Controlling liquid splash on superhydrophobic surfaces by a vesicle surfactant

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Deposition of liquid droplets on solid surfaces is of great importance to many fundamental scientific principles and technological applications, such as spraying, coating, and printing. For example, during the process of pesticide spraying, more than 50% of agrochemicals are lost because of the undesired bouncing and splashing behaviors on hydrophobic or superhydrophobic leaves. We show that this kind of splashing on superhydrophobic surfaces can be greatly inhibited by adding a small amount of a vesicular surfactant, Aerosol OT. Rather than reducing splashing by increasing the viscosity via polymer additives, the vesicular surfactant confines the motion of liquid with the help of wettability transition and thus inhibits the splash. Significantly, the vesicular surfactant exhibits a distinguished ability to alter the surface wettability during the first inertial spreading stage of ~2 ms because of its dense aggregates at the air/water interface. A comprehensive model proposed by this idea could help in understanding the complex interfacial interactions at the solid/liquid/air interface.

RESULTS

Figure 1 shows the impacts of droplets of pure water and aqueous solutions containing the same mass fraction of the micelle surfactant sodium dodecyl sulfate (SDS), trisiloxane molecules (TSs), and the vesicle surfactant sodium bis(2-ethylhexyl) sulfosuccinate [Aerosol OT (AOT)] on a Brassica oleracea L. leaf (Fig. 1A) at a velocity of 2.53 ± 0.11 m s⁻¹ using high-speed cameras (movie S1). In the experiment, the impact behavior was defined by measuring more than 30 different positions of the same sample and surfactant solutions. The B. oleracea L. leaf surface characterized by microstructured/nanostructured morphologies (Fig. 1, B and C) shows a water contact angle of 156.2 ± 4.3° (Fig. 1D), ensuring superhydrophobicity. The impacting water droplet, after reaching its maximum spreading at ~1.8 ms, breaks up into numerous droplets.
By adding a certain amount of surfactants, the receding splash can be inhibited by varying degrees (movie S1). Figure 1 (F and G) shows that aqueous droplets containing 1% SDS or 1% TSs partially reduced the receding splash but left several streams during retraction and finally broke up into several fragments. In contrast, by adding 1% AOT in the aqueous phase, the impacting drop first spread to a larger wetting area within 2 ms. Then, the liquid broke up and the receding laminar stream was substantially depressed (Fig. 1H) even after the maximum spreading stage (movie S1). Finally, a large wetting area was achieved and maintained. Partial and scarce receding behavior at low-speed impact was found in the micelle and vesicle regions (Fig. S1), respectively. Furthermore, on artificial superhydrophobic surfaces with varied structures and tilted angles, aqueous droplets containing 1% AOT would spread properly (movies S2 to S4). Notably, this kind of liquid deposition behavior is in contrast to previous works, where surfactant drops have been shown to bounce off the superhydrophobic surface (18), although surfactants can help the liquid wet the hydrophobic surface (movie S5) (25). AOT is therefore a unique surfactant that has a more pronounced effect than the others in controlling liquid deposition and in reducing unavoidable splash.

DISCUSSION

Compared with the mechanism of liquid deposition enhancement using polymer additives (1), surfactant additives cannot alter viscosity but can reduce the liquid’s surface tension. Although surfactants can decrease the surface tension of the liquid, helping it spread on a superhydrophobic surface under a low-speed impact (25), the reduction of surface tension also plays a major role in the increased instability and the enhanced droplet’s splash (20, 21). According to the Kelvin-Helmholtz instability, \( k_{\text{max}} = 2\pi \gamma / U_r^2 \), the key to reducing instability is via the retraction velocity \( U_r \), and the brevity of impact contact time should be enough for liquid droplets to wet the superhydrophobic surface (18). In our experiment, local pinning is observed for SDS (Fig. 1F) and TSs (Fig. 1G), and the entire pinning is found for AOT in the peripheral area of maximum spreading (Fig. 1H), where the retraction velocity \( U_r \) slows down to a low value, resulting in a small \( k_{\text{max}} \). For the AOT drop, the motion of spreading is greatly confined, leading to extremely low instability and thus retarding the splash (movie S1).

The exceptional molecular structure of AOT distinguishes it from the other two surfactants in reducing splash and in enhancing liquid deposition. Cryo-TEM (transmission electron microscope) imaging...
was used to prove our assumption, which was achieved by allowing a free-falling surfactant drop to impact the Cu mesh followed by immersion in liquid nitrogen. This mimics the surfactant packing stage during the impact process. The significant differences of the surfactant aggregates are shown in Fig. 2 (A1 to C1), where the multilamellar vesicles were closely packed at the air/water interface for the AOT drop with a mass fraction of 1%, whereas micelles only randomly and loosely existed for the other two surfactant solutions at the same mass fractions. Compared with the sample molecular structures of SDS, TSs, and the previously mentioned surfactants in reducing the liquid bouncing (18, 25), AOT has two alkyl chains and a relatively small hydrophilic head group. This particular molecular structure of AOT is the main reason for its compact and directed alignment and leads to the multilamellar vesicle structure (26). As shown in Fig. 2 (A2 to C2), among the three surfactants, the aqueous solution containing 1% AOT exhibits the lowest DST within a surface age of 80 ms. At the beginning of the bubble pressure measurement of ~10 ms, its DST could decrease to a low value of ~32 mN/m (Fig. 2C2), whereas both 1% SDS and 1% TSs have DSTs that begin in a high value of ~43 mN/m (Fig. 2, A2 and B2). Similar to the property reflected in the diffusion coefficients achieved through $^1$H nuclear magnetic resonance (NMR) spectrometry (fig. S2) and dynamic contact angles (fig. S3), the DST results indicate that AOT has the fastest diffusion speed to the air/water interface and thus has the strongest ability to reduce the surface tension when there are newly created surfaces.

Besides reducing splashing on natural superhydrophobic leaves, AOT is the most effective surfactant that inhibits the bouncing and splashing of the liquid drops on the artificial superhydrophobic surface at both low (~1.2 m s$^{-1}$) and high (~2.5 m s$^{-1}$) impact speeds. The artificial superhydrophobic surfaces include a microstructured/nanostructured superhydrophobic surface composed of 20-nm hydrophobic SiO$_2$ nanoparticle composites with a typical size and spacing of around 200 nm and a CuO nanosheet structured superhydrophobic surface with a typical size of about 3 to 6 μm in length and 200 to 600 nm in width. The water contact angles of these artificial superhydrophobic surfaces are 161.3 ± 0.5° and 159.1 ± 1.7°, respectively, which are much higher than those of the natural B. oleracea L. leaf. A fluorinated glass slide with a water contact angle of 112.8 ± 1.1° is

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**Fig. 2.** The molecular structure, dynamic surface tension, and impact behavior of SDS, TSs, and AOT. (A1 and B1) Cryo-TEM images of both 1% SDS and 1% TSs show the micelle aggregates at a mass fraction of 1%. (C1) Cryo-TEM image of 1% AOT shows that multilamellar vesicles have formed, indicating the dense aggregates of AOT molecules at the air/water interface. (A2) SDS has a long chain, and its dynamic surface tension (DST) slowly falls in the rapid fall region and cannot reach its equilibrium within a surface age of 100 ms. (A3) The droplets containing SDS are easy to rebound on the superhydrophobic surface even for highly concentrated solution. (B2) TSs have long induction periods in the first tens or hundreds of seconds. (B3) With the increase of the concentration, the induction period is shortened so that the impact behavior turns from bouncing, emission, to no rebound. On the inclined surface, it is still easy to partially rebound. (C2) AOT distinguishes itself from other surfactants in the fastest diffusion speed to form a densely packed molecular layer at the air/water interface. AOT directly approaches low surface tension of around 32 mN/m at the very beginning of the bubble pressure measurement, showing the lowest DST among the three surfactants within a surface age of 80 ms. The DSTs of 1% SDS and 1% TSs begin nearly at the same value of ~43 mN/m. TS quickly decreases to a lower value, and SDS slowly decreases to a higher value. (C3) AOT is the most effective surfactant that inhibits bouncing of the liquid drops on the superhydrophobic surface.
also used for comparison. As shown in movie S5, although the droplets containing SDS can properly deposit on a smooth hydrophobic surface, it is difficult to reduce the rebound on a superhydrophobic surface, no matter how low or how high the impact speed is, even for highly concentrated solutions. For TSs, with the increase in concentration, the induction period is shortened so that the low-speed impact behavior turns to emission from bouncing, whereas it is still easy to partially rebound after a high-speed impact. In contrast, for AOT, the liquid droplets can deposit on the hydrophobic surface at a low concentration of 0.1% and at any superhydrophobic surfaces with a concentration of 0.3% (movie S5).

A diagram is shown in Fig. 3 to explain how the receding splash can be substantially depressed by AOT. Driven by the inertia, the impacting liquid first spreads to a maximum diameter (27). As shown in the spreading state of the diagram, the liquid droplet experiences a large surface deformation during the high-speed impact, and the curved edge of the spreading drop is completely out of equilibrium when it reaches its maximum diameter. Then, surface tension acts on the liquid to retract the flow above the substrate. For water, the drop would break up into multiple droplets during the receding state and would splash in the final state (Fig. 1E). For the surfactant drops, if the surfactant molecules cannot replenish the newly created air/water interface in time, typically with high DST, then the surface tension of the deformed drop could not be uniform, where nonuniform receding behavior occurs (Fig. 3B). Examples can be found for the SDS drop (Fig. 1F), the TS drop (Fig. 1G), and the AOT drop in the micelle region (Fig. S4). In contrast, if the surfactant with a low beginning DST can effectively saturate the newly created surface within ~1.8 ms (corresponding to the spreading time) and maintain the homogeneous low surface tension at the air/liquid/solid interface, then the liquid can uniformly deposit on the superhydrophobic surface (Fig. 3C). As shown in Fig. 1H and fig. S4, a gentle and uniform receding contact line will be obtained similar to AOT in the vesicle region. These results provide direct evidence for the role of AOT in controlling the receding splash.

The underlying mechanism for the abovementioned transient knockdown of the receding velocity at the pinning area can be ascribed to the wettability transition in the spreading phase. At the peripheral area of maximum spreading, the impacting water drop slides over air cushions that are trapped on or beneath the superhydrophobic surface, and it is difficult for the water to enter the nanostructures (Fig. 3A). The upward increased capillary force induced by the squeezed air entrapment in the nanostructures easily makes the water drop take off the surface (28). Similar behavior is observed for the micelle surfactant drops (Fig. 3B). The final “floating” state of the micelle surfactant drop, the 0.1% AOT drop, indicates that micelle surfactant drops could not properly reverse surface wettability, which can be seen from the cryo-SEM image in fig. S5. In contrast, the reduction of surface tension induced by the vesicle surfactant leads to the dropdown, reverses the capillary force, and makes an easier and deeper entry of the impacting drop in the nanostructure (the side view in spreading state in Fig. 3C). Cryo-SEM was used to prove the reverse of surface wettability during the impact, where the vesicle surfactant drop (1% AOT drop) is trapped between the gaps of nanoneedles and fully wets the nanostructured superhydrophobic surface (fig. S5). The outward hydrophobic tails of the surfactants at the air/liquid interface act as bridges to connect the drop and the nanostructure by hydrophobic force and to change the wettability of the superhydrophobic surface. Through this process, the surfactant droplets can be pinned and thus reduce the receding velocity via the wettability transition at the peripheral area of maximum spreading. As a result, the high-speed impacting AOT drops can firmly and quickly deposit on the superhydrophobic surface.

The wettability transition at the central contact point is easier than at the peripheral area because capillary forces are overcome by inertial effects (29) at a high Weber number regime (We > 200). Both the water drop and the surfactant drop tend to become convex in the nanostructure of the superhydrophobic surface because of the downward hammer pressure and the dynamic pressure (8). However, the water repellency of structure chemistry and the huge upward Laplace pressure induced by the squeezed air entrapment in the nanostructure rebound the water drop, as shown in Fig. 1E.

AOT also manifests itself in inhibiting rebound and splash on tilted superhydrophobic surfaces. Superhydrophobic surfaces with tilted angles of 30°, 60°, and 75° are used. In the experiment, the SDS shows little effect on the liquid deposition within the tested concentration region (Fig. 2A), although it is a good choice to inhibit rebound on the hydrophobic surface, as shown in movie S5 (15, 16, 23). The TS

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**Fig. 3. Schematic illustration for splash inhibition on the superhydrophobic surface by surfactant additives.** (A) The impacting water drop mainly breaks up in the receding stage after spreading to the maximum lamellar liquid. The upward increased capillary force induced by the squeezed air entrapment in the nanostructure easily makes the water drop take off the surface. (B) For the surfactants in the micelle region, the surfactant molecules cannot replenish the newly created air/water interface (high DST), and the surface tension of the deformed drop is not uniform, explaining the nonuniform receding behavior. The nonuniform surface tension leads to partial wettability transition, and several scattered fragments stick on the substrate as SDS, TSs, and AOT in the micelle region. The reduced surface tension makes the entry of the impacting drop in the nanostructure much easier because of the reverse of capillary force. (C) Because of the lowest DST and dense aggregates at the air/water interface, AOT in the vesicle region effectively saturates the newly created surface within a short time and maintains a homogeneous low surface tension at the air/liquid/solid interface so that it can change the surface wettability as long as the drop contacts the surface, thus leading to hardly receding behavior and a large wetting area.
drop shows the impact behavior from bouncing, emission, to no rebound as the concentration increases from 0.01 to 1%, but it still rebounds partially on the oblique superhydrophobic surface (Fig. 2B3). The percentage of liquid that bounces off the surface can be quantitatively measured through an analytical microbalance, and the impact processes of surfactant drops on the horizontal and tilted superhydrophobic surfaces are shown in movie S3. Only AOT can suppress the rebound of aqueous droplets on both horizontal and oblique surfaces at a low mass fraction of 0.3% at any inclined angles (Fig. 2C3).

Figure S1 depicts the impact behaviors of aqueous drops containing the AOT additive in three regions. At concentrations lower than the critical micelle concentration, complete bouncing occurs along with complete receding behavior. At the micelle region, partial receding of the contact line is accompanied with partial splashing, partial rebound, and no rebound. Scarce receding of the contact line takes place only at the vesicle region, indicating that both the rebound and receding splashes have been greatly inhibited.

CONCLUSION

In conclusion, although we have mainly focused on a specific microstructured/nanostructured superhydrophobic surface with varying tilted angles to elucidate the role of the vesicle surfactant (AOT) in inhibiting the receding splash, the scarce or gentle receding behavior can also be generalized to apply to other artificially fabricated superhydrophobic surfaces and other single-drop impact and spray processes at varied impact velocities (Fig. 4 and movies S6 to S9). In addition, AOT is shown to be a stable surfactant molecule (fig. S6). This work helps advance our understanding of how to control liquid deposition on superhydrophobic surfaces. Therefore, this approach
can potentially be used to improve the efficiency of pesticide spraying and to reduce environmental pollution.

**MATERIALS AND METHODS**

**Superhydrophobic silicon nanowire structures**
A silicon wafer was cleaned with acetone, ethanol, and deionized water before it was immersed in 5 weight % hydrofluoric acid solution for 1 min to remove the oxidation layer. Then, it was put in a mixed solution of 4.8 M hydrofluoric acid and 0.5 mM silver nitrate for 1 min to deposit silver seed on the substrate. It was successively immersed in a solution of 4.8 M hydrofluoric acid and 0.15 M hydrogen peroxide for 30 min to realize metal-assisted etching of silicon, which resulted in the acquisition of silicon nanowire structures. The typical length of the nanowire was ~1.2 μm, and the space between nanowires was about 50 nm. The as-prepared silicon plate was O2 plasma-treated at 150 W for 30 s and then put in a sealed container together with a piece of glass coated with 0.5 ml of (heptadecafluoro-1,1,2,2-tetrade- cyl)trimethoxysilane. The container was evacuated with a vacuum pump. After 3 hours at 80°C, the plate showed surface superhydrophobicity with a contact angle of 154.5 ± 3.2°.

**Microstructured/nanostructured SiO2 surface**
The commercial glass plates were cleaned with acetone, ethanol, and deionized water. In accordance with our previous research (30), the polymer-particle dispensed solution was prepared by adding 1 ml of Capstone ST-200 (DuPont Co.) solution and 1 g of hydrophobic fumed silica nanoparticles (average particle size of 14 nm; Evonik Degussa Co.) in 5 ml of acetone and 20 ml of ethanol. The solution was mixed and stirred for 30 min in a closed bottle. Pre cleaned glass plates were dipped in this solution at a speed of 80 mm s⁻¹ and pulled out from the solution at a speed of 100 mm s⁻¹. Owing to the rapid evaporation of the solvent, the semitransparent membrane quickly transformed into a white coating with extremely high water repellency. From an SEM observation, the aggregate of SiO2 nanoparticles had random features of typical size and spacing of around 200 nm.

**Superhydrophobic CuO nanosheets**
The copper plate was first cleaned with acetone, ethanol, and purified water before modification. It was then immersed in a solution of 0.15 M ammonium persulfate and 2.5 M sodium hydroxide for 20 min and subsequently immersed in a 0.1 M perfluoroecanoic acid solution for 1 hour. The prepared CuO nanosheets were about 3 to 6 μm in length and 200 to 600 nm in width. After the copper plate was rinsed with distilled water and dried with N₂, it showed a high water repellency with a contact angle of 159.1 ± 1.7°.

**Patterned pillar-structured silicon substrate**
Silicon wafers (n-type doped with phosphorus, <100>-oriented, 525 μm thick) were patterned using standard photolithography techniques. A thin layer of positive resist was spray-coated onto the silicon wafer at a rotational speed of 3000 rpm, which was followed by an ultraviolet (UV) exposure process (Karl Suss MA6). Then, the UV-exposed Si wafer was immersed in the resist developer to remove the unexposed photoresist. Subsequently, deep reactive ion etching was performed. Micropillar has a diameter of 10 μm, a space of 10 μm, and a height of 20 μm. After the substrates were resist-removed (Microposit Remover 1165), they were cleaned with ethanol and acetone before the chemical modification process was performed. The as-prepared silicon plate was O2 plasma-treated and then put in a sealed container together with a piece of glass coated with 0.5 ml of (heptadecafluoro-1,1,2,2-tetrade-cyl)trimethoxysilane for 2 hours at 80°C.

**Characterization**
Analysis of the droplet deposition on the B. oleracea L. leaf surface and superhydrophobic substrates was recorded with i-SPEED 3 (Olympus) high-speed cameras from the oblique view and a FASTCAM Mini UX100 (Photron) from the side view, respectively. SEM images were obtained using a field-emission SEM at 10 kV (Hitachi S-4800). The images of cryogenic electron microscopy were carried out using a field-emission SEM (Hitachi S-4300) equipped with extra low–temperature equipment at 3 kV (cryo-electron microscope, Leica). Cryo-TEM images were obtained with FEI Tecnai Spirit BioTwin TEMs. Cryo-transfer holders were used to ensure low-temperature transfer and observation of frozen hydrated specimens. Contact angles were measured using a contact angle measurement device (OCA 20, DataPhysics), with droplets of 3 μl to be removed dynamically. Each reported contact angle was an average of at least five independent measurements. The diffusion rates were determined with a Bruker AVANCE 600 NMR spectrometer. The DSTs were carried out with an automatic maximum bubble pressure tensiometer (Krüss BP100), which measures the behavior of a surfactant over a wide speed range as part of a single, fully automatic measuring process and determines surface tension as a function of surface age. The measured range in the time window is from 10 ms to 10 s. The capillary diameter is 0.210 mm.

**SUPPLEMENTARY MATERIALS**
Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/3/e1602188/DC1

**REFERENCES AND NOTES**

Acknowledgments: The high-speed imaging, artificial superhydrophobic surface fabrication, and most of the work were performed in the Key Laboratory of Bio-inspired Materials and Interfacial Science, Technical Institute of Physics and Chemistry. The DSTs of surfactant drop, 3H NMR, and SEM (cryo-SEM) measurements were acquired in the Key Laboratory of Colloid and Interface Science, Institute of Chemistry. The B. oleracea L. leaf was provided by Henan Agricultural University. Cryo-TEM was performed in Tsinghua University. Funding: This work was financially funded by the National Research Fund for Fundamental Key Projects (grant 2014CB93220), the National Natural Science Foundation of China (NSFC) (grants 21121001 and 91127025), and the Key Research Program of the Chinese Academy of Sciences (grant KJZD-EW-M01). This work was also supported by NSFC (grants 51473172, 51473173, 5173190, and 21121001) and the “Strategic Priority Research Program” of the Chinese Academy of Sciences (grant XDA09020000). M.S. was funded by the National Key Projects (grant KJZD-EW-M01). This work was also supported by NSFC (grants 51473172, 51473173, 5173190, and 21121001) and the “Strategic Priority Research Program” of the Chinese Academy of Sciences (grant XDA09020000). M.S. was funded by the Fundamental Key Projects, 2014CB93220, in 2014. Author contributions: L.J. and Y.W. conceived and designed the experiments. M.S. and Z.D. performed the experiments. Z.D. fabricated artificial superhydrophobic surfaces. M.S., Y.W., and Z.D. analyzed the data. M.S. and Z.D. wrote the original manuscript, and L.J., Z.D., and Y.W. revised it. All authors discussed the results and commented on the manuscript. Competing interests: The authors declare that they have no competing interests. Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 9 September 2016
Accepted 15 December 2016
Published 1 March 2017
10.1126/sciadv.1602188

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Sci Adv 3 (3), e1602188.
DOI: 10.1126/sciadv.1602188

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