

Collaborative research between Prof. Woo Kyung Cho (Department of Chemistry, Chungnam National University, Korea) and a research team of the Center for Cell-Encapsulation Research (Korea)

Mussel-inspired, perfluorinated polydopamine for self-cleaning coating on various substrates

Two inspirations: Lotus leaf-inspired, superhydrophobic coating with self-cleaning property is achieved on various substrates (from left: gold, glass, PDMS, PET, TiO_2 , Zn foil, and V foil) by oxidative polymerization of a mussel-inspired, perfluorinated dopamine derivative. The photos were taken at and near Chungnam National University by Daewha Hong, the graphic was designed by Ji Hun Park.



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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 dust or contaminants, rolls off easily even at a slightly tilted angle of the leaves ($<10^{\circ}$) 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 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 into 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 strictly materialdependent 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 a one-step process, substrate-independent superhydrophobic coating. A substrate-independent coating was developed with inspiration from mussels in nature. The mussel, a marine organism, secrets 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 to show 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, selfcleaning 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.

In the oxidative dopamine polymerization, the catechol group is oxidized to *o*-quinone. The *o*-quinone moiety is suggested to

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(a)



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 NalO₄-mediated oxidation. The data obtained at 0 min indicate the absorbance from the solution containing only *f*-DOPA.

be transformed into leukodopaminechrome via intramolecular cyclization by primary amines (*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 1H,1H,2H,2H-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⁻¹) was diluted to 0.05 mg mL⁻¹, 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 symmetryforbidden transition (La-Lb) 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 progressed, 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 the catechol moiety in *f*-DOPA to *o*-quinone.¹⁵ In addition, the formation of dopaminechrome was evidenced by a weak, broad peak at around 480 nm. The UV-Vis spectra, therefore, confirmed that the reaction conditions employed were suitable for *f*-DOPA coating.

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⁻¹) containing a substrate an aqueous solution of NaIO₄ (100 mM) at the final ratio of 15:2 (v/v) was added. 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). X-ray photoelectron spectroscopy (XPS) analysis also confirmed the successful coating of 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 (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 a 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



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. Scale bar: 1 cm. (b) Wide-scan XPS spectrum of a *f*-DOPA-coated gold surface. (c) Narrow-scan XPS spectra of the bare and *f*-DOPA-coated gold surfaces.



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 that of 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 to be about 155° (Fig. 3). Interestingly, PTFE, which exhibits the low surface energy (19.1 mJ m⁻²) and is non-sticky,¹⁷ also became a self-cleaning, superhydrophobic surface with a 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 a low contact angle hysteresis of 9.9°. A water droplet on the substrate easily rolled off at a tilt angle of 5.3° , which is clear evidence of self-cleaning properties. All other f-DOPA-coated substrates also showed the low contact angle hysteresis and selfcleaning properties 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 $(\gamma_{\rm S}^{\rm D})$ and polar $(\gamma_{\rm S}^{\rm P})$ ones.¹⁷

$$(1 + \cos\theta)\gamma_{\rm L} = 2\sqrt{\gamma_{\rm S}^{\rm D}\gamma_{\rm L}^{\rm D}} + 2\sqrt{\gamma_{\rm S}^{\rm P}\gamma_{\rm L}^{\rm P}}$$

where θ is the measured contact angle of a liquid on the surface, and $\gamma_{\rm L}$ is the surface tension of the liquid.

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 m⁻², and the other substrates have the surface free energies between 0.2 and 0.9 mJ m⁻². These values are extremely low, probably because of both the structural roughness and the incorporated perfluoro groups. For comparison, the surface free energy of a smooth surface modified with CF₃ groups in hexagonal close-packing was reported to be 6.7 mJ m⁻².¹⁸ 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

 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_2I_2 contact angle (°)	Surface free energy $(\gamma_s) (mJ m^{-2})$
Gold	154.5	148.6	$0.279 (\gamma_{\rm S}^{\rm D}: 0.251, \gamma_{\rm S}^{\rm P}: 0.028)$
Glass	156.8	149.1	$0.256 (\gamma_{\rm S}^{\rm D}: 0.249, \gamma_{\rm S}^{\rm P}: 0.007)$
PDMS	155.6	148.6	$0.274 (\gamma_{\rm S}^{\rm D}: 0.258, \gamma_{\rm S}^{\rm P}: 0.015)$
PET	154.5	137.9	$0.929 (\gamma_{\rm S}^{\rm D}: 0.910, \gamma_{\rm S}^{\rm P}: 0.019)$
V foil	154.7	142.1	$0.581 (\gamma_{\rm S}^{\rm D}: 0.581, \gamma_{\rm S}^{\rm P}: 0.000)$
Zn foil	156.3	144.4	$0.458 (\gamma_{\rm S}^{\rm D}: 0.458, \gamma_{\rm S}^{\rm P}: 0.000)$
TiO_2	153.6	140.2	0.706 ($\gamma_{\rm S}^{\rm D}$: 0.706, $\gamma_{\rm S}^{\rm P}$: 0.000)

^{*a*} Contact angles are the averaged values from 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.

surface free energy and realization of superhydrophobic, selfcleaning properties.

Interestingly, the wetting characteristic of the *f*-DOPA films was changed to non-superhydrophobic by simple O_2 -plasma treatment: after 1 min of 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 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 m⁻²) without any additional fabrication. Although the *f*-DOPA coating was not transparent intrinsically because of the chemical nature of the 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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