Electronic Supplementary Information for

Antifogging antireflective thin films: Does the antifogging layer have to be the outmost layer?

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Methods

Chemicals: Poly(vinyl alcohol)(PVA, M_n=70000–90000 g/mol, 99% hydrolyzed, Aladdin) and poly (acrylic acid) (PAA, 53wt% in water, M_w=4000–7000) were purchased from Shandong Heli water treatment company. Tetraethyl orthosilicate (TEOS, 98+%) was obtained from Alfa Aesar. Aqueous ammonia (25%), absolute ethanol (99.5%) were purchased from Beihua Fine Chemicals. Ultrapure water with a resistivity higher than 18.2 MΩ•cm was used in all experiments, and was obtained from a three-stage Millipore Mill-Q Plus 185 purification system (Academic).

Preparation of hollow silica nanoparticles: In a typical procedure, 0.1-0.5 g of PAA dissolved in 3-5 mL of aqueous ammonia was mixed with 90 mL of absolute ethanol, followed by the injection of 5 aliquots of TEOS totaling 1-4 mL over a time interval of 1 h under vigorous magnetic stirring at room temperature. After 10 h, hollow silica nanoparticles were obtained.

Thin film preparation: Polymer thin films were deposited on substrates by one-step dip-coating followed by thermal cross-linking. First, slide glasses were sonicated in water for at least 10 min, and then treated with oxygen plasma (84 W, 5 min) at an oxygen flow of 800 mL·min^{-1}. The substrates were then immersed in an aqueous solution containing PVA and PAA for 40 s, where the molar ratio of hydroxyl groups to carboxyl groups was set to 6:1~15:1 (RH: 15%~40%), and withdrawn at a speed of 50 mm·min^{-1} from the solution. Finally, the polymer thin films were thermally cross-linked at 130–150°C for 5 min. After the substrates coated by the polymer were allowed to cool to room temperature, the polymer covered substrates were immersed in a hollow silica nanoparticles suspension for 30 s, and withdrawn at a speed of 150 mm·min^{-1} from the suspension.

Characterization of thin films: The as-prepared thin films were examined by scanning electron microscopy (SEM) on a Hitachi S-4300 scanning electron microscope operated at 5 kV. Transmission electron microscopy (TEM) images were taken on a JEOL JEM-2100F transmission electron microscope at 200 kV. Samples for TEM observations were prepared by first dispersing hollow silica nanoparticles in ethanol by ultrasonication, followed by dropping on holey carbon-coated copper grids and drying at room temperature. Transmission spectra in the wavelength range of 330–800 nm were recorded using a TU-1901 spectrophotometer (Beijing Purkinje General Instrument Co.). Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) analyses were carried out on a Varian Excalibur 3100 spectrometer. Water contact angles on the surface of different specimens

were measured at ambient temperature on a Kino SL200B3 automatic contact angle meter. The mass change of the polymer thin film arising from the antifogging test was monitored by quartz crystal microbalance (QCM). A drop-coating method was used to coat both sides (5 mm in diameter) of a silver-coated QCM resonator (9Hz, AT-cut piezoelectric quartz crystal, Beijing Chenjing Electronics) followed by thermal cross-linking. Frequencies were recorded by Agilent 53131A universal counter linked to a computer. For the examination of antifogging property, the glasses coated by 2HSNs, polymer, 2HSNs/polymer were cooled at ca. –6°C for 24 h in a refrigerator, and then exposed to humid laboratory air (room temperature : 20–30°C, relative humidity: 20-40%).

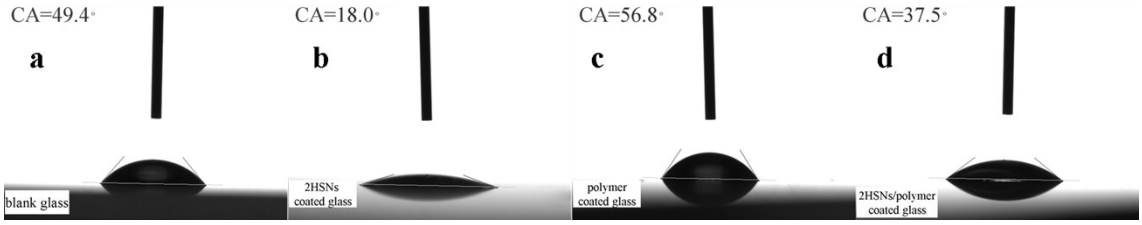

Fig. S1 Images of water contact angles on (a) blank glass, (b) 2HSNs coated glass, (c) polymer coated glass, and (d) 2HSNs/polymer coated glass. Water droplets of 4 μl were applied in the water contact angle measurements. The water contact angles are 49.4°, 18.0°, 56.8°, and 37.5°, respectively, on blank glass, 2HSNs coated glass, polymer coated glass, and 2HSNs/polymer coated glass.

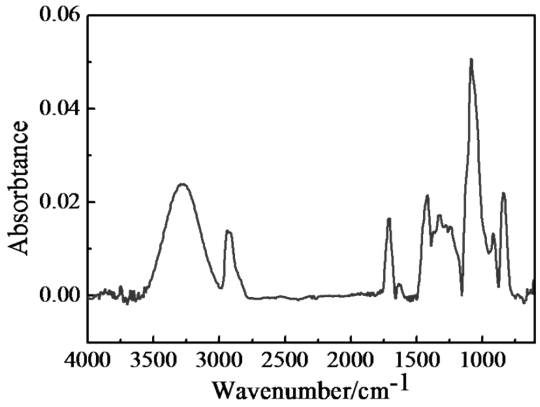

Fig. S2 ATR-FTIR spectrum of the polymer thin film.