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Supplementary Materials for

Robust Self-cleaning Surfaces that Function when Exposed to either Air or Oil

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Materials and Methods

Materials

Titanium oxide (anatase) nanoparticles (around 60-200 nm in diameter) and 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane ($C_8F_{13}H_4Si(OCH_2CH_3)_3$) were purchased from Sigma-Aldrich. TiO_2 P25 was purchased from Degussa. Laboratory solvents were purchased from Fisher Scientific and of the highest possible grade. All chemicals were analytical grade reagents and were used as received.

Coating preparation

1.00 g of 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane was placed into 99 g of absolute ethanol, and the solution was mechanically stirred for 2 hours. To the resulting solution, 6 g of titanium oxide nanoparticles (Aldrich) and 6 g of Degussa P25 TiO_2 were added to make a paint-like suspension. In the following experiments, we used dip-coating (120 cm /min), spray, or even simply a syringe needle (0.8*50 mm) to paint the substrates, the paint was dried in air for at least 180 s before testing (for cotton wool and filter paper, it would take a longer time for ethanol base to dry up).

Characterizations

Scanning Electron Microscopy (SEM) was performed to determine surface morphology using a JEOL JSM-6301F Field Emission SEM at an accelerating voltage of 5 kV. Images were captured using SEMAfore software. Samples were cut to 10 mm x 10 mm coupons and coated with a fine layer of gold to eliminate charging. Transmission electron microscopy (TEM) micrographs were collected using a JEOL JEM 2100 microscope at a beam acceleration of 200 kV. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Scientific K-alpha photoelectron spectrometer with monochromatic Al-Kα source to identify the chemical constituents and their oxidation states. High-resolution scans were done for the Ti (3d), O (1s) and C (1s) at a pass energy of 40 eV. The binding energies were adjusted to adventitious carbon (284.5 eV). The water contact angles were measured at ambient temperature via the sessile-drop method using an optical contact angle meter (FTA 1000, water droplet is 5 µL). The X-ray powder pattern of the hard and soft substrates were examined using D4 ENDEAVOR (Cu source, 10-60° 2θ range, 0.05°/step) in glancing angle mode (5^o) and STOE SEIFERT (Mo source radiation, 2-40° 2θ range, 0.495°/step) in transmission mode X-ray diffractometers (XRD). The XRD patterns were compared with respective standard patterns for TiO_2 anatase based on the radiation source used (*27*).

Supplementary Text

Superhydrophobicity of treated samples

Fig. S1 compares the untreated and superhydrophobic paint treated surfaces on the glass, steel, cotton wool and filter paper substrates. In this figure, the glass and steel were treated via spray, the cotton wool was treated with dip-coating and the filter paper was treated with syringe painting.

Water dropping test

The water dropping tests were studied using a Phantom V7.1 colour high-speed camera (2900 frame/s). Water droplets were dropped from a height of 40 mm (tip to surface) using a micro-syringe fitted with a 30 gauge dispensing tip. Droplets impacted the surface at approximately 0.89 m/s estimated by gravimetric calculation. The water droplets were around 6.3 ± 0.2 μL in size and were left to detach under their own weight. The substrates were the treated and untreated glass, steel, cotton wool and filter paper, respectively. Methylene blue was added to the water to aid visualization; this did not change the behavior of the water droplets on the surface. Another test is to use running water as “artificial rain drops” to impact the surfaces, the impacting velocities and drop sizes varied randomly from a 40 mm height. All the painted samples in this test were treated via dip-coating. Fig. S2 shows the water dropping tests on untreated samples.

Self-cleaning test in air

1. Dip-coated cotton wool was put into methylene blue dyed water. 2. Filter paper sprayed with the coating was placed on top at about 30 degrees relative to the untreated filter paper. MnO powder was put onto the treated surface acting as a mimic for dirt; water was then dropped onto the surface to test the self-cleaning property of the treated filter paper by removing the simulated dirt (Fig. S3). 3. Water droplets (dyed blue) were put onto dip-coated cotton wool and syringe-coated filter paper (that was fixed on the glass slide by double-sided tape) for 10 min, and then removed. 4. Self-cleaning tests on the dip-coated glass and steel were the same as those on the treated filter paper and were taken by the high-speed camera. Fig. S4 shows the results of these tests (self-cleaning test in air).

Self-cleaning test in oil

1. A half dip-coated glass slide was immersed in oil (hexadecane), water was dropped onto the treated and untreated areas respectively (Fig. S5A). 2. Water was dropped onto the oil-contaminated spray-coated surface to test the self-cleaning ability in air (Fig. S5B). 3. An oil-contaminated treated glass slide was in part immersed in oil; dirt was put onto the glass slide and positioned half in air and half in oil, water was then dropped onto the surface to test two types of self-cleaning properties: (1) dirt removal from the oil-contaminated treated surface in air; (2) dirt removal from the treated surface

immersed in oil (Fig. S5C). Fig. S6 shows the results of the test described in Fig. S5A. 4. The experiment shown in Fig. S5C was repeated but using soil (from the Gordon Square, London) and dust (from kitchens, offices and laboratories) as dirt; the substrates were treated by dip-coating; hexadecane and cooking oil (corn oil from Waitrose, London) were used as solvent (Fig. S7). Water in these tests was dyed with methylene blue to aid visualization.

Robustness test

In this test, adhesives (including the double-sided tapes from the Niceday and the spray adhesive – EVO-STIK multi-purpose impact) were used to promote the robustness of the painted superhydrophobic coatings. Both hard (glass and steel) and soft (cotton wool and filter paper) substrates were involved in the robustness tests, such as finger-wipe, knife-scratch and sandpaper abrasion. There are two cases in the sample preparation: when the tested substrate is glass, adhesives were directly coated onto the glass surface, and then the "glass + adhesive" surface was treated with the paint by dip-coating as shown in Fig. S8A; when the tested substrate is steel, cotton wool or filter paper, these substrates were initially fixed on a glass slide by double-sided tape in order to facilitate the experiment, and then adhesives were coated on the surfaces of these substrates, followed by treating with the paint via dip-coating as shown in Fig. S8B.

In consideration of actual conditions, what normally happens to a surface includes hand touch (i.e. on walls), scratches (i.e. on cars) and mechanical abrasion in industry. Thus we chose finger-wipe, knife-scratch and sandpaper abrasion as robustness tests on the substrates. Fig. S8C shows the scheme of the finger-wipe test, the three substrates were untreated, paint treated and "paint + adhesive" treated surfaces, respectively from left to right. Water was firstly dropped on these surfaces to test the wettability, and then a finger tried to remove the paint from the paint treated to the "paint + adhesive" treated surfaces, followed by the water dropping test to compare the robustness of painted surfaces with or without adhesives. Fig. S8D shows the scheme of the knife-scratch test, a knife (Sterile disposable scalpels from the Swann-Morton) was used to scratch the "paint + adhesive" treated surfaces along a meshy path, and then water was dropped to test the wettability. Fig. S8E shows that the surface robustness was tested via a sandpaper-abrasion method (*28*). The "paint + adhesive" treated surface was placed face-down to the sandpaper (Standard glasspaper, Grit No. 240, from the English Abrasives & Chemicals Ltd.). This surface was longitudinally and transversely (10 cm for each direction, or transversely and then longitudinally) abraded by the sandpaper under a weight at 100 g, respectively, this process is defined as 1 cycle as shown in Fig. S8F. 40 cycles of mechanical abrasion tests were carried out on a "paint + double-sided tape" treated (PDT) glass sample, and water contact angles were measured after each cycle's abrasion test. Water droplet travelling test: water droplets were guided by a needle to travel across the treated surface after the 11^{th}, 20^{th}, 30^{th}, and 40^{th} abrasion test, respectively.

Spray adhesives can be treated on both hard and soft surfaces and can be used in large scale industries. Robustness tests (finger-wipe, knife-scratch and sandpaper abrasion) were then carried out on the "paint + spray adhesive" treated (PSAT) substrates, including glass, steel, cotton wool and filter paper. The sample preparation methods and relevant tests were as shown in Fig. S8. Fig. S9 and Fig. S10 show the finger-wipe tests on PDT and PSAT substrates, respectively. Fig. S11 shows that the paint was abraded out when directly treated with the cotton wool in the sandpaper abrasion test, while the cotton wool treated with paint and spray adhesive was well protected and retained superhydrophobicity (Fig. S12). In addition, all of the substrates did not lose supehrydrophobicity after the sandpaper abrasion and knife-scratch tests (Figs. S12 and S13), indicating the “paint + spray adhesive” combination works well both on hard and soft substrates.

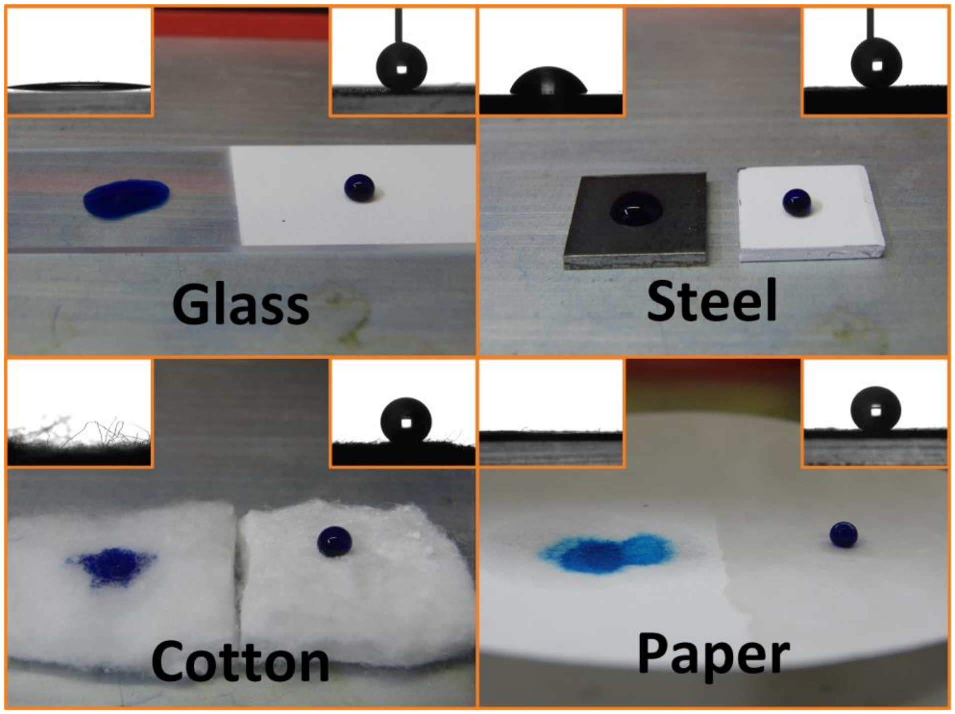

Fig. S1

Optical images are used to compare the untreated and treated surfaces on different substrates.

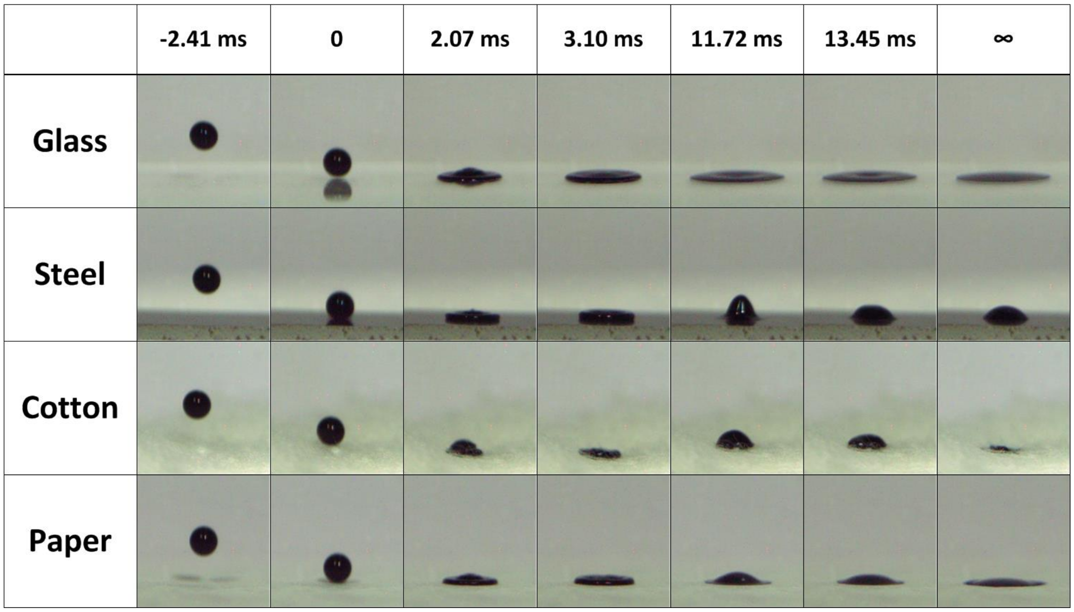

Fig. S2.

Water dropping tests on untreated glass, steel, cotton wool and filter paper, respectively (droplet size: *ca* 6.3 ± 0.2 μL).

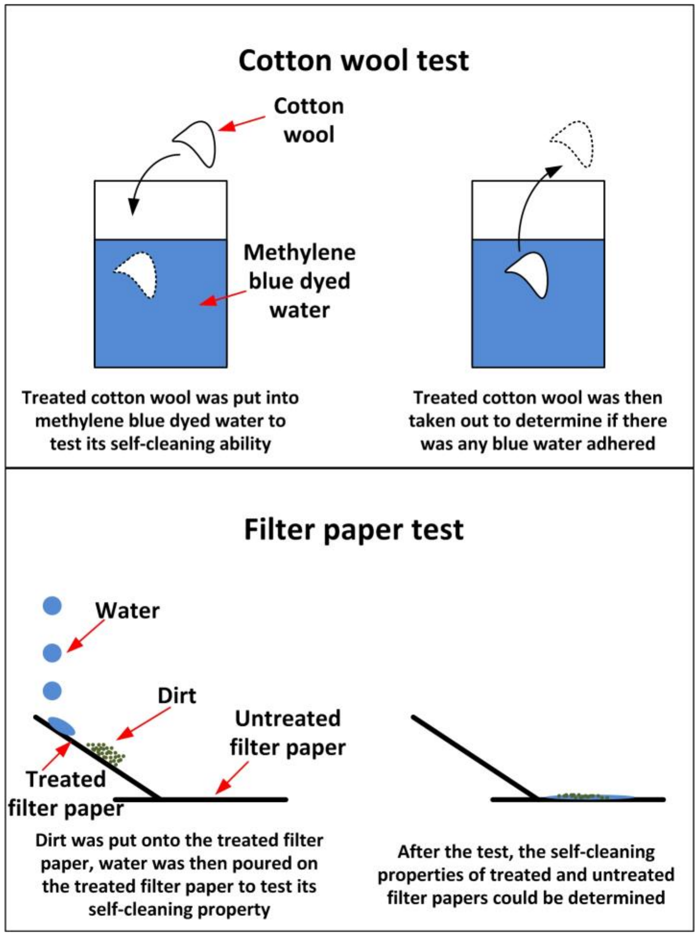

Fig. S3.

Self-cleaning test of dip-coated cotton wool and spray-coated filter paper.

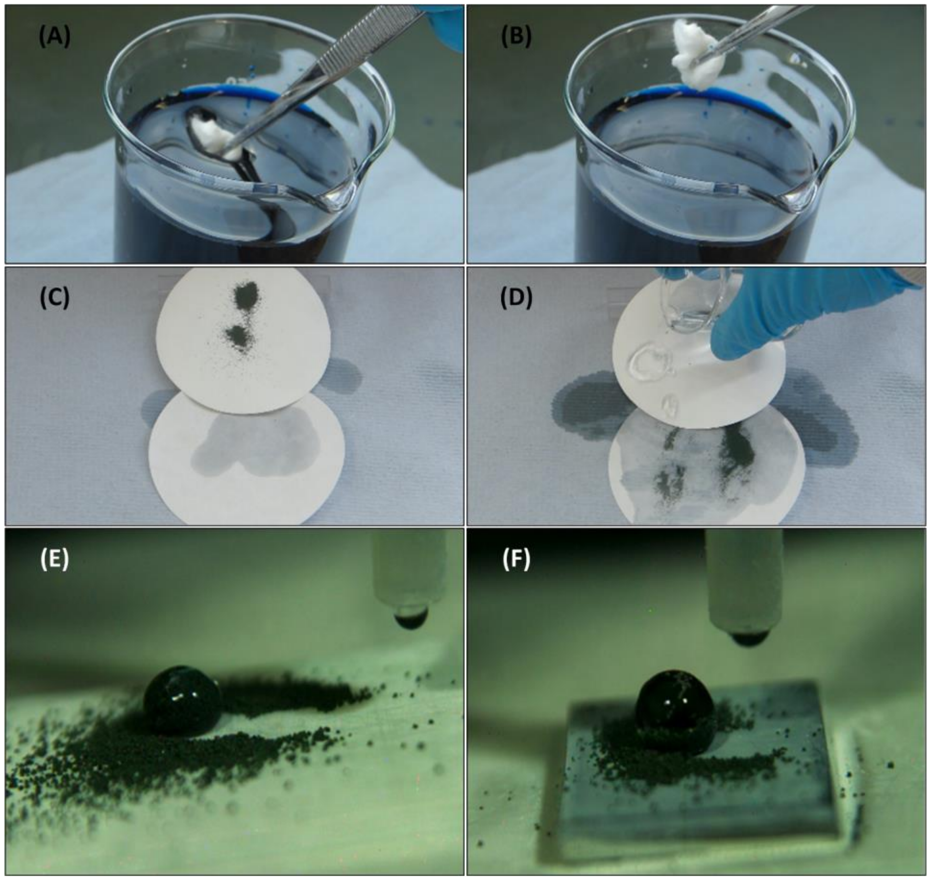

Fig. S4.

Self-cleaning tests were carried out on cotton wool, filter paper, glass and steel substrates. (A) and (B) show the dip-coated cotton wool was inserted into methylene blue dyed water, the cotton wool did not get dyed due to the self-cleaning properties; (C) and (D) show the poured water could easily remove the dust (MnO powder) from the spray-coated filter paper, in addition, the filter paper was not wetted by the fast running water while the untreated one was wet and polluted by the dirt. (E) and (F) show the dirt removal tests on dip-coated glass and steel surfaces via the high speed camera.

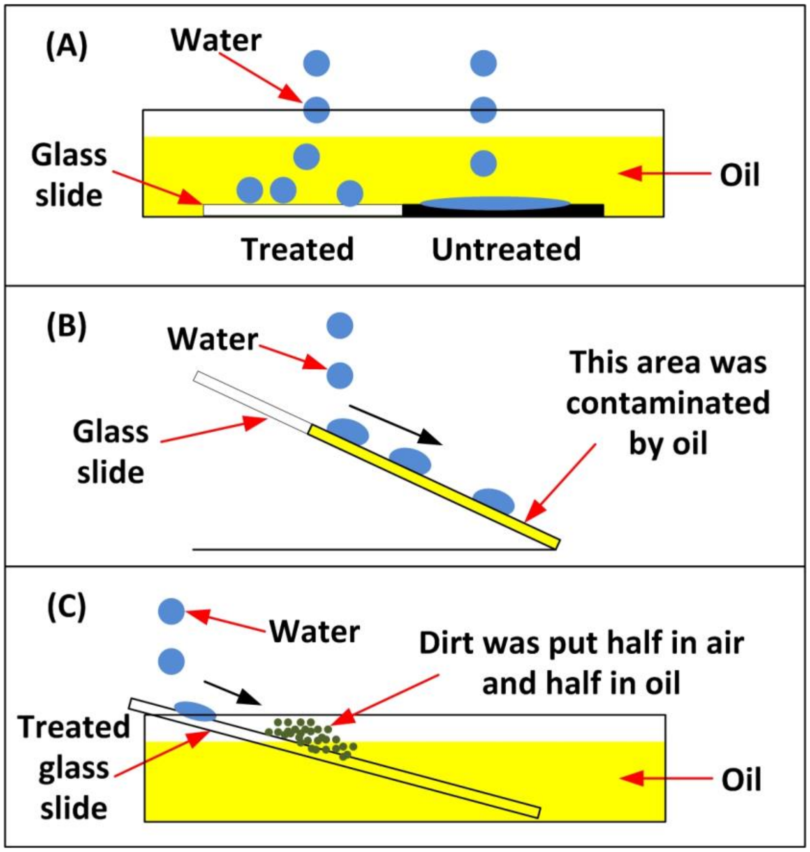

Fig. S5.

Scheme of self-cleaning tests in oil. (A) A half dip-coated glass slide was immersed in oil, water was dropped onto the treated and untreated areas respectively. (B) Water was dropped onto the oil-contaminated spray-coated surface to test the self-cleaning ability. (C) Dirt removal test on oil-contaminated treated surface both in air and under oil.

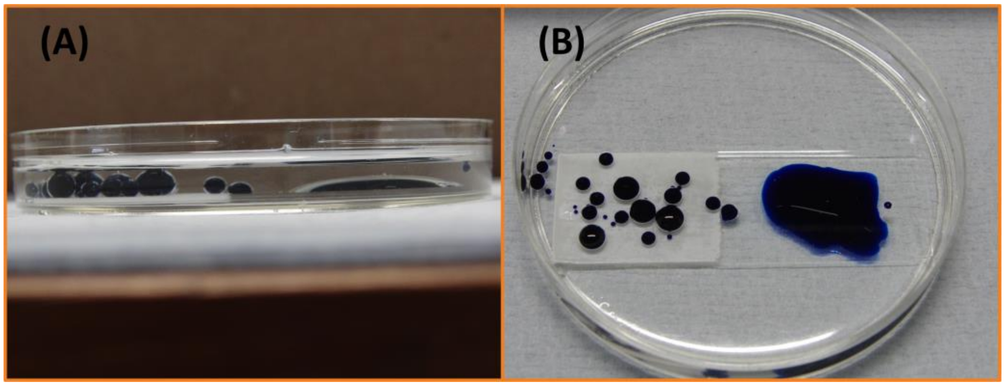

Fig. S6.

Water droplets placed on the half dip-coated sample that was immersed in oil, the left part was treated and the right part was untreated. (A) and (B) are the side and top views respectively.

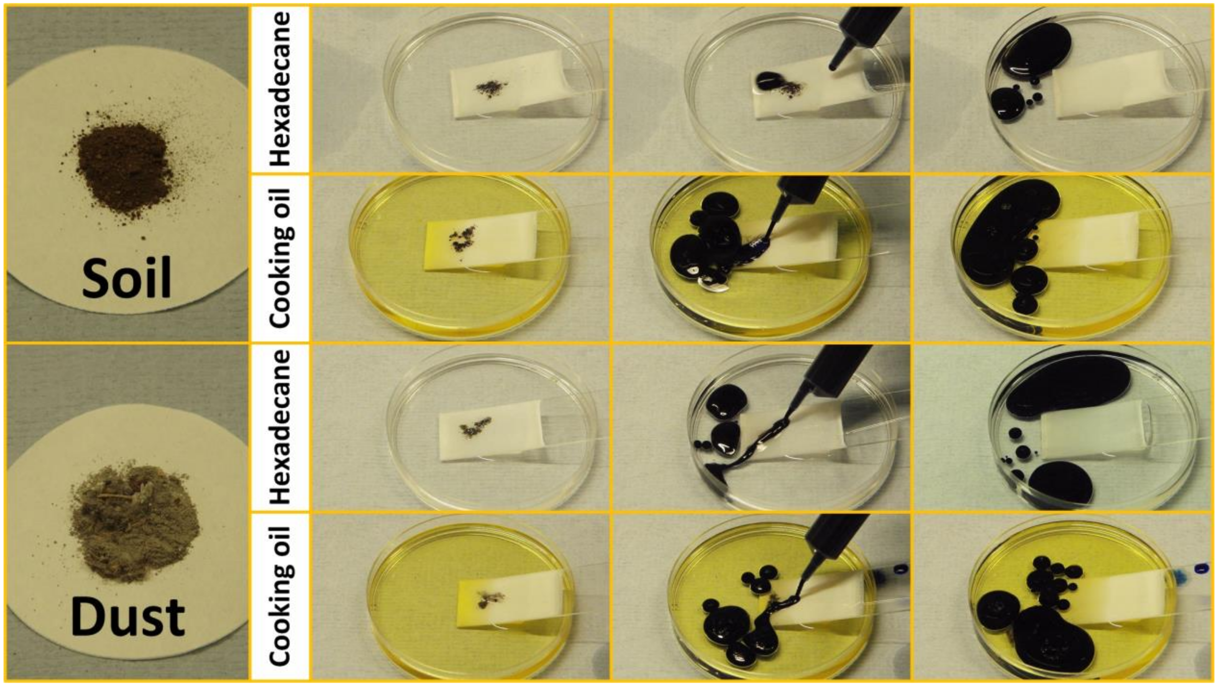

Fig. S7.
Dirt removal tests of dip-coated surfaces. Soil and dust were used as dirt and placed onto the treated surfaces partially immersed in hexadecane and cooking oil, respectively. Water was then dropped to remove the dirt from the oil-contaminated treated surfaces both in air and under oil.

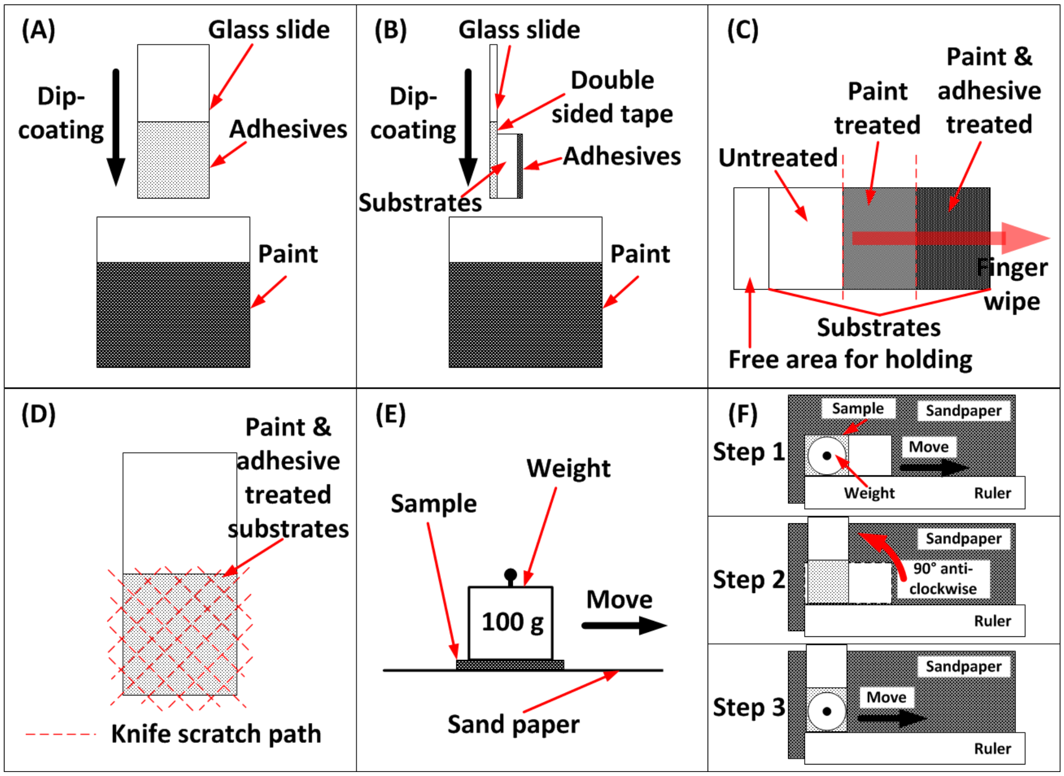

Fig. S8.

Scheme of robust sample preparation and robustness tests. (A) Preparation of "paint + adhesive" surfaces on glass substrates, which were firstly treated with adhesives and then dip-coated with the paint. (B) Preparation of "paint + adhesive" surfaces on steel, cotton wool and filter paper substrates, which were firstly fixed on glass, then treated with adhesives followed by dip-coating of the paint. (C) Finger-wipe test – a finger was wiped across the surface in an attempt to remove the paint from the paint treated and the "paint + adhesive" treated substrates to test the robustness. (D) Knife-scratch test – a knife was used to scratch the "paint + adhesive" treated substrates along the path of red dashed lines to test the surface robustness. (E) Sandpaper abrasion test – the "paint + adhesive" treated substrates weighed 100 g were faced down to the sandpaper, and (F) moved for 10 cm along the ruler, and then the sample was rotated anti-clockwise by 90°, followed by a 10 cm move along the ruler. This process is defined as 1 cycle of abrasion and just guarantees that the sample is abraded longitudinally and transversely (or transversely and longitudinally) in each cycle.

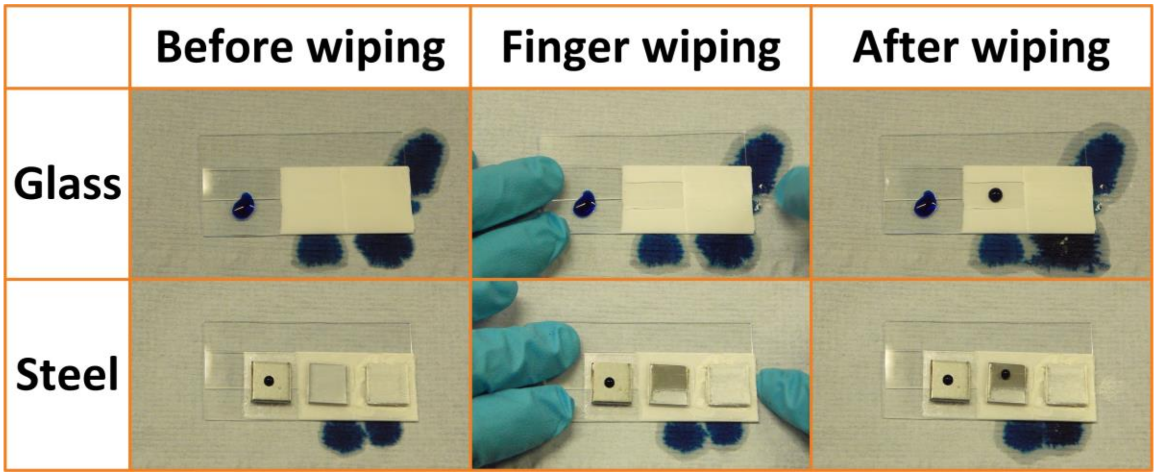

Fig. S9.

Finger-wipe tests on glass and steel substrates. The surfaces were untreated, paint treated and “paint + double-sided tape” treated, respectively (from left to right). The paint was easily removed by a finger wipe when it is directly treated to the substrates. However, the superhydrophobic glass and steel treated with paint & double-sided tape retained water proofing properties, indicating the coating becomes more robust after bonding with adhesives.

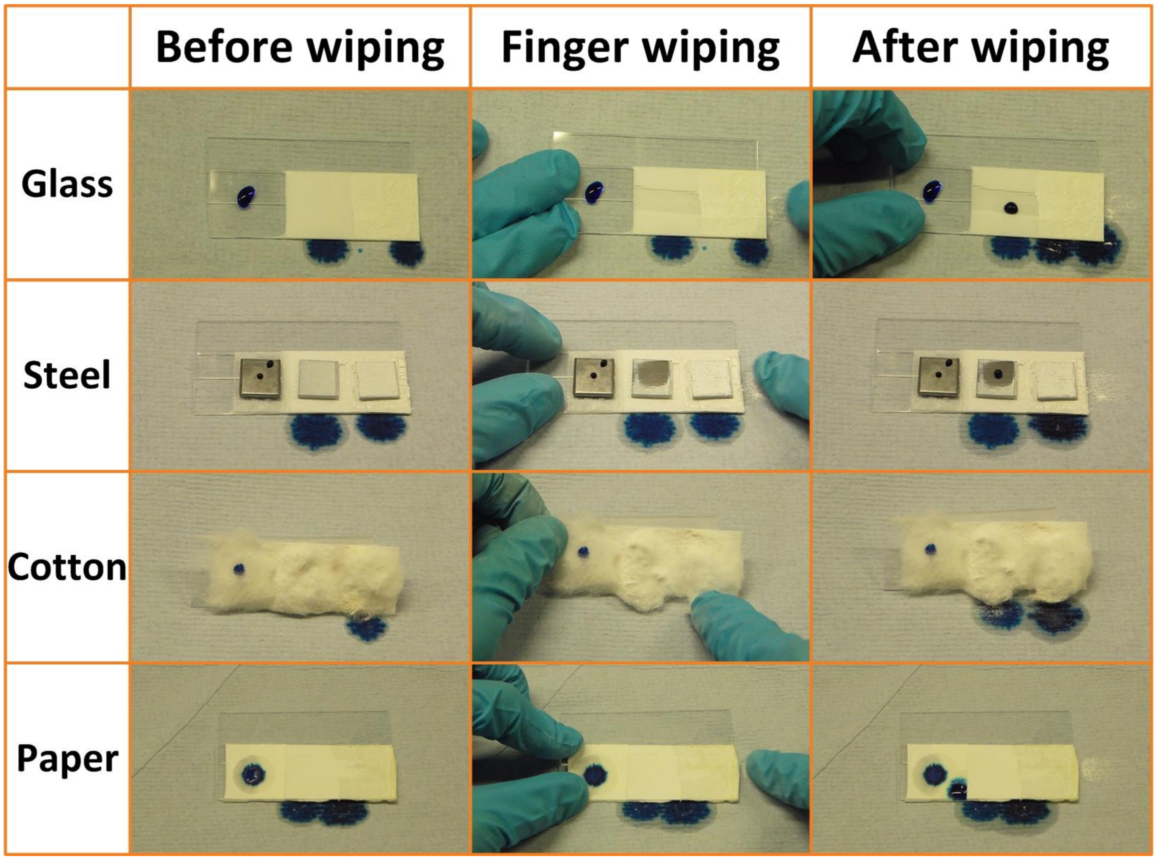

Fig. S10.
Finger-wipe tests on glass, steel, cotton wool and filter paper substrates. The surfaces were untreated, paint treated and "paint + spray adhesive" treated (PSAT), respectively (from left to right). The paint directly coated on hard substrates (glass and steel) were easily removed by the finger-wipe, while on soft substrates (cotton wool and filter paper), finger-wipe did not impact much as the paint was protected by the porous structures from the soft materials. However, on the PSAT surfaces, both hard and soft substrates retained superhydrophobicity after finger-wipe tests.

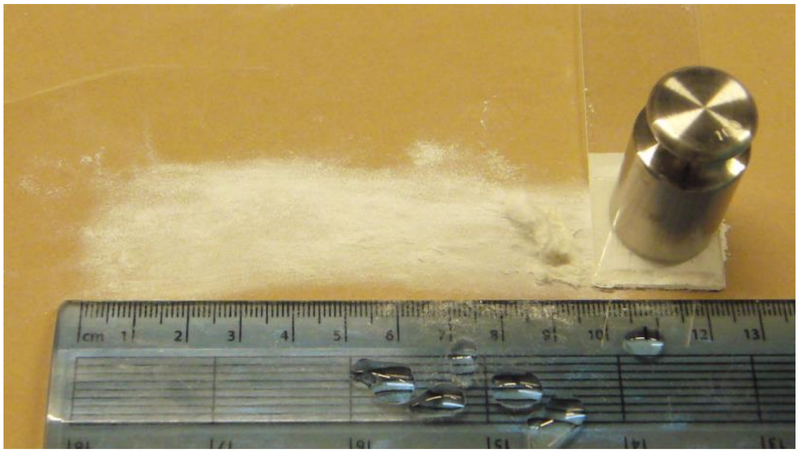

Fig. S11.
In the sandpaper abrasion test, the paint directly treated on the cotton wool was abraded out.

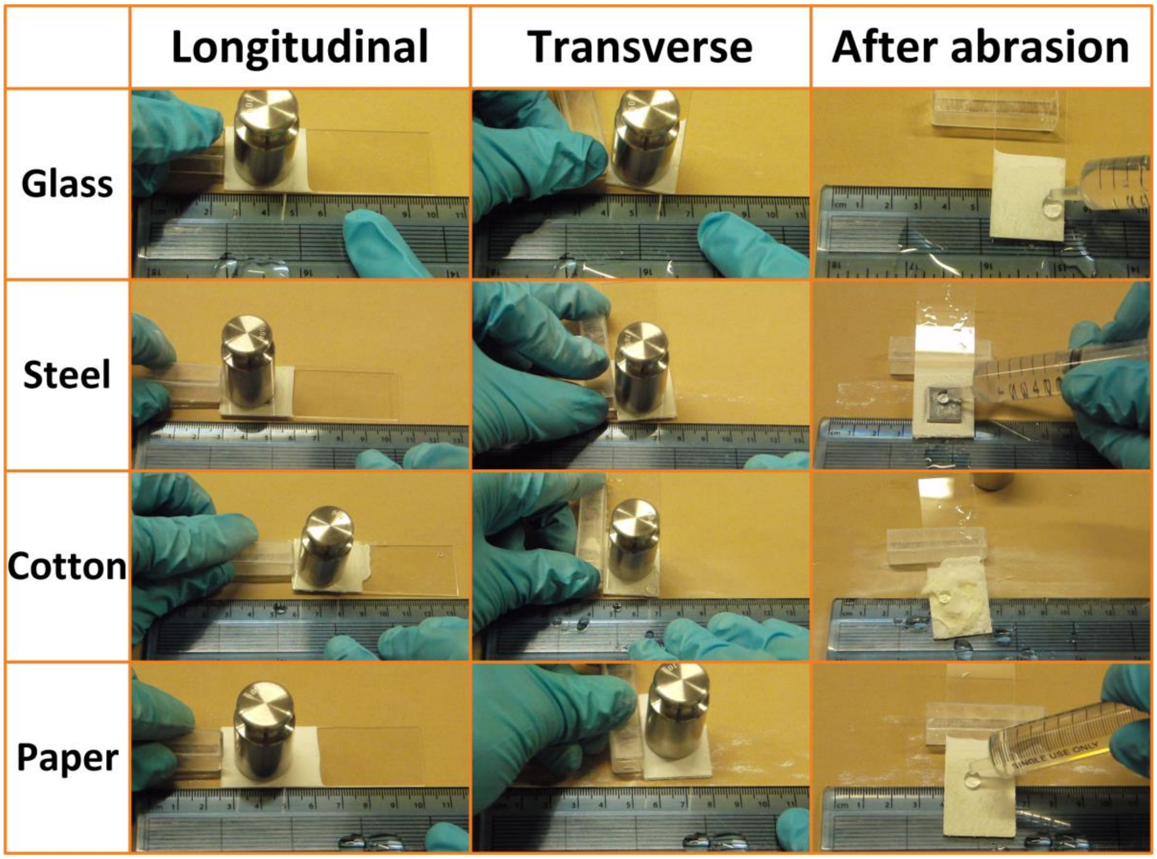

Fig. S12.

Sandpaper abrasion tests on the PSAT glass, steel, cotton wool and filter paper. In particular, paint was well "protected" by the adhesive and porous structures of cotton wool, indicating "paint + spray adhesive" can also be applied on soft substrates.

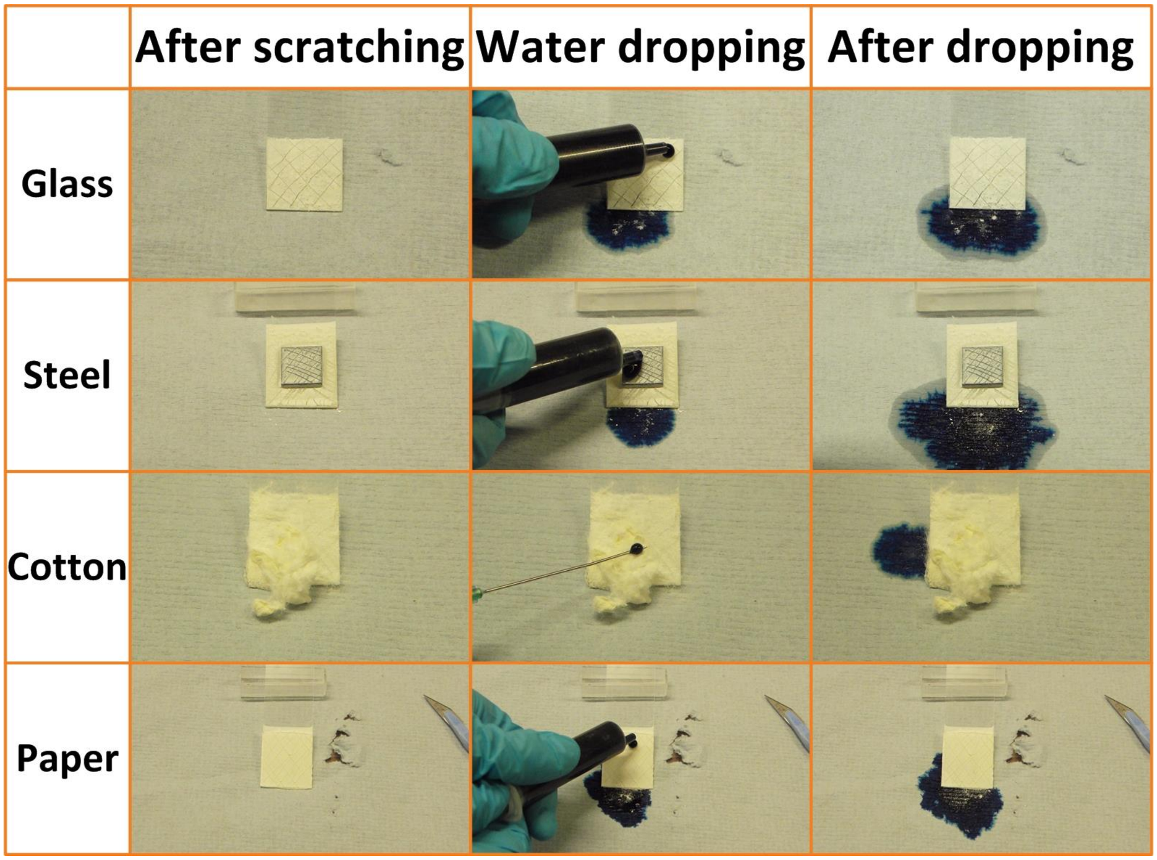

Fig. S13.
Knife-scratch tests on PSAT glass, steel, cotton wool and filter paper substrates. These surfaces retained water repellent after knife scratches.

Movie S1
An example of syringe coating the material on a filter paper, a syringe was used to treat half of the filter paper and the compressed air was used to dry the material. Water with methylene blue dropped on the treated area is repelled to the untreated area.

Movie S2
Water dropping tests on untreated and dip-coated glass, steel, cotton wool and filter paper, respectively. Water droplets were dropped from a height of 40 mm (tip to surface) using a micro-syringe fitted with a 30 gauge dispensing tip and the droplet sizes are around 6.3 ± 0.2 μL.

Movie S3
Artificial rain hit the dip-coated glass, steel, cotton wool and filter paper, the drop sizes varied with random impacting velocities, and all of the droplets could not wet the coated surfaces, indicating this paint has water proofing and self-cleaning properties.

Movie S4
Self-cleaning tests on the dip-coated cotton wool and spray-coated filter paper, this movie is divided into two parts. 1. Treated cotton wool was inserted into methylene blue dyed water and then taken out. 2. Running water was used to remove dirt (MnO powder) from the treated filter paper.

Movie S5
A time-lapsed video clip of water droplets (dyed blue) staying on the dip-coated cotton wool and syringe-coated filter paper for 10 min. When water droplets were removed, the cotton wool and filter paper retained dry and clean.

Movie S6
High speed video of the self-cleaning property on dip-coated glass and steel surfaces; MnO powder was used as dirt. The surfaces were cleaned along the path of the water droplet movement.

Movie S7
Water dropped on the half-dip-coated surface immersed in oil (hexadecane), the left part was treated while the right was untreated.

Movie S8
Self-cleaning tests of a spray-painted surface after oil (hexadecane) contamination. This movie is divided into three parts. 1. Water droplets slipped off from the surface which was immersed in oil; 2. Water droplets marble-formed on the surface immersed in oil; 3. In air, water droplets still slipped off from the oil-contaminated surface. These tests show the treated surface still functions after oil-contamination both in air and oil.

Movie S9

The fully oil-contaminated spray-coated surface was partly inserted into oil; dirt (MnO powder) was put partly in oil and air on the surface, and then water was dropped onto the surface to remove the dirt both in air and oil.

Movie S10

Robustness tests on "paint + double-sided tape" treated (PDT) substrates. This movie is divided into two parts. 1. Finger-wipe tests that compare untreated, paint treated and PDT glass and steel (from left to right), the PDT glass and steel retained superhydrophobic after the finger-wipe. 2. Knife-scratch test on the PDT glass surface, which retained water proofing properties after this test.

Movie S11

Sandpaper abrasion test. The PDT glass weighing 100 g was positioned face-down to sandpaper (Standard glasspaper, Grit No. 240) and moved for 10 cm along the ruler; the sample was rotated by 90° (face to the sandpaper) and then moved for 10 cm along the ruler. This whole process is defined as one abrasion cycle, which guarantees the surface is abraded longitudinally and transversely in each cycle even if it is moved in a single direction.

Movie S12

Water droplet travelling tests were performed on the PDT glass surface. A droplet was guided by the needle to travel around the PDT glass surface after the 11^{th}, 20^{th}, 30^{th} and 40^{th} cycle's abrasion, respectively.

Movie S13

Finger-wipe tests on glass, steel, cotton wool and filter paper substrates. The surfaces were untreated, paint treated and "paint + spray adhesive" treated (PSAT), respectively (from left to right).

Movie S14

Sandpaper abrasion tests on PSAT glass, steel, cotton wool and filter paper substrates. The process is the same as that of PDT glass.

Movie S15

Knife-scratch tests on PSAT glass, steel, cotton wool and filter paper substrates. The process is the same as that of PDT glass.

References and Notes:

27. M. Horn, C. F. Schwerdtfeger and E. P. Meagher, *Z. Kristallogr* **136**, 273 (1972).
28. Y. Lu *et al.*, *J. Mater. Chem. A*, **2**, 11628 (2014).