

# Silica-Core Perfluorinated Polymer-Shell Composite Nanoparticles for Highly Stable and Efficient Superhydrophobic Surfaces

*Eun-Ho Sohn,<sup>1,†</sup> Hong Suk Kang,<sup>1,†,\*</sup> Jeong-Cheol Bom,<sup>1,2</sup> Jong-Wook Ha,<sup>1</sup> Soo-Bok Lee,<sup>1</sup>  
and In Jun Park<sup>1,\*</sup>*

<sup>1</sup>Interface Materials and Chemical Engineering Laboratory, Korea Research Institute of Chemical Technology, Daejeon 305-343, Korea

<sup>2</sup>Present address: Research Center, Nicca Korea Co. Ltd., Daegu 704-801, Korea

<sup>†</sup>These authors contributed equally to this work.

\*Corresponding author: Dr. Hong Suk Kang (hongsukk@kriect.re.kr) and Dr. In Jun Park (ijpark@kriect.re.kr)

## Experimental Section

**Materials.** The hydrophilic fumed silica (Aerosil 200, Evonik) used in this study had a specific surface area of  $200 \pm 25$  m<sup>2</sup>/g (as determined by the Brunauer-Emmett-Teller method) and a mean particle diameter of 12 nm. It was dried at 120 °C under  $10^{-2}$  mbar overnight. Perfluoroalkylethyl acrylate (FA, F(CF<sub>2</sub>)<sub>8</sub>CH<sub>2</sub>CH<sub>2</sub>COOCH=CH<sub>2</sub>, Daikin) was passed through a neutral alumina column, distilled under vacuum in the presence of copper(I) chloride, and stored at -30 °C until required. Toluene was distilled with sodium after refluxing overnight using benzophenone as an indicator. Triethylamine and 1,1,2-trichloro-trifluoroethane (Freon-113) were dried by distillation over CaH<sub>2</sub> and CaCl<sub>2</sub>, respectively. Dimethylchlorosilane was also purified by distillation. All reagents described above were purified under an argon atmosphere. Deionized water was used for all the experiments. Other chemicals were commercially obtained and used without further purification.

**Preparation and characterization of silica@PFA NPs.** 4,4'-azobis-(4-cyanopentanoic acid-(3'-chlorodimethylsilyl)propyl ester) (ADS) was prepared following the literature procedure for the hydrosilylation of 4-(3-allyloxycarbonyl-1-cyano-methyl-propyazo)-4-cyano-4-methyl-butyric acid allyl ester with dimethylchlorosilane and using hexachloroplatinic acid as the catalyst. Surface polymerization was carried out after immobilization of ADS on the silica nanoparticles, and subsequent radical polymerization with the FA monomer.<sup>[S1]</sup> Silica NPs were dispersed using an ultra-tip sonicator (Fisher Scientific, FB 705) operating at a power of 180–200 W for 30 s before use. Immobilization of the initiator onto silica was performed under an argon atmosphere by adding 1 g of ADS and 1 mL of triethylamine to 3 g of silica as a solution in 50 mL of dry toluene. After degassing at ca. 1 mbar until no gas evolution from the silica could be observed, the mixture was stirred for 24 h. The immobilized silica was extracted with toluene, methanol, and acetone, and dried under vacuum at  $10^{-2}$  mbar. Radical polymerization was carried out in neat FA monomer (initiator immobilized silica/FA = 1/20, w/w) at 60 °C under argon atmosphere after degassing by repeated freeze-thaw cycles. After polymerization was complete, the free polymer adsorbed on the nanoparticle surface was washed away in the repeated extraction cycles involving sonification in Freon-113 under reduced pressure and decantation using a high-speed refrigerated centrifuge (Supra 22K, Hanil).

Quantitative information about the graft densities of silica@PFA NPs was obtained by using a thermogravimetric analyzer (TGA, TA TGA 2950, 10 °C/min, N<sub>2</sub>). The thermal behavior of PFA attached to silica nanoparticles was observed by differential scanning calorimetry (DSC,

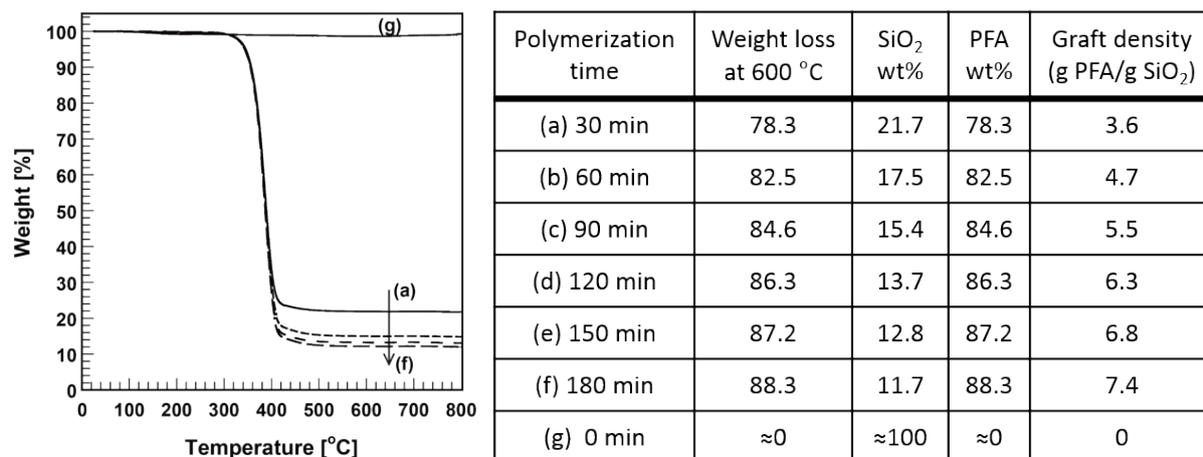
TA DSC Q1000, 10 °C/min, N<sub>2</sub>). X-ray photoelectron spectroscopy (XPS) was performed using a V.G. Scientific ESCALAB MK II spectrometer with an AlK $\alpha$  X-ray source (15 keV), a filament current of 20 mA, and a take-off angle of 90°. All binding energies in XPS measurements were referenced to the C1s peak for neutral carbon, which was assigned a value of 285.0 eV. The morphology and average particle sizes of the silica@PFA NPs were investigated using a high-resolution transmission electron microscope (HRTEM, Philips F20) operating at 200 keV. The samples for HRTEM observation were prepared by putting a drop of a diluted Freon-113 suspension (1 mg/100 mL) on carbon-coated Cu grids and allowing the sample to dry in air.

**Characterization and preparation of superhydrophobic surfaces.** The superhydrophobic surfaces were prepared by a very simple and convenient method of spray coating the silica@PFA NPs on an epoxy resin (IBL)-coated slide glass. The thermosetting epoxy resin (EP 1160, KCC) was coated on a clean glass slide (S-1111, Matsunami, 1 mm) using a spin coater (2000 rpm, 10 s). The superhydrophobic surface was obtained by spraying of the PFA/silica nanocomposite particles using an air atomizing nozzle (SU 11, Internal mix, Spraying Systems) above the substrate and curing for 12 h at 60 °C. AK-225 was used as the spraying solvent. The concentration and spraying time for all experiments were 0.5 wt% and 10 min, respectively. The thickness of the composite particle layer was ~150–200  $\mu$ m. The residual particles, not fixed on the surface, were thoroughly blown off using a clean air gun with a pressure of 5 kg<sub>f</sub>/cm<sup>2</sup>.

A scanning electron microscope (SEM, Leo 1455VP, K.E. Developments) equipped with a quadrant backscattered electron detector (type 225) was used to obtain images of the NP-coated surfaces. The micro roughness of the silica@PFA NP-coated slide glass was measured using SurfTest SV-402 (Mitutoyo). The measurements were performed at the speed of 1 mm/s with a resolution of 0.1  $\mu$ m and a Gaussian filter (PC50). The arithmetic mean deviation ( $R_a$ ), root-mean-square deviation ( $R_q$ ), maximum height of the profile ( $R_y$ ), and mean spacing of local peaks (S) were measured for estimating microroughness.

Contact angles were measured using an optical goniometer (DSA 100, Krüss) with 15  $\mu$ L of water and methylene iodide at 20 $\pm$ 1 °C. The wetting behavior of the silica@PFA NP-coated surfaces was investigated by contact angle measurements and estimation of the surface free energy. Contact angles were measured with water, methylene iodide, and hexadecane at five different points for each sample and the average values were calculated. The sliding angle measurement was done using DSA 100 (Krüss) with a tilting stage. Before each measurement,

the samples were blown with ionized air to eliminate static electricity on the surface.

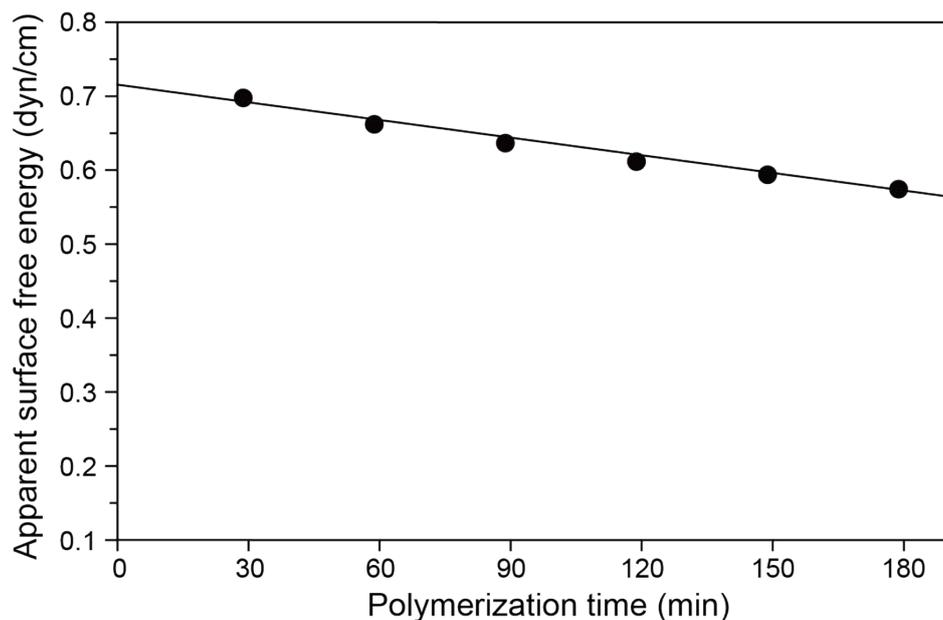


**Figure S1.** TGA curves (left) of silica@PFA NPs according to polymerization time and corresponding calculated graft densities (right): (a) 30 min, (b) 60 min, (c) 90 min, (d) 120 min, (e) 150 min, (f) 180 min, and (g) fumed silica. The silica@PFA NPs showed a significant weight loss from 400 °C, which could be attributed to polymer degradation.

The graft densities presented in Figure 1e were calculated from TGA data as shown in Figure S1. The total PFA content was determined from the mass loss occurring at 600 °C because pure PFA displayed ~100% mass loss at 600 °C. Therefore, the graft densities (Figure 1e) were calculated based on the “mass loss percentage (decomposition of surface-bound PFA)” divided by the “residual mass percent (silica component)” at 600 °C. The calculated graft densities are presented in the right panel in Figure S1.

Notably, there were no residual organic components such as that of PFA that was unattached to silica NPs in the TGA sample. This is because the synthesized NPs were washed thrice in the repeated extraction cycles after polymerization (i.e., sonification in Freon-113 under reduced pressure and decantation using a high-speed refrigerated centrifuge). Hence, such weight loss as shown in Figure S1 only occurred from PFA that covered the silica NPs.

We additionally carried out MALDI-TOF (Bruker Autoflex III, Bruker Daltonics) to measure the molecular weight of perfluorinated shell polymer. For this measurement, we first removed the silica from silica@PFA NPs by multiple washing and centrifugation processes with diluted HF solvent (concentration of 2.5 wt% in water). Subsequently, we dispersed the obtained PFA polymer in R113 solvent at a concentration of 0.1 wt% for the measurement. We used the DHB matrix for MALDI-TOF measurement. From the results, we found that the average molecular weight increased from 7883 Da to 11025 Da with increasing polymerization time from 60 min to 120 min.

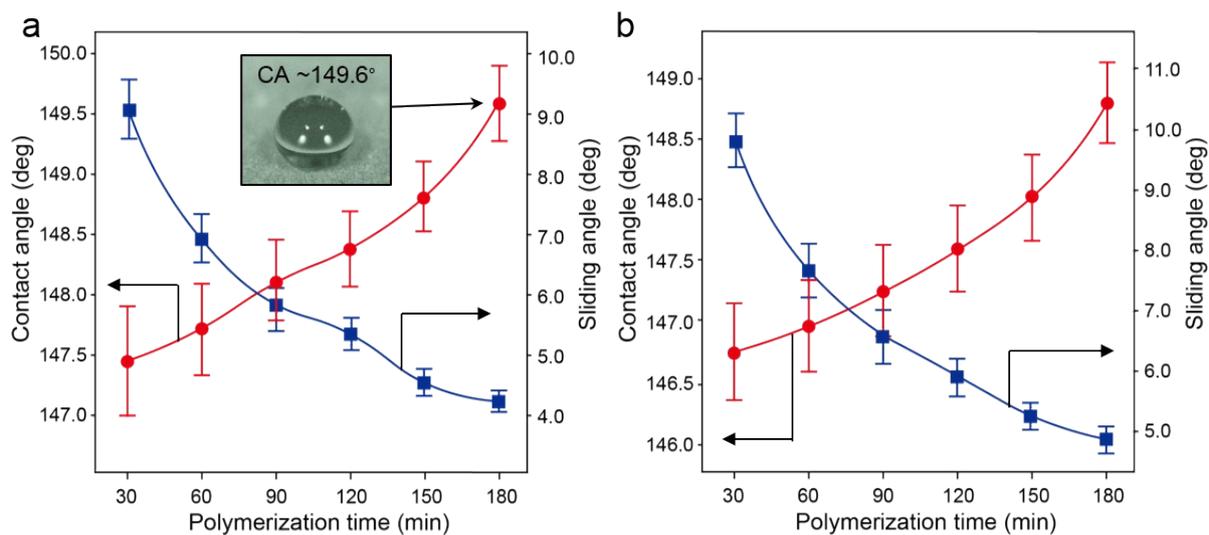


**Figure S2.** Variation of surface free energy as a function of polymerization time of silica@PFA NPs as calculated by Fowkes' equation.

Total surface free energies ( $\gamma$ ) and their polar ( $\gamma^p$ ) and dispersion ( $\gamma^d$ ) components were calculated by Fowkes' equation as follows:

$$\gamma_{SV} (1 + \cos \theta) = 2(\gamma_{SV}^d \gamma_{LV}^d)^{1/2} + 2(\gamma_{SV}^p \gamma_{LV}^p)^{1/2}$$

where p and d are the polar and dispersion components of each surface free energy,  $\theta$  is the contact angle, and  $\gamma_{SV}$ ,  $\gamma_{LV}$ , and  $\gamma_{SL}$  are interfacial tensions at the solid-vapor, liquid-vapor, and solid-liquid interfaces, respectively.<sup>[S2]</sup> The calculated values of the apparent surface free energies decreased with the increasing polymerization time, and showed an extremely low value of less than 0.58 dyn/cm at the polymerization time of 180 min.



**Figure S3.** Contact and sliding angles of (a) methylene iodide and (b) hexadecane droplets on silica@PFA NP-coated surfaces as a function of surface polymerization time. Inset in (a): Photograph of methylene iodide droplet on silica@PFA NPs (polymerization time of 180 min)-coated surface.

## References

- [S1] Prucker, O.; Rhe, J. *Macromolecules* **1998**, 31, 592.  
 [S2] Fowkes, F. M. *Ind. Eng. Chem.* **1964**, 56, 40.