# Supporting Information

# Transparent, Thermally and Mechanically Stable Superhydrophobic Coating Prepared by Electrochemical Template strategy

Lianyi Xu, Dandan Zhu, Xuemin Lu, and Qinghua Lu\*

#### 1. Preparation of PEDOT films

Electrochemical synthesis of PEDOT films was performed in an electrochemical cell with a three-electrode system by using a computer-controlled CHI 630E electrochemical analyzer (Figure S1a). The working electrode consisted of indium tin oxide (ITO) glass (<10  $\Omega$  sq<sup>-1</sup>, 0.9 cm × 5 cm), which was washed successively under ultrasonication with deionized water and absolute ethanol, and then dried with a stream of N<sub>2</sub> before use. The counter electrode was a platinum wire (1 mm diameter), which was cleaned before each examination. An Ag/AgCl wire was used as a quasi-reference electrode. The electrochemical experiments were performed at room temperature and less than 40% relative humidity. PEDOT was electrodeposited on ITO electrodes by cyclic voltammetry (CV) between -0.8 V and +1.5 V in 0.01 M EDOT/ACN solution containing 0.2 M LiClO<sub>4</sub> as a supporting electrolyte (Figure 1a). The as-prepared PEDOT films were rinsed three times with ethanol (95%) and dried under an air stream at room temperature.



**Figure S1.** (a) The electrochemical cell. (b) The superhydrophilicity of the PEDOT film with a WCA  $\approx 0^{\circ}$ .

#### 2. Preparation of silica coatings.

To encase the PEDOT films with silica layers, chemical vapor deposition (CVD) of tetraethoxysilane (TEOS) was performed at room temperature for 30 h. To this end, PEDOT films were placed in a closed desiccator together with two open vessels containing about 2 mL of TEOS and 1 mL of aqueous ammonia solution, respectively.<sup>9</sup> A silica layer was formed on each PEDOT film by hydrolysis and condensation of TEOS under catalysis by ammonia.<sup>10</sup> Calcination of the silica-layer-encased PEDOT films at 500 °C for 2 h in air led to combustion of the internal PEDOT, and the generated gas diffused through the silica layer.<sup>9,19</sup> After annealing, the resultant silica coating is superhydrophilicity (Figure 2a (left)). For the generation of the superhydrophobic surface, the silica coatings were fluoridized by CVD of POTS at room temperature for 12 h in a similar closed desiccator. For this, the silica

coatings were placed together with two open vessels containing 0.2 mL of POTS and 0.2 mL

of aqueous ammonia solution, respectively.



Figure S2. XPS spectrum of the superhydrophobic silica coating.

#### 3. Measurement of contact angle

Static contact angle (CA) measurements in air were performed by the sessile drop method using an OCA 20 contact angle system (Data Physics Instruments GmbH, Germany). The reported CAs are the mean values of measurements on a 4  $\mu$ L water droplet or 5  $\mu$ L organic droplet at three different positions on each sample. Sliding angles (SA), advancing angles ( $\theta_A$ ), and receding angles ( $\theta_R$ ) were determined by slowly tilting the sample stage until the 4  $\mu$ L water droplet or 5  $\mu$ L organic droplet started to move.

#### 4. Characterization

Field-emission scanning electron microscopy (FE-SEM) was performed with a Nova NanoSEM instrument (FEI, U.S.A.). The high-speed video and sequential photography images of impacting water-droplet on the coating were captured at 1200 fps using a high-speed camera (Motion Studio Cameras SDK, IDT, Inc.) The chemical compositions of the surfaces were determined by XPS on a Kratos Axis Ultra<sup>DLD</sup> spectrometer (Kratos Analytical, Ltd., Manchester, U.K.) using monochromatic Al- $K_{\alpha}$  radiation (1486.6 eV) and a takeoff angle of 90°. Transmittance measurements were performed using a Perkin-Elmer Lambda 20 UV/Vis spectrophotometer in double-beam mode. Refractive index and coating thickness

were measured using W-VASE on an AutoRetarder<sup>TM</sup> variable-angle spectroscopic ellipsometer (J.A. Woollam, U.S.A.). Photographs were acquired with a camera.

#### 5. Transparency of coatings.

As shown in Figure S3, the UV/Vis transmittance spectrum of the pure ITO glass indicated a maximum transmittance of 88.7% at 602 nm. Compared with the pure ITO glass, the ITO glass annealed at 500 °C in air for 2 h exhibited an increase in transmittance with a maximum of 91.1% at 643 nm. The increase in its optical transmittance after annealing can be attributed to an increase in the structural homogeneity and crystallinity of the ITO.<sup>20–22</sup>

The annealed ITO layer on the glass had a refractive index ( $n_{\rm ITO}$ ) of about 1.69 and its thickness was about 180 nm. Since the refractive index of ITO ( $n_{\rm ITO}$ ) is higher than that of glass ( $n_{\rm sub} \approx 1.51$ ), it would be detrimental to reduce the glass substrate surface reflection in the visible light range by using the ITO layer alone according to the equation  $n_c =$  $(n_{\rm air}n_{\rm sub})^{1/2}$ .<sup>14</sup> The superhydrophobic porous silica coating (EC of PEDOT: 16.6 mC cm<sup>-2</sup>) had an effective  $n_c$  of 1.29 and an average thickness of 215.9 nm. The porous silica coating together with the underlying ITO layer formed a matched refractive index gradient. Thus, this porous silica coating enhances the transmittance of ITO glass. The highly porous nanostructured silica coating reduced the reflectance, thereby enhancing the transmission of light over a broad wavelength range.<sup>14</sup> Its reflection resistance can be directly proved by comparing their photographs of the glass slide, porous silica coating, and annealed ITO glass taken in strong reflected light with a reflection angle of about 65° (Figure S4b).



**Figure S3.** UV/Vis transmittance spectra of the pure ITO glass (green dashed line), the annealed ITO glass (blue line), and the superhydrophobic silica coating on ITO glass (red line).



**Figure S4.** (a) A 4  $\mu$ L water droplet was placed on the fluorinated silica-coated surface without using electrodeposited PEDOT as a template during covering with silica; it shows a water contact angle of just 111.2° ± 1°. (b) Photograph of a glass slide (a1), porous silica coating (a2), and annealed ITO glass (a3) taken in strong reflection light with a reflection angle of about 65°. Sample a2 shows clearer letters beneath the silica-coated ITO glass than samples a1 and a3. (c) Capturing and releasing a water droplet. A water droplet deposited on

low-adhesion superhydrophobic coatings (C2 to C8) could be captured easily by highadhesion superhydrophobic coating (C1) that had stronger adhesion force. When water droplet contacted on the hydrophobic coating surface, it could be released without mass loss.



**Figure S5.** UV/Vis transmittance spectra of the superhydrophobic silica coatings (marked as C1 to C8), whereby PEDOT films were electrodeposited with charges of 7.5, 10.5, 17.8, 23.9, 29.9, 35.3, 43.5, and 56.7 mC cm<sup>-2</sup>, respectively. The short-dash line is the transmittance spectrum of the pure ITO glass annealed at 500 °C in air for 2 h. The transmittance at 530 nm shows a slight decrease with increasing EC of the PEDOT templates.



**Figure S6.** ITO glasses coated with the transparent superhydrophobic silica coatings (from C2 to C8) placed on labeled paper.

#### 6. Water-droplet impact resistance

To assesse the durability of the superhydrophobic silica coating, the long-term water-drop impact experiment was preformed. The silica coating was placed with a 45-degree tilted angle and water drops (radius of 2.3 mm) impacted the superhydrophobic surface from 12 cm height ( its impact velocity of about 1.53 m s<sup>-1</sup>) with a dropping rate of 2 droplets per second for 24 hours (Figure S7b). After the long-term water-drop impact experiment, the water contact angle measurement was preformed in the position of the water-droplet impact (inset in Figure S7b).



**Figure S7.** (a) Sequential photography images of a 22  $\mu$ L water droplet impacting the surface with a higher velocity of 4.43 m s<sup>-1</sup> (the red line on the ITO glass (top) indicates a division between the superhydrophobic fluorinated porous silica coating surface on the right and the hydrophobic fluorinated silica surface without porous structure on the left, which only showed a water contact angle of  $111.2^{\circ} \pm 1^{\circ}$ ). A great coronary water ring can be observed at water-droplet impacting moment. The scale bars represent 5 mm. (b)The sketch of the long-term droplet impact tested by dropping water drops (50  $\mu$ L) from a height of 12 cm to impinge a silica coating with a tilt angle of 45°. Inset: the water contact angle of 162.5°  $\pm 1^{\circ}$ .

# 7. Thermal stability.

To evaluate the thermal stability of the superhydrophobic silica coating, a sample was annealed at various temperatures from 22 to 400 °C, for 1 h at each selected temperature. After each annealing step, its water contact and sliding angles were measured at room temperature. When the annealing temperature reached 450 °C, the silica coating lost its superhydrophobicity and showed a superhydrophilic surface instead (Figure 2a).

### 8. Tape peeling test.

To determine the adhesion between the silica coatings and ITO substrate, double-sided sticky tape was pressed at about 100 kPa (about  $1.1 \text{ kg/cm}^2$ ) onto the superhydrophobic silica coating (EC of PEDOT: 15.2 mC cm<sup>-2</sup>). After releasing the pressure, the tape was rapidly peeled off from the porous silica coating, and bulk adhesive was seen to be left on the silica coating by SEM (Figure S8). After successively washing the silica coating with toluene, dichloromethane, and ethanol, it remained intact without any obvious damage (Figure 6a). To further assess its robustness, the same sample was re-tested under the same conditions. After cleaning the surface, the water CA of the silica coating was measured as about 158.5°  $\pm$  2° (inset in Figure 6a).



**Figure S8.** SEM image of the superhydrophobic silica coating after peeling off double-sided sticky tape. The silica coating underneath the tape remained in place very well without any obvious damage. On the contrary, bulk adhesive was left on the silica coating after peeling off the tape, indicating strong adhesion between the silica layer and ITO substrate.

#### 9. Hydraulic pressure test.

The stability of the superhydrophobicity of the porous silica coating towards hydraulic pressure was tested. The sample was placed in a watertight glass syringe filled with water (Figure S9a). The diameter of the piston (*d*) was about 1.23 cm. The force (*F*) acting on the water was applied by means of an MTS Criterion Model 43 electromechanical universal test system (MTS Systems Corporation, U.S.A.). Before applying pressure, the coating in water could form a reflective interface like a mirror (inset in Figure 6b (left)). A 4 µL injected air bubble could rapidly spread into the coating surface placed upside down under water at a depth of about 0.5 cm (Figure S9b). With the increase of *F*, the mirror-like reflective interface was seen to gradually fade by observing it with the naked eye. When *F* was about 77.2 N (7.9 kg) for 60 s, the mirror-like reflective interface faded significantly (inset in Figure 6b (right)). According to the equation: P = F/S ( $S = \pi(d/2)^2$ ; *d* is the diameter of the piston), the corresponding hydraulic pressure *P* was about 650 kPa, which was maintained for 60 s. After releasing the pressure, the sample was taken out from the water. The water sliding angle of the coating was measured directly without any drying treatment (Figure 6b).



**Figure S9.** (a) Diagram of the hydraulic pressure device for testing the stability of the superhydrophobic coating under a hydrostatic pressure of 650 kPa for 60 s. By applying a certain force *F*, the hydraulic pressure *P* can be created (P = F/S, where  $S = \pi (d/2)^2$ , *d* is the diameter of the piston). Before pressurizing, the sample was immersed in water. (b) Before pressurizing, a 4 µL air bubble could rapidly spread into the coating surface placed upside down in the water.

#### 10. sand abrasion test

To assess the mechanical abrasion resistance of the silica coating, the sand abrasion test was performed. The 20 g sand grains with the diameter of  $150 \pm 100 \mu$ m impacted onto the tilted 45-degree silica coating from a height of 20 cm (Figure 7a). After 50 second sand abrasion and wishing the coating with water, water CA of the silica coating was measured.

**Movie S1.** Lateral movement of the water droplet hanging at the tip of a needle on the surface of the porous superhydrophobic silica coating.

**Movie S2.** High-speed video of a 22  $\mu$ L water droplet impinging and bouncing off the porous superhydrophobic silica coating with an impacting velocity of 0.75 m s<sup>-1</sup>, leaving the surface dry.

**Movie S3.** High-speed video of a 22  $\mu$ L water droplet impinging the superhydrophobic silica coating with an impacting velocity of 4.43 m s<sup>-1</sup>.

**Movie S4.** Sand contaminants are removed from the self-cleaning silica coating by a  $20-\mu L$  water droplet dropped down with a velocity of 0.78 m s<sup>-1</sup>.

**Movie S5.** The video of sand grains abrading the superhydrophobic silica coating from an impact height of 20 cm. After abrading, the silica coating still showed the anti-wetting property.

# References

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