

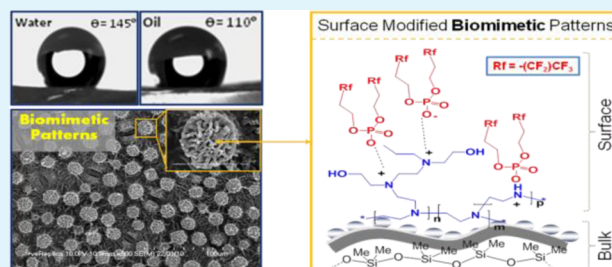
Water-Based Layer-by-Layer Surface Chemical Modification of Biomimetic Materials: Oil Repellency

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ABSTRACT: Biomimetic materials possessing hierarchical surface roughness thrive when complementary terminal chemical functionality is introduced. However, incorporating terminal functionality on the biomimetic material is the challenge, especially, when its roughness needs to be preserved. Hence, we report surface chemical modification of biomimetic materials through water-based layer-by-layer deposition. The amine terminated biomimetic replica PDMS-replica^{Silica/NH₂} was prepared by treating silica-modified replica (i.e., PDMS-replica^{Silica}) with the aqueous solution of branched ethoxylated polyethylenimine (EPEI). Next, -CF₃ terminal PDMS-replica^{Silica/NH₂/CF₃} was obtained by treating PDMS-replica^{Silica/NH₂} with the aqueous solution of phosphate ester fluorosurfactant. PDMS-replica^{Silica/NH₂/CF₃} showed superhydrophobicity (advancing $\theta_{\text{water}} \approx 140^\circ$) and high oil repellency (advancing $\theta_{\text{oil}} \approx 110^\circ$). X-ray photoelectron spectroscopy (XPS) revealed well-organized terminal -CF₃ groups present on the PDMS-replica^{Silica/NH₂/CF₃} surface. During the process of layer-by-layer deposition, the surface topography was monitored using scanning electron microscopy (SEM). This method could be extended to get desired terminal chemical functionality on the biomimetic materials which would furnish interesting surface properties in air or under water.

KEYWORDS: oil repellency, biomimetic patterns, surface modification



INTRODUCTION

Biomimetic materials possessing hierarchical surface roughness thrive when complementary terminal chemical functionality is introduced. Understanding interactions of surface modified biomimetic materials with the organic matter would provide key information in the development of nonstick coating, antimicrobial and antifouling applications. In general, oil repellent surfaces^{1–5} possess surface energy (γ_s) of ~ 10 mJ/m² because of the presence of close-packed -CF₃ terminal functionality. Theoretically,^{6–8} oil having a surface tension (γ_{oil}) of 36 mJ/m² should exhibit a maximum contact angle (θ_{oil}) of 87° on such flat -CF₃ terminal surfaces. This oil contact angle can be further enhanced only when -CF₃ terminal functionality is combined with the hierarchical surface roughness.^{9–16}

Previously,^{17,18} materials possessing complementary combination of re-entrant surface texture and -CF₃ terminal functionality showed superoleophobic properties. These materials were prepared by electrospinning a blend containing fluorosilsesquioxane and polymethylmethacrylate (PMMA) to form roughened structure on the silicon wafer. Similarly, oil repellent porous silicon,¹⁹ cotton,^{20–23} cellulose,^{24,25} and wool²⁶ were developed either by vapor deposition of tridecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane (*n*-C₆F₁₃CH₂CH₂SiCl₃) or by in situ deposition of fluorinated silica particles on their surface. Previously, we prepared superhydrophobic and highly oil repellent biomimetic materials²⁷ (i.e., PDMS-replica), by introducing -CF₃ terminal functionality on the hierarchical surface pattern.

All the previous publications described preparation of oil repellent materials either through electro-spinning or chemical vapor deposition of well-organized -CF₃ terminal functionality. Recently,²⁷ we found that incorporating terminal functionality on the biomimetic polymeric material is difficult; especially when its roughness needs to be preserved. We observed that the surface roughness present on the biomimetic materials undergoes significant damage, when plasma-mediated surface modification methods are employed. Hence, we report simple water-based layer-by-layer surface modification; by maintaining surface roughness of biomimetic materials. This deposition method generated well-organized -CF₃ terminal functionality on the biomimetic materials; by keeping their complementary surface roughness intact. Surface modified biomimetic materials offered superhydrophobic (advancing $\theta_{\text{water}} \approx 140^\circ$) and oil repellent (advancing $\theta_{\text{oil}} \approx 110^\circ$) properties. X-ray photoelectron spectroscopy (XPS) revealed presence of well-organized terminal -CF₃ groups on the replica surface. During the process of layer-by-layer deposition, the surface topography was monitored using scanning electron microscopy. This method could be extended to get desired terminal chemical functionality on the biomimetic materials that would furnish interesting surface properties in air as well as under water.

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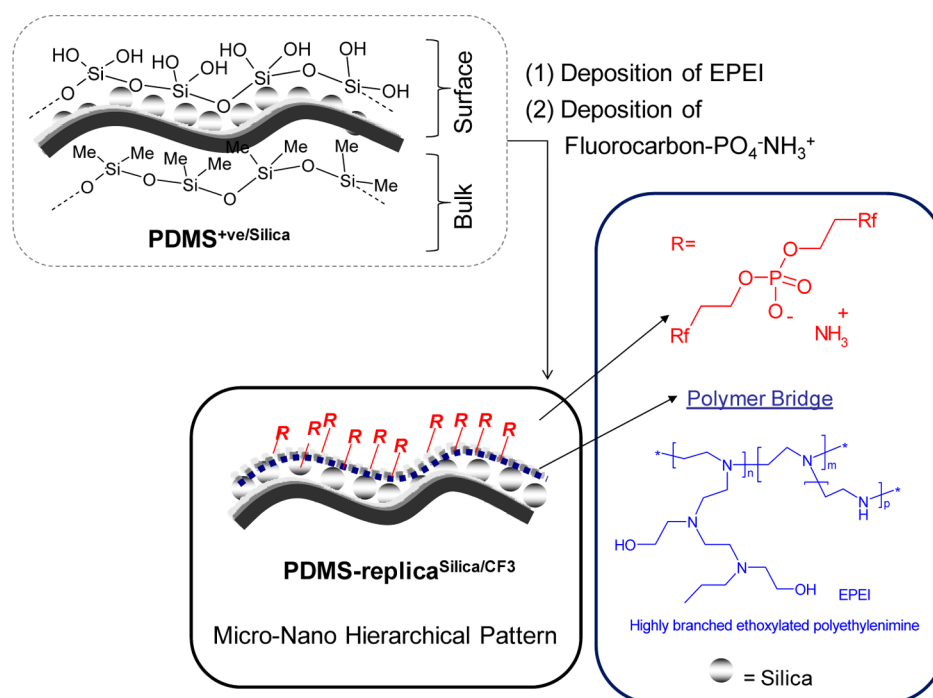


Figure 1. Layer-by-layer surface chemical deposition on the PDMS-replica $\text{Rf} = -(\text{CF}_2)\text{CF}_3$.

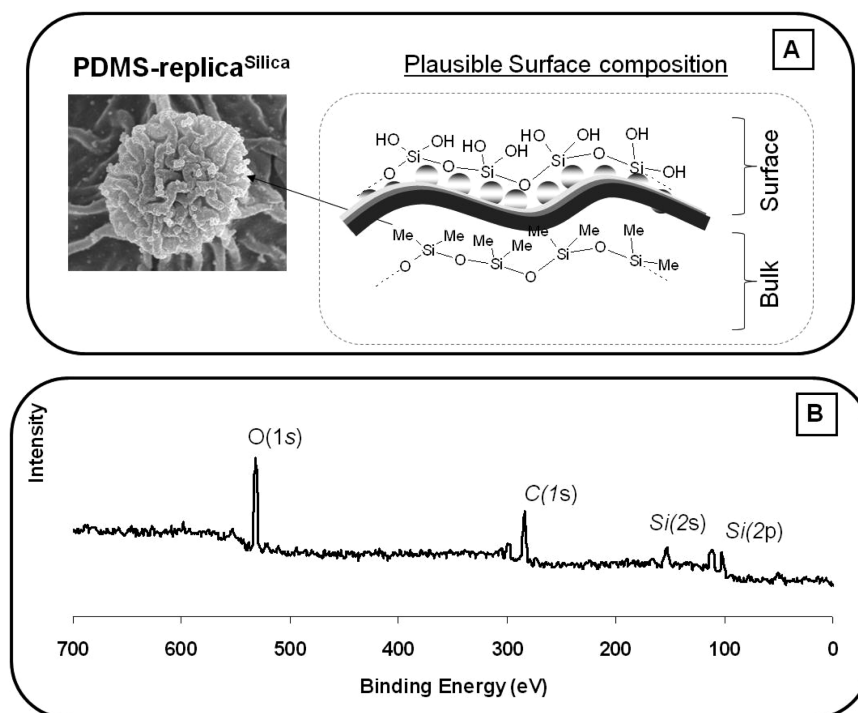


Figure 2. (A) Surface and bulk chemical structure of PDMS-replica^{Silica} and (B) XPS survey spectrum of PDMS-replica^{Silica} surface at 90° take off angle from.

EXPERIMENTAL SECTION

Materials. Fluoroaliphatic phosphate ester fluorosurfactant (22%, Masurf FS-120PS, $[\text{CF}_3(\text{CF}_2)_8\text{CH}_2\text{CH}_2\text{O}]_2\text{-PO}_2^- \text{NH}_3^+$), perfluoroalkylethyl phosphate (Masurf FS-130 EB), C8–18 perfluoroalkylethyl betaine (Masurf FS-330), ammonium fluoroaliphatic carboxylates (Masurf FS-1030), and fluoroaliphatic oxyethylene adduct (Masurf FS-1725EB) were purchased from Mason Chemical, U.S.A., and used as 5% active solution in water. Heptadecafluoro-1,1,2,2-tetrahydrodecyl trichlorosilane was purchased from Gelest (USA). Polyethylenimine,

80% ethoxylated solution (EPEI, 35–40 wt % in H_2O , average $M_w \approx 70\,000$), 30% hydrogen peroxide solution, 30% ammonia solution, and tetraethyl orthosilicate (98%) were purchased from Sigma Aldrich. Silicone elastomer base and curing agents (Sylgard 184) were purchased from Dow Corning.

Preparation of PDMS-replica. The reactive blend containing silicone elastomer base (100 g) and curing agent (10 g) was prepared.²⁸ The viscous blend was poured on the bottom surface of the leaf, placed in a polystyrene Petri dish (100×15 mm). The trapped air bubbles present in the blend were removed under vacuum.

The blend was cured at 25 °C in a dust-free chamber for 24 h. The solid blend attached to the leaf was kept in the oven at 60 °C for 1 h. It was peeled off carefully from the leaf as the negative replica; washed gently with distilled water, and purged with nitrogen. The negative replica (area 8 cm², thickness 2 mm) was exposed to the vapors of heptadecafluoro-1,1,2,2-tetrahydrodecyl trichlorosilane for 1 h, under reduced pressure (~1 mm of Hg). It was further cured in the oven at 60 °C for 1 h to form -CF₃ terminal negative PDMS-replica. The viscous silicone elastomer blend was again poured on the patterned negative PDMS-replica, placed in a polystyrene Petri dish. Similar curing procedure was followed and solid blend was peeled off from negative replica to obtain positive PDMS-replica.

Preparation of Silica Modified Positive Replica (PDMS-replica^{Silica}). Positive PDMS-replica (area ~4 cm², thickness ~5 mm) was treated with a solution containing hydrogen peroxide (30%, 4 mL), hydrochloric acid (36%, 4 mL), and water (8 mL) for 10 min. The hydroxyl terminal oxidized PDMS-replica (i.e., PDMS-replica^{OH}) was washed with distilled water and dried under nitrogen. The dry PDMS-replica^{OH} was treated with a solution^{33,34} containing tetraethylorthosilicate (1 mL), ammonia (1 mL), and ethanol (15 mL) for 2 h. The silica-modified positive replica (PDMS-replica^{Silica}) was washed with ethanol and dried under nitrogen.

Preparation of -CF₃ Functional PDMS-replica^{Silica}. Amine-terminated biomimetic PDMS-replica^{Silica/NH₂} was prepared by rinsing PDMS-replica^{Silica} with 10% aqueous solution of branched ethoxylated polyethylenimine (EPEI) with PDMS-replica^{Silica}. PDMS-replica^{Silica/NH₂} formed was further rinsed with 5% aqueous solution of fluoroaliphatic phosphate ester fluorosurfactant (Masurf FS-120PS, [CF₃(CF₂)₈CH₂CH₂O]₂-PO₂⁻ NH₃⁺). PDMS-replica^{Silica/NH₂/CF₃} showed superhydrophobic (advancing $\theta_{\text{water}} \approx 140^\circ$) and highly oil repellent (advancing $\theta_{\text{oil}} \approx 110^\circ$) properties.

Scanning Electron Microscopy (SEM) of PDMS Replicas. Surface topography of PDMS-replica was monitored using HITACHI S-47 scanning electron microscope, with an acceleration potential of 10 kV. All the replicas were coated with 10 nm gold layer using HITACHI capital ϵ -1010 ion sputter-coater. Operation parameters: working pressure, 0.05 mbar; distance, 50 mm; current, 30 mA; and time, 120 s.

Wettability Method. Contact angles water and oil (glyceryl trioleate, surface tension 34.7 dyn/cm) with the replica surface were measured using KRUSS (GmbH Germany) G10 Goniometer. The advancing and receding contact angles were measured using sessile drop technique.²⁹

X-ray Photoelectron Spectroscopy (XPS). X-rays were generated using a high intensity rotating Al K α source at a power of 150 W. The surface chemical structure of the PDMS-replica^{Silica}, PDMS-replica^{Silica/NH₂}, and PDMS-replica^{Silica/NH₂/CF₃} were determined using XPS, Model ESCA-3000 from VG Scientific U.K. The survey spectra were recorded using pass energy of 50 eV. The region spectra for silicon 2p (102 eV), silicon 2s (152 eV), carbon 1s (284 eV), nitrogen 1s (400 eV), oxygen 1s (532 eV) and fluorine 1s (688 eV) were recorded using pass energy of 50 eV at 90° take off angle. All the spectra were interpreted by referring Scienta ESCA300 database^{30,31} followed by Gaussian peak deconvolution analysis using Peak fit, version 4.11, software (SPSS Inc.).

RESULTS AND DISCUSSION

Oil Repellent PDMS-replica^{Silica/CF₃} via Chemical Functionalization of PDMS-replica. Biomimetic PDMS-replica possessing hierarchical surface pattern was prepared using soft lithography.²⁷ As reported previously,²⁷ SEM image of the biomimetic replica (PDMS-replica) showed hierarchical array of flower-shaped protuberance (of average diameter of 12 μm) with a spatial distance of ~20 μm . The magnified SEM image further showed presence of fiber-like mesh structure on each protuberance. PDMS-replica^{Silica} was prepared using procedure described by the Experimental Section.³²

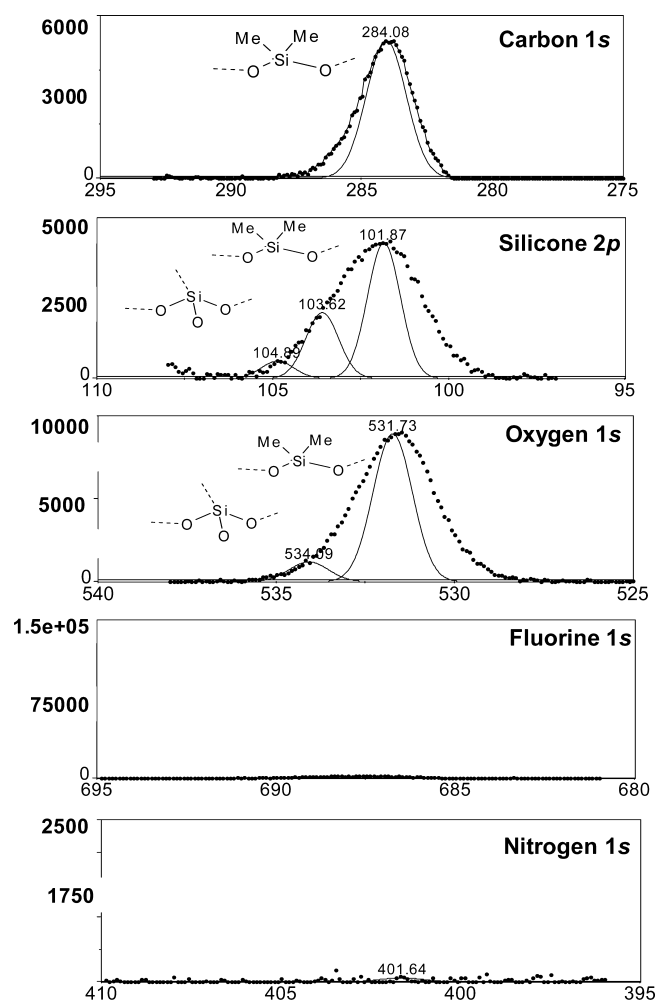


Figure 3. XPS spectra of carbon 1s, silicon 2p, oxygen 1s, fluorine 1s, and nitrogen 1s regions at 90° take off angle from the PDMS-replica^{Silica} (··· data; — Gaussian sum).

Next, PDMS-replica^{Silica} was rinsed with various fluorocarbons shown in the Materials section. However, our X-ray photoelectron spectroscopy data showed presence of both fluorocarbon and silica as the mixed surface composition. This mixed composition did not offer desired oil repellence. Practically,²⁷ for superior oil repellency PDMS-replica^{Silica} should possess closed packed organization of only -CF₃ terminal groups. Hence, we decided to deposit bridging chemical composition for enhanced deposition of fluorocarbon. As seen in Figure 1 the amine terminated biomimetic replica PDMS-replica^{Silica/NH₂} was prepared by rinsing silica modified replica (i.e., PDMS-replica^{Silica}) with the aqueous solution of branched ethoxylated polyethylenimine (EPEI). Next, -CF₃ terminal PDMS-replica^{Silica/NH₂/CF₃} was obtained by rinsing PDMS-replica^{Silica/NH₂} with the aqueous solution of fluoroaliphatic phosphate ester fluorosurfactant.

Surface Chemical Structure of PDMS-replica^{Silica}. Surface compositions of PDMS-replica^{Silica} were determined using XPS. The surface and bulk chemical structures of PDMS-replica^{Silica} are shown in Figure 2A. SEM image of PDMS-replica^{Silica} (in Figure 2A) also indicated uniform coating of nano-silica particles on the fiberlike mesh structure present on protuberance. The presence of silica particles on the PDMS-replica^{Silica} surface was confirmed by XPS. In Figure 2B, XPS spectrum of PDMS-replica^{Silica} showed peaks at binding

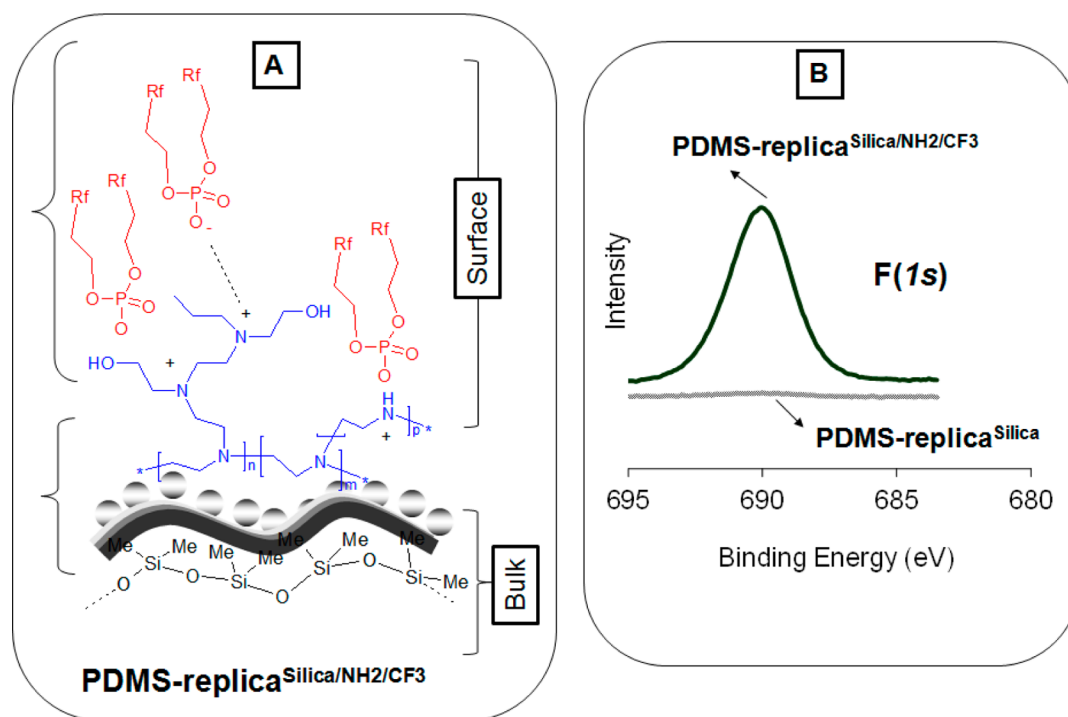


Figure 4. (A) Plausible surface chemical composition of PDMS-replica^{Silica/NH₂/CF₃} indicating enriched fluorocarbon layer. (B) XPS region spectra of fluorine 1s at 90° takeoff angle from PDMS-replica^{Silica} and PDMS-replica^{Silica/NH₂/CF₃}.

energies of 532, 284, 152, and 102 eV because of oxygen 1s, carbon 1s, silicon 2s, and silicon 2p, respectively.

In Figure 3, high-resolution region spectra showed strong peaks at 101.87 (Si_{2p}), 284.08 (C_{1s}), and 531.73 (O_{1s}) eV because of the $-\text{Si}(\text{CH}_3)_2\text{O}-$ groups from PDMS-replica. The peaks due to silicon and oxygen from the silica network appeared at 103 (Si_{2p}) and 534.9 (O_{1s}) eV respectively. Peaks at 401 and 688 eV because of fluorine 1s and nitrogen 1s, respectively, were absent.

Surface Chemical Structure of PDMS-replica^{Silica/CF₃}.

Previously, it was demonstrated that for high oil repellence it is necessary to have surface composition enriched with $-\text{CF}_3$ terminal group. As indicated earlier, conventional method of preparation of oil repellent materials describe either electrospinning or chemical vapor deposition of well-organized $-\text{CF}_3$ terminal functionality. Our newly developed water based layer-by-layer deposition process lead us to biomimetic surfaces having terminal fluorocarbon ($-\text{CF}_3$) groups. PDMS-replica^{Silica/NH₂/CF₃} was prepared using procedure described by the Experimental Section. First PDMS-replica^{Silica} was modified with bridging layer namely branched ethoxylated polyethylenimine (EPEI). This was followed by deposition of various fluorocarbon surfactants, such as fluoroaliphatic phosphate ester ($\text{CF}_3(\text{CF}_2)_8\text{CH}_2\text{CH}_2\text{]-PO}_4^- \text{NH}_3^+$), C8-18 perfluoroalkylethyl betaine, ammonium fluoroaliphatic carboxylates, fluoroaliphatic oxyethylene adduct, etc. Out of these, fluoroaliphatic phosphate ester showed effective deposition on the EPEI modified PDMS-replica^{Silica}. This was reconfirmed by identifying intense XPS fluorine 1s peak against other peaks due to oxygen 1s, carbon 1s, silicon 2s, and silicon 2p. Surface compositions of PDMS-replica^{Silica/NH₂/CF₃} were determined using XPS. The surface and bulk chemical structures of PDMS-replica^{Silica/NH₂/CF₃} are shown in Figure 4A. The presence of silica terminal functionality on the PDMS-replica^{Silica/NH₂/CF₃} surface was determined by XPS. The XPS survey spectrum of

PDMS-replica^{Silica/NH₂/CF₃} showed significantly low intensity peaks at 533, 400, 290, and 106 eV due to oxygen 1s, nitrogen 1s, carbon 1s, and silicon 2p, respectively. It showed relatively high intensity peak at 690 eV due to fluorine 1s. Figure 4B shows region spectrum, which showed peak corresponding to fluorine atom, specifically, $-\text{CH}_2(\text{CF}_2)_7\text{CF}_3$ appeared at 690 eV from PDMS-replica^{Silica/NH₂/CF₃}. This peak was absent in the case of PDMS-replica^{Silica}.

In Figure 5, High-resolution region spectra also showed peaks at 106 (Si_{2p}), 291 (C_{1s}), 401 (N_{1s}), 533 (O_{1s}), and 690 (F_{1s}) eV due to the fluorocarbon and polyamine from PDMS-replica. The original peaks at 101.87 (Si_{2p}), 284.08 (C_{1s}), and 531.73 (O_{1s}) eV because of the surface $-\text{Si}(\text{CH}_3)_2\text{O}-$ groups from PDMS-replica^{Silica/CF₃} were dominated by high intensity peak due to the terminal $-\text{CF}_3$ groups. This indicated that PDMS-replica^{Silica/NH₂/CF₃} surface was enriched with $-\text{CF}_3$ possibly leading to high oil repellence on the biomimetic surface. The peaks due to carbon atom bonded to fluorine, namely $-\text{SiCH}_2\text{CH}_2\text{CF}_2(\text{CF}_2)_6\text{CF}_3$ appeared at 291.1 and 293.4 eV. The peaks due to silicon and oxygen from silica network appeared at 106 (Si_{2p}) and 533.5 (O_{1s}) eV, respectively. The weak intensity peak due to nitrogen, specifically signals because of polyamine appeared at 401.7 (N_{1s}) eV.

Figure 6A, that is, SEM image of biomimetic PDMS-replica^{Silica/NH₂/CF₃} showed hierarchical pattern of flower-shaped protuberance. Figure 6B and 6C showed uniform coating of nono-silica particles on the fiber-like mesh structure present on protuberance. These particles possess particle size of less than 400 nm. As seen in Figure 6D, PDMS-replica^{Silica/CF₃} showed superhydrophobic property with advancing and receding contact angles (θ_{water}) of $\sim 152^\circ$ and 140° , respectively. PDMS-replica^{Silica/CF₃} also showed high oil repellency with advancing and receding contact angles (θ_{oil}) of $\sim 112^\circ \pm 3$ and

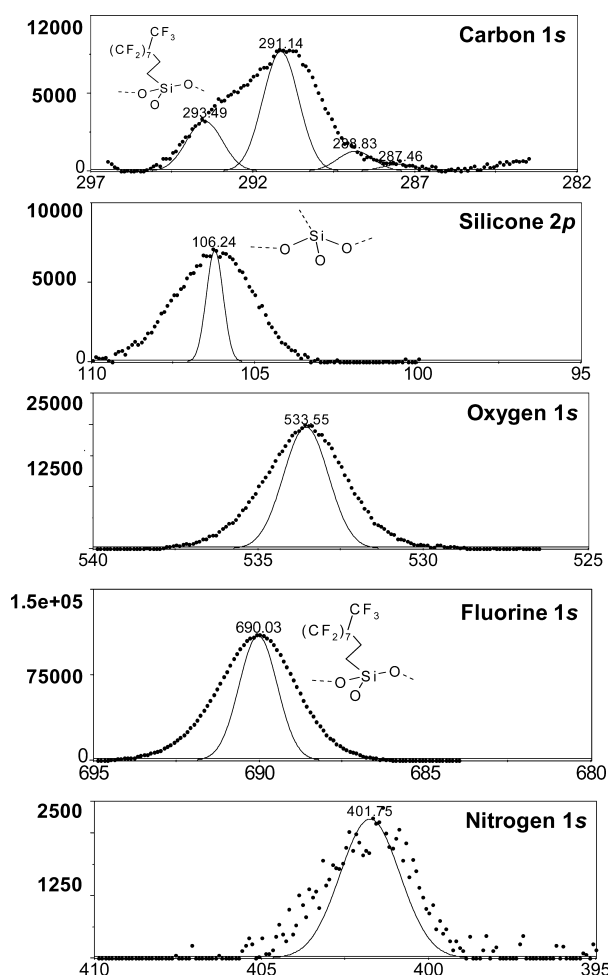


Figure 5. XPS spectra of carbon 1s, silicon 2p, oxygen 1s, fluorine 1s, and nitrogen 1s regions at 90° take off angle from the PDMS-replica_{Silica/CF₃} (··· data; — Gaussian sum).

$104^\circ \pm 4$, respectively. Glycerol trioleate (oil) having surface tension 34.7 dyn/cm was used for the contact angle study.

CONCLUSION

Surface chemical modification of biomimetic material was achieved by preserving its complementary micronano roughness. Water-based layer-by-layer sequential deposition of ethoxylated polyethylenimine and phosphated fluorocarbon on the biomimetic material produced superhydrophobic ($\theta_{\text{water}} \approx 152^\circ$) and high oil repellency properties (advancing $\theta_{\text{oil}} \approx 112^\circ$). This method could be extended to get diverse terminal chemical functionality on the biomimetic materials, which would furnish interesting surface properties in air or water

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Notes

The authors declare no competing financial interest.

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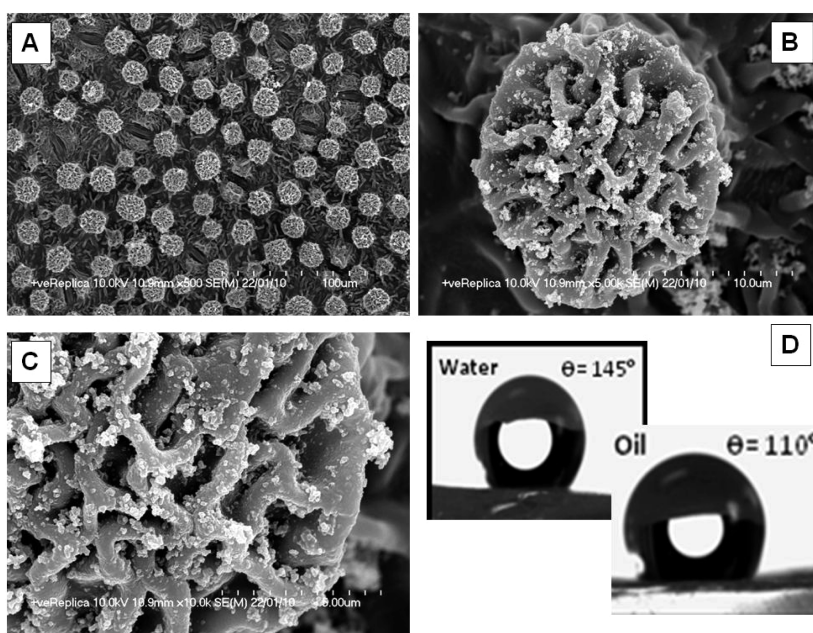


Figure 6. SEM images of PDMS-replica_{Silica/CF₃} showing (A) pattern of flower-shaped protuberance (scale bar = 100 μm), (B) silica-coated protuberances (scale bar = 10 μm), (C) silica-coated fiber-like mesh structure present on each protuberances (scale bar = 5 μm), and (D) the goniometer images of oil and water drops on the PDMS-replica_{Silica/CF₃} surface.

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