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Superomniphobic Surfaces for Effective Chemical Shielding

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Ⓢ *Supporting Information*

ABSTRACT: Superomniphobic surfaces display contact angles >150° and low contact angle hysteresis with essentially all contacting liquids. In this work, we report surfaces that display superomniphobicity with a range of different non-Newtonian liquids, in addition to superomniphobicity with a wide range of Newtonian liquids. Our surfaces possess hierarchical scales of re-entrant texture that significantly reduce the solid–liquid contact area. Virtually all liquids including concentrated organic and inorganic acids, bases, and solvents, as well as viscoelastic polymer solutions, can easily roll off and bounce on our surfaces. Consequently, they serve as effective chemical shields against virtually all liquids—organic or inorganic, polar or nonpolar, Newtonian or non-Newtonian.

Superhydrophobic surfaces display apparent contact angles $\theta^* > 150°$ and low contact angle hysteresis $\Delta\theta^*$ (the difference between the advancing and receding contact angles) with water, while superoleophobic surfaces display $\theta^* > 150°$ and low $\Delta\theta^*$ with low surface tension liquids.[1−4] Superomniphobic surfaces display both superhydrophobicity and superoleophobicity. While surfaces that display superomniphobicity with various Newtonian[5] liquids have been previously engineered,[6−17] there are few, if any, articles that report superomniphobicity with non-Newtonian[5] liquids. In this work, we report surfaces that display superomniphobicity with non-Newtonian liquids (e.g., viscoelastic polymer solutions) in addition to a wide range of Newtonian liquids including concentrated organic and inorganic acids, bases, and solvents. Virtually all liquids—organic or inorganic, polar or nonpolar, Newtonian or non-Newtonian—easily roll off and bounce on our surfaces, thereby making our surfaces ideal candidates for effective chemical shielding. We envision that our surfaces will have numerous applications including stain-free clothing and spill-resistant, breathable protective wear,[11] enhanced solvent-resistance,[16] biofouling resistant surfaces,[18] self-cleaning,[19] drag reducing,[20] and lightweight corrosion-resistant coatings.[21]

Hierarchically structured surfaces possess more than one scale of texture (a finer length scale texture on an underlying coarser length scale texture). When a hierarchically structured surface supports a contacting liquid droplet in the so-called Cassie–Baxter state,[22] the liquid droplet displays high apparent contact angles and low contact angle hysteresis.[19,23−25] Previous work[1,2,6,8,9,26−32] has explained the significance of re-entrant curvature in designing surfaces that can support low surface tension liquids in the Cassie–Baxter state. Consequently, hierarchically structured surfaces possessing re-entrant curvature are expected to be very useful in developing surfaces that are extremely repellent to low surface tension liquids.[33]

In this work, we have employed an electrospun coating of cross-linked poly(dimethylsiloxane) (PDMS) + 50 wt% fluorodecyl polyhedral oligomeric silsequioxane (POSS) (solid surface energy, $\gamma_{sv} \approx 11.5$ mN/m; see Supporting Information (SI) section 1) on top of stainless steel wire meshes to fabricate hierarchically structured surfaces (see Figure 1A). We chose PDMS in this work because upon cross-linking it exhibits excellent chemical resistance against a range of different chemicals. The low solid surface energy of the cross-linked PDMS + 50 wt% fluorodecyl POSS blends is due to the preferential segregation of fluorodecyl POSS ($\gamma_{sv} \approx 10$ mN/m) molecules to the surface[2] (see Figure 1B and SI section 2). Our hierarchically structured surfaces possess re-entrant

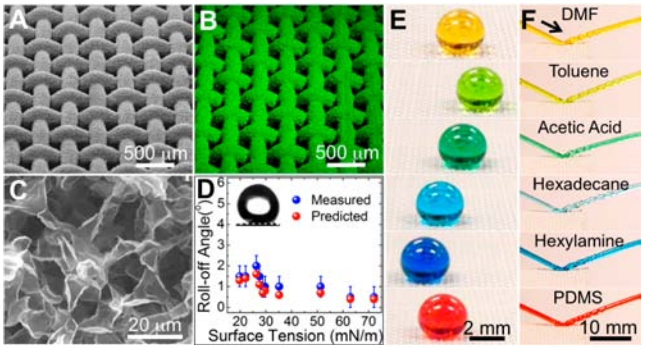

Figure 1. (A) SEM image of the hierarchically structured surface illustrating the electrospun coating of cross-linked PDMS + 50 wt% fluorodecyl POSS on a stainless steel wire mesh 70. (B) Elemental mapping of fluorine on the hierarchically structured surface. The high surface fluorine content is expected to be due to the surface migration of the fluorodecyl POSS molecules. (C) SEM image illustrating the re-entrant curvature of the electrospun texture. (D) Roll-off angles for various Newtonian liquids on the surface shown in (A). The inset shows an ethanol droplet rolling on the surface at a roll-off angle ω = 2°. (E) Droplets of various low surface tension Newtonian liquids showing very high contact angles on the surface shown in (A). (F) Jets of different Newtonian liquids shown in (E) bouncing on the surface shown in (A).

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curvature at both the coarser length scale (see Figure 1A) and the finer length scale (see Figure 1C). The hierarchical texture (spacing ratio[1,2,26] $D^*_{\text{particle}} = 12.7$ and $D^*_{\text{fiber}} = 1.7$, see SI section 3) along with the re-entrant curvature and the low surface energy of the coating results in high apparent contact angles (see Figure 1E) for a range of different polar and nonpolar low surface tension Newtonian liquids, including various acids, bases, and solvents. Further, the surfaces display low contact angle hysteresis (see SI section 4) and low roll-off angles ($\omega \leq 2°$, see Figure 1D) for essentially all Newtonian liquids. There have been very few reports of surfaces displaying such low contact angle hysteresis and low roll-off angles with extremely low surface tension liquids ($\gamma_{\text{lv}} < 25$ mN/m). Our surfaces display such low contact angle hysteresis and low roll-off angles because of the hierarchical structure with re-entrant curvature. The experimentally measured roll-off angles match reasonably well with the predictions based on the work by Furmidge.[34,35] Due to the low contact angle hysteresis, even jets of a range of different Newtonian liquids easily bounce on our hierarchically structured surfaces (see Figure 1F and movie S1).

Our hierarchically structured surfaces display exceptional chemical resistance as they can cause virtually all organic and inorganic Newtonian liquids to bounce and roll off. Figure 2A,B shows time sequence images of droplets (radius, $R_{\text{o}} \approx 1$ mm) of an organic acid (acetic acid, $\gamma_{\text{lv}} = 27.7$ mN/m) and an organic base (hexylamine, $\gamma_{\text{lv}} = 25.8$ mN/m), respectively, dropped under gravity from a height $h \approx 4.5$ mm, bouncing on our hierarchically structured surfaces (also see movie S2). The Weber number, $We = \rho V^2 R_{\text{o}}/\gamma_{\text{lv}}$, for acetic acid and hexylamine on first impact is 3.5 and 2.8, respectively. Here, $V = (2gh)^{1/2}$ is the impact velocity of the droplet with radius $R_{\text{o}} \approx 1$ mm. Each droplet bounces approximately four times before rolling off from the surface. Droplets of inorganic acids and bases, which typically have higher surface tension values, are repelled much more easily by our surfaces.

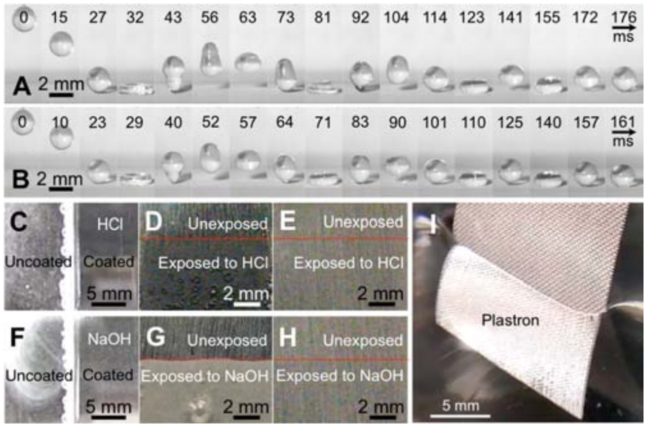

Figure 2. (A,B) Series of images illustrating droplets ($R_{\text{o}} \approx 1$ mm) of acetic acid and hexylamine, respectively, bouncing on the hierarchically structured surface that is tilted by 2° relative to the horizontal. (C,F) Side view of an aluminum plate, immersed in concentrated hydrochloric acid (HCl) and concentrated sodium hydroxide (NaOH), respectively. One side of the plate is uncoated, while the other side is coated with an electrospun coating of cross-linked PDMS + 50 wt% fluorodecyl POSS. The uncoated aluminum surface reacts violently with HCl or NaOH, releasing bubbles of hydrogen gas, but the coated aluminum surface (on the right) remains unaffected. (D,G) The uncoated aluminum surface appears rough and damaged after immersion in HCl and NaOH, respectively. (E,H) The coated aluminum surface remains unaffected after immersion in HCl and NaOH, respectively. (I) A bright plastron layer is visible when the surface is immersed in a liquid bath of PDMS.

We have also tested the chemical shielding effectiveness of our surfaces by immersing an aluminum plate coated with electrospun cross-linked PDMS + 50 wt% fluorodecyl POSS blend in concentrated acids and concentrated bases. While an uncoated aluminum surface reacts violently, releasing bubbles of hydrogen gas when immersed in concentrated hydrochloric acid (12 M; see Figure 2C) or concentrated sodium hydroxide (19 M; see Figure 2F),[36,37] the coated aluminum surface remains unaffected (also see movie S3). Upon examining the surface after a few minutes of immersion, significant damage is evident on the uncoated aluminum surface immersed in concentrated hydrochloric acid (Figure 2D) or concentrated sodium hydroxide (Figure 2G). In contrast, the coated surfaces do not display any macroscopic damage (see Figure 2E,H) or microscopic damage (see SI section 5), indicating effective chemical shielding.

Our electrospun coatings can similarly cause a wide range of other concentrated inorganic chemicals including concentrated sulfuric acid, which is known to attack cross-linked PDMS, to bounce and roll-off. A wide range of organic chemicals including toluene and chloroform, which readily wet/swell cross-linked PDMS, are also easily repelled. Even when our surfaces are immersed in a liquid bath of PDMS ($M_{\text{n}} = 800$ Da, $\gamma_{\text{lv}} = 19.8$ mN/m), a plastron[38] (air pockets) layer that is indicative of a robust Cassie–Baxter state is formed (see Figure 2I). The plastron layer was stable and remained unchanged even upon extended exposure to un-cross-linked PDMS. Note that PDMS is a major constituent of the electrospun beads. The observation of a stable plastron layer even when the surface is submerged under PDMS is extremely unique and indicates that the surface does not reconfigure, even when exposed to an enthalpically favorable solvent.[39−42] Thus, our surface remains unaffected even when exposed to liquids that adversely affect PDMS. In Table S1 (see SI section 4) we report the extremely low contact angle hysteresis and roll-off angles for 35 different Newtonian liquids, including organic and inorganic concentrated acids, concentrated bases, and solvents, on our electrospun cross-linked PDMS + 50 wt% fluorodecyl POSS blend surface.

A unique and remarkable feature of our hierarchically structured surfaces is that they display superomniphobicity even with non-Newtonian liquids. The impact of non-Newtonian liquid droplets on solid surfaces is of importance for a range of practical applications such as inkjet printing and spray-coating.[43] Previous studies[43−46] on the bouncing dynamics of non-Newtonian liquid droplets have typically been limited to high surface tension liquids. Our superomniphobic surfaces can provide a platform to systematically study the bouncing dynamics of low surface tension non-Newtonian liquid droplets as well. For example, droplets of viscoelastic polymer solutions such as 10 mg/mL poly(methylmethacrylate) (PMMA, $M_{\text{w}} = 35\,000$ Da) in dimethylformamide (DMF) display high apparent contact angles (Figure 3A), low contact angle hysteresis, and low roll-off angles (see Figure 3C and SI section 6) on our surfaces. Even jets of PMMA in DMF solutions easily bounce on our surfaces (see Figure 3B and movie S1). On a surface bent into a U-shape, a droplet of PMMA in DMF solution rolls back and forth at least four times before coming to rest (Figure 3d and

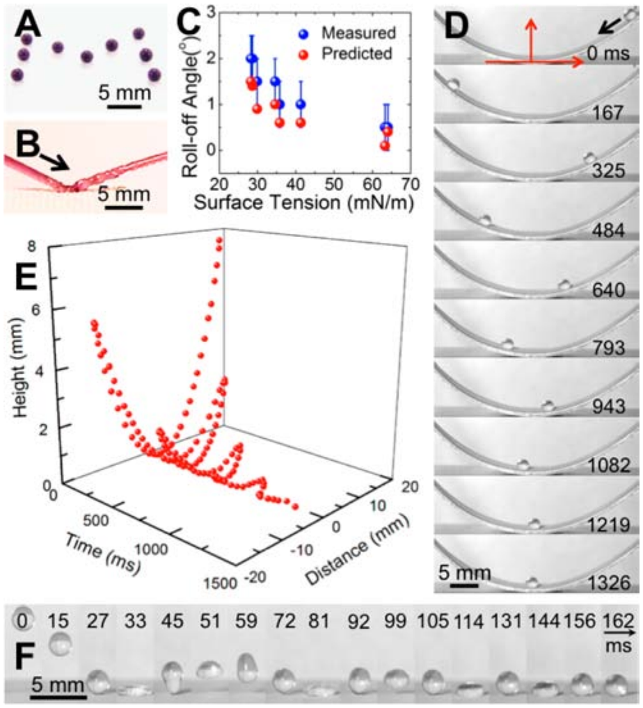

Figure 3. (A) Droplets of PMMA in DMF solution showing high apparent contact angles on the hierarchically structured surface. (B) A jet of PMMA in DMF solution bouncing on the surface. (C) Roll-off angles for various polymer solutions (see SI section 6) on the surface. (D) Series of images showing a droplet of PMMA in DMF solution rolling back and forth on the surface bent into a U-shape. (E) Trajectory of the droplet shown in (D) as a function of time. (F) Series of snapshots showing droplets ($R_o \approx 1$ mm) of PMMA in DMF solution bouncing on the surface tilted by 2° relative to the horizontal.

movie S4). By taking a ratio of the successive maximum heights in the trajectory of the droplet (Figure 3E), we estimate that an average of 46% of the energy is lost per half cycle. The energy lost is due to both viscous dissipation and contact angle hysteresis.[47] Because the contact angle hysteresis for a droplet of PMMA in DMF solution on our surfaces ($\Delta\theta^* = 4°$) is very low, we expect that the majority of the energy is lost due to viscous dissipation. The low contact angle hysteresis also allows droplets of PMMA in DMF solution ($R_o \approx 1$ mm) dropped under gravity from a height $h \approx 4.5$ mm to bounce at least three times before rolling off from our surface (Figure 3F and movie S2). Similarly, our surfaces also display superomniphobicity with a wide range of polymer solutions of different polymer molecular weights, concentrations, and solvents. In Table S2 (see SI section 6) we report the extremely low contact angle hysteresis and roll-off angles for 25 different non-Newtonian liquids on our electrospun cross-linked PDMS + 50 wt% fluorodecyl POSS blend surface. Due to such effective repellency, our surfaces provide effective chemical shielding against non-Newtonian liquids, in addition to Newtonian liquids.

In conclusion, we have developed a simple technique, based on electrospun coatings of cross-linked PDMS + 50 wt% fluorodecyl POSS, to fabricate hierarchically structured superomniphobic surfaces with re-entrant curvature at both coarser and finer length scales. The low surface energy and significantly reduced solid−liquid contact area allow our surfaces to exhibit high contact angles, low contact angle hysteresis, and low roll-off angles with virtually all liquids—organic or inorganic, polar or nonpolar, Newtonian or non-Newtonian. Consequently, our surfaces can serve as effective chemical shields against virtually all contacting liquids.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental methods, additional data and discussion, and movies. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Tuteja, A.; Choi, W.; Mabry, J. M.; McKinley, G. H.; Cohen, R. E. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 18200.

(2) Tuteja, A.; Choi, W.; Ma, M.; Mabry, J. M.; Mazzella, S. A.; Rutledge, G. C.; McKinley, G. H.; Cohen, R. E. *Science* **2007**, *318*, 1618.

(3) Tuteja, A.; Choi, W.; McKinley, G. H.; Cohen, R. E.; Rubner, M. F. *MRS Bull.* **2008**, *33*, 752.

(4) Chhatre, S. S.; Choi, W.; Tuteja, A.; Park, K. C.; Mabry, J. M.; McKinley, G. H.; Cohen, R. E. *Langmuir* **2010**, *26*, 4027.

(5) Batchelor, G. K. *An introduction in fluid dynamics*; Cambridge University Press: Cambridge, UK, 1970.

(6) Tsujii, K.; Yamamoto, T.; Onda, T.; Shibuichi, S. *Angew. Chem., Int. Ed.* **1997**, *36*, 1011.

(7) Li, H. J.; Wang, X. B.; Song, Y. L.; Liu, Y. Q.; Li, Q. S.; Jiang, L.; Zhu, D. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 1743.

(8) Cao, L.; Price, T. P.; Weiss, M.; Gao, D. *Langmuir* **2008**, *24*, 1640.

(9) Ahuja, A.; Taylor, J. A.; Lifton, V.; Sidorenko, A. A.; Salamon, T. R.; Lobaton, E. J.; Kolodner, P.; Krupenkin, T. N. *Langmuir* **2008**, *24*, 9.

(10) Hsieh, C. T.; Wu, F. L.; Chen, W. Y. *J. Phys. Chem. C* **2009**, *113*, 13683.

(11) Leng, B. X.; Shao, Z. Z.; de With, G.; Ming, W. H. *Langmuir* **2009**, *25*, 2456.

(12) Steele, A.; Bayer, I.; Loth, E. *Nano Lett.* **2009**, *9*, 501.

(13) Wang, D. A.; Wang, X. L.; Liu, X. J. E.; Zhou, F. *J. Phys. Chem. C* **2010**, *114*, 9938.

(14) Fujii, T.; Aoki, Y.; Habazaki, H. *Langmuir* **2011**, *27*, 11752.

(15) Darmanin, T.; Guittard, F.; Amigoni, S.; de Givenchy, E. T.; Noblin, X.; Kofman, R.; Celestini, F. *Soft Matter* **2011**, *7*, 1053.

(16) Zhang, J. P.; Seeger, S. *Angew. Chem., Int. Ed.* **2011**, *50*, 6652.

(17) Deng, X.; Mammen, L.; Butt, H.-J. R.; Vollmer, D. *Science* **2011**, *335*, 67.

(18) Genzer, J.; Efimenko, K. *Biofouling* **2006**, *22*, 339.

(19) Sun, T. L.; Feng, L.; Gao, X. F.; Jiang, L. *Acc. Chem. Res.* **2005**, *38*, 644.

(20) Lee, C.; Kim, C.-J. *Phys. Rev. Lett.* **2011**, 106.

(21) Ishizaki, T.; Saito, N. *Langmuir* **2010**, *26*, 9749.

(22) Cassie, A. B. D.; Baxter, S. *Trans. Faraday Soc.* **1944**, *40*, 0546.

(23) Bhushan, B.; Jung, Y. C. *Biomimetics Inspired Surfaces for Superhydrophobicity, Self-cleaning, Low Adhesion, and Drag Reduction*; Springer: Berlin, 2011.
(24) Ma, M.; Hill, R. M. *Curr. Opin. Colloid Interface Sci.* **2006**, *11*, 193.
(25) Quere, D. *Rep. Prog. Phys.* **2005**, *68*, 2495.
(26) Choi, W.; Tuteja, A.; Chhatre, S.; Mabry, J. M.; Cohen, R. E.; McKinley, G. H. *Adv. Mater.* **2009**, *21*, 2190.
(27) Marmur, A. *Langmuir* **2008**, *24*, 7573.
(28) Coulson, S. R.; Woodward, I.; Badyal, J. P. S.; Brewer, S. A.; Willis, C. *J. Phys. Chem. B* **2000**, *104*, 8836.
(29) Coulson, S. R.; Woodward, I. S.; Badyal, J. P. S.; Brewer, S. A.; Willis, C. *Chem. Mater.* **2000**, *12*, 2031.
(30) Herminghaus, S. *Europhys. Lett.* **2000**, *52*, 165.
(31) Marmur, A. *Langmuir* **2003**, *19*, 8343.
(32) Nosonovsky, M. *Langmuir* **2007**, *23*, 3157.
(33) Kota, A. K.; Li, Y.; Mabry, J. M.; Tuteja, A. *Adv. Mater.* **2012**, *24*, 5838.
(34) Furmidge, C. G. *J. Colloid Sci.* **1962**, *17*, 309.
(35) Choi, W.; Tuteja, A.; Mabry, J. M.; Cohen, R. E.; McKinley, G. H. *J. Colloid Interface Sci.* **2009**, *339*, 208.
(36) Belitsku, D. *J. Electrochem. Soc.* **1970**, *117*, 1097.
(37) Abdallah, M. *Corros. Sci.* **2004**, *46*, 1981.
(38) Shirtcliffe, N. J.; McHale, G.; Newton, M. I.; Perry, C. C.; Pyatt, F. B. *Appl. Phys. Lett.* **2006**, *89*, 104106.
(39) Kakehi, H.; Muira, M.; Isu, N.; Sawada, H. *Polym. J.* **2008**, *40*, 1081.
(40) Sherman, P. O.; Smith, S.; Johannes, B. *Text. Res. J.* **1969**, *39*, 449.
(41) Vaidya, A.; Chaudhury, M. K. *J. Colloid Interface Sci.* **2002**, *249*, 235.
(42) Kota, A. K.; Kwon, G.; Choi, W.; Mabry, J. M.; Tuteja, A. *Nat. Commun.* **2012**, *3*, 1025.
(43) Luu, L.-H.; Forterre, Y. *J. Fluid Mech.* **2009**, *632*, 301.
(44) Bartolo, D.; Boudaoud, A.; Narcy, G.; Bonn, D. *Phys. Rev. Lett.* **2007**, *99*, 174502.
(45) Bertola, V. *Int. J. Heat Mass Trans.* **2009**, *52*, 1786.
(46) Guemas, M.; Marin, A. G.; Lohse, D. *Soft Matter* **2012**, *8*, 10725.
(47) Richard, D.; Quere, D. *Europhys. Lett.* **2000**, *50*, 769.