

Supplementary Information for

Deforming water droplet with a superhydrophobic silica coating

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The introductions of the movies

Movie 1: Behaviors of powder on the surfaces of normal and deformed droplets

This movie compares the behaviors of hydrophobic fumed silica powders when they are sprayed onto the surfaces of normal and deformed water drops, separately. As demonstrated, the powder particles move freely over the surface of the normal water drop, and can be driven to move again (after stopping) with the disturbance of air flow. In contrast, whether blowing or shocking the pedestal, the powder particles don't change their positions on the deformed water drop, and can be blown away from the droplet surface. The movability of powder reflects the free movement of water molecules, and vice versa. So it can be said that the deformed droplet loses its surface liquidity.

Movie 2: Deforming a normal droplet

This movie demonstrates the process of deforming a normal water drop on a superhydrophobic surface. As is seen, repeated squeezing and rubbing gave rise to a stable deformation.

Movie 3: Transforming a deformed droplet

This movie demonstrates how a deformed water drop is further transformed. As is seen, the protrusion of the deformed droplet is elongated by the droplet being pressed by a tool of tube.

Movie 4: Continuous transformation of a deformed droplet

This movie demonstrates the process of transforming a deformed water drop continuously.

Materials and methods

The preparation of the superhydrophobic silica coating

The superhydrophobic silica coating is derived from a hexamethyldisilazane (HMDS) treated silica sol, which was synthesized by the hydrolysis and condensation of TEOS in ethanol (EtOH) solvent. The mole ratio was TEOS: EtOH: NH₃:H₂O=1:38:0.54:1.53 (All the water was from the 28% ammonia solution, and the volume ratio was TEOS: EtOH: Ammonia=5: 50: 0.9). First, half of EtOH was mixed with TEOS and the other half was with ammonia and water and the two solutions were stirred for 10 minutes. Afterwards, the solution with NH₃ was added, dropwise, into the TEOS solution with stirring. Lastly, the mixed solution was aged at room temperature for 5-7 days to become a silica sol, then a certain quantity of HMDS (0.6 TEOS) was added into the sol with stirring for 1 day; after that, the sol needed to settle for at least 1 day and was ready for use. Glass slide (7.5×2.5×1.2 mm) and tube (diameter about 1 mm) were coated with this silica sol by a dip-coating method. In brief, the glasses were immersed in the sol for a short time (about 5 seconds), and then were lifted at a uniform speed of ~1.4 mm/s. It was not necessary to heat the coating, and just two minutes drying in air was enough to obtain the superhydrophobic surface. The resulting surface consisted of -CH₃ groups that were from HMDS, unhydrolyzed -OC₂H₅ groups that were from TEOS, and unmodified -OH

groups on the silica particles.

The preparation of another workable surface using hydrophobic fumed silica

In addition to the sol-gel silica coating, another superhydrophobic surface, with very weak binding force, was found also capable to carry out the droplet manipulation in this work. This superhydrophobic surface was derived from a commercial hydrophobic fumed silica powder (made up of ~15 nm particles) that was dispersed in ethanol forming 3% silica suspension. Dip-coating method was also feasible to form the surface with this suspension, using glass as the substrate. The aggregation of the particles made the coating present as white, and endowed the surface with relatively high roughness, which reduced the water adhesion and so the manipulation was not as easy as when using the sol-gel coating.

Characterization

The SEM image was measured by a Zeiss Ultra Plus scanning electron microscope. The EDS data were from a Zeiss Ultra Plus energy-dispersive X-ray spectroscope. The transmittance spectra were measured by a Jasco V-570 UV/Vis/NIR spectroscope. The droplet images were photographed by an ordinary digital camera and an optical contact-angle meter system (home-made).

Discussions and Figures

Test of silica particles left by the deformed water drop

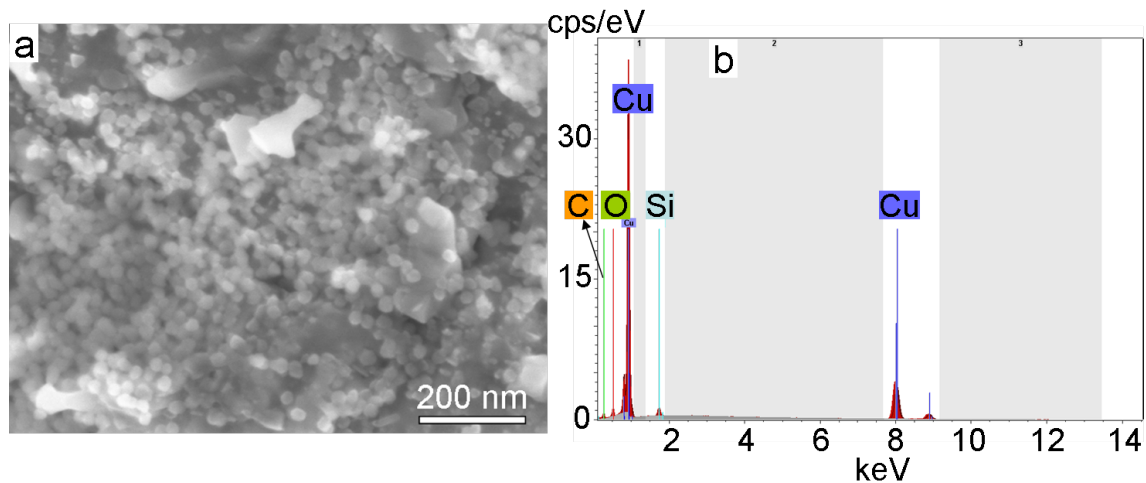


Figure S1. (a) SEM image of residues of a dried deformed water drop settled on a copper sheet surface. (b) EDS spectrum of the particles area displayed in (a).

A deformed water drop was settled on a clean copper sheet surface and was then dried at 150°C. Afterwards, the copper carrying residues left by the droplet was characterized with scanning electron microscopy (SEM, Zeiss Ultra Plus) and energy-dispersive X-ray spectroscopy (EDS, Zeiss Ultra Plus). The SEM image shows that the residues consist of particles of ~25 nm (**Fig. 1a**) which are in accordance with those in the sol-gel silica coating. The EDS result (**Fig. 1b**) displaying the existence of high ratios of Si, O, and C further confirms these particles being modified silica. (The copper sheet itself and the one that carried a pure water drop after drying were also tested for comparison. The elements of Si, O, and C were also found but their ratios were very small, which were attributed to the minuscule contaminants and the reactions of Cu with environmental substances such as O₂, H₂O and CO₂. The atom ratios of elements detected in the EDS experiment were compared in **Table. S1**; as shown, the ratio of Si in the deformed droplet sample is as 10 times more than in the other two samples.)

Table S1. The atom ratios of O, C, Si, and Cu on the surfaces of three different samples tested by EDS.

Element	The copper substrate	The pure water-covered copper substrate	The deformed water-covered copper substrate
O (orm. at%)	1.436618	1.458348	7.243915
C (orm. at%)	15.60853	12.5217	18.85462
Si (orm. at%)	0.312947	0.310729	3.156878
Cu (orm. at%)	82.6419	85.70923	70.74459

Estimation of the amount of the transferred silica particles

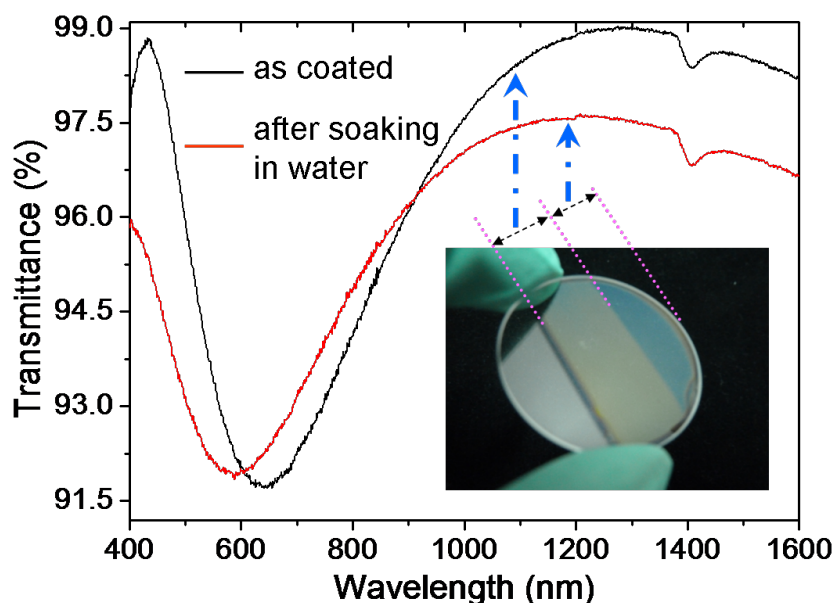


Figure S2. Transmittance spectra of two coating areas with different coating thicknesses. The different colors of the two areas (soaked and as-coated) in the inset are related to the shooting angle.

The superhydrophobic sol-gel coating used in this work has particles on top interacting very weakly with the interior and thereby can be removed by contacting with water. To make certain the depth of the removable particles, part of the coated glass was soaked in water and was then lifted, resulting in different transmittance of this soaked area compared with the unsoaked one (**Fig. S2**). The difference in transmittance was attributed to the reduction of coating thickness and the increase of refractive index which

could be obtained by modeling the transmittance spectrum using FilmWizard32 software. The results showed that the original refractive index and thickness of the coating were about 1.32 and 250 nm respectively, and that those of the soaked area were about 1.38 and 220 nm respectively. The increase of refractive index might result from water invasion to the pores of the coating, and the ~30 nm reduction of coating thickness was assigned to the depth of the removable silica particles.

Given that the contact area between droplet and the superhydrophobic surface was about 10 mm^2 for a typical droplet of 10^{-2} g (10~100 μl), and that the density of the coating was about 1.5 g/cm^3 , the mass of the removable particles could be calculated as $30 \text{ nm} \times 10 \text{ mm}^2 \times 1.5 \text{ g/cm}^3 = 4.5 \times 10^{-7} \text{ g}$. In other words, particles transferred to the droplet during manipulation were $\sim 10^{-7} \text{ g}$.