Robust Anti-Reflective Silica Nanocoatings: the Abrasion Resistance Enhanced via Capillary Condensation of APTES

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Materials and instruments

Tetraethoxysilane (TEOS), ammonia (NH₃·H₂O, 38wt% aqueous solution), toluene (CH₃C₆H₅, 99.9%) and dehydrated ethanol were purchased from Beijing Chemical Works Plant. 3-aminopropyl triethoxysilane ((CH₃CH₂O)₃SiCH₂CH₂NH₂, APTES) was obtained from Alfa Aesar. All of the chemical reagents were used as received without further purification. Deionized water was used in all manipulations. All substrates were subjected to ultrasonic cleaning in ethanol and deionized water, respectively, followed by blow-drying with N₂ before use.

Morphology of the samples was characterized by scanning electron microscopy (Hitachi S4800, Japan) with an accelerating voltage of 15 kV. Transmittance of the films was investigated by UV-vis spectrometer (Lamda-950, PerkinElmer, USA). Surface roughness was measured by atomic force microscopy (AFM, Multimode 8, Bruker, Germany). Measurement of thickness and refractive index (RI) was performed by ellipsometer (M-2000V, J. A. Woollam Co. Inc., US), fitting by a Cauchy Model. All thickness and RI values specified in the text were averaged at least 5 individual measurements. Mass change of the films was measured by quartz crystal microbalance with dissipation analysis (QCM-D, Suzhou Institute of Nano-Tech and Nano-
Preparation of silica AR coatings

Dispersions of silica nanoparticles (SiO$_2$ NPs) with average diameters of 20 nm and 100 nm, respectively, were synthesized through a typical Stöber method$^{1}$. To avoid gelation, ammonia was removed by evacuation. Extra ethanol (with a volume ratio to the original dispersion of 5:1) is added to adjust the concentration of the final dispersion. Uniform films were prepared by spin-coating the dispersions on as-cleaned substrates (1500 rpm, 30 s).

Capillary condensation

All the chambers and vials used in this step were rinsed with toluene, and then were blow-drying with N$_2$. Capillary condensation was implemented at 80 °C in a sealed chamber, where the substrate with AR coating, a drop of diluted NH$_3$·H$_2$O solution in a vial and 500 μL APTES contained in another vial were enclosed. For diverse samples, different durations, 1 h, 2 h, 4 h and 7 h, were maintained. To avoid film-like condensation, at the end of this procedure, substrates were taken out quickly before they were cooled down.

Abrasion resistance test

For the abrasion resistance test on hard substrates, the AR coatings were fabricated on 5 MHz QCM chips as the process described in Preparation of silica AR coatings. Then, the frequencies of these chips ($f_1$) with coatings were recorded by QCM. Prior to this, the frequencies of the bare chips ($f_0$) were recorded as references. After capillary condensation process, the frequencies were recorded again as $f_2$. Then the samples were wiped by lens paper for 5 times with forces that we usually applied to the touch screen of the cellphones and the post-frequencies were recorded as $f_i$. $\Delta f_1$, $\Delta f_2$ and $\Delta f_i$ were determined by the differentials between $f_i$ and $f_0$, $f_1$; and $f_1$, $f_2$ and $f_5$, respectively. Based on the Saubrey equation (Equation 1 in the main text), $\Delta m_1$, $\Delta m_2$ and $\Delta m_3$, could be obtained.

For the abrasion resistance test on PET substrates, the fabrication of AR coatings was carried out in the same way as mentioned above, the transmittance curves were recorded as references. After capillary condensation of APTES, the samples were wiped by lens paper for 100 times with forces that we usually applied to the touch screen of the cellphones. The transmittance curves of the samples were tested after being wiped for 5, 10, 15, 20, 30, 40, 50, 65, 80, 100 times, respectively.
Fig. S1 SEM images of 100-nm silica NPs coatings with further prolonging capillary condensation process: (A) 4 h, (B) 7 h and (C) 24 h.
**Fig. S2** Morphology of 30-nm SiO2 NPs coating before capillary condensation: (A) SEM and (B) AFM images; (C) Roughness curve of the coating through AFM and (D) the corresponding 3D image of (B).
Fig. S3 The AFM images of coatings treated by capillary condensation at 80 °C with different durations: 1 h (A), 2 h (B), 4 h (C) and 7 h (D). (E) - (H): The 3D-height images of (A) - (D), respectively. (I) - (L): The profile height curves corresponding to images (A) - (D).

References: