Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

A facile approach to TiO_2-based superhydrophobic-superhydrophilic patterns by UV or solar irradiation without photomask

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Materials and Experimental section

Materials:

Organosilicon adhesive and curing gent were purchased from Guangzhou delta organosilicon technology development Co., Ltd. Titanium oxide (anatase) nanoparticles (around 30-60 nm in diameter) were purchased from Hangzhou wanjing new material Co., Ltd. TiO_2 P25 was purchased from Degussa. 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane was purchased from Hubei jusheng technology Co., Ltd. All chemicals were analytical grade reagents and were used as received.

Experimental section:

Organosilicon adhesive preparation:

The organosilicon adhesive is mixed with the curing gent in mass ratio 100:3. The mixture is mechanically stirred for 2 min and standed for a while until the bubbles are completely discharged.

TiO_2-FAS paint preparation:

1 g FAS is placed into 99 g of absolute ethanol, and the solution is mechanically stirred for 1 hour. To the resulting solution, 6 g of titanium oxide nanoparticles and 6 g of Degussa P25 TiO_2 are added to make a paint-like suspension.

Fabrication method and wettability transition of TiO_2 superhydrophobic surface to SH-SL patterns:

Fabrication of TiO_2-based surface with spot-, line- or letter-shaped SH-SL patterns: Firstly, the glass is coated with the organosilicon adhesive with a spot- or line-shaped patterns by screen printing (the letter-shaped patterns by hand-making) and cured at the room temperature for about 2 min. Then, the TiO_2-FAS paint is coated on the above surface by dip-coating, spray or spin-coating and dried in air for at least 2 min. The superhydrophobic surface is formed. Finally, the formed superhydrophobic surface is exposed by UV light (254 nm, ~24 W) or sunlight for at least 2 min, and the SH-SL patterns are presented.

Fabrication method and wettability transition of TiO_2 superhydrophilic surface to SH-SL patterns:

Firstly, the cleaned substrate is coated by the organosilicon adhesive with a certain pattern through hand drawing, dispensing gun, screen printing or other methods. The organosilicon adhesive/substrate is cured at the room temperature for about 2 min. The choice of substrates is flexible and it can be Cu, Al, Si, glass, plastics, and paper. Secondly, the TiO_2 paint is coated on the organosilicon adhesive/substrate by dip-coating, spray or spin-coating and dried in air for at least 2 min. The areas with and without the organosilicon adhesive below become superhydrophilic. Thirdly, the formed superhydrophilic area is exposed by the UV light or sunlight for at least 2 min. Finally, the SH-SL patterns can be obtained. The superhydrophilic areas without organosilicon adhesive below maintain the original wettability. Meanwhile, the superhydrophilic areas with organosilicon adhesive below become superhydrophobicity. The reason is that the organosilicon below TiO_2 has been partly decomposed into small molecules after the UV irradiation, and the small molecules which has low surface energy transfers to the surface of TiO_2 nanoparticles. (see Fig. S4)

Artificial weathering test of fabricated superhydrophobic-superhydrophilic (SH-SL) patterns:

The artificial weathering tests have been carried out in the radiation chamber with a medium-voltage silica tube mercury vapor arc lamp without ozone whose wavelength is 290~800 nm. The SH-SL patterns are placed at the sample stage which is about 150 mm away from the lamp with operating power of 750 W. The rotating bowel with sample stage is rotated around the lamp with a speed of 2 r/min (see Fig. S8).

Characterizations of the superhydrophobic or superhydrophilic surfaces:

The chemical modifications of the samples are investigated using a Fourier transform infrared spectrophotometer (FTIR, Tensor27 Bruker). Scanning electron microscopy (SEM) is performed to determine surface morphology using a HITACHIS-4800 field emission SEM at an accelerating voltage of 2 kV. The surface chemical compositions are determined by X-ray photoelectron spectroscopy (XPS, thermo scientific Escalab 250Xi). The Ti and Si ions are examined by secondary ion mass spectroscopy (TOF-SIMS IV, ION-TOF, German). The water contact angles are measured at ambient temperature via the sessile-drop method using an optical contact angle meter (Dataphysics OCA 20LHT, water droplet is 5 μL). The water droplet roll-off angles are measured with a volume of 10 μL, and in the experiment we use the mean value of the five samples.

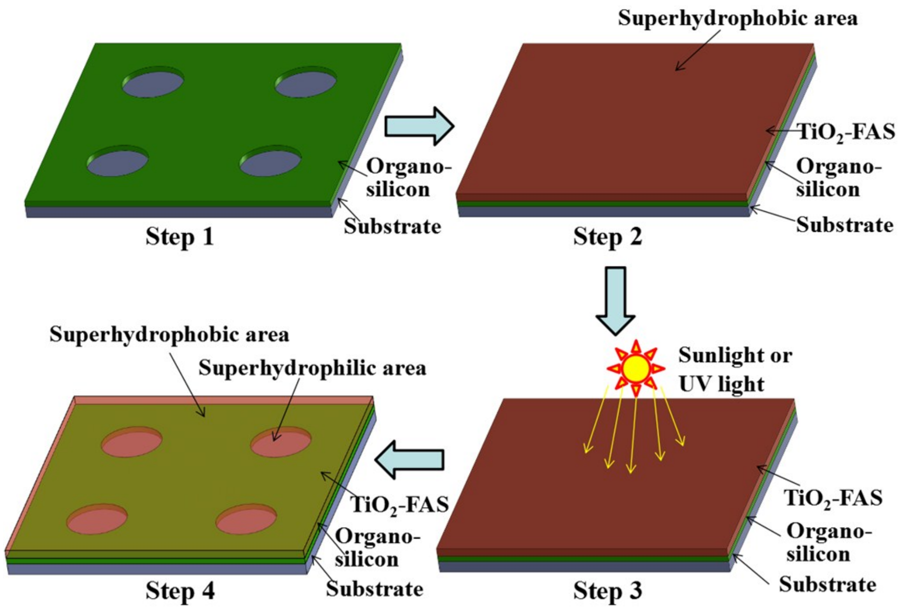

Fig. S1. Schematic representation of the method for creating SH-SL patterns on TiO_2 superhydrophilic surface by sun or UV irradiation without photomask.

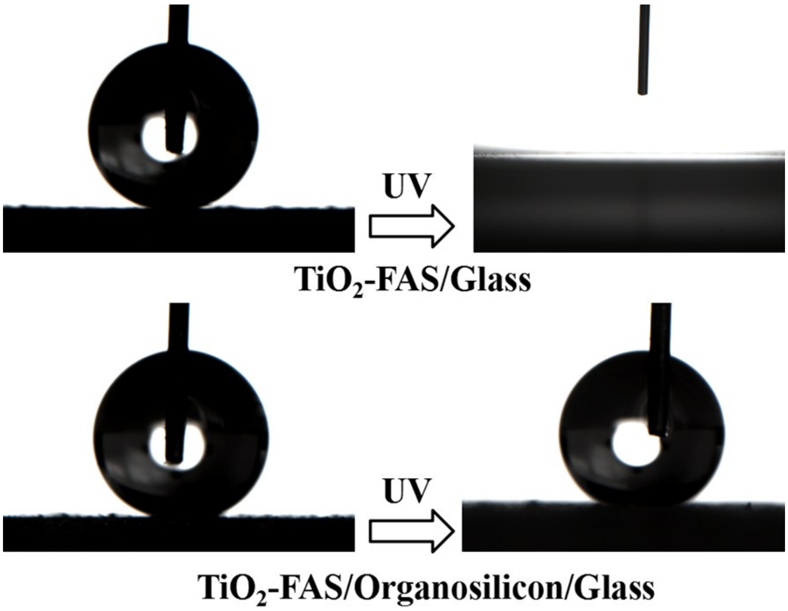

Fig. S2. Wettability conversions of the TiO_2-FAS surface with or without organosilicon below by UV irradiation.

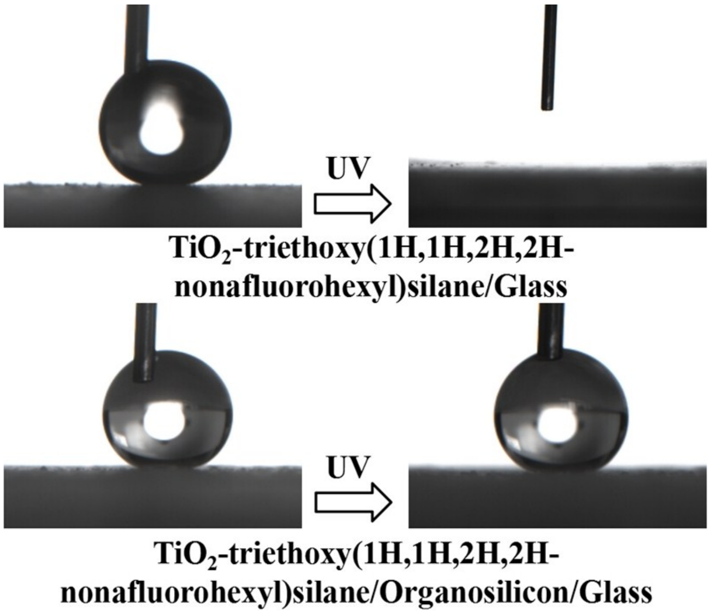

Fig. S3. Wettability conversions of the TiO_2-triethoxy(1H,1H,2H,2H-nanafluorohexyl)silane surface with or without organosilicon below by UV irradiation.

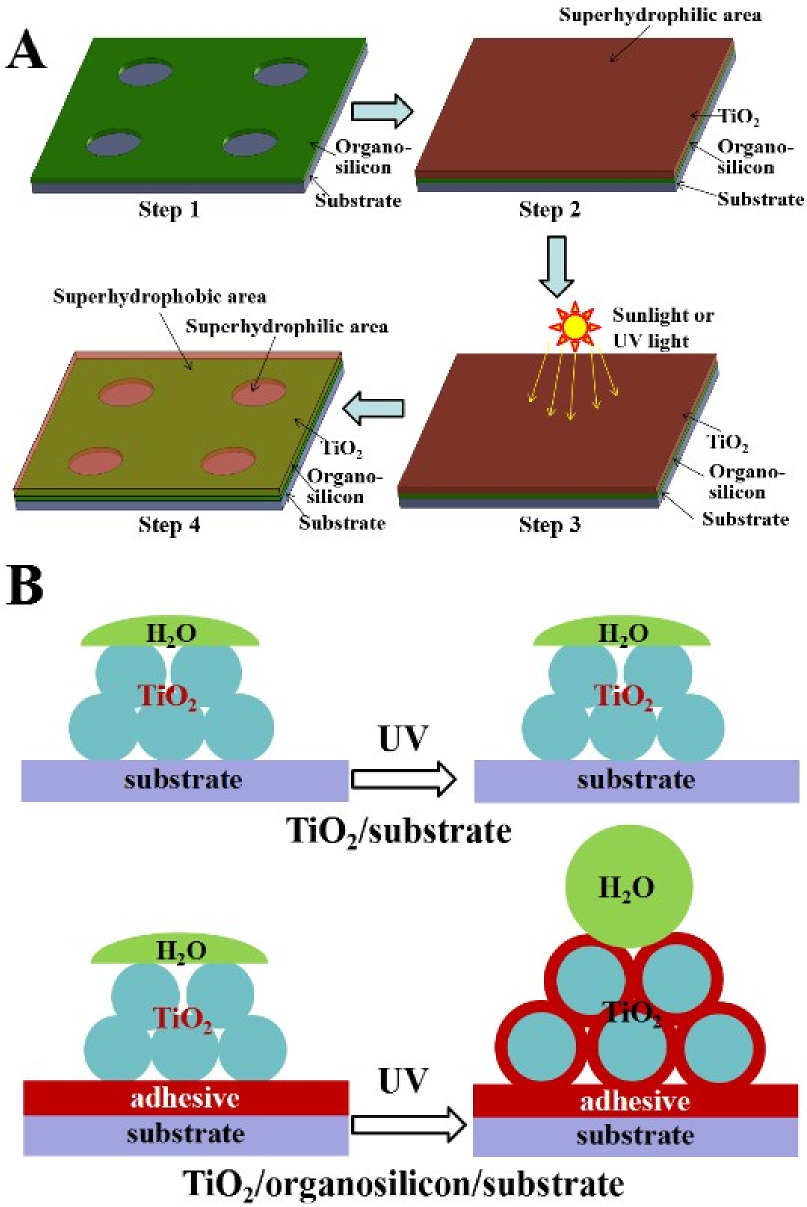

Fig. S4. (A) Schematic representation of the method for creating SH-SL patterns on TiO_2 superhydrophilic surface by sun or UV irradiation without photomask. (B) Cartoons illustrating the wettability transition induced by changes in surface structure and chemical composition before and after UV irradiation.

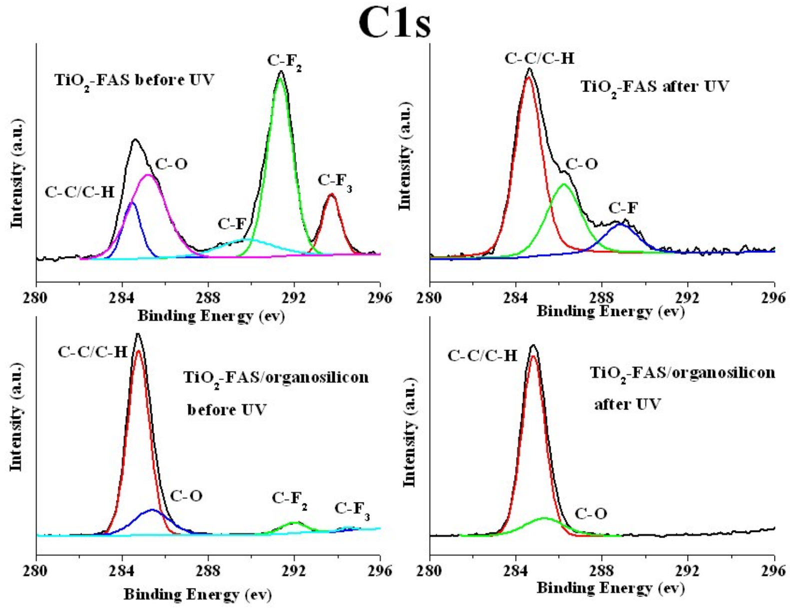

Fig. S5. Peak-fitted of C*1s* of the surfaces of TiO_2-FAS and TiO_2-FAS/organosilicon before and after UV irradiation

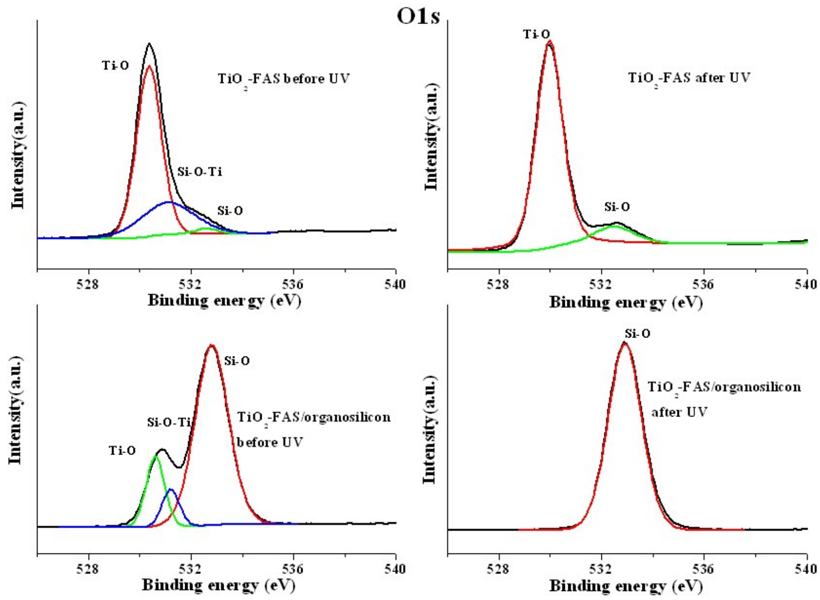

Fig. S6. Peak-fitted of O*1s* of the surfaces of TiO_2-FAS and TiO_2-FAS/organosilicon before and after UV irradiation

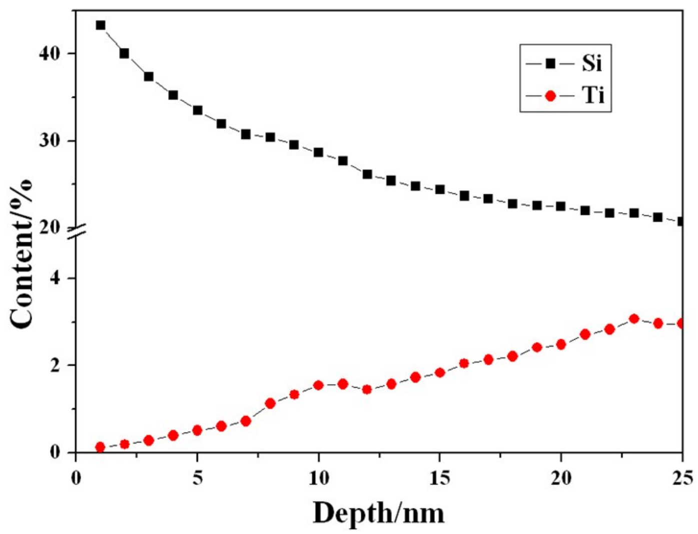

Fig. S7. Secondary ion mass spectroscopy for Si and Ti distribution in the depth of TiO_2-FAS/organosilicon sample after UV irradiation.

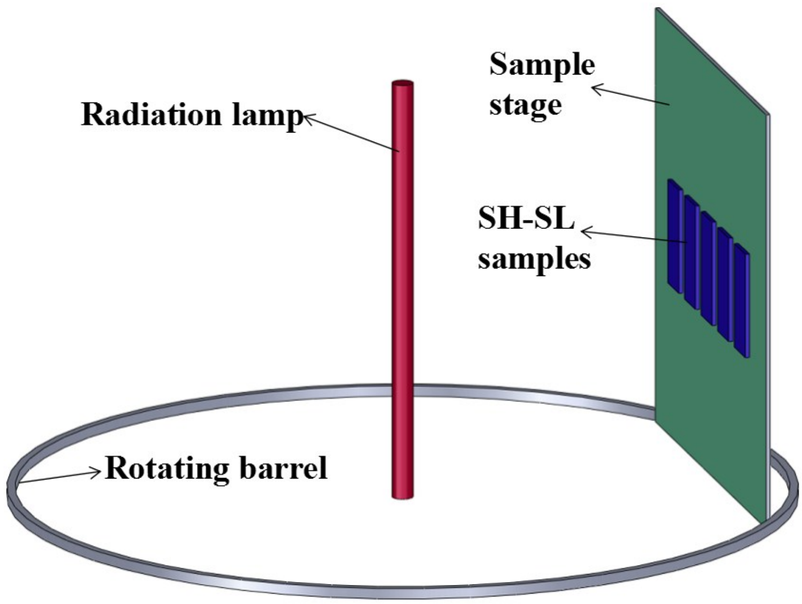

Fig. S8. Schematic diagram of artificial weathering test.

Table.S1 The atomic% of elements

Element	TiO_2-FAS befor e UV	TiO_2-FAS after UV	TiO_2-FAS/organosilicon befo re UV	TiO_2-FAS/organosilicon after UV
F	34.26	2.18	8.95	0.24
O	30.75	61.12	35.46	37.86
Ti	14.09	20.26	5.17	0
C	18.75	8.02	30.61	32.75
Si	2.15	8.42	19.81	29.15

Movie S1

Tape peeling tests on the TiO_2-FAS/organosilicon surface. The tape was pressed against the fabricated TiO_2-FAS/organosilicon sample and then peeled off.

Movie S2

Sandpaper abrasion tests on TiO_2-FAS/organosilicon surface. The sample with a weight of 100 g above was placed face-down to the sandpaper (mesh number 1000) and moved for 10 cm distance along the ruler, then the sample was rotated by 90o and moved again. This process which contains longitudinal and transverse abrasion is defined as one abrasion.

Movie S3

Water droplet travelling tests were proformed on the TiO_2-FAS/organosilicon surface. A droplet was guided by the needle to travel around the surface after 10^{th}, 20^{th}, 30^{th}, 40^{th} cycle's abrasion, respectively.

Movie S4

Knife-scratch tests on TiO_2-FAS/organosilicon surface. The surface was cut in cross-shape by knife.