

Supplementary Information

PS/OTS superhydrophobic coatings with hierarchical morphology

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Materials & Methods. Polystyrene (PS; 230,000 g/mol) was purchased from Sigma-Aldrich, octadecyltrichlorosilane (OTS) and tetrahydrofuran (THF, 99%) were obtained from Merck. The glass substrates (Menzel-Glaser, Braunschweig, Germany) were first rinsed with distilled water, soaked in Piranha solution for 15 min, rinsed with deionized water and dried under nitrogen. The coating solution was prepared in a glass vial by dissolving 120 mg of PS in 4 ml THF and adding desired volume of OTS drop wise. The resulting solution was sonicated for 30 min for homogeneity. The solution was then transferred to a beaker and the clean glass substrates were immersed into it for dip-coating. Each dipping cycle consisted of 5 min immersion time followed by air drying. Coatings were prepared with OTS volume in solution varying between 0-0.5 ml and number of dipping cycles between 1-6.

The water contact angles were measured using the sessile drop method with a water drop volume of 8 μ l on a contact angle system (DataPhysics Instruments, Germany) at ambient temperature. More than five different positions were measured on a given sample and the average values were plotted. Three different liquids having different polarity were used as probes for surface free energy calculations: water, diiodomethane (Sigma-Aldrich) and isopropanol (Sigma-Aldrich). Surface energies of the coatings were calculated using the Owens, Wendt, Rabel and Kaelble (OWRK) method using the instrument software.

The surface morphology of the coatings was characterized by scanning electron microscopy (Zeiss EVO LS-15 SEM). The thickness of the coatings was measured from SEM images captured at 45° tilt angle.

The infrared spectra were obtained using Fourier transform infrared spectrometer (Nicolet Impact 400D).

Surface energies of the coatings.

The Owens, Wendt, Rabel and Kaelble (OWRK) method was used to estimate the surface energy of the coatings by measuring the static contact angle of three different polarity liquids on a given sample. Surface energy values were tabulated in Table S1.

PS: THF: OTS (120mg:4ml:Xml)	Surface Energy (S. E.) Measurements (mN/m) of the coatings			
	1 dipping cycle	2 dipping cycles	4 dipping cycles	6 dipping cycles
X = 0	31.5	31.05	29.76	29.12
X = 0.1	17.45	12.37	12.13	12.13
X = 0.2	12.09	8.46	5.07	4.85
X = 0.3	11.76	5.41	4.04	4.75
X = 0.4	11.80	11.84	11.40	10.36
X = 0.5	15.36	11.98	11.76	10.03

Table S1. The surface energies of PS/OTS coatings at various OTS concentrations and after various dipping cycles.

SEM characterization.

In SEM images of Fig. 2, the bright regions correspond to the solid materials, namely PS and OTS, and dark regions to the pores. The amount of bright and dark regions changed with OTS concentration. When the OTS concentration was increased further above the peak WCA, the curved sheets were seen to orient more in the plane of the top surface (Fig. 2e-2f) which increased the amount of bright regions. The changes in SEM images of Fig. 2 were analyzed and plotted in Fig. S1. The images were first converted to black&white images, and then the black&white pixels were counted. As shown in Fig. S1, the dark regions (the pores) decreased when OTS concentration was increased further above the peak WCA.

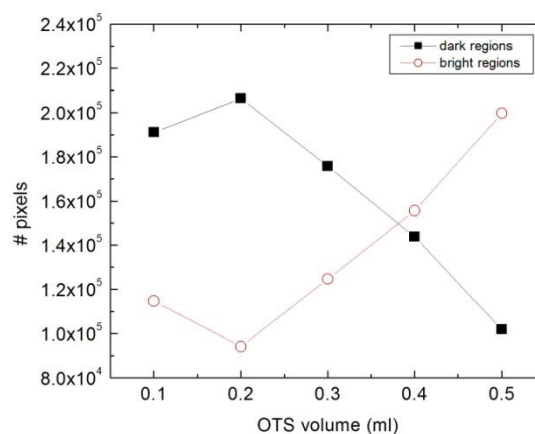


Fig. S1 The change of the amount of bright and dark regions with OTS concentration in the SEM images of Fig. 2. The horizontal axis shows the OTS volume for 4 ml THF, 120 mg PS.

SEM images were also taken at 45° tilt to determine extent of surface morphology from top surface to the substrate and to determine coating thickness.

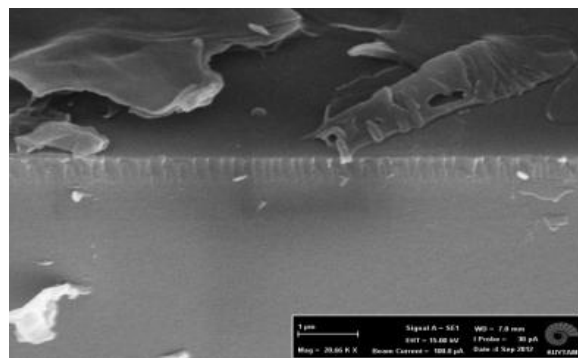


Fig. S2. SEM image at 45° tilt of the coating prepared from solution containing 0.3 ml OTS/4.0 ml THF/120 mg PS after the first dipping cycle.

Effect of immersion time on WCA and surface morphology.

To obtain hierarchical surface morphology and superhydrophobic behaviour, going through discrete dipping cycles (5 min immersion time and air drying) was required. When the glass substrates were dipped in PS/OTS solutions and kept

continuously in solution for 24 hours, a similar dependence of WCA on OTS concentration was observed as shown in Fig. S3. But, the peak WCA was only $\sim 120^\circ$.

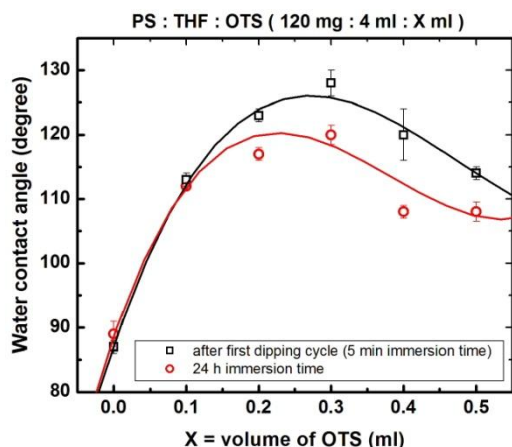


Fig. S3. The dependence of water contact angle on OTS concentration after one dipping cycle of 5 min immersion time (squares) and after 24 h immersion time (circles). The solid lines were drawn to guide the eye.

Fig. S4 shows the surface morphologies of the coatings prepared by dipping in solutions containing 4.0 ml THF/120 mg PS and various volumes of OTS for 24 h. The surface did not show any hierarchical morphology. The surfaces were rather smooth with holes. These surface morphologies clearly explain the rather low WCAs (Fig. S3) obtained on these coatings.

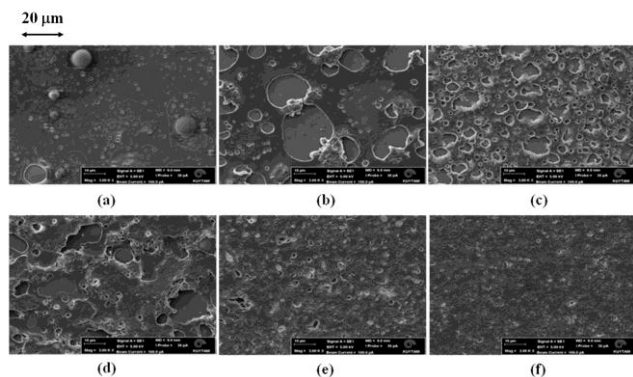


Fig. S4. SEM images of the coatings after immersing in solutions containing 120 mg PS, 4.0 ml THF and varying volumes of OTS: (a) 0 ml, (b) 0.1 ml, (c) 0.2 ml, (d) 0.3 ml, (e) 0.4 ml, (f) 0.5 ml.

FTIR characterization of coatings.

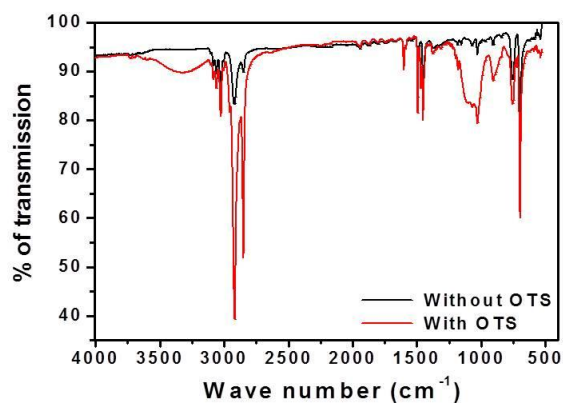


Fig. S5. FTIR spectra of the coatings with and without OTS.

Characterization of the durability and uniformity of coatings

The glass substrates having superhydrophobic PS/OTS coatings on both sides floated on water surfaces. The mass of the glass substrates varied between 0.5-3.0 g. The samples were observed for a period of 1 week. None of the substrates were observed to sink in water within this period.

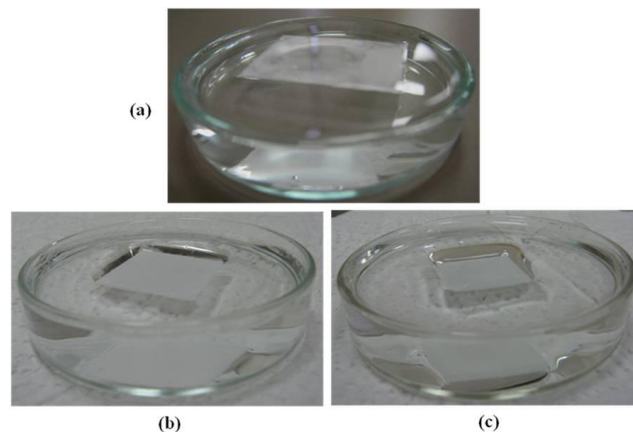


Fig. S6. Photographs of coated glass substrates of mass (a) ~ 0.5 g, (b) ~ 2.0 g, and (c) ~ 3.0 g floating on water.

These observations show that the superhydrophobic property of the coatings is maintained at least for 1 week when in touch with water. When soaked in water, the coatings were not superhydrophobic right after they were taken out of water, but they recovered their hydrophobicity after drying. Stable floatation on water also indicates that the coatings have good uniformity in larger areas. Fig. S7 shows a set of water droplets on superhydrophobic PS/OTS coating confirming this uniformity.

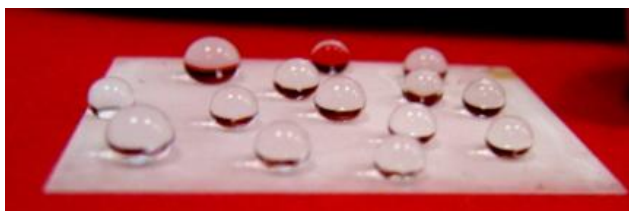


Fig. S7. Photograph of the water droplets having different sizes on the superhydrophobic PS/OTS coating.