

Supplementary Information for:

## **A facile two-step dipping process based on two silica systems for superhydrophobic surface**

Xiaoguang Li, Jun Shen

### **The preparation of the silica microspheres**

Silica microspheres with the size of about 550 nm were synthesized by the hydrolysis and condensation of Tetraethylorthosilicate (TEOS) in isopropanol (IPA) solvent at the present of ammonium hydroxide. All the reagents were purchased from Sinopharm Chemical Reagent Co. Ltd without further purification. The reactions were carried out at the mole ratio of TEOS: IPA: NH<sub>3</sub>:H<sub>2</sub>O=1:17:0.81:6.25. First, a certain amount of deionized H<sub>2</sub>O, NH<sub>3</sub> and isopropanol were blended for 10 min, and then a known volume of TEOS was added into the above solution at room temperature under magnetic stirring. After that, the clear solution gradually turned opaque due to the formation of a white silica suspension, and it was continuously stirred for 4 h. The silica microspheres were centrifugally separated from the suspension and washed with ethanol for 3 times, and then they were dried in an oven at 150 °C for 2 hours. Eventually, these microspheres were dissolved in ethanol at certain ratio (from 0.3 wt % to 1.3 wt %). The distribution density of the microspheres on the substrate is mainly decided by the concentration of the suspension, and when the concentration is certain, increasing or decreasing the immersing time hardly affects the density.

### **The impact of the dispersity of the microspheres**

The dispersity of the microspheres is very important to the hydrophobicity. If the microspheres gather seriously as shown in Fig. S1, the network of sol-gel silica film can't wrap them nicely so that the hydroxyl groups on the microspheres are widely exposed, and in this case, the hydrophobicity of the surface is very poor. In our system, usually the larger the size is, the easier for the microspheres to gather. We eventually chose the size of about 550 nm when the dispersity is quite good and so the hydrophobicity is good. While it doesn't mean other sizes don't work if the dispersity can be good.

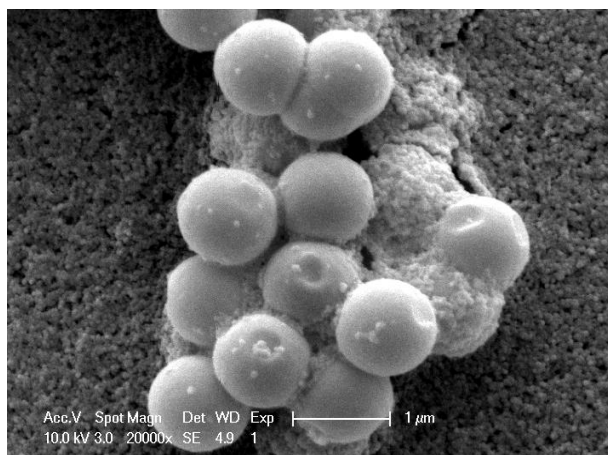


Figure S1. SEM image of the surface after the two-step dipping process when the microspheres are seriously gathered.

### The preparation of the silica sol

Silica sol with the particle size of about 10 nm was synthesized by the hydrolysis and condensation of TEOS in ethanol (EtOH) solvent. All the reagents were purchased from Sinopharm Chemical Reagent Co. Ltd without further purification. The mole ratio was TEOS: EtOH:  $\text{NH}_3$ : $\text{H}_2\text{O}$ =1:38:0.54:2. First, half of EtOH was mixed with TEOS and the other half was with ammonia and water and the two solutions were stirred for 15 min. afterwards, the solution with  $\text{NH}_3$  was dropwise added into the TEOS solution with stirring. At last, the solution was allowed to stand at room temperature for a minimum of three days to become a silica sol, then a certain quantity of HMDS (0.6 TEOS) was added into the sol with stirring for 1 days, after that, the sol needed to settle for at least 1 day and was ready for use. Fig. S2 shows the size distribution of particles in this silica sol.

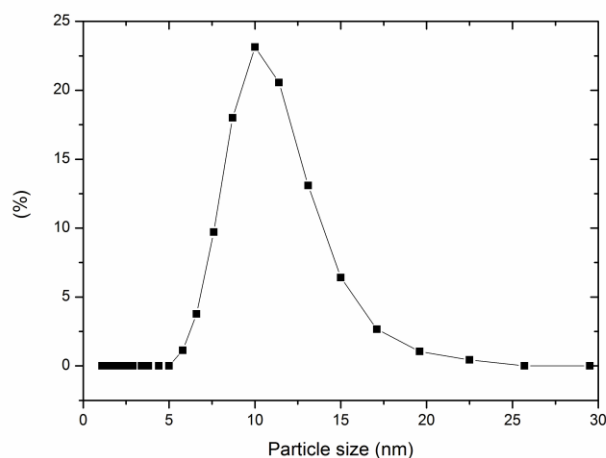
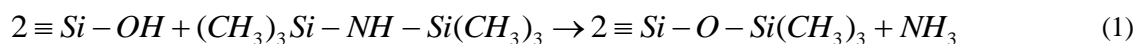


Figure S2. The size distribution of particles in the silica sol measured by dynamic light scattering device.

### The components and structure of the sol-gel silica coating

Silica film derived from the HMDS-treated silica sol without any post treatment can be superhydrophobic because the low surface energy has already been realized in the sol. The chemical reaction is described below and the Fourier Transform Infrared Spectroscopy (FTIR) spectra of resulting coatings are shown in Fig. S3.



As shown, the coating (black trace) from the traditional silica sol without HMDS modification is abundant of hydroxyl groups. As a comparison, the coating (red trace) from the HMDS-treated silica sol is abundant of methyl groups and at the same time, the residual hydroxyl groups are very rare. It should be noted that only the sol-gel silica coating is abundant of hydrophobic methyl groups so the sequence of the dipping in this work can't be exchanged.

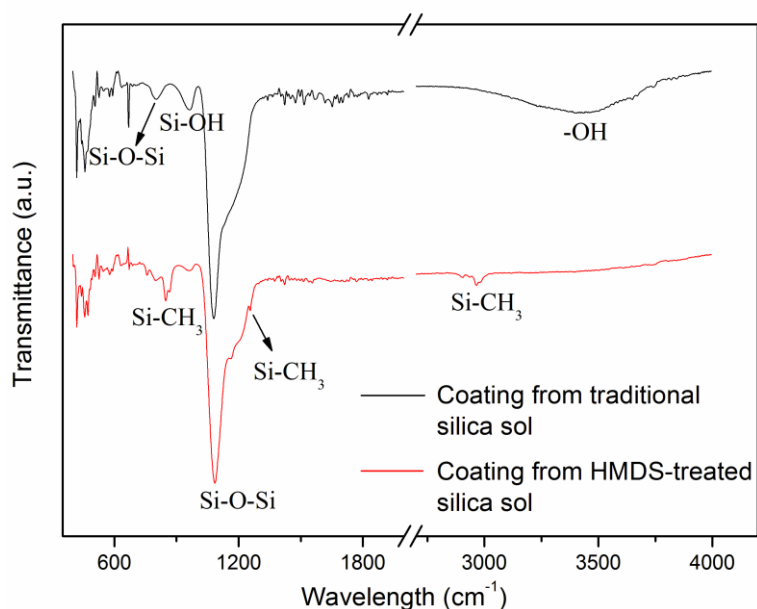


Figure S3. FTIR spectra of the silica coatings from two kinds of silica sols.

The sol-gel silica coating features a porous structure, for which it has a very low refractive index that is decisive for antireflection. Fig. S4 shows a TEM image of this kind of coating scratched off the substrate, revealing a clear porous structure. In this work, this porous structure is not only responsible for the antireflection but also responsible for the high adhesive force by providing a large-area contact with the droplet.

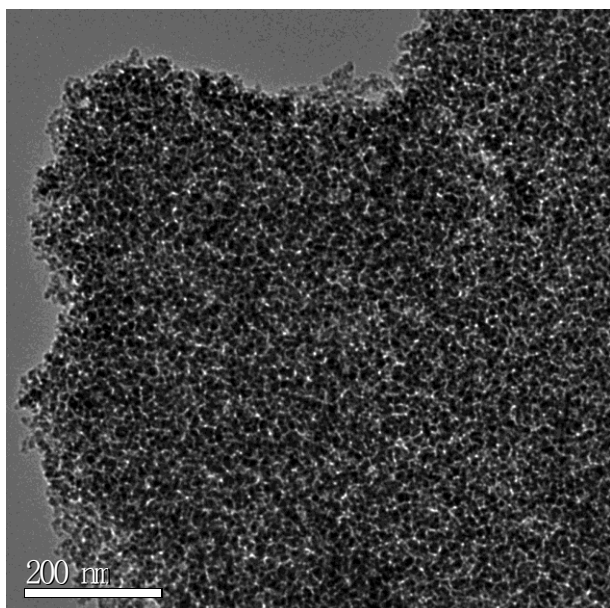


Figure S4. TEM image of the silica coating scratched from the substrate.

### Transparencies of the two kinds of superhydrophobic areas

When the concentration of microspheres in the suspension is between 0.3 wt % to 1.3 wt % or a bit more, the sphere-wrapped surface can always present excellent superhydrophobicity but present decreasing transparencies as the concentration increases. This is because the size of the microspheres is so large as to cause strong diffuse reflection. As shown in Fig. S5, the average transmittances of the sphere-wrapped areas are between 30-85% in visible light zone. As a comparison, the micro-fluctuant area e.g. the sol-gel silica coating is highly transparent with the peak transmittance of 99.8%.

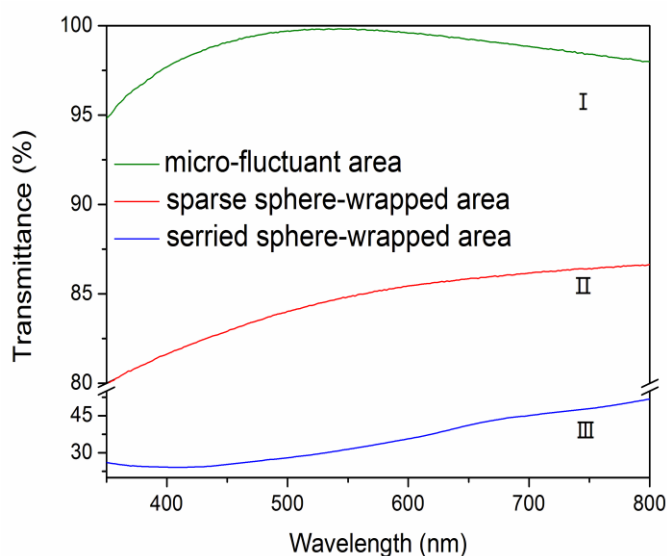


Figure S5. Transmission spectra of the micro-fluctuant area and the sphere-wrapped areas with different

microsphere concentrations.

### **Characterization**

The surface structures were observed using a field-emission scanning electron microscope (SEM, Philips-XL30FED) and an atomic force microscope (AFM, Veeco Dimension 3100) in the non-contact mode. The structures of the silica microspheres and sol were observed using a transmission electron microscope (TEM, CM 200 FEG). The water-repellent and adhesive properties of the sample surfaces were characterized using an optical contact-angle meter system (home-made). The FTIR spectra were obtained from a BRUKER TENSOR-27 spectrometer. The transmission spectra were obtained from a Jasco V-570 UV/Vis/NIR spectroscopy. The refractive index of films were acquired by spectroscopic ellipsometer (Ellip-A). The size of the particles in the silica sol is measured by TEM and dynamic light scattering device (HORIBA LB 550).