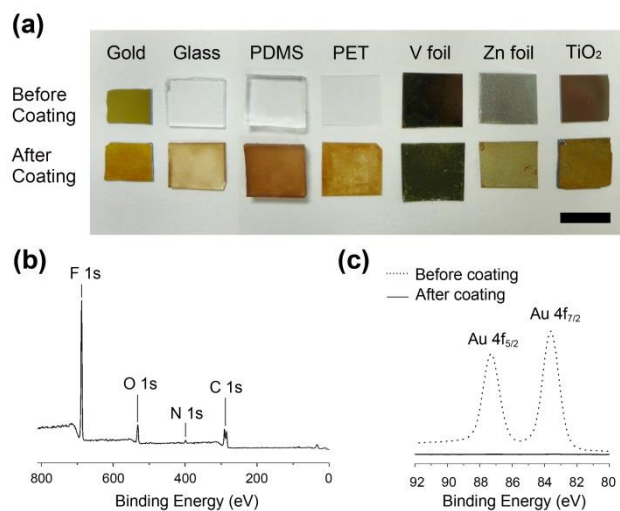


Fig. 2 (a) Optical photographs of bare and *f*-DOPA-coated substrates. The upper and lower lines show the bare and *f*-DOPA-coated substrates, respectively. (b) Wide-scan X-ray photoelectron (XPS) spectrum of *f*-DOPA-coated gold surface. (c) Narrow-scan XPS spectrum of the bare and *f*-DOPA-coated gold surfaces.

In the oxidative dopamine polymerization, the catechol group is oxidized to *o*-quinone. The *o*-quinone moiety is suggested to be transformed into leukodopaminechrome via intramolecular cyclization by primary amine (i.e., 1,4-conjugate addition), which is oxidized further to dopaminechrome.¹¹ The isomerized 5,6-dihydroxyindole moiety is highly involved in the polymerization process of dopamine and its derivatives.^{11,12} The suggested mechanism indicated that it was required to keep the catechol and amine groups for proper polymerization and subsequent coating; therefore, we attached the perfluoro group onto the carboxylic acid in L-DOPA to increase the hydrophobicity of the resulting polymer films (Fig. 1a). It was reported that a substituent at the benzylic position was compatible with the polymerization, exemplified by norepinephrine polymerization.¹³ Briefly, L-DOPA was coupled with 1*H*,1*H*,2*H*,2*H*-heptadecafluoro-1-decanol via esterification with protection/deprotection of the hydroxy and amine groups. Prior to substrate coating, the oxidation process of *f*-DOPA in solution was investigated by UV-Vis spectroscopy (Fig. 1b). The acetonitrile stock solution of *f*-DOPA (4 mg/mL) was diluted to 0.05 mg/mL, and 0.5 mL of the diluted solution was used for reliable UV-Vis

analysis. The UV-Vis spectrum of *f*-DOPA showed a characteristic peak at 283 nm, corresponding to the symmetry-forbidden transition (L_a-L_b) of the catechol moiety in *f*-DOPA.¹⁴ The peak intensity at 283 nm decreased upon the addition of the aqueous sodium periodate (NaIO₄) solution (1.25 mM; 0.13 mL). As the reaction time went, a new peak appeared as a shoulder over the peak at 283 nm and was observed clearly at 330 nm after 2 h. The peak at 330 nm indicated the oxidation of catechol moiety in *f*-DOPA into *o*-quinone.¹⁵ In addition, the formation of dopaminechrome was evidenced by a weak, broad peak around at 480 nm. The UV-Vis spectra, therefore, confirmed that the reaction conditions employed were suitable for *f*-DOPA coating.

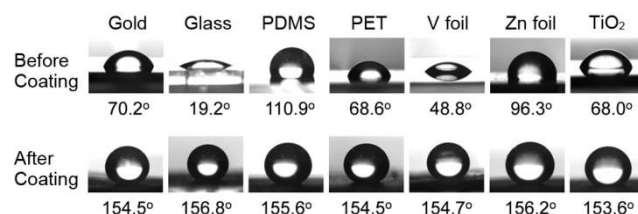


Fig. 3 Static water contact angles of the bare and *f*-DOPA-coated substrates.

We coated various substrates with polymerized *f*-DOPA, such as gold, glass, PDMS, PET, V foil, Zn foil, and TiO₂. To the acetonitrile solution of *f*-DOPA (4 mg/mL) containing a substrate was added an aqueous solution of NaIO₄ (100 mM) at the final ratio of 15:2 (v/v). After 12 h, the substrate was washed with acetonitrile, and the coating process was repeated with a fresh *f*-DOPA solution. After coating, all the substrates became brownish or dark-colored, indicating the formation of *f*-DOPA films, except for the V foil that was black before coating (Fig. 2a). The X-ray photoelectron (XPS) spectra also confirmed the successful coating for all the substrates tested. For example, the characteristic peaks of *f*-DOPA at 688.0 (F 1s) and 290.7 eV (C 1s) were observed after coating on gold (Fig. 2b), and the surface elemental ratio (C/F) was 1.03, which was nearly consistent with that of *f*-DOPA (1.12). In addition, Au peaks at 83.6 eV (Au 4f_{7/2}) and 87.3 eV (Au 4f_{5/2}) disappeared after *f*-DOPA coating, indicating the formation of thick *f*-DOPA films with the thickness of 10 nm or more (Fig. 2c).⁶ The intensity of the characteristic XPS peak(s) for glass, PDMS, V foil, Zn foil or TiO₂ also decreased significantly after coating (Fig. S1, ESI[†]). In addition to the incorporation of fluorine, the *f*-DOPA films were structurally heterogeneous (i.e., rough), fulfilling the basic characteristics of superhydrophobic surfaces. The scanning electron microscopy (SEM) images showed that the substrate was coated with *f*-DOPA microparticles, ranging from 1.0 to 2.0 μm in diameter, which were hierarchically composed of smaller nanoparticles (Fig. S2a, ESI[†]). The root-mean-square roughness was measured to be 533.92 nm in the atomic force microscopy (AFM) image (Fig. S2b, ESI[†]). We believe that the coating of the polymerized *f*-DOPA involved the same processes as the polydopamine coating, which was thought to result from the presence of the catechol and amine groups,^{6,16} although the adhesion strength would be lower than polydopamine due to the perfluorinated group in *f*-DOPA.

Fig. 3 shows the static water contact angles before and after coating, confirming that all the *f*-DOPA-coated substrates were superhydrophobic. Regardless of different contact angles before coating, the coating made the contact angle of all the substrates be about 155° (Fig. 3). Interestingly, PTFE, which exhibits the low surface energy (19.1 mJ/m²) and is non-sticky,¹⁷ also became a self-cleaning, superhydrophobic surface with the static water contact angle of 149° after *f*-DOPA coating (Data not shown). The wetting properties were further investigated by the tilting-plate method that measured the dynamic contact angles, because it was essential in the

confirmation of self-cleaning properties to investigate the dynamic water contact angles and surface free energies. The advancing (θ_{adv}) and receding (θ_{rec}) water contact angles of *f*-DOPA-coated substrates were measured, and the contact angle hysteresis (i.e., ($\theta_{adv} - \theta_{rec}$)) of each substrate was calculated (Table S1, ESI[†]). For example, the gold substrate, after coating, showed low contact angle hysteresis of 9.9°. A water droplet on the substrate easily rolled off at a tilt angle of 5.3°, which was a clear evidence of self-cleaning property. All other *f*-DOPA-coated substrates also showed the low contact angle hysteresis and self-cleaning property with low sliding angles of 2.5° to 6.7°. In addition, the surface free energy (γ_s) was calculated based on the Owens-Wendt geometric mean equation that divides the surface free energy into the dispersive (γ_s^D) and polar (γ_s^P) ones.¹⁷

$$(1 + \cos\theta)\gamma_L = 2\sqrt{\gamma_s^D\gamma_L^D} + 2\sqrt{\gamma_s^P\gamma_L^P}$$

where θ is the measured contact angle of a liquid on the surface, and γ_L is the surface tension of the liquid.

Table 1 Static water and CH₂I₂ contact angles on the substrates and the surface free energies of the substrates.^a

Substrate	Water contact angle	CH ₂ I ₂ contact angle	Surface free energy (γ_s) (mJ/m ²)
Gold	154.5°	148.6°	0.279 (γ_s^D : 0.251, γ_s^P : 0.028)
Glass	156.8°	149.1°	0.256 (γ_s^D : 0.249, γ_s^P : 0.007)
PDMS	155.6°	148.6°	0.274 (γ_s^D : 0.258, γ_s^P : 0.015)
PET	154.5°	137.9°	0.929 (γ_s^D : 0.910, γ_s^P : 0.019)
V foil	154.7°	142.1°	0.581 (γ_s^D : 0.581, γ_s^P : 0.000)
Zn foil	156.3°	144.4°	0.458 (γ_s^D : 0.458, γ_s^P : 0.000)
TiO ₂	153.6°	140.2°	0.706 (γ_s^D : 0.706, γ_s^P : 0.000)

^aContact angles are the averaged values from the three different samples. The surface free energies, and their dispersive and polar components are calculated with the averaged contact angles based on the Owens-Wendt geometric mean equation.

The surface free energy (γ_s ; $\gamma_s = \gamma_s^D + \gamma_s^P$) of each surface was determined by measuring the contact angles with water and diiodomethane (CH₂I₂) (Table 1). The surface free energy of the *f*-DOPA-coated gold surface was calculated to be 0.279 mJ/m², and the other substrates had the surface free energies between 0.2 and 0.9 mJ/m². These values were extremely low, probably because of both the structural roughness and the incorporated perfluoro groups. For a comparison, the surface free energy of a smooth surface modified with CF₃ groups in hexagonal close-packing was reported to be 6.7 mJ/m².¹⁸ In our system, the simple *f*-DOPA coating, therefore, led to structurally heterogeneous rough films of perfluorinated materials without any further treatments, which definitely contributed to reduction of surface free energy and realization of superhydrophobic, self-cleaning property.

Interestingly, the wetting characteristic of the *f*-DOPA films was changed to be non-superhydrophobic by simple O₂-plasma treatment: after 1-min treatment, the static water contact angle of the *f*-DOPA-coated gold substrate was changed from 154.45° to 124.18°. The spatio-selective oxidation of the film could be utilized for manipulation of water droplets and flow. For example, when a small square area of the film was made relatively hydrophilic surface by plasma treatment, a water droplet was captured at that hydrophilic area after fast rolling on superhydrophobic area with slight tilting. Droplet-based microfluidic channels could be fabricated with ease, demonstrated by a hydrophilic line on the superhydrophobic surface (Fig. S3, ESI[†]).

In summary, we demonstrated a simple coating method for generating superhydrophobic, self-cleaning surfaces by using a perfluorinated dopamine derivative (*f*-DOPA) as a polymerization precursor. *f*-DOPA was coated on various

substrates via oxidative polymerization, forming a rough structure of low surface free energy (0.2-0.9 mJ/m²) without any additional fabrications. Although the *f*-DOPA coating was not transparent intrinsically because of the chemical nature of polydopamine moiety, we believe that the universality of the coating method would widen the substrate scope for certain applications of self-cleaning, superhydrophobic surfaces.

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Notes and references

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[†]Electronic Supplementary Information (ESI) available: Detailed experimental procedures for the synthesis of *f*-DOPA, coating methods, and surface characterizations. See DOI: 10.1039/c000000x/

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