Supporting information

A Facile and Large-area Fabrication Method of Superhydrophobic Self-cleaning Flourinated Polysiloxane/TiO_2 Nanocomposite Coatings with Long-term Durability

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Experimental

Materials and preparation: A certain amount of Disperbyk-180 (BYK Chemicals, 1.5 wt% relative to the weight of nano-TiO_2 particles) and 60 g of butyl acetate (chemical grade, Sinopharm Chemical Reagent Co., Ltd) were added into a 250 mL plastic beaker and stirred for 10 min at low speed. Then, 8 g of α,ω-bis(hydroxyl)-terminated, 2,2,3,3,4,4,4-heptafluoro-poly(methylsiloxane) (PMSF, Mw= 8000 g/mol, Guangzhou Kang-Gu-Jia Chemical Technology Co., Ltd.), 1.2 g of α,ω-bis(hydrogen)-terminated poly(dimethylsiloxane) (PDHS, Mw=1200 g/mol, Aladdin Chemicals) and TiO_2 nanoparticles (primary size: 27 nm, P25, Degussa) were added to this plastic beaker and stirred for 2 h at a speed of 1000 r/min for 2 h. Just before application, Karstedt catalyst (platinum (0)-1,3-divinyl-1,1,3,3-tereamethyldisioxane complex, Sigma-Aldrich) was added into the above mixture based on the molar ratio of [Pt]/[Si-H]=4.0×10^{-6} to get fluorinated polysiloxane/TiO_2 nanocomposite coatings. Other inorganic nanoparticles-based composite coatings were prepared as the same procedure. The coatings were cast on tin plate using a drawdown rod (120 μm) and dried at room temperature for several days to directly obtain superhydrophobic surfaces.

Characterization: Water contact angle (WCA) and sliding angle were determined with an OCA15 contact angle analyzer (Dataphysics, Germany) using a 5 μL deionized water droplet and obtained from the average value of five parallel measurements. To investigate the pH influence on the WCA, the probe water was added with hydrochloric acid or sodium hydroxide and then carried out WCA analysis.The surface images of the coatings were observed with a filed emission scanning electron microscope (FESEM, JSM-6701F, JEOL Co., Ltd, Japan) at an accelerated voltage of 10 kV. The specimens were sputtering-coated with gold prior to FESEM imaging. The wear resistance of the fluorinated Polysiloxane/TiO_2 nanocomposites was measured by tape abrasion using an A4 paper tape with 100 g load, the weight loss of a unit area was used to evaluate the mechanical properties of the as-prepared nanocomposites coatings. AFM studies were performed using a SPM-9500J3 (SHIMADZ, Inc., Japan) microscope with silicon tips of 10 nm in radius, a spring constant of 5.5–22.5 N m-1 and frequency of 190–325 KHz. Tapping mode was adopted to map the 3-D topography of the coatings at ambient conditions. The surface composition of coating was measured by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000C ECSA) using Al K radiation at a 90° take-off angle. All the binding energy values were calibrated using the reference peak of C1S at 284.6 eV. The dried films of TiO_2-based nanocomposite coatings were tested in a QUV accelerated weathering tester (QUV/se, Q-Panel Co., Ltd., USA). UV lamps with wavelength of 340 nm were used and the accelerated weathering cycle was set as follows: UV-irradiation for 8 h at 50 ^oC and irradiation intensity of 0.68 W/m^2, and condensation for 4 h at 40 ^oC. The resistance of coatings to oily contaminant was evaluated using salad oil as the model pollutants. A thin layer of salad oil was sprayed on the coating surfaces. Then, the coatings were put under the UV lamp (365 nm, 20 mW/cm^2). The WCAs were measured after one hour of time interval. The formation of ice on the superhydrophobic nanocomposite coating (containing 35 wt% of TiO_2 nanoparticles) and the hydrophobic coating (containing 10 wt% of TiO_2 nanoparticles) were determined by putting them in an oven with a temperature of -10 ^oC. Water fogs was sprayed into the oven through a hole. The amount of ice was qualitatively examined with naked eyes. The adhesive force of ice with the coatings was determined using a pull-off adhesion tester (PosiTest AT, DeFelsko Co., USA). Aluminum dollies with 20 nm surface diameter were eroded with diluted HCl solution to get the hydrophilic surface. Afterthat, the dolly was covered with a thin layer of water and put on the coated panel. The panel together with the dolly was moved into an oven with a temperature of -10 ^oC and kept there for 15 min. The panel was then taken out from the oven and quickly carried out a pull test by the adhesion tester. The adhesion force was obtained by three parallel pulls.

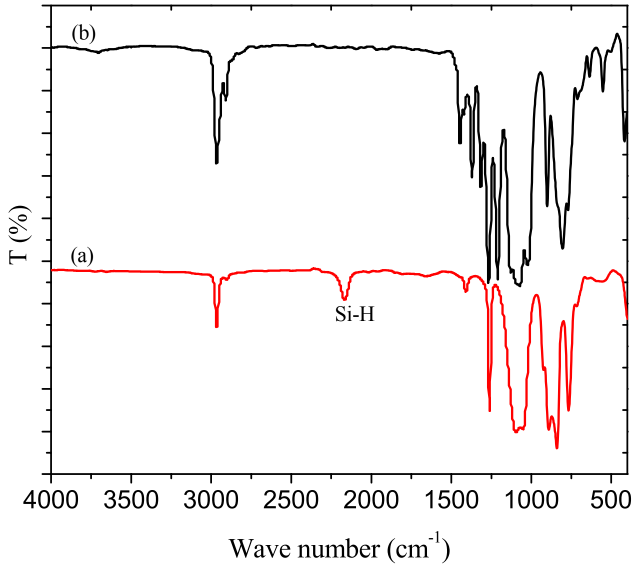

Figure S1. FT-IR spectra of (a) PDHS and (b) the dried coating film.

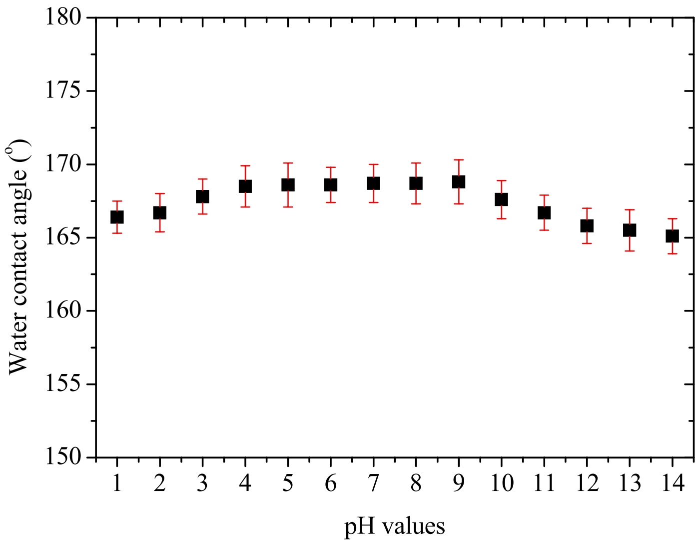

Figure S2. The relationship between pH value and WCA on the as-prepared superhydrophobic coating containing 35 wt% TiO_2.

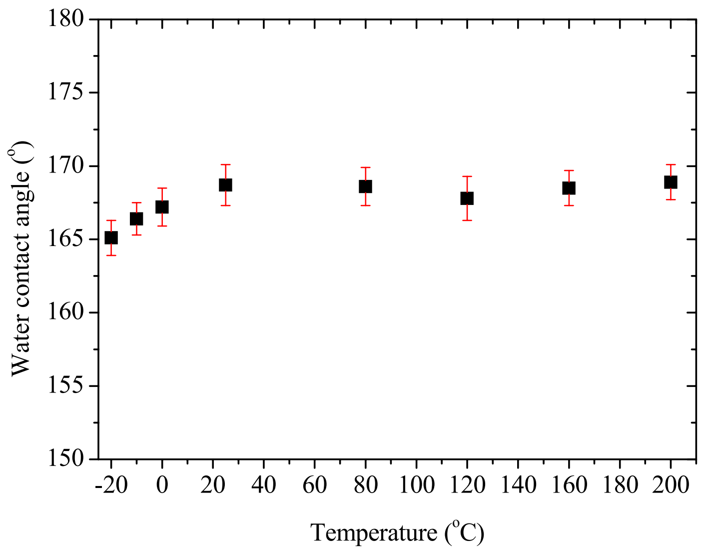

Figure S3. Plot of WCA as a function of temperature. All the WCA measurements were carried out at room temperature after the cooling/ heating treatment.

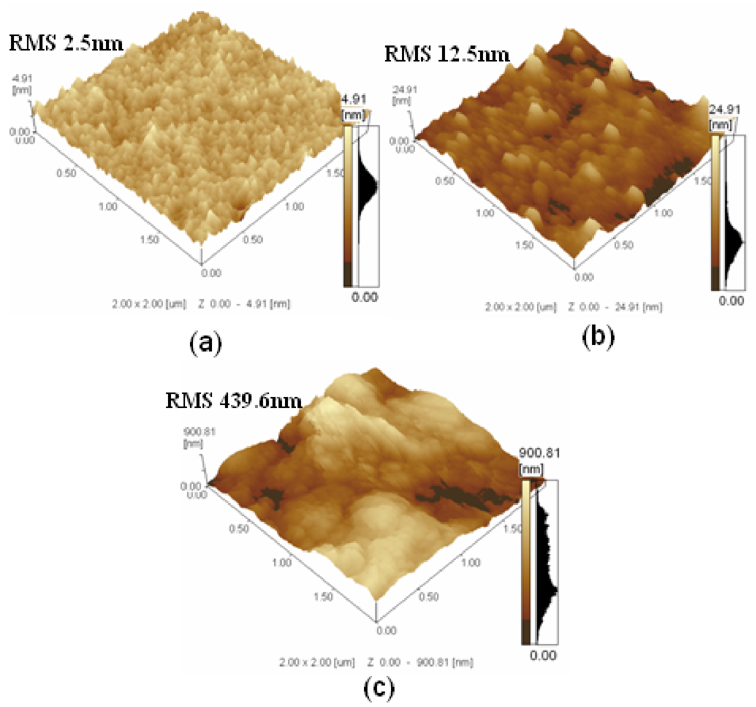

Figure S4. AFM 3D height images of the TiO_2-based nanocomposite coatings with various TiO_2 content: (a) 0, (b) 5, and (c) 35 wt%, respectively.

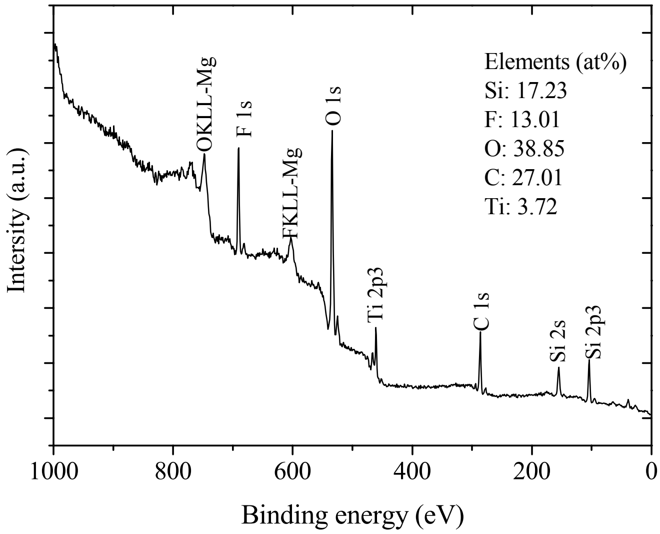

Figure S6. XPS spectrum of superhydrophobic coatings with 35% of TiO_2 content.

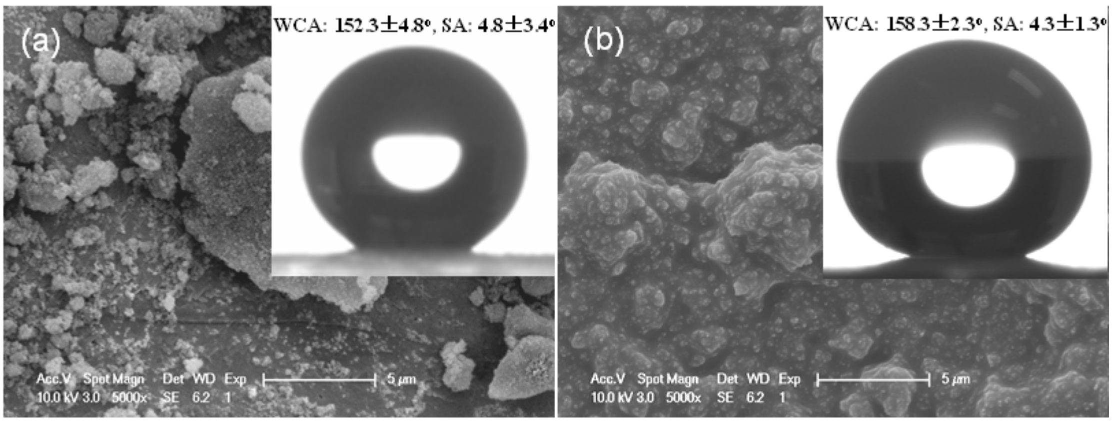

Figure S5. SEM images of fluorinated polysiloxane/Al_2O_3 nanocomposite coatings with 40 wt% Al_2O_3 content (a) and 56 wt% Fe_3O_4 content (b). (inserted pictures: a water droplet on the surfaces and its WCA and sliding angle).

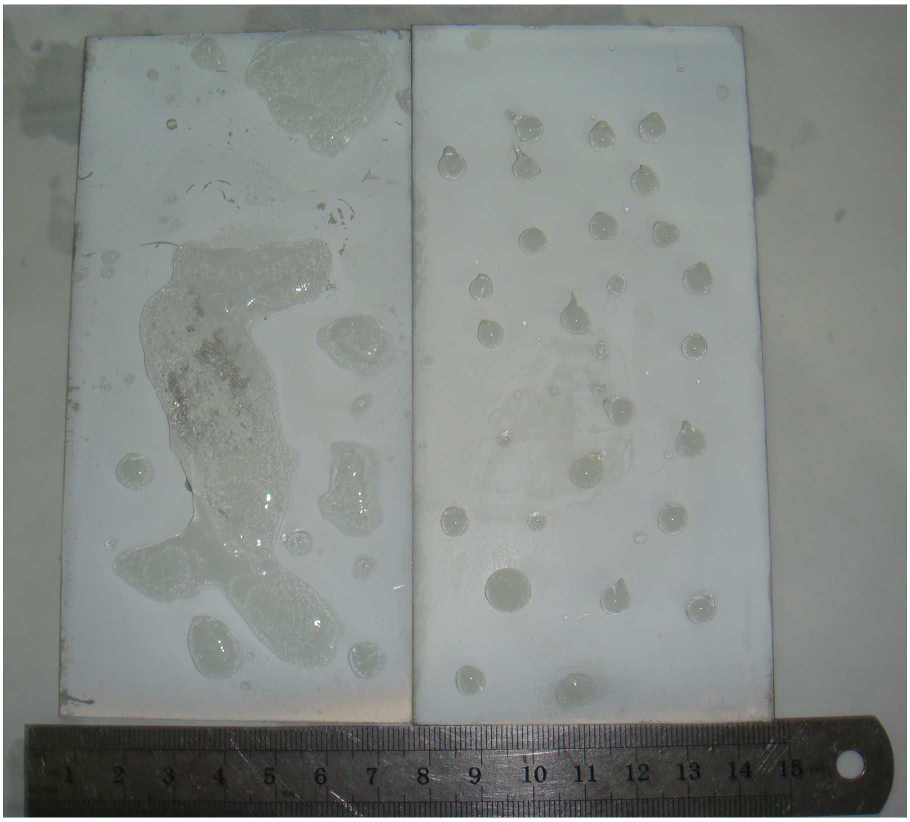

Figure S6. The amount of ice formed on the surface of hydrophobic coating (left, 10 wt% of TiO_2 content) and superhydrophobic coating (right, 35 wt% of TiO_2 content) at a temperature of -10 ^{o}C.