One-Step Synthesis of Statically Amphiphilic/Dynamically Amphiphobic Fluoride-Free Transparent Coatings

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Supporting Information

ABSTRACT: Although amphiphobic materials have attracted tremendous attention recently owing to their many important applications, there remain some critical challenges such as complex or expensive fabrications, poor long-term stability, nontransparency, etc. Herein, we develop a novel kind of amphiphobic materials—statically amphiphilic but dynamically amphiphobic fluoride-free transparent coating—through one-step reaction. The obtained transparent coating can be readily applied to different kinds of substrates including flat surfaces, curved surfaces, or inner walls of some tubes and bottles, and demonstrate excellent repellency against various high/low-surface-tension liquids and outstanding stability against external damages.

KEYWORDS: amphiphobic, liquid-like, transparent, fluoride-free, coatings

INTRODUCTION

Although numerous superhydrophobic materials with significantly dewetting property against water have been investigated in the past decades, through mimicking natural nonwetting structures, such as lotus leaves,1 feathers,2 insect legs,3 and wings,4,5 they are easily contaminated by oily liquids or mechanical damages.6,7 Accordingly, development of high-quality amphiphobic materials that completely resist wetting from both water and oily liquids is highly desirable because of their great application value in antifouling,8-10 anti-icing,11 self-cleaning,12-14 corrosion prevention,15-17 oil transportation,18 etc.

The current strategies to develop amphiphobic materials might be divided into two categories, according to the interaction mechanisms between material surfaces and applied liquids, in which fabrication of a robust hierarchical structure with perfluorinated chemistry treatment is regarded as the dominant concept.19,20 Liquid droplets on such kind of surfaces have apparent contact angles of above 150°, and the formed air cushion is crucial to facilitate easy rolling-off of the standing liquid droplets at relatively low sliding angles (SA) (typically <10°). Although this strategy is effective to repel various high/surface-tension liquids, it is very difficult to fabricate the well-designed hierarchical structure of complex overhang,21-24 convex curvature,25 or re-entrant morphology,26,27 which usually involves complicated technologies such as plasma etching,28 reverse nanoimprint,29 photolithographic,30,31 etc. And, the hard-won surface coatings are usually nontransparent and very fragile.32 The second kind of amphiphobic material is mainly inspired by the Nepenthes pitcher plant,33-36 which is termed as slippery liquid-infused porous surfaces. The introduced lubricant is locked in place by nano/microstructured substrates to form an overlying film between the test liquids and the protected substrates, the applied foreign liquids can slide off from the matched slippery surface with a tiny tilt angle due to dynamic fluidity. However, the weak interaction between infused lubricants and substrates is not sufficient to ensure a long-term stable dewetting property of the materials, especially for oil volatilization under high-temperature environment or oil loss in flow condition.37

To explore high-quality liquid-repellent coatings for practical applications, in this study, we fabricate a statically amphiphilic but dynamically amphiphobic fluoride-free transparent coating in a simple and environment-friendly way. Through the reaction between aminopropyl-terminated poly(dimethylsiloxane) (H2N-PDMS—NH2) oligomer, 3-isocyananotopropyltriethoxysilane (IPTS), and tetraethyl orthosilicate (TEOS), the prepared transparent coating can be easily coated on various flat and curved surfaces, endowing the surfaces with durable nonwetting property toward various high- or low-surface-tension liquids even after harsh environmental attacks and physical damages.

EXPERIMENTAL SECTION

Materials. Aminopropyl-terminated poly(dimethylsiloxane) (H2N-PDMS—NH2, Mn ~2500) was purchased from Sigma-Aldrich. Tetraethyl orthosilicate (TEOS), fluorescein isothiocyanate (FITC),...
glycol, acetonitrile, diglycol, and *N*,*N*-dimethylformamide (DMF) were received from Aladdin Chemical Reagent Corp. Erioglaucine disodium salt, oil red O, sunset yellow FCF, absolute ethanol, 3-isocyanatopropyltriethoxysilane (IPTS, ≥95%), ditin butyl dilaurate (≥95%), olive oil, concentrated hydrochloric, sodium hydroxide, and sodium chloride were bought from Sinopharm Chemical Reagent Co., Ltd (China). Poly(dimethylsiloxane) (PDMS, SYLGARD 184) was received from Dow Coming Corp. Fluorinert FC-40 was supplied by Shanghai Silver-Tech Co., Ltd, and deionized water was used throughout the experiments.

**Preparation of Liquid-Repellent Coating.** Typically, *H*₂*N*-PDMS–NH₂ (2.5 g), TEOS (0.274 g), IPTS (0.274 g), and ditin butyl dilaurate (0.01 g) were added into a 50 mL round-bottom flask and stirred magnetically at 40 °C for 6 h. The obtained transparent coating was casted on various substrates and dried at 80 °C for 24 h.

**Preparation of PDMS Coating.** A mixture of PDMS prepolymer and curing agent (mass ration, 10:1) was degassed and then casted on the substrates. After cross-linking at 80 °C for 2 h, the prepared coating was used as the control group to test the liquid-repellent property.

**Characterization.** Fourier transform infrared spectra (FTIR) were recorded on Nicolet Nexus 470 (Thermo Fisher). X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000C ECSA) with Al Mg radiation at a 90° take-off angle was used to detect the surface composition of the coating film. Scanning electron microscopy (SEM XL30FEG) and atomic force microscopy (AFM, Dimension 3100, Digital Instruments) were applied to observe the surface morphology and roughness of the samples, respectively. Oil/water contact angles (WCA/OCA) and sliding angles (SA) were measured on OCA15 contact angle analyzer (Data-physics, Germany); more than five experimental points were recorded to calculate the average.

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**Scheme 1. Schematic Diagram for the Structure of the Amphiphobic Coating**

**Figure 1.** (a) FTIR spectra of the reactants and the coating film. XPS scan of the prepared coating (b) and the fitting curve of peak of N 1s (c). Digital photographs and the corresponding confocal laser scanning microscopy images of bare glass (d) and coated glass (e) after immersion into FITC ethanol solution for 24 h.

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value. UV–vis spectra were recorded on a Beckman Coulter DU520 UV–vis spectrophotometer (Fullerton). Confocal laser scanning microscopy (Nikon, Japan) was selected to observe the surface fluorescence phenomenon.

## RESULTS AND DISCUSSION

As illustrated in Scheme 1, our statically amphiphilic but dynamically amphiphobic fluoride-free transparent coating is fabricated via reaction between H₂N–PDMS–NH₂ and IPTS as well as TEOS to produce highly flexible coating in which TEOS and IPTS can co-hydrolyze to enhance the intensity of the prepared coating films, whereas some free PDMS segments consist of polymer brushes.

Figure 1 demonstrates the FTIR spectra of the coating film and its reactants, as well as the XPS scans of the coating film. The typical FTIR characteristic peaks of the isocyanate group that belong to IPTS disappeared from the prepared coating, accompanied by new peaks of amide groups (Figure 1a), indicating the reaction between the amino and the isocyanate groups has indeed occurred. The XPS scan indicates the presence of free amine from the fitting curve of peaks of N 1s (Figure 1b,c), which strongly suggests that the polysiloxane chain segment in the prepared solid film is still in a highly mobile state. To further prove it, the coated and bare glass slides were immersed in FITC ethanol solution to make a comparison because iso-thiocyanate group is prone to react with the amine group at room temperature. As shown in Figure 1d,e, unlike the uncoated glass without fluorescence observed under confocal laser scanning microscope, the coated surface turns FITC-like yellow and exhibits an obvious green fluorescence, further confirming the existence of free amino group and the highly mobile PDMS segments of the prepared coating, which can endow the coating with “liquid-like” nature and excellent liquid-repellent property.38,39
The as-prepared coating can be directly applied on various substrates. As shown in Figure 2a, the glass, polyethylene terephthalate (PET), and tinplate substrates can be well coated, and the coated glass and the PET display a relatively high transparency over their bare counterparts (Figure 2a,b). Using coated glass as an example, one can see the coated surface is smooth with a quite low root-mean-square roughness of approximately 3.95 nm ($100 \times 100 \ \mu m^2$), without an obvious bump structure (Figure 2c,d). Besides, the prepared coating film is stretchy and firmly bonded to the substrates and general bending, twisting, or rubbing does not damage the coating obviously (insets of Figure 2b).

It is generally known that the static contact angle alone does not reflect the actual dewetting performances of the materials because liquids with high static contact angles sometimes are in the typical Wenzel state and therefore strongly adhere to the surfaces without rolling off. On the contrary, dynamic sliding angles can more accurately characterize the wetting/dewetting properties of the liquid-repellent surfaces. Figure 3a,b illustrates the surface wettability of the as-prepared
coating against various organic solvents and oil liquids using static contact angles and dynamical sliding angles, respectively. Although the OCAs of the tested organic solvents and oils on the coating surface are lower than 90°, indicating an oleophilic surface, their SAs are less than 10° due to the highly mobile PDMS segments of the deposited coating. Even after immersion in FITC ethanol solution for 24 h, with the reaction of the free amino group of the PDMS segments with FITC, the SAs only increase by 4.6 and 3.5° for glycol and DMF, respectively. Accordingly, these organic solvents and oils can slide off readily from the coated substrates, as shown in Figure 3c and Movies S1–S6 with glycol (46.5 mN m⁻¹, dyed with oil red O) and DMF (25.7 mN m⁻¹, dyed with sunset yellow FCF) as probe liquids, whereas the corresponding bare substrates and commercial cross-linked PDMS coating show poor oil-resistant property (Figure S1 and S2). These results demonstrate that the deposited coating can provide the surfaces of materials with prominent oil repellency, which can efficiently prevent the substrates from oil contaminations.

When the DMF and water droplets are dropped onto the coated glass at a slant angle of 10, the DMF droplet slides off smoothly from the surface, whereas the water droplet (dyed with erioglaucine disodium salt) is pinned at the initial position without any movement (see Figure 4a and Movie S7). This is ascribed to the poor interaction between the DMF and the amine group of the coating surface but a strong hydrogen bond between the water molecule and the amine group. Nevertheless, the coating surface still possesses the evident dynamic dewetting property against water. As shown in Figure 4b,c, the water droplet on the flat glass slide with a WCA of 82.4° can be absorbed rapidly by napkin or automatically slide off at a slant angle of 20°, without leaving any residues (Movies S8 and S9). Additionally, even strong acid (pH 1), alkaline (pH 14), and saturated salt water droplets leave no traces on the coating surfaces (Figure 4d). All these results indicate that the prepared coating possesses outstanding liquid repellency against water and oils, with special statically amphiphilic but dynamically amphiphobic feature.

Figure 6. Antifouling performance of the prepared coating on the concave surfaces (a), convex surfaces (b), and inner walls of the test tubes (c) and the reagent bottles (d). The blue, red, and orange liquids represent water, glycol, and DMF, respectively.

Figure 7. Comparison of the antigraffiti performance between uncoated (a) and coated glasses (b) with aqueous (green trace) and oily pastels (red trace).
To investigate the liquid-repellent stability of the prepared coating, we further simulated several harsh environments that may be confronted in practical applications. As shown in Figures 5a–c and S3, the coating surfaces still present low sliding angles toward the applied liquids even after treatment with UV irradiation (310 nm, 120 W), freezing at $-20\,^\circ\text{C}$, and heating at 100 $^\circ\text{C}$ for 120 h, respectively. After the abrasion test (200 g of load placed over coarse sandpaper to rub the coated glass back and forth for 50 times, Figure 5d), although the damaged coating surface is slightly roughed (Figure 5e), the transparency and the liquid repellency do not deteriorate significantly (Figures 5f and S4).

Considering the possible target objects with different textures and shapes in practical applications, we further investigated the liquid-repelling property of the curved surfaces coated by our coating material. As shown in Figure 6a,b, the liquid droplets on the coated curved surfaces freely roll off rather than spread out on the uncoated surfaces. Similarly, the coated test tubes and reagent bottles also exhibit excellent liquid repellency, whereas the inner walls of the uncoated test tubes and reagent bottles are completely stained by the applied liquids (Figure 6c,d). This indicates that the coated inner surfaces of the feeding bottles, soy crucets, etc. can efficiently prevent the loss of the loaded stuff.

Figure 7 further demonstrates the antigraffiti performance of our coating. No matter which marker (oily or aqueous) is used, the writings on the bare glasses are clear, and they are almost impossible to be erased by napkin (Figure 7a). On the contrary, the marks on the coated glasses can be slightly wiped off thoroughly (Figure 7b). These drawn glasses observed through digital microscope show that the marked liquids fully spread out on the bare glasses but aggregate into small droplets on the coated surfaces, which are easily erased.

**CONCLUSIONS**

We have demonstrated a novel amphiphobic materials—statically amphiphilic but dynamically amphiphobic fluoride-free transparent coating—via one-step reaction of $\text{H}_2\text{N-}$PDMS$-\text{NH}_2$, IPTS, and TEOS, without using any organic solvents or other toxic reagents. The prepared coating can be easily used on various flat and curved surfaces to repel various high/low-surface-tension liquids even in harsh environments, e.g., high or low temperatures, UV irradiation, and mechanical damage. Owing to its efficient and environment-friendly preparation method, outstanding optical transparency, and dewetting property against various liquids, this novel amphiphobic coating offers promise to meet the emerging needs in self-cleaning, anti-icing, fuel transport, and anti fouling fields, especially in some transparent demands such as lenses, mobile phones, laptops, cameras, solar panels, optical devices, etc., and antifingerprint or self-cleaning transparent protective films.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b16485.

Sliding behavior of glycol and DMF droplets on the uncoated surfaces; sliding behavior of glycol and DMF droplets on the commercial cross-linked PDMS coating surface; sliding performance of the tested water liquids on the coated surface, which were treated for 120 h under UV irradiation, freezing at $-20\,^\circ\text{C}$, and heating at 100 $^\circ\text{C}$, respectively; UV–vis transmission spectrum of the rubbed coated glass (PDF).

Liquids sliding behavior on the prepared statically amphiphilic but dynamically amphiphobic fluoride-free transparent coating (ZIP).

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**Notes**

The authors declare no competing financial interest.

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