Supporting Information

One-step sol-gel electrochemistry for fabrication of superhydrophobic surface

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Experimental details

Films preparation: Indium tin oxide (ITO) glass (R_S = 10-20 Ω, LaiBao Co. Ltd. Shenzhen, China) was used as the substrate for electrodeposition of sol-gel films. Before deposition, the as-received ITO glass was ultrasonicated in ethanol, acetone and de-ionized water for 15 min, respectively, followed by drying at room temperature. The exposed area of the electrodes is ~3.0 cm^2.

To prepare DTMS sol-gel solutions, 2 mL of DTMS (95%, Wuda Chemical, Wuhan, China) was added into 80 mL of ethanol and the pH was adjusted to 3.0 ± 0.1 by using 10 wt. % HCl. After stirring for 5 min, 20 mL aqueous solution of 0.2 M KNO_3 was added slowly within 40 min. Finally, the precursor solution was continuously stirred for 6 h at 25 ± 1.0 °C before use. Silica-incorporated sol-gel solutions were prepared by directly adding 2 mL of TEOS (99.9%, Aladdin, Shanghai, China) into DTMS sol-gel solutions. Electrodeposition was performed on a CHI 630b electrochemical workstation (CH Instruments, Shanghai, China) at 25 ± 1.0 °C. Three-electrode configuration was used, with ITO glass as the working electrode, a Ag/AgCl (in saturated KCl solution) as the reference electrode and a platinum plate with an exposed area of ~ 4 cm^2 as the counter electrode. After a certain time of electrodeposition, samples were taken out from the precursor, thoroughly rinsed with water and blow-dried with nitrogen to remove any excess liquid. The film electrodes were stored in air for 10 min before testing.

Characterization: The morphology of the films was characterized by field emission scanning electron microscopy (FE-SEM, Corl ZeisD Ultra55, operated at 5 kV equipped with energy dispersive X-ray (EDX) microanalysis (Oxford EDS Inca Energy Coater 300, operated at 10 kV). The specimens were sputter-coated with a thin platinum film to increase conductivity. The transmission electron microscopy (TEM,) micrographs were acquired on a HT-7700 (Hitachi) microscope at an acceleration of 100 kV. Fourier Transform Reflection-Absorption Infrared Spectroscopy (FTRA-IR) was measured at sol-gel films-coated substrates. FT-IR spectra were recorded on a Nicolet 470 spectrophotometer (Thermo Nicolet, USA). Signals of 32 scans at a resolution of 8 cm^{-1} were averaged before Fourier transformation. A Varian 500-MS ion trap mass spectrometer (Varian, USA) equipped with an atmospheric pressure chemical ionization (APCI) interface was used for mass spectroscopy (MS) measurement of sol-gel films. The as-prepared DTMS films were scraped off from the substrate, and dispersed into 5 mL of methanol, followed by sonication for 30 min. The suspension was filtrated by a 0.22 μm filter, and then the obtained filtrate was directly infused to the mass spectrometer with a syringe pump at a flow rate of 10 μL/min. $[M+H]^+$ ions were generated in the positive ion mode for the compounds of interest. Nitrogen was used as nebulizing gas at a pressure of 35 psi and drying gas (350 °C) at a flow rate of 10 psi. The capillary voltage was 65 V. The mass scan range was 200–3000 m/z with a scan speed of 15000 u/s. Thermogravimetric analysis (TGA, Netzsch STA 409 PG/PC) measurements were carried out at a heating rate of 10 °C/min in air atmosphere. Water contact angles of the as-prepared surfaces were measured in open air with a JC2000X static dropping contact angle measuring instrument (Shanghai, China) with the aid of a high speed CCD camera for image capture. The water droplet size used for the measurements was 5 μL. Contact angle data were obtained by averaging the measurements on three randomly selected positions of the examined surface. The thickness and the roughness of the silica films were measured by profilometry (Dektak 150, Veeco, USA), and a notch was manually made by a wooden stick. The indentation tests of the superhydrophobic film samples were preformed in a DUH-211S dynamic ultra hardness tester (Shimadzu, Japan) equipped with a conospherical diamond tip, consisting of a 115 º conical indenter with a spherical end of effective radius of 0.1 μm. Load-displacement curves were generated by increasing the indenter load at a constant velocity of 0.1 mN/s up to a maximum of 19.6 mN with preset depth to 1.0 μm. The maximum load was maintained for 15 s, after which the load was removed from the samples at the same rate. The hardness and elastic modulus values were calculated by averaging the measured data at three randomly selected spots.

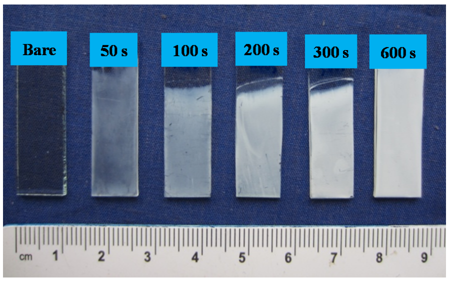

Fig. S1 Optical image of the E-DTMS films fabricated on ITO glass at -1.3 V vs. Ag/AgCl for different times.

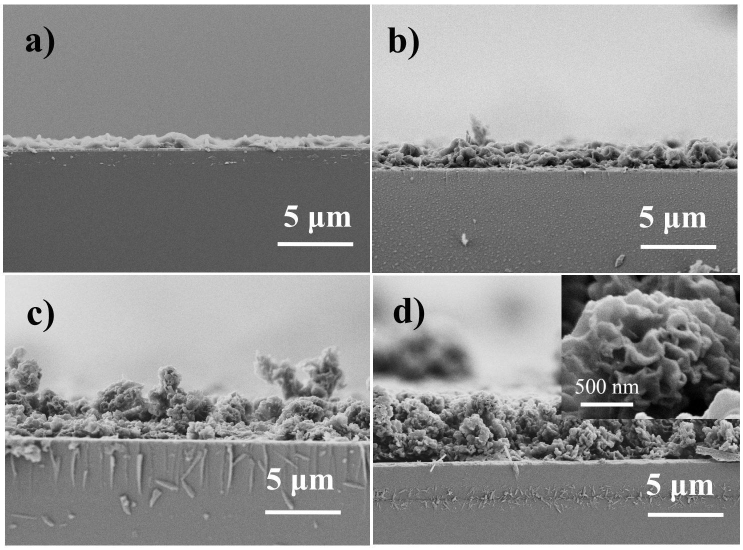

Fig. S2 Cross-section SEM images of the E-DTMS films prepared on ITO glass at -1.3 V vs. Ag/AgCl for different times: 50 s (a), 100 s (b), 200 s (c), 300 s (d). The inset in (d) is the high-resolution SEM image of the “nano-flower”.

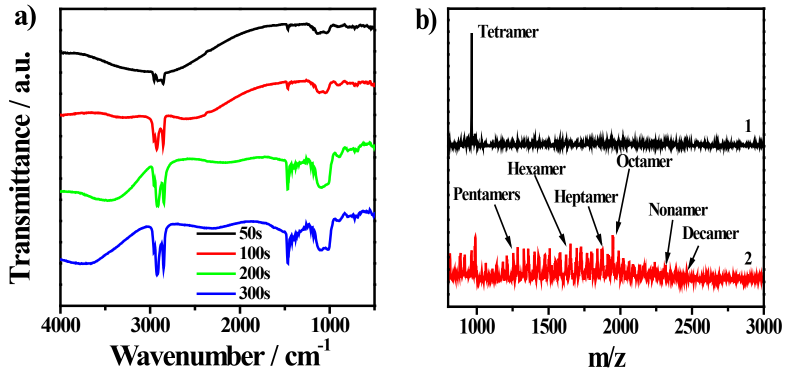

Fig. S3 a) FTIR spectra of the E-DTMS films deposited at -1.3 V on ITO for different times. b) APCI-MS spectra of the E-DTMS films electrodeposited for 100 s (1) and 600 s (2). The MS spectra were obtained from the filtrated solution which was prepared by detaching the films from substrate and then dispersing into methanol via sonication, followed by the filtration of the suspension.

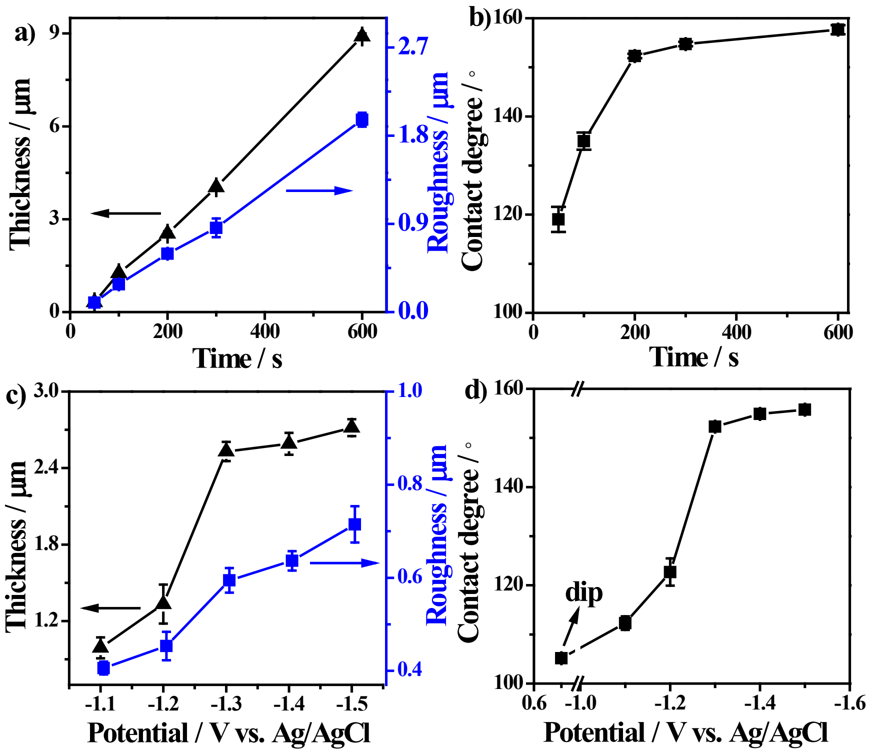

Fig. S4 (a, b) Electrodeposition time-dependent thickness and roughness (a) and water contact angle (b) of E-DTMS films prepared at -1.3 V vs. Ag/AgCl on ITO glass. (c, d) Electrodeposition potential-dependent thickness and roughness (c) and water contact angle (d) of E-DTMS films fabricated on ITO glass for 200 s. The error bars are derived from one sample by three independent measurements. Contact angle of dip-coating DTMS surface is also given in (d).

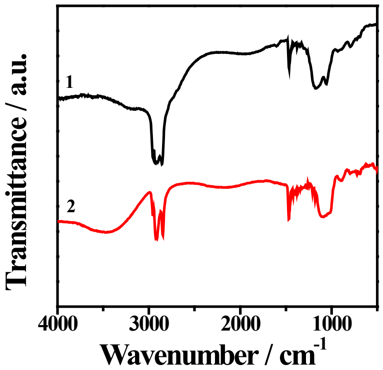

Fig. S5 FTIR of E-DTMS films before (1) and after (2) heated at 80 °C for 10 min. Curve 1 in this figure was re-plotted from Figure S3.

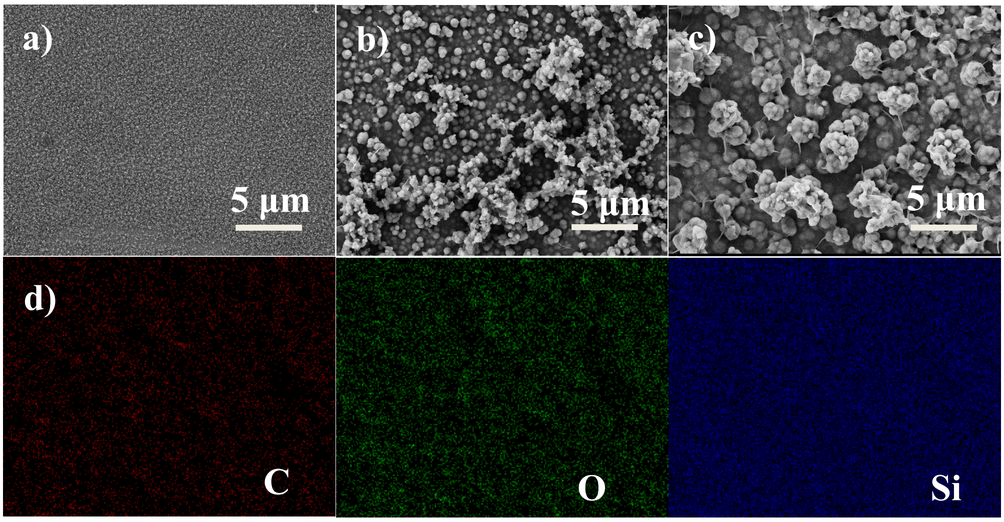

Fig. S6 FE-SEM images of the inorganic and organic hybrid silica films electrodeposited at -1.3 V for 20 s (a), 100 s (b), and 300 s (c), and the energy dispersive X-ray element mapping of the film prepared at -1.3 V for 200 s on ITO glass.

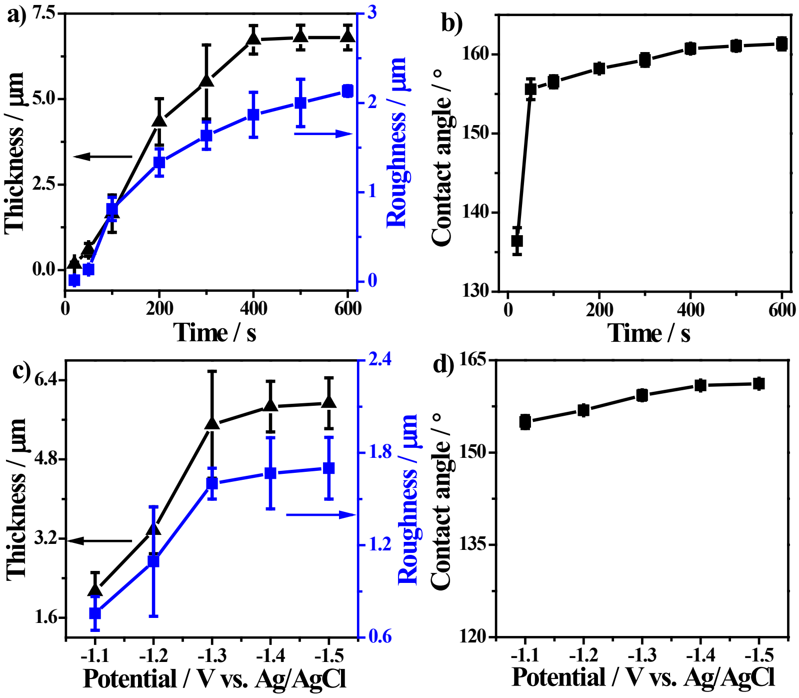

Fig. S7 (a, b) Electrodeposition time-dependent thickness and roughness (a) and water contact angle (b) of the hybrid films prepared at -1.3 V vs. Ag/AgCl on ITO glass. (c, d) Electrodeposition potential-dependent thickness and roughness (c) and water contact angle (d) of the hybrid films fabricated on ITO glass for 300 s. The error bars are derived from one sample by three independent measurements.