AIChE Letter: Separations: Materials, Devices and Processes

Durable Superoleophobic Fabric Surfaces with Counterintuitive Superwettability for Polar Solvents

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Significance

Smart superoleophobic (SOP) cotton fabric surfaces are created only through a controlled fluorosilanization treatment, exhibiting the first-ever extreme wetting behaviors displaying ultrarepellency to nonpolar oils and counterintuitive superwettability for all polar solvents. The smart durable SOP surfaces, demonstrated chemically, thermally, and mechanically, render great potential practical and industrial applications in robust oil shielding, effective antifouling, highly energy efficient self-cleaning, and solely gravity-driven oil–water separations. © 2014 American Institute of Chemical Engineers *AIChE J*, 60: 2752–2756, 2014

Keywords: surface chemistry, composite materials, membrane separations, self-cleaning clothing, superoleophobicity

Surfaces with special wetting properties have been attracting world-wide scientific interests in recent years due to their desirable practical applications.[1–6] A surface is considered to be superoleophobic (SOP) if the apparent contact angle θ^* for a contacting low surface tension oil droplet is greater than 150°.[7] While a few SOP surfaces have been previously engineered,[8–10] there are very few stimuli-responsive SOP surfaces reported displaying switchable oil wetting properties[11,12] and even significantly fewer[13,14] functioning as a both SOP and superhydrophilic ($\theta^*_{\text{water}} \sim 0°$) coating in air. In this work, we have fabricated remarkably durable smart surfaces that, for the first time, exhibit clever solvent-responsiveness of extreme wetting behaviors that display both superoleophobicity with a wide surface tension range of nonpolar oils and quick switch to *counterintuitive* superwettability with virtually all the contacting polar liquids. Our smart surfaces, allowing nonpolar oil liquids, even for ultra-low surface tension gasoline, such as hexane (18.5 mN m^{-1}) and heptane (20.6 mN m^{-1}), to easily bead up on the surface with a robust extreme oil-repellent composite Cassie-Baxter state,[15] can cleverly and spontaneously manifest fully wetted Wenzel state[16] displaying apparent contact angles of about 0° for almost all the aprotic and protic polar solvents covering an extensive range of surface tension, thus permitting such liquids like water (72.8 mN m^{-1}), dimethylformamide (37.4 mN m^{-1}), and ethanol (22.1 mN m^{-1}) to readily spread and permeate through. Such a clever solvent-responsive wetting and dewetting ability, thereby, make our surfaces ideal candidates not only for effective oil shielding but for highly energy efficient *surface self-cleaning*[17,18] and *oil–water separations*.[13,19]

Wettability of chemically homogeneous substrates[18] is dominated by the surface tension of the contacting fluids, thus, SOP surfaces are always superhydrophobic ($\theta^*_{\text{water}} > 150°$) owing to the higher surface tension of water,[10] which results in the respective higher Young's contact angle.[20,21] Homogeneous liquid-repellent coatings on cellulose-based materials were extensively reported on superhydrophobicity and/or oleophobicity recently.[22,23] Only a few studies[13,14,18,24] have reported surfaces performing higher oil contact angles than that of water, most all of which, however, are oleophilic thus displaying limited oil repellency. To obtain counterintuitive superhydrophilicity on an oil-repellent surface, the introduction and regulation of heterogeneity in surface chemistry plays a vitally important role.

Commercially available cotton fabrics (see Figure 1A) and dip-coated polyester fabrics (see Figure 1B) are intrinsically

Additional Supporting Information may be found in the online version of this article.

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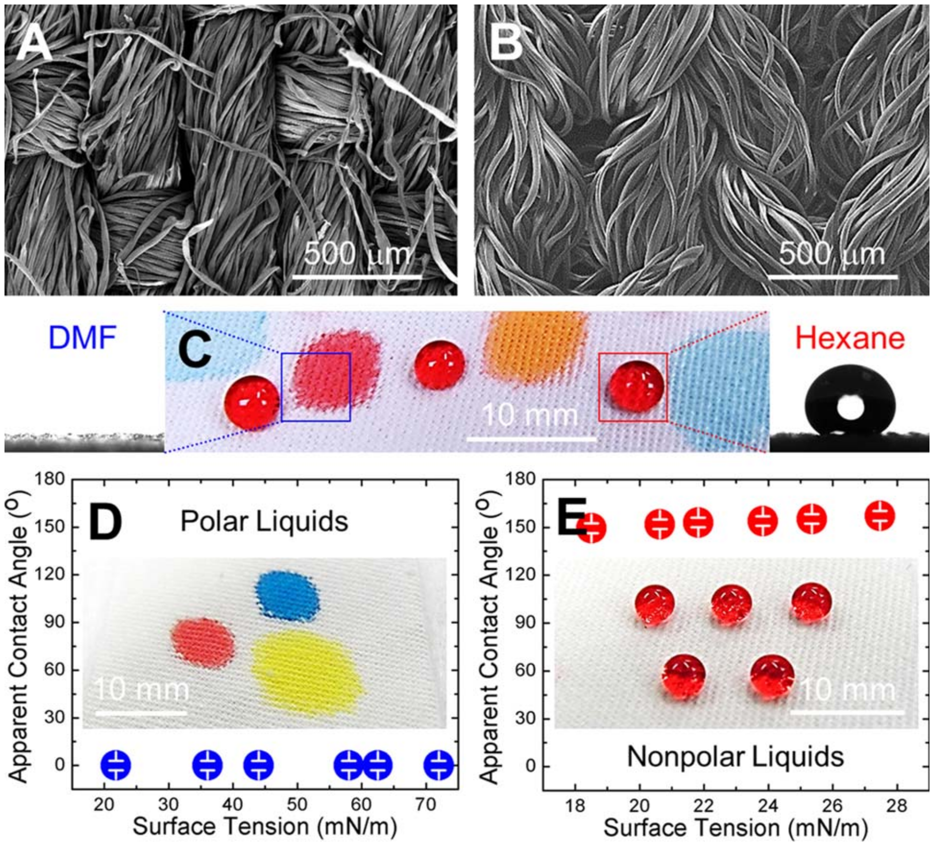

Figure 1. Counterintuitive surface extreme wettability for contacting nonpolar oils and polar solvents.

SEM images of smart SOP commercial cotton fabric (A) and (B) polyester fabric. (C) Smart fabric with nonpolar alkanes beading up (dyed red, from left to right, hexadecane, decane and hexane, respectively) and polar liquids permeating through (from left to right, dimethylformamide DMF red, ethanol orange and water blue, respectively). (D, E) Apparent contact angles for liquids with different polarity on the smart fabric surface shown in (A). Insets in (D, E) demonstrate the counterintuitive wettability for polar and nonpolar liquids. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

superwettable. In this Letter, (tridecafluoro-1,1,2,2-tetrahydrooctyl)triethoxysilane is chosen (see Supporting Information Section 1) for the one-step fabric modification because on fluorosilanization it exhibits excellent oil resistance to a wide range of low surface tension hydrocarbons due to the low solid surface energy[25] of its self-assembled molecule layers ($\sim$11.5 mN m^{-1}, see Supporting Information Section 2). The intrinsic reentrant porous structure[7] in conjunction with a reasonable fluorine coverage confirmed by the elemental map (see Supporting Information Section 3) results in high apparent contact angles for various nonpolar hydrocarbons, even for extreme-low surface tension gasoline, such as hexane ($\theta^{*}_{\text{hexane}} \sim 151°$), thus revealing supreme oil-shielding performance (see Figures 1C, E). Note that very few studies[11] have reported oil repellency with surface tension lower than 20.0 mN m^{-1}. Surface extreme oil repellency for other hydrocarbons, halogenated hydrocarbons, and aromatic hydrocarbons is discussed in Supporting Information Section 3. General estimate of oil contact angles is discussed in Supporting Information Section 4. The measured sliding angles match reasonably well with that of predictions, indicating our SOP fabrics are within a regime between a fully developed Cassie-Baxter state and a more wetted state when contacting with nonpolar oils[26] (see Supporting Information Section 5).

However, as is revealed from the energy dispersive X-ray scattering spectrum (EDAX) (see Supporting Information Section 3), a low fluorine ratio is evident after surface fluorosilanization owing to relatively low reactivity of triethoxysilanes at room temperature. Moreover, consider the intrinsic superwettability of cotton fabrics, the abundant intact cellulose chains would migrate to the surface to increase their interfacial area with contacting polar liquids in respect to the principle of "like dissolves like," thus facilitating the surface reconfiguration[13,18] and enthalpic gains through hydrogen bonding, leading to a smart switch to superwettability for contacting polar liquids (see Figures 1C, D). Detailed surface wettability for polar aprotic and protic liquids is discussed in Supporting Information Section 3. Note that, example of superwettability (for virtually all contacting polar liquids) coexisting with extreme oil repellency has never been reported before. Moreover, this fabrication technique is universal for all other cellulose based materials (e.g., filter paper).

Such an unprecedented surface extreme wetting behavior corresponding to physically different polar and nonpolar liquids renders great opportunity in industrial and practical applications. As to cleanup the oil-fouled clothing (oil loving), water needs to first sneak underneath and then replace the oil stain, the process of which is thermally and dynamically difficult as the surface is preferably to be wetted by oil. Thus, surfactants

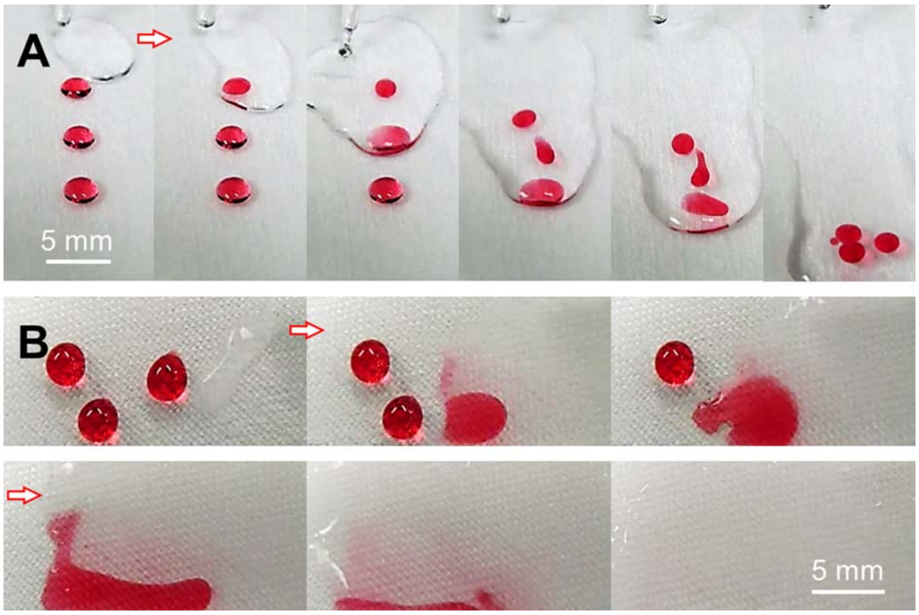

Figure 2. Process of oil replacement and surface self-cleaning.

(A) Flat smart coating and (B) smart SOP cotton fabrics: oil stains (hexadecane, dyed red) can be easily replaced and rinsed off by water without any detergent. Time interval is ~1 s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(like detergent or washing powder, which are always environmentally and ecologically unfriendly) have to be applied to decrease the interfacial surface tension. While as for water loving and oil hating surfaces shown in Figure 2 (see Experimental Section), preset oil stains could be readily replaced by water within seconds in the absence of any surfactants, the oil replacement during which, for comparison, is a spontaneous process as water wetting is a preferable way leading to a lower system free Gibbs Energy. The oil replacement and self-cleaning property of the smart fabric are demonstrated by ways

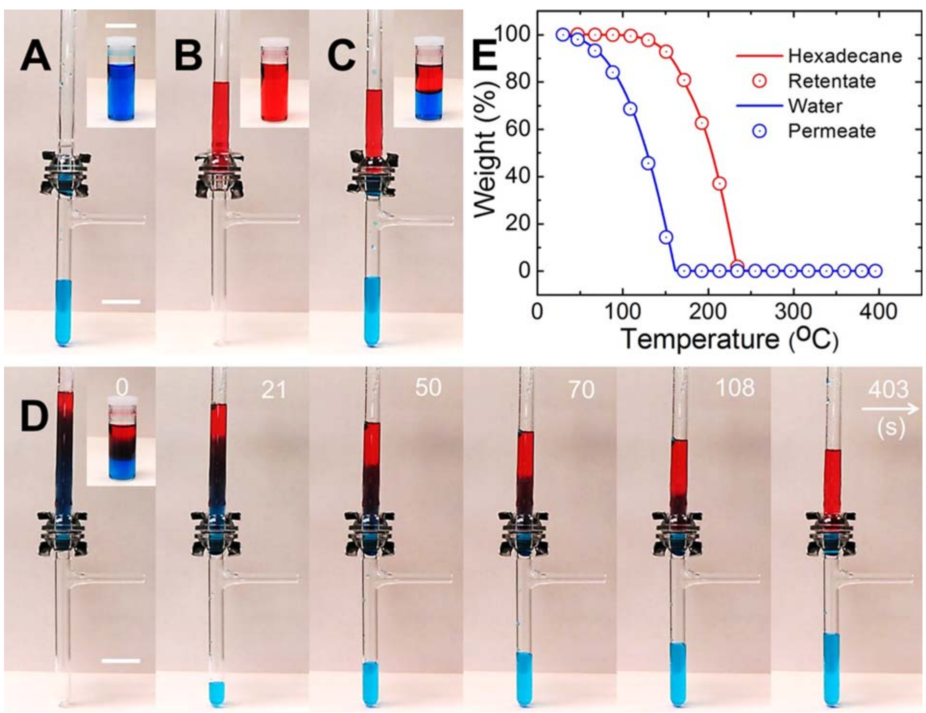

Figure 3. Solely gravity-driven oil–water separations.

(A) Water permeates through and (B) hexadecane retains above the membrane. (C) Effective separation of free water–oil mixture. (D) Series of images showing the separation of four-component oil–water mixtures. (E) TGA data of permeate and retentate of (D). The insets in (A–D) are free water, free oil, free water–oil, and four-component oil–water mixtures, respectively. Water is dyed blue and hexadecane red. Scale bar, 2 cm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

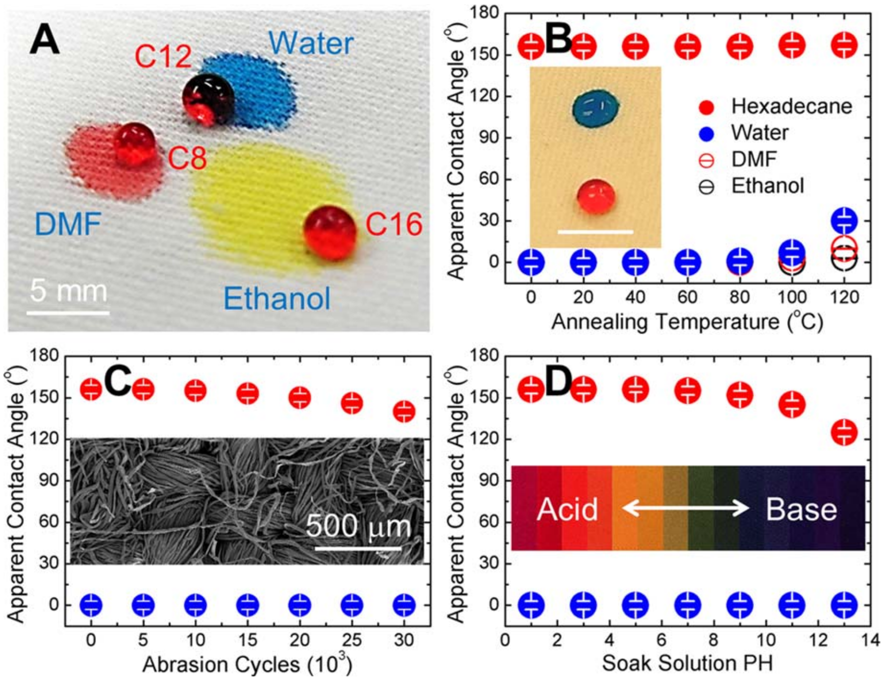

Figure 4. Durability of the smart fabric.

(A) Oil droplets exhibit unchanged high contact angles on domains prewetted by water, DMF, and ethanol, respectively. Dependence of liquid contact angles on annealing temperature (B), abrasion cycles (C), and PH of soak solution (D). Oil (hexadecane) is denoted red circle and water blue. Inset of (B) shows slightly increased water contact angle when treating the fabrics at 120°C for 24 h. Scale bar, 1 cm. Inset of (C) is a SEM image of abraded fabrics for 20,000 times. Inset of (D) indicates the intensity of acidity and basicity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of rinse washing and dip washing in Supporting Information Movie S1 (even dried oil stains with dye can also be replaced and removed completely by water within seconds, see Part 4 of Movie S1). Note that the water-assisted self-cleaning process is economically effective and environmentally friendly as no detergent is needed during the entire cleaning process.

Conventional liquid–liquid separation technologies require more than one separation units and consume a lot of external energy.[27,28] However, waste oil–water mixtures can be further separated readily only by a solely gravity-driven separation unit, in which the as-prepared smart fabric is tightly sandwiched between two glass tubes (see Figures 3A–D). Pure water is collected as permeate as the fabric cleverly allows water to pass through and retains oil above it as retentate (see Figures 3A–C). A possible highly energy efficient way of industrial waste separation is demonstrated by feeding a complicated four component oil–water mixture (including free oil and water, oil-in-water emulsions, water-in-oil emulsions) into the single separation unit (see Figure 3D). Very high purity of permeate and retentate is revealed by thermogravimetric analysis (see Figure 3E). The effective solely gravity-driven oil–water separations are also demonstrated in Supporting Information Movie S2. Water flux[29] during separation and a quasiempirical rating respect to surface self-cleaning and oil–water separation is discussed in Supporting Information Section 6.

Remarkable durability of our surfaces has also been demonstrated chemically, thermally and mechanically in various ways shown in Figure 4. Oil droplets exhibit almost unchanged high contact angles on domains prewetted by polar solvents (see Figure 4A), revealing a robust and reversible responsiveness for polar and nonpolar liquids. Our membranes show long-term durability within an environmentally relevant temperature range of 0–100°C (see Figure 4B). After 20,000 cycles of abrasion test, the fabric was found to be still maintaining the superoleophobicity and superwettability for polar liquids (see Figure 4C). Oil contact angles remain unchanged at low PH, while high basicity (PH > 12) may damage the Si—O—C bonding thus resulting in the slightly decrease of oil repellency (see Figure 4D). Detailed discussion is in Supporting Information Section 7.

In summary, we have demonstrated a simple technique for fabricating smart SOP membranes for effective oil-replacing applications. The low surface energy combining with surface reconfiguration renders both excellent oil resistance even for ultra-low surface tension nonpolar oils and extreme wettability for virtually all polar liquids. These smart fabrics exhibit prominent chemical, thermal, and mechanical durability. Consequently, our surfaces can serve as effective oil replacement media and are promising for applications in self-cleaning, antifouling, breathable oil-shielding clothing, cleanup of oil spills, wastewater treatment, separation of commercially relevant emulsions, and fuel purification.

Experimental Section

Textured surface

A piece of ultrasonically cleaned cotton wipe and 10 μL (tridecafluoro-1,1,2,2-tetrahydrooctyl)triethoxysilane were placed in the vacuum desiccator, and then chemical vapor deposition was carried out at room temperature for 24 h. Finally, the silanized fabric was subsequently washed with ethanol and dried for use.

Nontextured surface

Silicon wafers were first spin-coated with 10 mg mL^{-1} solutions of hydroxypropyl cellulose +5 wt % glyoxal in water, subsequently cross-linked. Same CAD procedure was carried out as described above.

Characterization

The surfaces were imaged using a JSM-6700F scanning electron microscope. The contact angles with a typical average error within $\pm 3^{\circ}$ throughout were obtained by measuring at least six times at different locations by advancing or receding a small volume of liquid ($\sim$5 μL) onto the fabric surface using a KRUSS DSA100 goniometer. Separation efficiency was evaluated using a HENVEN HCT-1 thermal gravimetric analyzer (TGA).

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S. Pan and R. Guo designed and performed the experiments, analyzed data and wrote the manuscript. W. Xu conceived and supervised the project. The authors declare no competing financial interest. We thank the National Science Foundation of China for funancial support under grants J0830415 and J1210040, and the Research Fund for the Doctoral Program of Higher Education of China (20120161110024).

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