Supplementary Information

Strategy toward fluorinated polyhedral oligomeric silsesquioxane wrapping nanoparticles for superomniphobic surfaces

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Experimental

Synthesis of poc-F_{13}POSS-2OH

In a typical 100-mL round-bottom flask filling with 20 mL THF and 0.2 mL H_2O, 2.55 g FAS-13 and 200 mg NaOH was added in sequence, followed by magnetic stirring and refluxing at 70 ℃ for 5 h. Then, the round-bottom flask was kept at room temperature for 12 h. A sticky product was obtained after solvent removal in a rotary evaporator at 50~60 ℃ and washing with 20 mL THF for 3 times at room temperature. The washing with THF as a purification step was necessary for separating side-products. The high-purity sticky matter (the yield exceeded 85%), *i.e.*, poc-F_{13}POSS-2OH, was yellowish and stored in absolute ethanol (0.11g ml^{-1}).

Preparation of poc-F_{13}POSS-wrapped materials

In a typical 100-mL round-bottom flask filling with 50 ml absolute ethanol, 1.6 g materials (*e.g.*, SiO_2 nanoparticles, TiO_2 nanoparticles , ATP (attapulgite) nanorods, GO (graphene oxide) nanosheets, PS microspheres) and 5 mL poc-F_{13}POSS-2OH (0.11g

ml^{-1}) was added and followed by magnetic stirring (1000 rpm) for 10 min and ultrasonication for 5 min. With a constant-pressure dropping funnel, 10 mL HCl (0.1 M) was added dropwise (a drop per 10 s) under magnetic stirring (500 rpm). The protonation was completed after 5 h incubation at room temperature. Through a 12 h drying, poc-F_{13}POSS-wrapped materials were yielded.

Construction of poc-F_{13}POSS-wrapped material-based superomniphobic surfaces

In a 20 ml of ordinary engineering resin system (*e.g.*, polyacrylate resins, polyurethane resins, organic silicon resins) with a typical solid content of 5%, 1.5 g of poc-F_{13}POSS-wrapped material (*e.g.*, poc-F_{13}POSS-wrapped SiO_2 nanoparticles and poc-F_{13}POSS-wrapped SiO_2 microparticles) were added and dispersed by magnetic stirring at 1500 rpm for 10 min. After 30 min standing for spontaneous removal of bubbles, a stable suspension was born without any assistance of additives. The suspension was spray-coated on a majority of usual engineering substrates (*e.g.*, glass sheets, metal sheets, plastic sheets, ceramic sheets and even paper sheets). After air-drying at room temperature, a superomniphobic coating with 15 μm in thickness was fabricated.

Characterization and tests

Characterization-1: NMR spectroscopy (Magritek GmbH Spinsolve 60, Germany) was utilized to qualitatively characterize poc-F_{13}POSS-2OH (^{1}H-NMR: 500 MHz, C_6D_6/C_6F_6; ^{29}Si-NMR: 400 MHz, C_2D_6O; ^{19}F-NMR: 471 MHz, CD_4O). The EDX spectroscopy (Oxford INCA, Britain), CHN analyzer (PerkinElmer 2400 Series II, USA) and Fourier-transform infrared (FTIR) spectroscopy (Bruker Vector 33, Germany) were applied to analyze the chemical composition of as-obtained products. Both FE-SEM (ZEISS Ultra 55, Germany) and TEM (JEOL JEM-2100F, Japan) were employed to probe the topography of specimens.

Characterization-2 (contact angle measurement): The contact angle measurements (including static contact angles, roll-off angles, advancing contact angles) of specimens were performed using a surface contact angle analyzer (KSV Helsinki CAM200, Finland) with a 2 μL of liquid droplet at ambient temperature. The liquid droplets included liquids with various surface tension (Table S1) and kinematic viscosity (dimethyl silicon oil), and a series of non-Newtonian liquids. The non-Newtonian

liquids covered milk, tomato sauce, soy sauce, egg white, goat blood, silicone oil, crude oil, sodium alginate (2 wt%) in water, chitosan (2 wt%) in acetic acid solution (1 wt%), PMMA (polymethyl methacrylate, 10 mg mL^{-1}) in DMF (dimethyl formamide), PMMA (10 mg mL^{-1}) in NMP (methyl pyrrolidone), PS (polystyrene, 10 mg mL^{-1}) in DMF, PS (10 mg mL^{-1}) in NMP, PVDF (polyvinylidene fluoride, 10 mg mL^{-1}) in DMF, PVDF (10 mg mL^{-1}) in NMP, PVDF-HFP (poly(vinylidene fluoride-co-hexafluoropropylene, 10 mg mL^{-1}) in DMF, PVDF-HFP (10 mg mL^{-1}) in NMP, PVP (polyvinyl pyrrolidone, 10 mg mL^{-1}) in DMF, PVP (10 mg mL^{-1}) in NMP.

Characterization-3 (adhesive force assessment): The adhesive force of water droplet on superomniphobic surfaces was assessed on a high-sensitivity micro-electromechanical balance system (Dataphysics DCAT11, Germany) by the Du Noüy ring method. A water droplet (*ca.* 5 μL) was suspended with a metal ring. The specimens placed on a balance table were approached at a speed of 0.01 mm s^{-1} until the specimen surfaces contacted the water droplet. Then the specimens were retracted at the same speed until the water droplet left their surfaces. In this retraction process, the force was gradually increased and sharply decreased to 0 after it reached its maximum (the moment of droplets were pulled away from surfaces).

Drag reduction of liquid flowing test: The plastic pipes were parallelly cut open to expose their inner space. Then, the coatings (*i.e.*, organic silicon resin coatings, poc-F_{13}POSS-wrapped SiO_2 nanoparticle-based superomniphobic coatings, and poc-F_{13}POSS-wrapped SiO_2 microparticle-based superomniphobic coatings) were introduced onto the partially open pipes. An initial velocity V_0 of water droplet with known weight was acquire by making it slide down a superomniphobic surface-decorated pipe with a specific tilting angle and length. The water droplet with V_0 was applied to slide on another horizontal pipe (decorated with one of aforementioned three coatings) until it stopped (final velocity $V_t = 0$), the acceleration a of water droplets and coefficients of friction μ of pipe surfaces could be calculated.

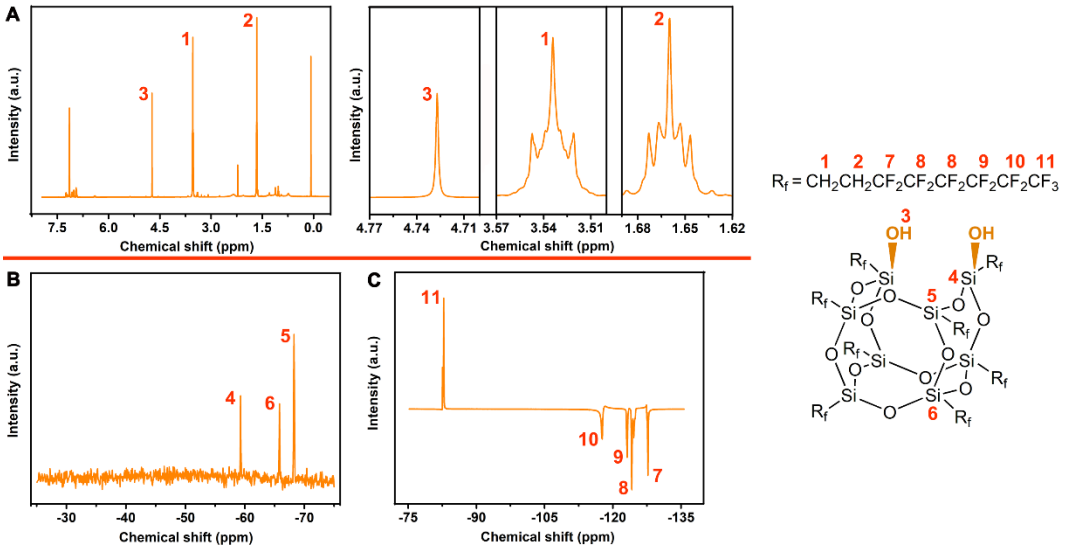

Fig. S1 (A) ^{1}H-NMR, (B) ^{29}Si-NMR and (C) ^{19}F-NMR spectra of poc-F$_{13}$POSS-2OH. In the ^{1}H-NMR spectrum, the δ 4.73 (2H), 3.53 (16H) and 1.66 (16H) was attributed to the protons of -OH at site-3, -CH$_2$ at site-1 and -CH$_2$ at site-2, respectively (δ 7.15: C$_6$D$_6$-solvent; δ 2.21: ethyl acetate-contaminant; δ 0.07: tetramethylsilane-internal reference). The protons of -CH$_2$ at both site-1 and at site-2 expressed multiple resonance signals, on account of the visible cracking affected by both adjacent -CH$_2$ and -CF$_2$. In the ^{29}Si-NMR spectrum, δ -59.27 (2Si), -65.83 (2Si) and -68.25 (4Si) could be assigned to the Si at site-4, site-6 and site-5, respectively. In the ^{19}F-NMR spectrum, δ -82.79 (3F), -117.62 (2F), -123.15 (2F), -124.18 (4F), -127.72 (2F) corresponded to the F at site-11, site-10, site-9, site-8 and site-7.

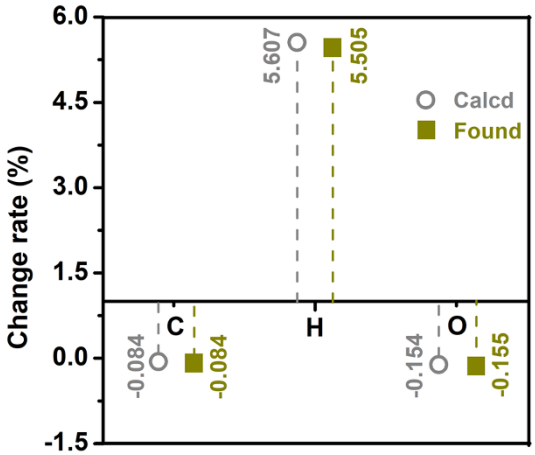

Fig. S2 Plot of element change rate of poc-F$_{13}$POSS-2OH$_2^+$ relative to poc-F$_{13}$POSS-2OH.

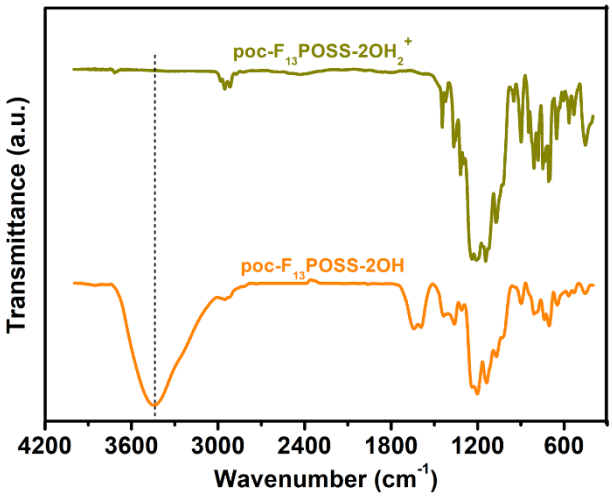

Fig. S3 FTIR spectra of poc-F_{13}POSS-2OH and poc-F_{13}POSS-$2OH_2^+$. In poc-F_{13}POSS-2OH profile, a band at *ca.* 3420 cm^{-1} was attributed to stretching vibration of Si-OH. In poc-F_{13}POSS-$2OH_2^+$ profile, the band at 3420 cm^{-1} disappeared, which was closely related with -OH protonation.

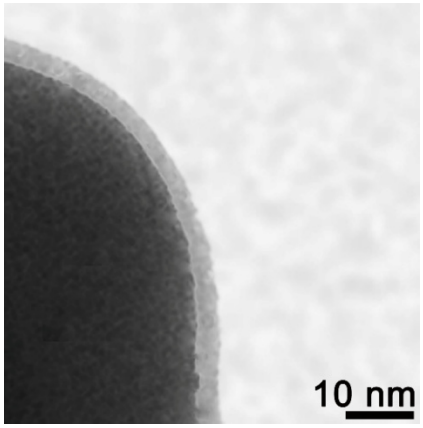

Fig. S4 TEM image of poc-F_{13}POSS-wrapped ZrO_2 nanoparticle.

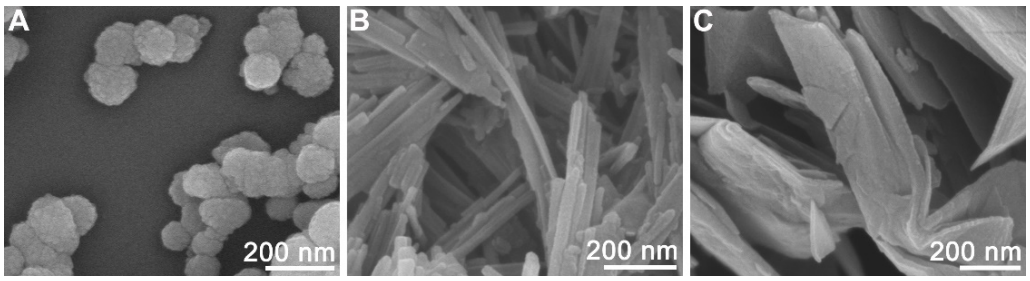

Fig. S5 FE-SEM images of (A) ZrO_2 nanoparticles, (B) ATP nanorods and (C) GO nanosheets.

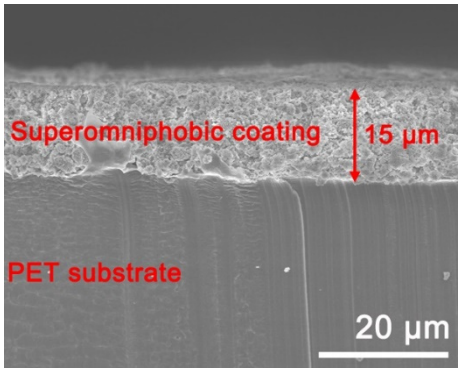

Fig. S6 FE-SEM image of cross-sectional poc-F_{13}POSS-wrapped SiO_2 nanoparticle-based coatings on a polyethylene terephthalate (PET) substrate.

Table S1 List of liquids with various surface tension.

Liquid	Surface tension (mN m^{-1})	Liquid	Surface tension (mN m^{-1})
Hydrogen peroxide	79.7	n-hexadecane	27.5
Water	72.3	Diesel	26.8
Glycerol	63.4	n-dodecane	25.4
Diiodomethane	50.8	Cyclohexane	24.3
Ethylene glycol	48.2	n-decane	23.8
Dimethyl sulfoxide	42.7	Polydimethylsiloxane	19.8
N,N-dimethyl formamide	35.6		

Table S2 List of liquids (with various surface tension) *versus* their roll-off angles, advancing contact angles and contact angle hysteresis on poc-F_{13}POSS-wrapped SiO_2 nanoparticle-based surfaces.

Liquid	Roll-off angle (°)	Advancing contact angle (°)	Contact angle hysteresis (°)
Hydrogen peroxide	0.5±0.3	157.0±0.2	1.4±0.5
Water	0.4±0.2	155.9±0.5	3.4±0.6
Glycerol	5.2±1.5	154.9±1.0	6.5±2.1
Diiodomethane	1.6±0.9	153.5±1.1	7.0±1.7
Ethylene glycol	2.3±1.0	155.5±1.0	4.4±1.2
Dimethyl sulfoxide	2.5±0.5	153.6±0.8	5.5±2.4
N,N-dimethyl formamide	7.1±2.4	154.0±1.4	7.2±2.7
n-hexadecane	2.8±0.7	153.0±0.5	3.5±0.7
Diesel	4.2±1.0	153.1±0.3	8.3±1.4
n-dodecane	2.7±0.8	153.6±0.9	5.6±1.9
Cyclohexane	3.6±0.9	151.6±0.3	4.6±1.0
n-decane	1.2±0.6	152.4±0.7	5.2±1.8
Polydimethylsiloxane	22.8±3.9	143.6±1.3	10.3±1.7

Table S3 List of kinematic viscosity of dimethyl silicone oil *versus* their roll-off angles on poc-F_{13}POSS-wrapped SiO_2 nanoparticle-based surfaces.

Kinematic viscosity of dimethyl silicone oil ($mm^2 s^{-1}$)	Roll-off angle (°)
1000	19.1±2.4
10000	22.6±7.4
50000	26.2±5.9
100000	24.5±3.1
500000	29.7±3.5
1000000	28.2±2.1

Table S4 List of non-Newtonian liquid *versus* their roll-off angles on poc-F_{13}POSS-wrapped SiO_2 nanoparticle-based surfaces.

Non-Newtonian liquid	Roll-off angle (°)	Non-Newtonian liquid	Roll-off angle (°)
Milk	1.1±0.6	PMMA in DMF	2.6±0.9
Tomato sauce	1.8±1.0	PMMA in NMP	2.6±0.7
Soy sauce	0.5±0.1	PS in DMF	2.0±1.6
Egg white	1.8±0.7	PS in NMP	2.0±0.5
Goat blood	0.8±0.4	PVDF in DMF	3.4±1.0
Silicone oil	22.6±7.4	PVDF in NMP	1.3±0.6
Crude oil	30.8±3.1	PVDF-HFP in DMF	3.3±1.2
Sodium alginate in water	1.0±0.4	PVDF-HFP in NMP	4.0±0.9
Chitosan in HAc solution	1.9±1.3	PVP in DMF	2.7±0.5
		PVP in NMP	1.5±0.8

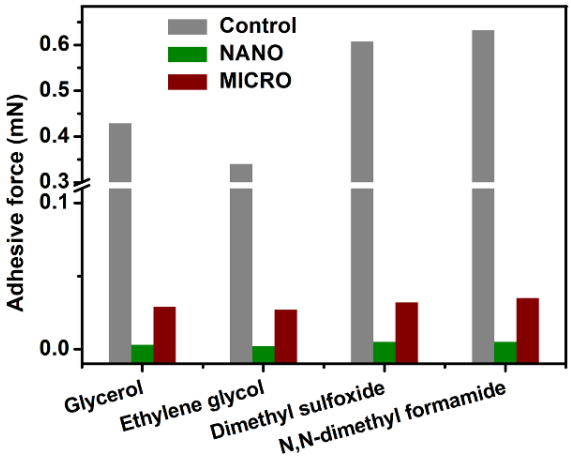

Fig. S7 Plot of adhesive force of contacted glycerol, ethylene glycol, dimethyl sulfoxide and N,N-dimethyl formamide droplets. The values of adhesive forces were acquired

from force-distance curves recording the liquid droplets contacting and leaving the three surfaces.