Supporting Information for

Universal Self-assembly of Organosilanes with Long Alkyl Groups into Silicone Nanofilaments

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Materials

Glass slides (Menzel, Braunschweig, Germany) of 22 mm × 50 mm (1#) were used as the substrates. Tetraethoxysilane (TEOS, 99.9%), tetrachlorosilane (TCS, 99%), *n*-octyltriethoxysilane (OTES, 97%), *n*-dodecyltriethoxysilane (DDTES, 95%), *n*-hexadecyltriethoxysilane (HDTES, 95%), *n*-octadecyltriethoxysilane (ODTES, 95%), 1*H*,1*H*,2*H*,2*H*-perfluorooctyltrichlorosilane (PFOTS, 97%), 1*H*,1*H*,2*H*,2*H*-perfluorodecyltrichlorosilane (PFDTS, 97%), 1*H*,1*H*,2*H*,2*H*-perfluorodecyltriethoxysilane (PFDTES, 97%) and 1H,1H,2H,2H-perfluorotetradecyltriethoxysilane (PFTDTES) were purchased from Gelest. 1*H*,1*H*,2*H*,2*H*-perfluorododecyltrichlorosilane (PFDDTS, 97%) was purchased from Sigma-Aldrich. All the silanes were handled under water free conditions and used without further purification. Toluene (99.85%, extra dry over molecular sieve) was purchased from Acros Organics. Diiodomethane, mineral oil, *n*-dodecane and *n*-decane were purchased from China National Medicines Corporation Ltd. The cotton (211#), polyester/cotton (65/35, 213#), wool (402#), silk (403#), viscose (404#), polyacrylnitrile

(408#) textiles were kindly supplied by EMPA Testmaterials AG, Switzerland. Detailed information for these fabrics can be seen from our previous paper.[1] The commercial polyester textile, wood sheet, polyethylene sheet and copper sheet were also used as substrates.

Table S1. CA and SA of water on the SNs coatings prepared using the $RSiCl_3$/TEOS precursors. The reaction conditions were optimized using the PFDTS/TEOS precursor and applied to the others (0.030 mmol of $RSiCl_3$, 0.45mmol of TEOS, C_{water} = 72ppm).

$RSiCl_3$	SNs?	CA/ °	SA/ °
PFDTS	Yes	171.7 ±1.7	0.2 ±0.3
PFDDTS	Yes	79.4 ±1.1	-

Table S2. CA and SA of water on the SNs coatings prepared using the $R'Si(OEt)_3$/TCS precursors. The reaction conditions were optimized using the HDTES/TCS precursor and applied to the others (0.068 mmol of $R'Si(OEt)_3$, 0.13mmol of TCS, C_{water} = 181 ppm).

$R'SiCl_3$	SNs?	CA/ °	SA/ °
OTES	Yes	134.0 ±0.9	-
DDTES	Yes	172.4 ±1.5	4.3 ±0.6
HDTES	Yes	174.7 ±3.2	1.3 ±0.6
ODTES	Yes	172.2 ±0.7	1.2 ±0.3
PFDTES	Yes	169.8 ±2.7	3.7 ±2.1
PFTDTES	Yes	172.8 ±1.4	0.3 ±0.3

Table S3. CA and SA of water on the SNs coatings prepared using the $R''SiCl_3$/TCS precursors. The reaction conditions were optimized using the PFOTS/TCS precursor and applied to the others (0.065 mmol of $R''SiCl_3$, 0.21mmol of TCS, C_{water} = 200ppm).

$R''SiCl_3$	SNs?	CA/ °	SA/ °
PFOTS	Yes	175.2 ±0.8	0.7 ±0.3
PFDTS	Yes	172.8 ±2.5	4.7 ±1.5
PFDDTS	Yes	172.1 ±1.2	2.2 ±0.3

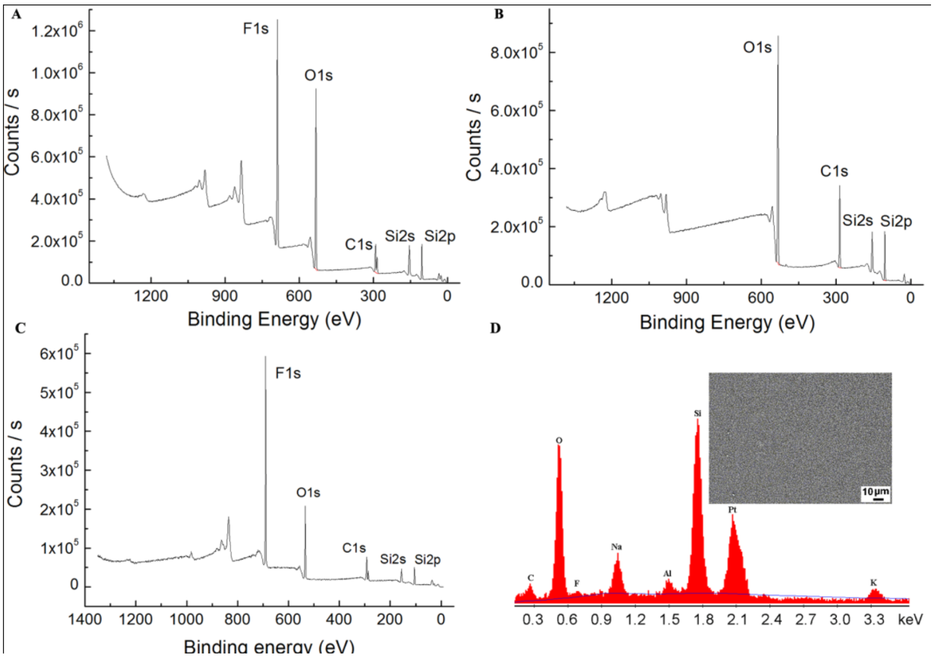

Figure S1. XPS spectra of the (A) PFDDTS/TEOS, (B) ODTES/TCS, (C) PFOTS/TCS and (D) EDAX spectrum of the PFOTS/TCS SNs coatings on glass slide.

Table S4. XPS analysis of the surface elemental composition of the PFDDTS/TEOS, ODTES/TCS and PFOTS/TCS SNs coatings.

PP At. %	Precursors		
	PFDDTS/TEOS	ODTES/TCS	PFOTS/TCS
F1s	30.51	0	50.69
O1s	34.09	38.02	18.05
C1s	14.82	25.27	18.76
Si2p	20.58	36.70	12.5
Molar ratio of alkylsilane to TEOS (or TCS)	1:15.7	1:25	1:4.3

Effects of precursor composition and C_{water} on the Growth of SNs

The effects of precursor composition and C_{water} on the growth of the PFDDTS/TEOS, PFTDTES/TCS and PFOTS/TCS SNs were investigated in this section. The water content needed for precursor (red lines in Figures S2C, S3C, S4C, S6C, S8C, S10C, S12C, S14C and S16C) was calculated considering complete hydrolysis of the precursor injected into the reaction chamber. The water content needed for the relatively more reactive component in the precursor (blue lines in Figures S2C, S3C, S4C, S6C, S8C, S10C, S12C, S14C and S16C) was calculated considering complete hydrolysis of it and no hydrolysis of the other one.

(1) Growth of the PFDDTS/TEOS SNs

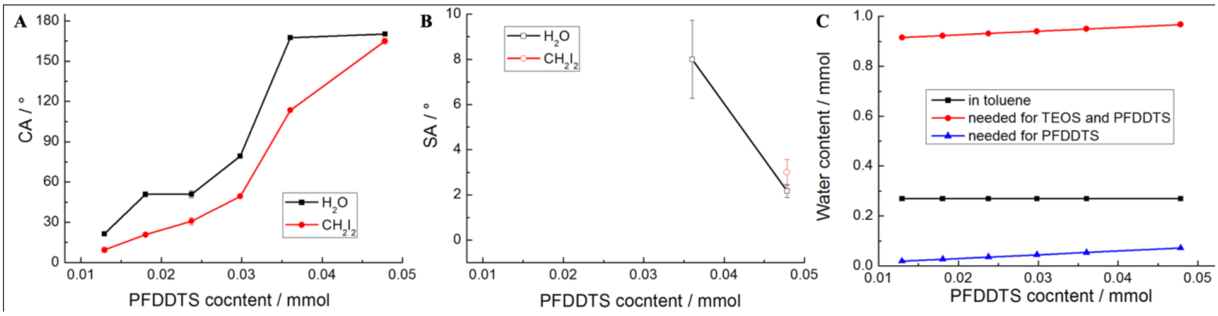

Figure S2. Variation of (A) CA and (B) SA of water and CH_2I_2 on the PFDDTS/TEOS coated glass slides as well as (C) water content needed for the hydrolysis of PFDDTS and TEOS with PFDDTS content (0.45mmol of TEOS, C_{water} = 72ppm).

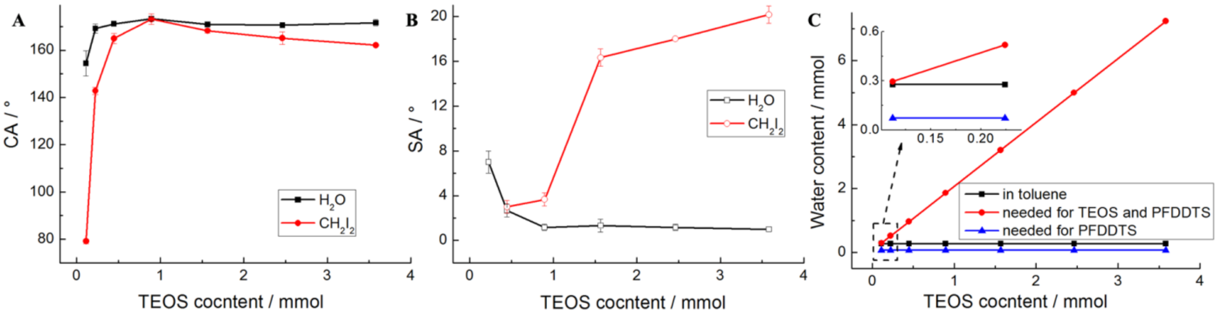

Figure S3. Variation of (A) CA and (B) SA of water and CH_2I_2 on the PFDDTS/TEOS coated glass slides as well as (C) water content needed for the hydrolysis of PFDDTS and TEOS with TEOS content (0.048mmol of PFDDTS, C_{water} = 72ppm).

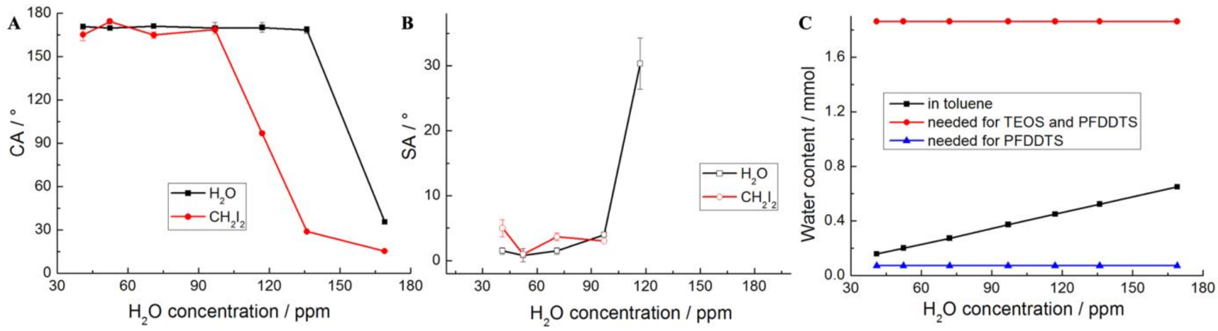

Figure S4. Variation of (A) CA and (B) SA of water and CH_2I_2 on the PFDDTS/TEOS coated glass slides as well as (C) water content needed for the hydrolysis of PFDDTS and TEOS with C_{water} (0.048mmol of PFDDTS, 0.90mmol of TEOS).

(2) Growth of the PFTDTES/TCS SNs

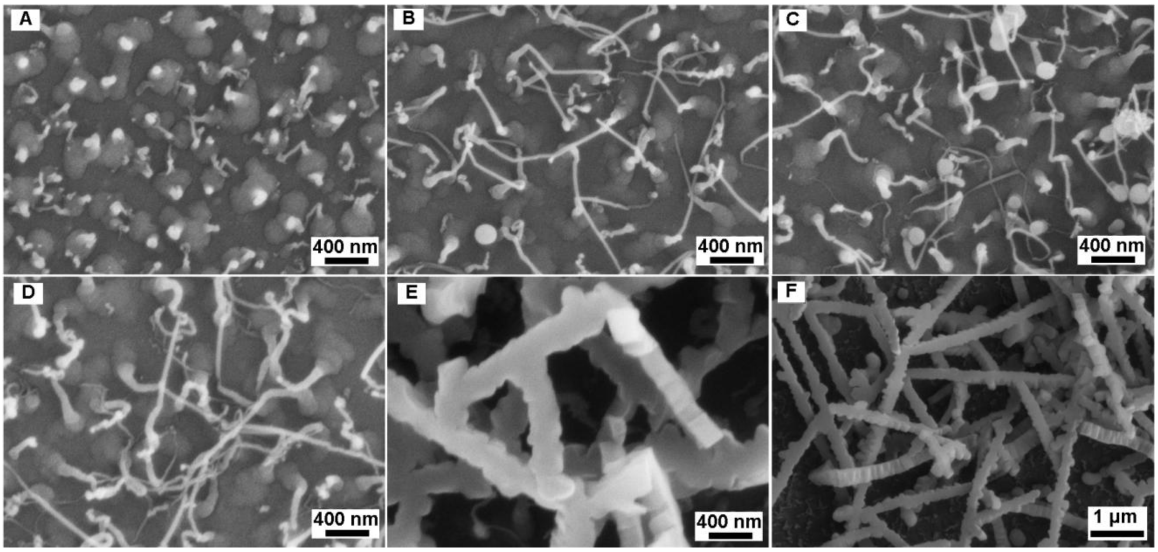

Figure S5. SEM images of the PFTDTES/TCS coated glass slides with a PFTDTES content of (A) 0.022, (B) 0.030, (C) 0.038, (D) 0.046 and (E, F) 0.053 mmol (0.07mmol of TCS, C_{water} = 162ppm).

Once injected into toluene, TCS will hydrolyze first and the released HCl will catalyze the hydrolysis of PFTDTES and their copolymerization. The water content in toluene is enough for the complete hydrolysis of both PFTDTES and TCS in the range of PFTDTES content, TCS content and water concentration investigated (Figures S6C, S8C and S10C). The effects of PFTDTES content, TCS content and C_{water} on growth of the PFTDTES/TCS SNs and their wettability were studied in this section.

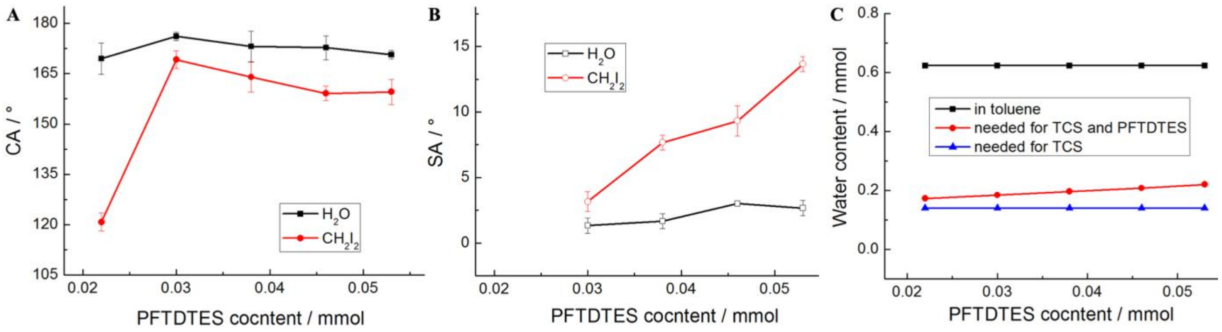

Figure S6. Variation of (A) CA and (B) SA of water and CH_2I_2 on the PFTDTES/TCS coated glass slides as well as (C) water content needed for the hydrolysis of PFTDTES and TCS with PFTDTES content (0.07mmol of TCS, C_{water} = 162ppm).

PFTDTES plays an important role in the growth of the PFTDTES/TCS SNs. Without PFTDTES, TCS could only form dense nano-islands on glass slide (Figure S18B). Once trace amount of PFTDTES (0.022mmol) was added into 80 mL of toluene, the asymmetric growth of PFTDTES/TCS was observed (Figure S5A). The root of the SNs and very short SNs can be seen clearly. The aspect ratio of the PFTDTES/TCS SNs evidently increases with increasing the PFTDTES content to 0.030mmol (Figure S5B). No obvious change of surface morphology was observed with further increasing the PFTDTES content to 0.046mmol. However, new quadrangular nano-prisms with a diameter of 220~260nm and a length of several micrometers were formed on top of the SNs when the PFTDTES content reaches 0.053mmol (Figure S5E-F). These nano-prisms should be attributed to the condensation of excess PFTDTES catalyzed by HCl. Two surfaces of the prisms are flat, whereas the other two surfaces are serrated. The CA of water remained almost constant (CA = 169 ° ~ 173 °) in the range of PFTDTES content studied (Figure S6). The CA of CH_2I_2 increases to 169.2 ° with increasing PFTDTES content to 0.030mmol, and then gradually decreases to 159.6 ° with further increasing PFTDTES content to 0.053 mmol. The droplets of water and CH_2I_2 are sticky on the coatings when the PFTDTES content is less than 0.030mmol. The SA of water remained in the range of 2 ° to 4.5 °, whereas the SA of CH_2I_2 gradually increases with increasing the PFTDTES content from 0.030 to 0.053mmol.

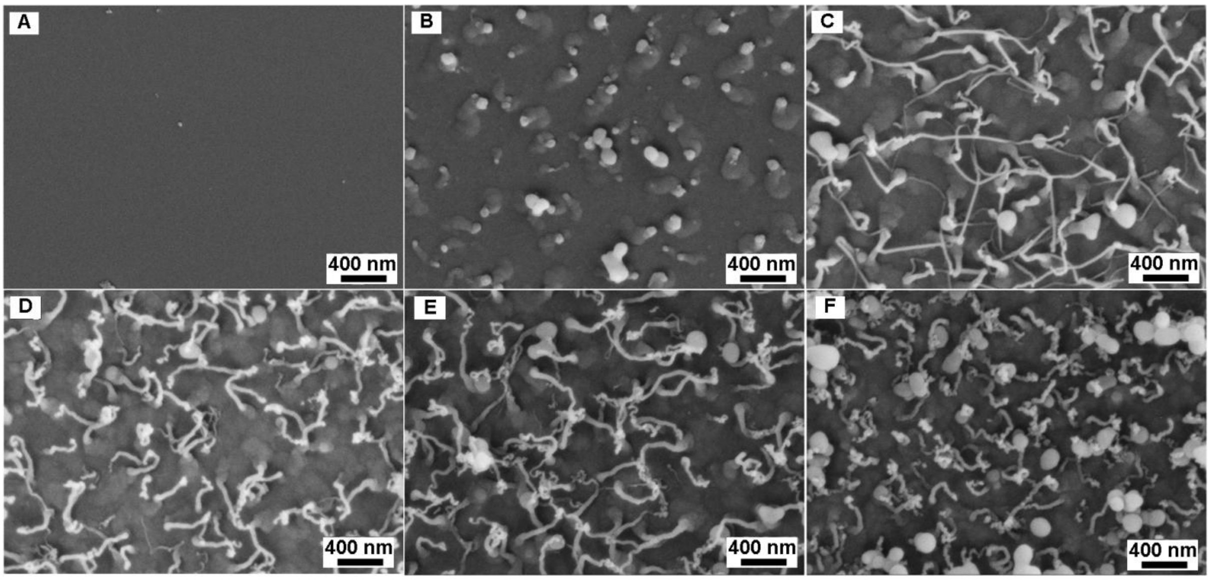

Figure S7. SEM images of the PFTDTES/TCS coated glass slides with a TCS content of (A) 0, (B) 0.035, (C) 0.052, (D) 0.070, (E) 0.087 and (F) 0.105 mmol (0.030mmol PFTDTES, C_{water} = 162ppm).

TCS is necessary for the growth of the PFTDTES/TCS SNs. Without TCS, we cannot get anything on glass slide (Figure S7A). A lot of SNs seeds were successfully grown onto glass slide after 0.035mmol of TCS was mixed with PFTDTES as the precursor (Figure S7B). The aspect ratio of the SNs increases evidently with increasing the TCS content to 0.052mmol. No obvious change on surface morphology was observed with further increasing the TCS content to 0.087mmol. However, the SNs become smaller and a lot of nanoparticles appear when the TCS content reaches 0.105mmol (Figure S7F). This is because the content of PFTDTES is insufficient in regulating hydrolysis and condensation of so much TCS. The variation of CA and SA of water and CH_2I_2 fits very well with the growth of SNs (Figure S8). The appearance of the nanoparticles has no influence on the CA and SA of water and CH_2I_2.

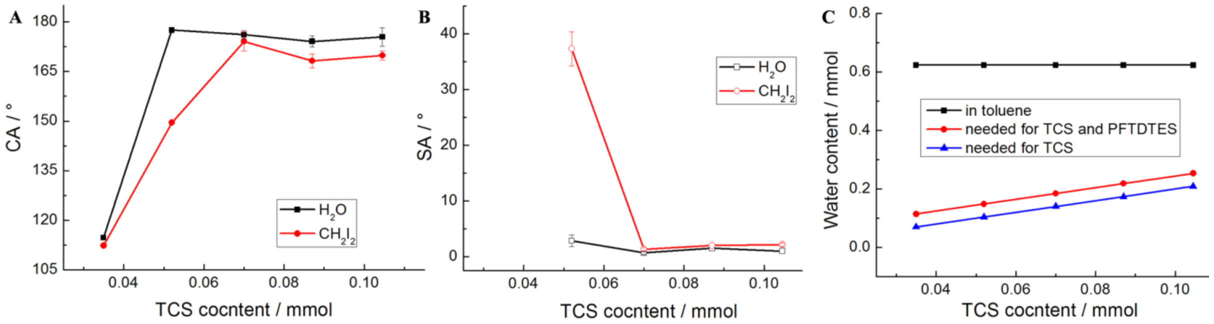

Figure S8. Variation of (A) CA and (B) SA of water and CH_2I_2 on the PFTDTES/TCS coated glass slides as well as (C) water content needed for the hydrolysis of PFTDTES and TCS with TCS content (0.030mmol PFTDTES, C_{water} = 162ppm).

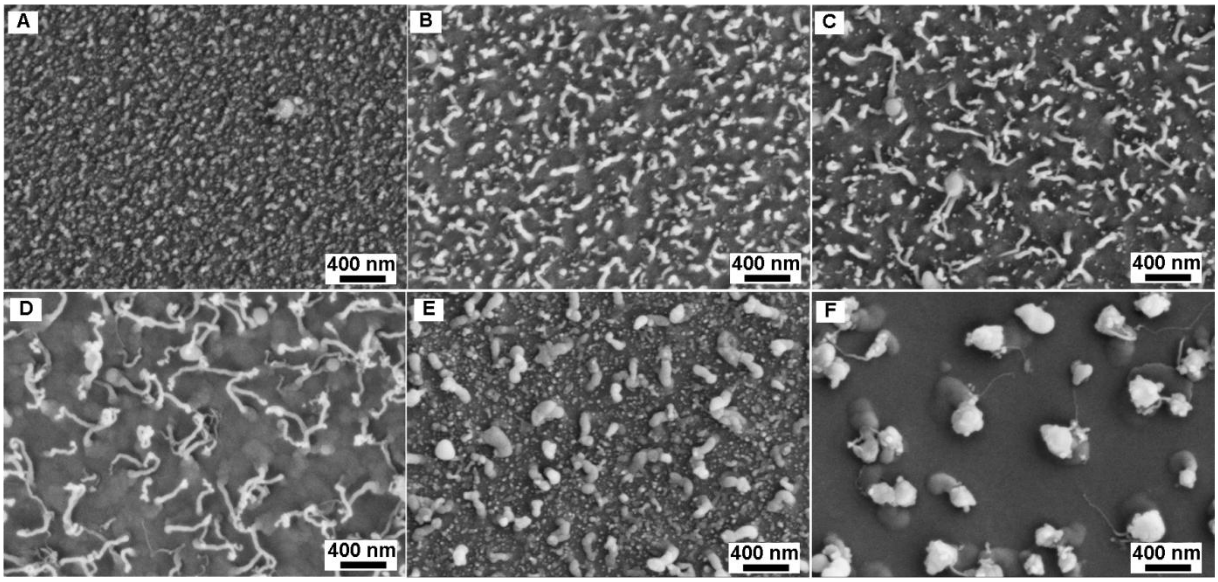

Figure S9. SEM images of the PFTDTES/TCS coated glass slides with a C_{water} of (A) 84, (B) 117, (C) 134, (D) 162, (E) 195 and (F) 230 ppm (0.030mmol PFTDTES, 0.07mmol TCS).

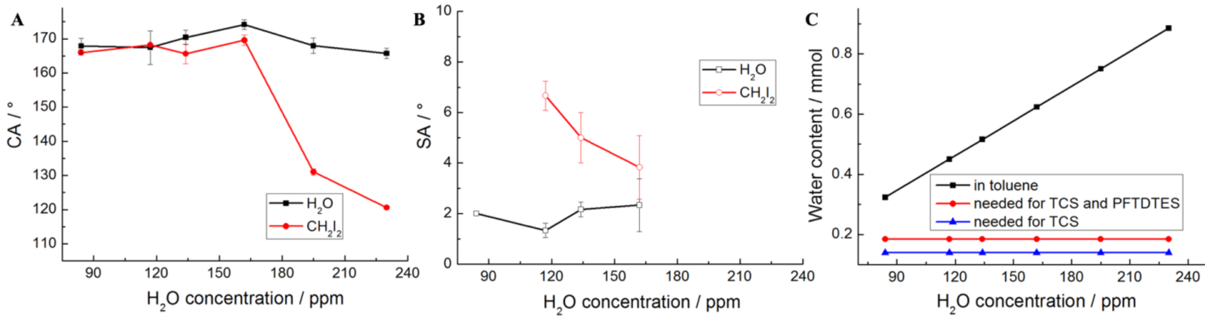

Figure S10. Variation of (A) CA and (B) SA of water on the PFTDTES/TCS coated glass slides as well as (C) water content needed for the hydrolysis of PFTDTES and TCS with C_{water} (0.030mmol PFTDTES, 0.07mmol TCS).

The influence of C_{water} on growth of the PFTDTES/TCS SNs was shown in Figure S9. The SNs can only be formed at proper C_{water}. At C_{water} = 84ppm, the surface morphology (Figure S9A) is very similar to that coated with TCS (Figure S18B) and the SNs are too short to be seen clearly. The reactivity of PFTDTES is low compared to TCS and its hydrolysis is slow at such low C_{water}. Consequently, TCS quickly hydrolyzed and condensed on glass slide, whereas PFTDTES cannot participate in forming the reactive components in time. Thus, PFTDTES has no chance to regulate hydrolysis and condensation of TCS. However, the coating is superhydrophobic with very low SA because of anchoring of PFTDTES onto the condensed TCS. The asymmetric growth was observed when C_{water} increases to 117ppm and the SNs are still short until C_{water} increases to134ppm. The SNs with high aspect ratio were prepared at C_{water} = 162ppm. At proper C_{water}, PFTDTES hydrolyzes quickly and more PFTDTES participates in forming the reactive components, which regulate the hydrolysis and condensation of TCS effectively. However, the SNs become shorter and their diameter increases with further increasing C_{water} to 195ppm. The SNs failed in elongation and only very big SNs roots can be seen when C_{water} reaches 230ppm.

(3) Growth of the PFOTS/TCS SNs

The effects of PFOTS content on surface morphology and wetting behaviors of the PFOTS/TCS SNs coatings are shown in Figures S11 and S12. When the PFOTS content is 0.032mmol, the glass slide is coated with aggregated particles and sparse SNs. This is because the PFOTS content is insufficient and can only induce a part of TCS growing into SNs. The surface is perfectly superhydrophobic (ultra high CA and low SA) and oleophobic although only sparse SNs are grown on it. With increasing PFOTS content to 0.065mmol, the SNs grow better and the surface is covered with a uniform layer of SNs, which is responsible for the excellent superamphiphobicity. The SNs tend to aggregate together and even gradually disappear with further increasing PFOTS content to 0.178mmol. As discussed above, PFOTS induces asymmetric hydrolysis of TCS and finally generates SNs. When the PFOTS content is over the optimal content, it will seriously restrict polymerization of TCS and the elongation of the SNs is stopped earlier, which should be the main reason for the aggregation and even disappearance of the SNs.

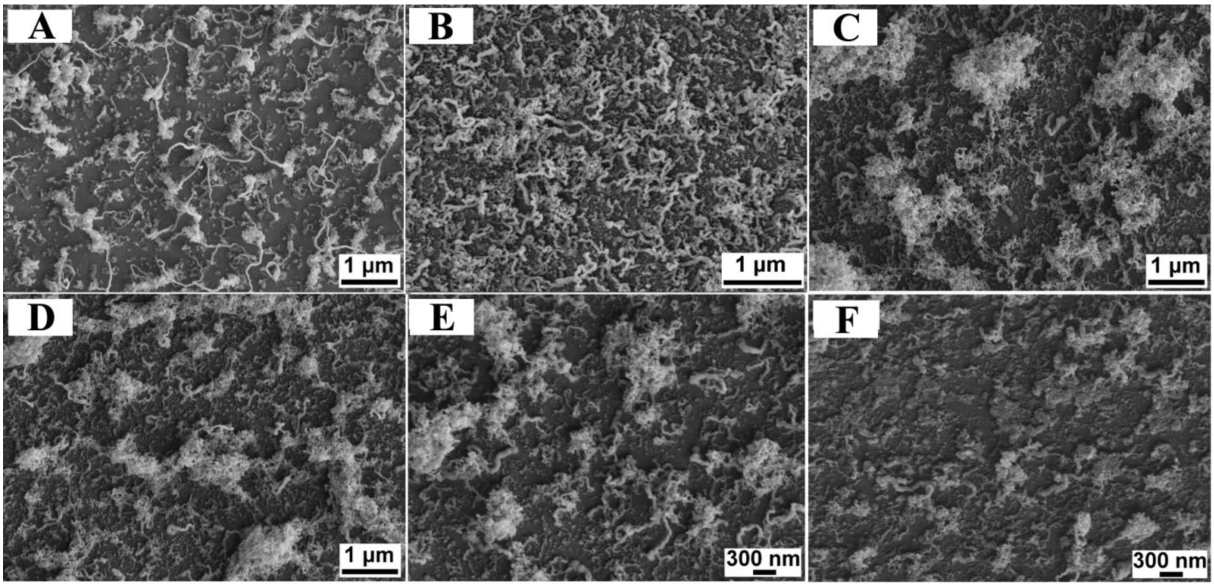

Figure S11. SEM images of the PFOTS/TCS coated glass slides with a PFOTS content of (A) 0.032, (B) 0.065, (C) 0.081, (D) 0.097 and (E) 0.130 and (F) 0.178 mmol (0.21mmol of TCS, C_{water} = 208ppm).

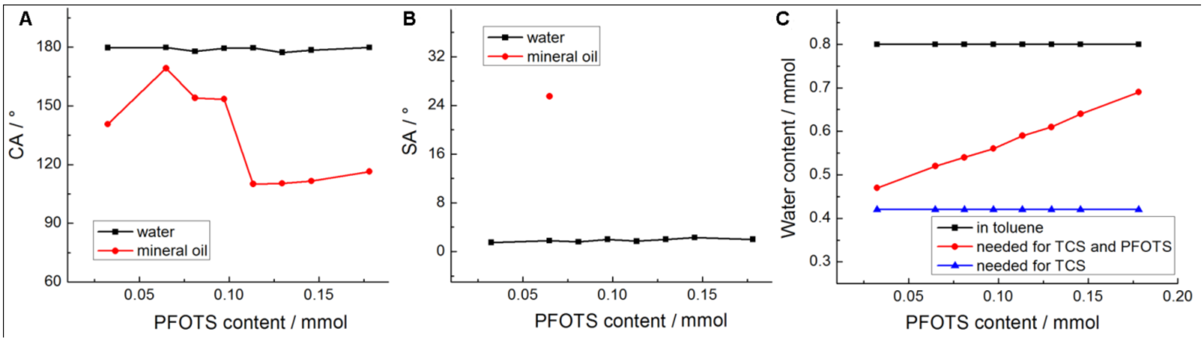

Figure S12. Variation of (a) CA and (b) SA of water and mineral oil on the PFOTS/TCS coated glass slide as well as (C) water content needed for the hydrolysis of PFOTS and TCS with PFOTS content (0.21mmol of TCS, C_{water} = 208ppm).

Table S5. XPS analysis of the surface elemental composition of the PFOTS/TCS coatings with different PFOTS content.

PP At. %	PFOTS content / mmol		
	0.032	0.065	0.176
F1s	45.78	50.69	45.86
O1s	21.45	18.05	22.46
C1s	18.17	18.76	18.61
Si2p	14.6	12.5	13.07
Molar ratio of PFOTS to TCS	1:5.4	1:4.3	1:4.6

The effects of TCS content on surface morphology and wetting behaviors of the SNs coatings are shown in Figures S13 and S14. When the TCS content is 0.10mmol, the surface cannot be coated uniformly and is full of wrinkles with a small amount of SNs on it. This may be because the PFOTS molecules anchor onto the glass slide before TCS when the TCS content is very low, which inhibit attachment of TCS onto the surface. Although the SNs are not grown very well, the surface is superhydrophobic (water drops pinned on the surface) and oleophobic. With increasing TCS content to 0.21 mmol, the SNs can be grown very well, and the surface becomes superamphiphobic with very high CA and low SA. It should be noted that the growth of the SNs is very sensitive to TCS content. For example, when the TCS content increases to 0.26mmol, the droplet of mineral oil pins stably on the surface and the CA slightly decreases. With further increasing TCS content, the CA of water and mineral oil decreases evidently. The surface even becomes hydrophilic and oleophilic when the TCS content is higher than 0.42mmol. This is because the water content becomes insufficient for the hydrolysis and condensation of TCS and PFOTS with increasing TCS content over 0.42 mmol (Figure S14C). Consequently, the SNs cannot grow very well and the surface is only coated with slightly elongated silica particles with a small amount of PFOTS on it.

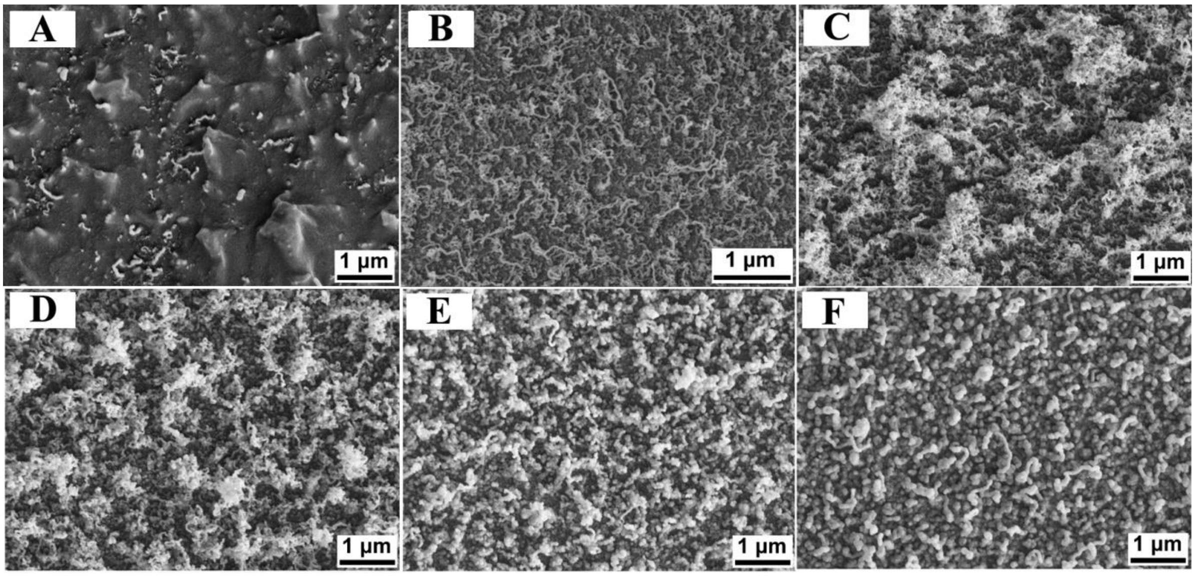

Figure S13. SEM images of the PFOTS/TCS coated glass slides with a TCS content of (A) 0.10, (B) 0.21, (C) 0.26, (D) 0.37 and (E) 0.42 and (F) 0.57 mmol (0.065mmol of PFOTS, C_{water} = 203ppm).

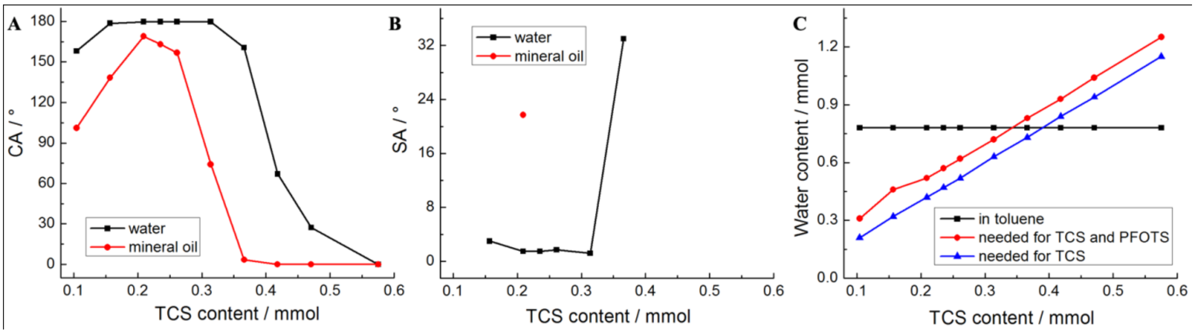

Figure S14. Variation of (a) CA and (b) SA of water and mineral oil on PFOTS/TCS coated glass slide as well as (c) water content needed for the hydrolysis of PFOTS and TCS with TCS content (0.065mmol of PFOTS, C_{water} = 203ppm).

Table S6. XPS analysis of the surface elemental composition of the PFOTS/TCS coatings with different TCS content.

PP At. %	TCS content / mmol	
	0.21	0.57
F1s	50.69	12.15
O1s	18.05	45.06
C1s	18.76	15.57
Si2p	12.5	27.22
Molar ratio of PFOTS to TCS	1:4.3	1:13.0

The effects of C_{water} on the growth of PFOTS/TCS SNs and CA and SA of water and mineral oil are shown in Figures S15 and S16.

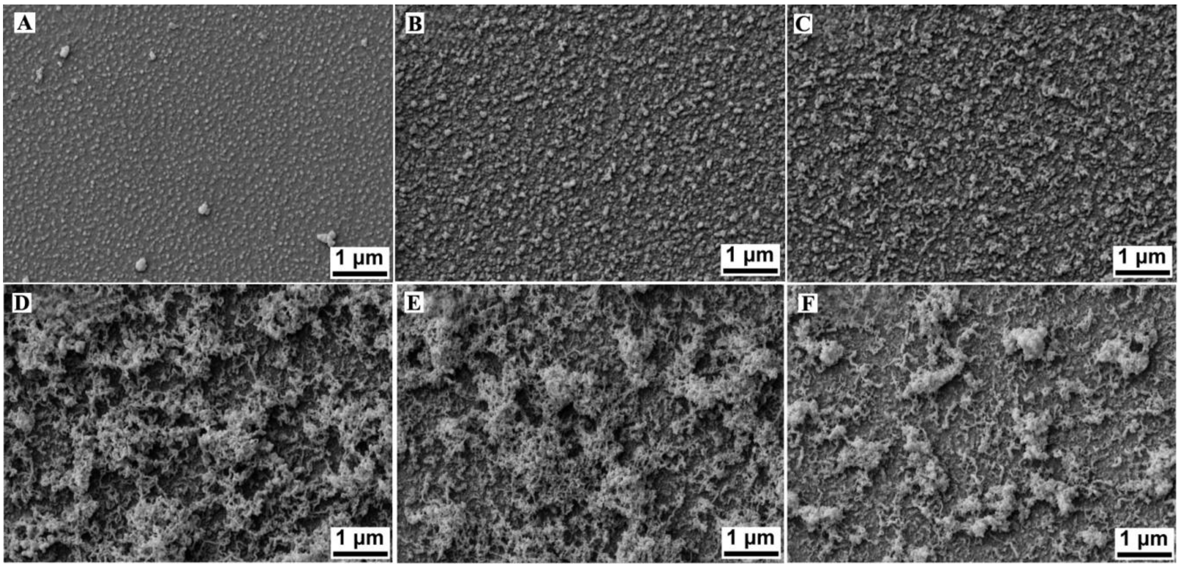

Figure S15. SEM images of the PFOTS/TCS coated glass slides with a C_{water} of (A) 40, (B) 61, (C) 125, (D) 145, (E) 190 and (F) 219 ppm (0.21mmol of TCS, 0.065mmol of PFOTS).

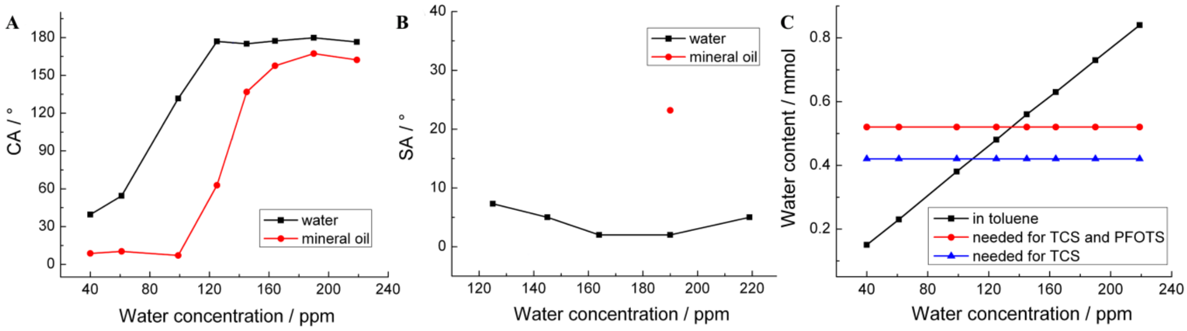

Figure S16. Variation of (a) CA and (b) SA of water and mineral oil on the TCS/PFOTS coated glass slides as well as (c) water content needed for the hydrolysis of PFOTS and TCS with C_{water} (0.21mmol of TCS, 0.065mmol of PFOTS).

Once the PFOTS/TCS mixture was injected into toluene, TCS quickly hydrolyzed and condensed in the presence of water and surface silanols of glass slide. The hydrolysis and condensation of PFOTS depends on water and TCS contents in toluene because of its lower reactivity compared to TCS. When C_{water} is very low (40 ppm), it is only enough for partly hydrolysis of TCS. Consequently, only some silica particles were covalently attached onto the surface because of hydrolysis and condensation of TCS in three dimensions (Figure S15A). [2,]

[3] The CA of water and mineral oil is pretty low (Figure S16A) and no SA is detectable, which also prove that the particles formed at very low C_{water} are mainly composed of hydrophilic silica. With increasing C_{water} to 99 ppm, the water content in toluene is still not enough for the complete hydrolysis of TCS, however, the surface becomes rougher and the particles grow asymmetrically. Correspondingly, the CA of water increases gradually, whereas the CA of mineral oil is still very low. This tendency indicates that a small amount of PFOTS have anchored onto the silica particles and make the surface hydrophobic although the water content is still not enough for the complete hydrolysis of TCS. The surface coated with TCS at 100 ppm is relatively smooth (Figure S18B) compared to those PFOTS/TCS coated surfaces and is very hydrophilic (CA ~ 0°), which also prove the attachment of PFOTS onto the silica particles. The sample prepared at 125ppm (The water content is enough for complete hydrolysis of TCS, but not enough for both TCS and PFOTS.) is very interesting. It has a similar morphology with those prepared at lower water concentration, whereas the surface becomes superhydrophobic (CA = 177° and SA = 7.3°) and the increase of CA of mineral oil was also observed. With further increasing C_{water}, more PFOTS molecules participate in copolymerization with TCS, which results in formation of SNs. The CA of water keeps very high and the SA gradually decreases to 2°. The CA of mineral oil increases gradually to 167.3° and a SA of 23.2° was recorded at 190 ppm. When C_{water} is too high (219 ppm), most of the SNs aggregate together, which results in slight decrease of the oleophobicity.

Table S7. XPS analysis of the surface elemental composition of the PFOTS/TCS SNs coatings with different C_{water}.

PP At. %	C_{water} / ppm	
	40	203
F1s	13.42	50.69
O1s	45.45	18.05
C1s	16.39	18.76

Si2p	24.74	12.5
Molar ratio of PFOTS to TCS	1:11.1	1:4.3

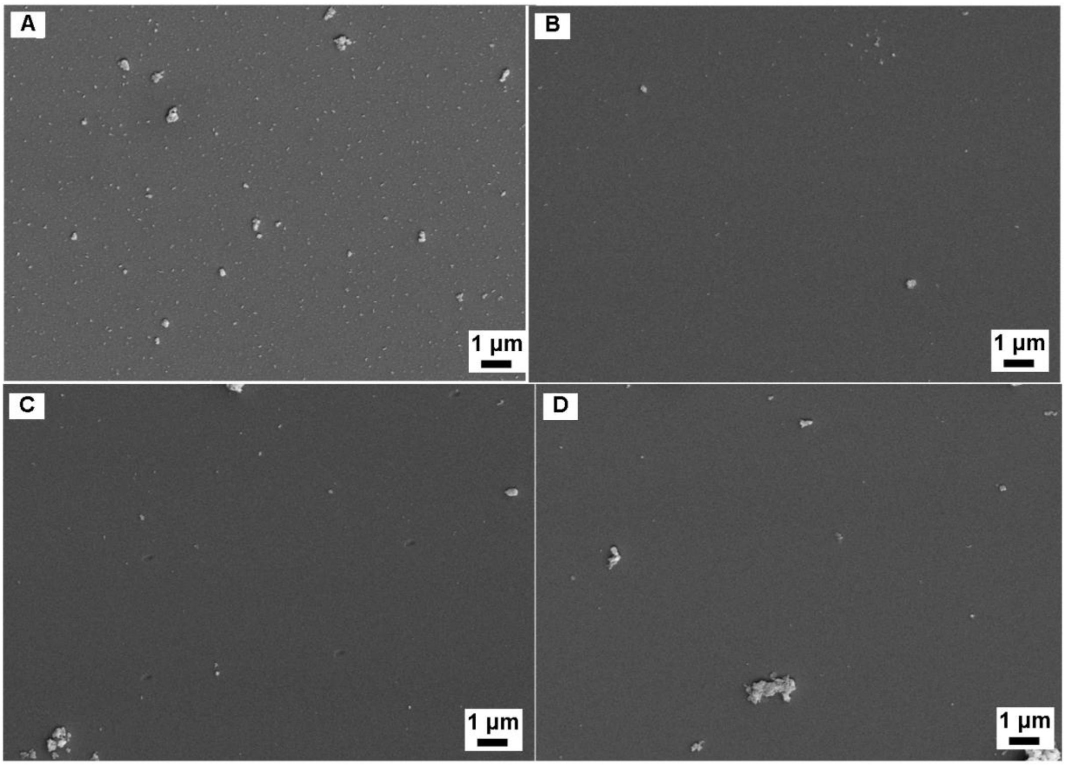

Figure S17. SEM images of the alkylsilanes coated glass slides (0.065mmol of alkylsilanes, C_{water} = 200ppm). (A) PFDTS, (B) PFDTES, (C) OTES and (D) HDTES.

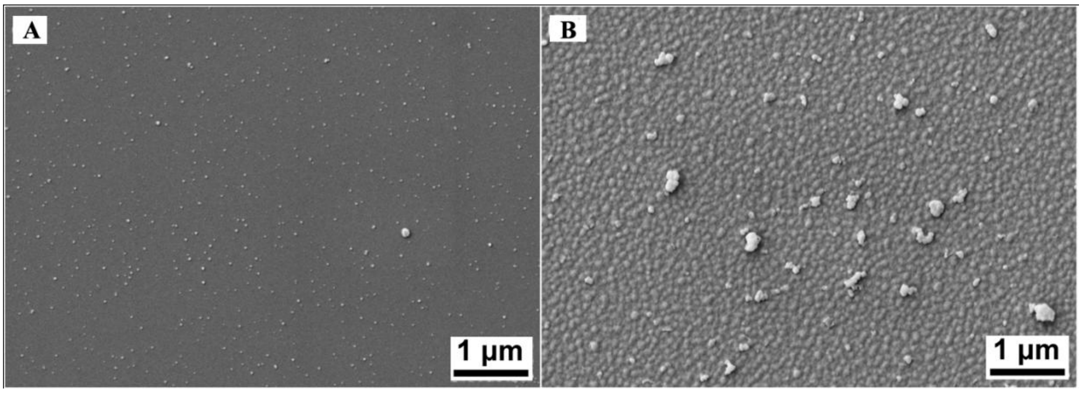

Figure S18. SEM images of the (A) TEOS (0.45mmol of TEOS, C_{water} = 72ppm) and (B) TCS (0.21mmol of TCS, C_{water} = 200ppm) coated glass slides.

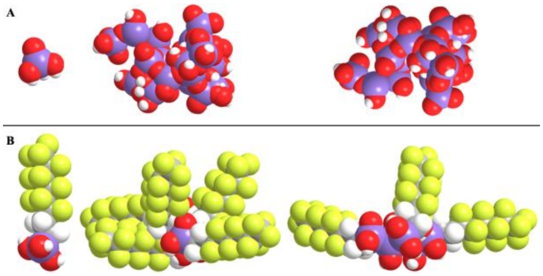

Figure S19. Schematic illustration of (A) Hy and (B) Ol. The composition of Hy and Ol depends on the TEOS (or TCS) content, alkylsilane content and C_{water} in toluene.

The SA and SHA of every liquid on coated glass slide are comparable as shown in Table S8, which means SHA is a reliable index to evaluate the surface repellent properties of macroscopically rough surfaces towards liquids.

Table S8. CA, SA and SHA of various liquids on PFOTS/TCS SNs coated glass slide (0.21mmol of TCS, 0.065mmol of PFOTS, C_{water} = 204ppm).

	CA / °	SA / °	SHA / °	Surface tension (mN/m, 20 ℃)
H_2O	179.7	1.8	1.0	72.8
CH_2I_2	176.6	2.0	1.0	50.8
Mineral oil	167.1	21.7	24.0	32

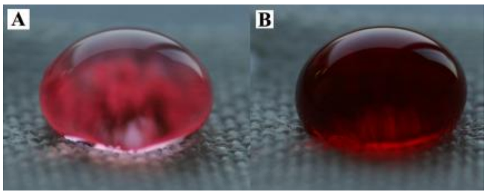

Figure S20. The droplets of (A) *n*-odecane and (B) *n*-decane on PFOTS/TCS coated polyester/cotton textile (0.21mmol of TCS, 0.065mmol of PFOTS, C_{water} = 204ppm).

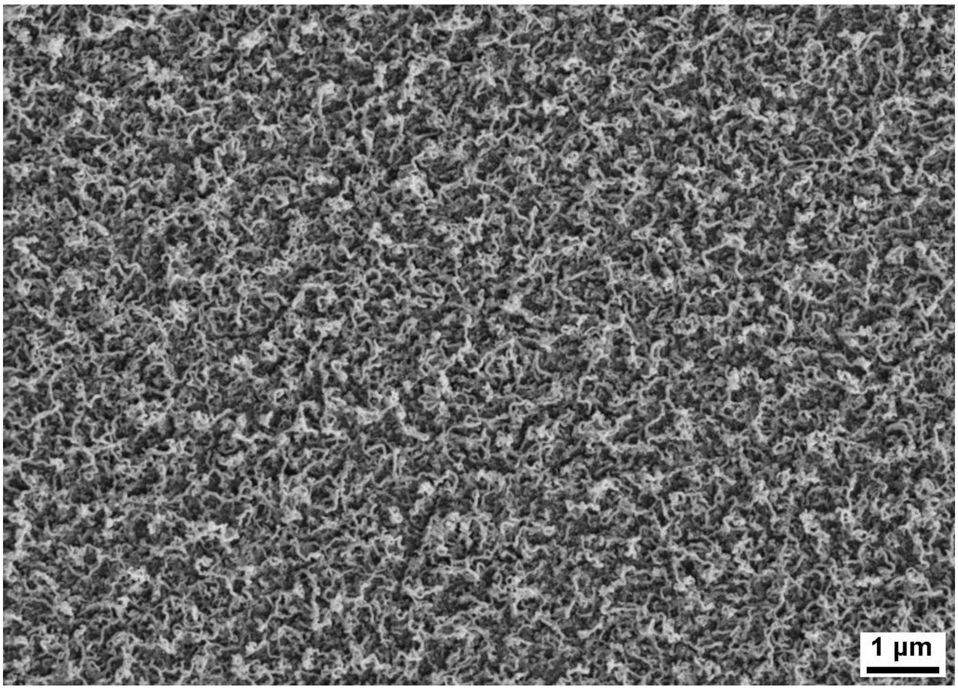

Figure S21. Representative SEM image of the PFOTS/TCS SNs coated glass slide (0.21mmol of TCS, 0.065mmol of PFOTS, C_{water} = 204ppm).

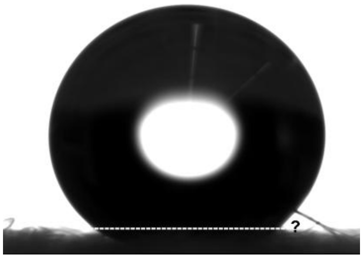

Figure S22. Typical image of a water droplet on the PFOTS/TCS coated textile surface.

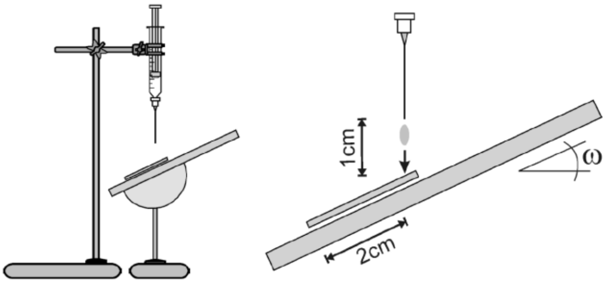

Figure S23. Principle setup employed for measuring SHA (ω).

Movie S1. Dropping CH_2I_2 (part 1) and water (part 2) on the horizontal PFOTS/TCS SNs coated glass slide. Water droplet rolls off the slightly tilted (1 °) PFOTS/TCS SNs coated glass slide (part 3). This video highlights the excellent anti-wetting properties of the coating.

Movie S2. Interaction between water droplet and the PFOTS/TCS SNs coated glass slide. This video demonstrates the very weak interaction between water droplet and the coating.

Movie S3. Bouncing of a water droplet (6μL, height: 15 mm) on a SNs coated glass slide. The video highlights the well conservation of the kinetic energy of water droplet by surface deformation and the very low dissipation of the kinetic energy by work of adhesion during the impact against the SNs coated surface.

References

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