Supporting Material

A facile layer-by-layer deposition process for the fabrication of highly transparent superhydrophobic coatings

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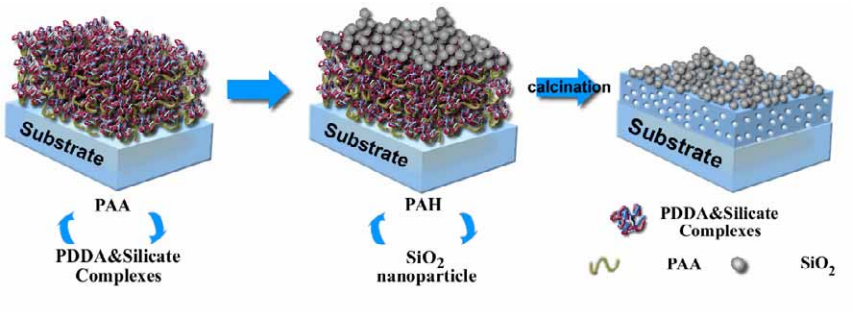
Materials. Poly(diallyldimethylammonium chloride) (PDDA, 20 wt%, *M*w ca. 100000-200000), poly(acrylic acid) (PAA, *M*w ca. 2000), poly(allylamine hydrochloride) (PAH, *M*w ca. 52000), 14 nm silica nanoparticle and sodium silicate solution were all purchased from Sigma-Aldrich. 1H,1H,-2H,2H-perfluorooctyltriethoxysilane (POTS) was purchased from Degussa. Quartz slides with a thickness of 1.0 mm were used for film deposition.

Characterization. UV-vis absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Scanning electron microscopy (SEM) observations were carried out on an XL30 ESEM FEG scanning electron microscope. Atom force microscopy (AFM) images were taken on a Nanoscope IIIa atom force microscope (Digital Instruments, Santa Barbara, CA). Water contact angle - sliding angle measurements were performed with an OCA20 contact-angle analysis system (Dataphysics, Germany) at ambient temperature. A water droplet of 4 μL was used as the indicator.

Preparation of Complexes of PDDA and Sodium Silicate.[1] To a stirring aqueous solution of PDDA (1.0 mg/mL), aqueous sodium silicate (34.4 mg/mL) was added dropwise. The ultimate volume ratio of PDDA and sodium silicate solutions was 60:5. The pH value of the aqueous PDDA-silicate complexes solution was adjusted to 4.0 using 1 M HCl.

Fabrication of Highly Transparent Superhydrophobic Coatings. The procedure of fabrication highly transparent superhydrophobic coatings is shown in

Scheme 1. Slides of quartz were immersed in a slightly boiled piranha solution (3:1mixture of 98% H_2SO_4 and 30% H_2O_2) for 20 min and rinsed with copious amount of water and dried with N_2 flow. *Caution: Piranha solution reacts violently with organic materials and should be handled carefully.* The freshly cleaned quartz slides were sequentially immersed into PDDA (1.0 mg/mL) and PAA (1.0 mg/mL, pH = 5.0) solutions for 20 min to obtain a precursor layer of PDDA/PAA film, with an intermediate water rinsing and N_2 drying. Then multilayer films of PDDA-silicate/PAA were deposited on the substrates according to the following general protocol:[1] i) Substrates were immersed in a solution of PDDA-silicate complexes for 20 min, followed by rinsing with water for 1 min and drying with N_2 flow. ii) Substrates were immersed in a solution of PAA (1.0 mg/mL, pH 5.0) for 20 min, followed by rinsing with water for 1 min and drying with N_2 flow; Steps of i and ii were repeated until a (PDDA-silicate/PAA)*12 film was fabricated. Next, the quartz substrate covered with a (PDDA-silicate/PAA)*12 film was immersed into aqueous PAH solution (1mg/mL, pH 7.5) for 3 min. The substrate was then rinsed with water and dried with N_2 flow. After the deposition of PAH layer, the substrate was immersed into SiO_2 nanoparticle solution (0.4 w% in 3:1 (v/v) water: ethanol, 14 nm in diameter) for 2 min**,** followed by extensive rinsing with water and drying with N_2 flow. A 4-bilayer PAH/SiO_2 nanoparticle film (noted as (PAH/SiO_2)*4) was deposited on top of the (PDDA-silicate/PAA)*12 film. The quartz covered with a (PDDA-silicate/PAA)*12/(PAH/silica)*4 film was calcined at 500˚C for 2 h to burn out the polymeric components and concomitantly cross-link the silicate sodium and the top layers of SiO_2 nanoparticles. A highly transparent superhydrophobic coating was finally obtained by CVD of a layer of 1H,1H,-2H,2H-perfluorooctyltriethoxysilane (POTS) at 120˚C for 3 h.



Scheme 1. Schematic illustration of the fabrication of highly transparent superhydrophobic coatings.

Reference:
(1) L. B. Zhang, Y. Li, J. Q. Sun, J. C. Shen, *Langmuir*, 2008**, 24**, 10851-10857.