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Supporting Information for

Super-durable, non-fluorinated superhydrophobic free-standing items

Xia Zhang[1], Danfeng Zhi[1], Lei Sun[1], Yanbao Zhao[1], Manish K. Tiwari[2*], Claire J. Carmalt[3], Ivan P. Parkin[3], Yao Lu[2*]

[1] National & Local Joint Engineering Research Center for Applied Technology of Hybrid Nanomaterials, Henan University, Kaifeng 475004, P.R. China.

[2] Nanoengineered Systems Laboratory, UCL Mechanical Engineering, University College London, London, WC1E 7JE, UK. Email: yao.lu@ucl.ac.uk (Y. Lu); m.tiwari@ucl.ac.uk (M. K. Tiwari)

[3] Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, UK.

Experimental

1. Sample preparation

1.1 Materials

Hydrophobic SiO_2 nanoparticles were prepared according to our previous work.[S1] Hydrochloric acid (25 mL, 0.18 M) was added into the Na_2SiO_3 water solution (50 mL, 0.15 M). After half of the hydrochloric acid had been added, 1,3,3,3-hexamethyldisilazane (HMDS, 25 mL, 12.5 mM) was added dropwise to the Na_2SiO_3 water solution together with the remaining hydrochloric acid. The resulting suspension was stirred for 4 h at 60 °C, and then it was separated into two phases upon cooling to room temperature, with white foam floating at the top of the liquid phase. The foam was purified by filtration and cleaned repeatedly using a solution containing water and ethanol until Cl^- could not be detected by silver nitrate solution by visual examination. The desired hydrophobic SiO_2 nanoparticles were obtained after drying for 4 h at 120 °C.

Polyhexamethylene adipamide (PA610) was purchased from Yixing Chemical Reagent Factory. Polypropylene (PP), Mw = 100000, was purchased from Linyi Goldman Sachs Weibang Chemical Co., Ltd. Polystyrene (PS): Mw=104.14 and methyl silicone resin (MSR) were purchased from Aladdin. Toluene and Xylene were purchased from Tianjin Chemical Reagent Factory. Formic acid was purchased from Tianjin Ke Miou Chemical Reagent Co., Ltd.

1.2 Preparation of SiO_2/PA610 superhydrophobic blocks

1.5 g of hydrophobic SiO_2 nanoparticles, 4 g of polyhexamethylene adipamide were added into 30 ml of formic acid, and the mixture was condensate reflux magnetically stirred at 110 °C for 3 h. The solution was cooled and dried at 80 °C to get the SiO_2/PA610 composite powder. The powder was placed into a mold and pressed under a pressure of 5, 10, 30 and 40 MPa at room temperature, respectively. After about three minutes, the sample was demolded and removed from the smooth layer on the surface. The samples were then manually abraded for 2-3 times using sandpaper (SiC, 800 Cw).

1.3 Preparation of SiO_2/PS superhydrophobic blocks

1 g hydrophobic SiO_2 nanoparticles and 1 g polystyrene were added into 20 ml toluene; the mixture was magnetically stirred and refluxed at 110 °C for 2 h. Then the solution was cooled and dried at 80 °C to get the SiO_2/PS composite powder. The powder was placed into a mold and pressed under a pressure of 5, 10, 30 and 40 MPa at room temperature, respectively. After about three minutes, the sample was demolded and removed the smooth layer on the surface. The samples were then manually abraded for 2-3 times using sandpaper (SiC, 800 Cw).

1.4 Preparation of SiO_2/PP superhydrophobic blocks

1 g of hydrophobic SiO_2 nanoparticles and 2 g of polypropylene were added into 20 ml of xylene, and the mixture was magnetically stirred and refluxed for 3 h at 140 °C. Then the solution was cooled and dried at 80 °C to get the SiO_2/PP composite powder. The powder was placed into a mold and pressed under a pressure of 5, 10, 30 and 40 MPa at room temperature, respectively. After about three minutes, the sample was demolded and removed the smooth layer on the surface. The samples were then manually abraded for 2-3 times using sandpaper (SiC, 800 Cw).

1.5 Preparation of SiO_2/MSR superhydrophobic blocks

1 g of hydrophobic SiO_2 nanoparticles, 2 g of polyhexamethylene adipamide were added into 20 ml of toluene, and the mixture was magnetically stirred and refluxed at 90 °C for 2 h. Then the solution was cooled and dried at 80 °C to get the SiO_2/MSR composite powder. The powder was placed into a mold and pressed under a pressure of 5, 10, 30 and 40 MPa at room temperature, respectively. After about three minutes, the sample was demolded and removed the smooth layer on the surface. The samples were then manually abraded for 2-3 times using sandpaper (SiC, 800 Cw).

2. Characterization

Surface morphology of the samples was examined using a JSM-6701F field-emission scanning electron microscope (FESEM, JEOL, Japan). The chemical composition of the samples was investigated using an X-ray photoelectron spectroscopy (XPS), which was conducted on a PHI-5702 electron microscope. The static water contact angle (WCA) and sliding angle (WSA) were measured by a DSA100 contact angle instrument (Germany) using 10 ml water droplets. The WCA and WSA were obtained by calculating the average of the data that was measured at five different positions on an individual sample. The optical images were captured with a digital camera (Nikon, P600). Thermal stability of the samples was characterized using a thermogravimetry (TG, NETZSCH STA 449 C) at a heating rate of 10 °C/min.

3. Various mechanical tests

3.1 Scratch tests in air and water (on SiO_2/PP block)

(a) The sample was tested by knife scratch, finger print and then tape peeling in air with respective water dropping tests after each mechanical test.

(b) The sample was scratched by a knife in water, and then removed. Water was dropped onto the sample to test the wettability.

(c) The sample was abraded by a file in air, and then water was dropped onto the sample.

(d) The sample was scratched by a file in water, and then removed. Water was dropped on the sample in air.

3.2 Liquid nitrogen test

The SiO_2/PP block was dipped into liquid nitrogen for ~10 s and then removed. The sample was heated using a hair dryer followed by water dropping tests.

3.3 Newton meter press

The SiO_2/PA610 block was pressed by a Newton meter at ~200 N and then water was dropped onto the surface to test its wettability.

3.4 Hammer beat test

The SiO_2/PA610 block was broken into pieces by hammer beat, water was dropped onto the broken area to test the wettability of the inside parts of the samples.

3.5 Dropping sand and running water tests

The SiO_2/PA610 block was strongly impacted by running sand followed by running water.

4. Sandpaper abrasion test

Superhydrophobic blocks were abraded by sandpaper (SiC, 1000 Cw). During abrasion, the samples were loaded 80 g weights with the abrasing area of 7.065 cm^2. The original mass of the SiO_2/polymer samples were 2 ± 0.3 g. WCA, WSA and retention ratio were measured and calculated when the samples were abraded after every 200 cm of travel.

5. Friction tests using a tribotester

A pin-on-disk friction tribotester (CZM-1A) was used to understand the factors that lead to superhydrophobicity and the abrasion-resistance of these SiO_2/polymer blocks. In this test, the SiO_2/PS blocks were used as an example, which was positioned onto the disk. Sandpapers (SiC, 320, 600, 800, and 1200 Cw) were fixed on the upper stationary pins (440C stainless steel), respectively. During the friction process, the disk spun at 60 r/min for 10 min, and different weights of 20, 40, 60, and 80 g were loaded, respectively.

Surface roughness was measured using a 3D surface profiler (Contour GTK-1).

6. Chemical stability tests

Two independent methods were used to study the chemical durability of the SiO_2/polymer blocks in corrosive conditions.

6.1 Acidic/alkali droplet contact tests

An acidic (pH = 1) or alkali (pH =14) liquid droplet was dropped on the sample surface and the evolution of contact angles was studied as a function of time that corrosive droplets contacted with the sample surfaces.

6.2 Acidic/alkali soak tests

The sample was soaked in strong acidic (pH = 1) and alkali (pH = 14) solution for a certain time, respectively. After a definite time of immersion, the sample was removed from the corrosive liquids, dried with a filter then a water droplet was dropped onto the surface to investigate the influence of the corrosive solution on the wettability.

Supporting figures and tables

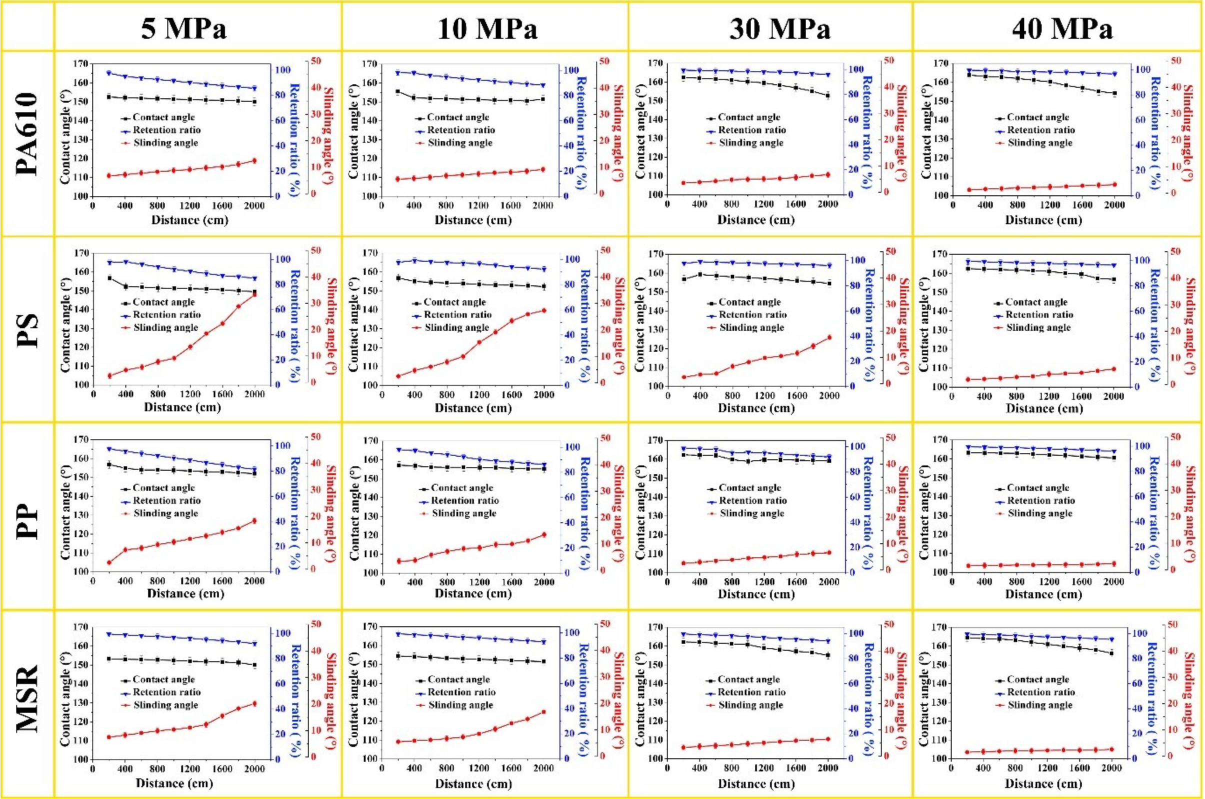

Figure S1. Plot of water contact angle, sliding angle and retention ratio as a function of sandpaper abrasion distance on SiO_2/polymer blocks under different fabrication pressure. The polymers are polyhexamethylene adipamide (PA610), polystyrene (PS), polypropylene (PP), and methyl silicone resin (MSR), respectively.

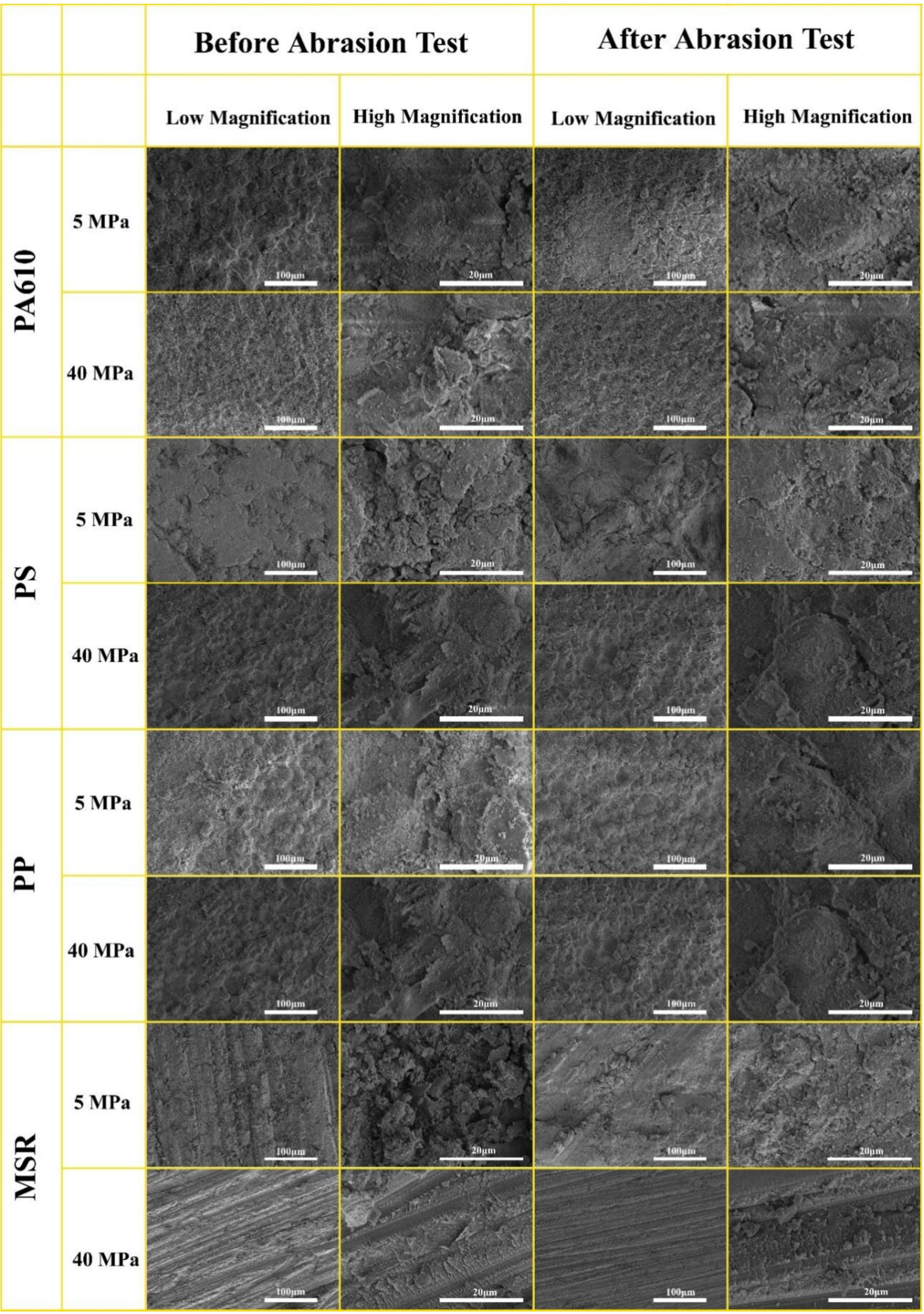

Figure S2. SEM images of four SiO$_2$/polymer blocks that were fabricated under 5, 10, 30, and 40 MPa before and after abrasion test for 2000 cm. The polymers are polyhexamethylene adipamide (PA610), polystyrene (PS), polypropylene (PP), and methyl silicone resin (MSR), respectively.

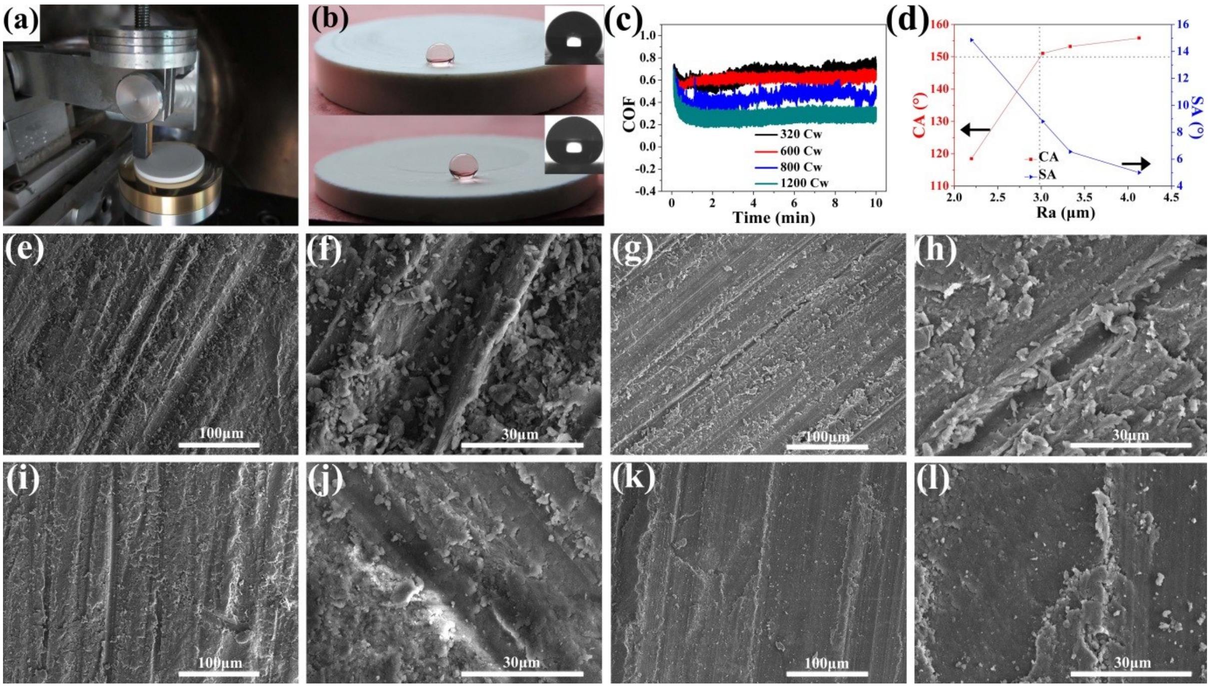

Figure S3. (a) Photograph of friction test on the pin-on-disk tribotester under the load of 40 g; (b) Water droplet sitting on the SiO_2/PS blocks after friction under sandpaper (SiC) grits of 1200 Cw (upper) and 320 Cw (bottom). (c) Plot of the coefficient of friction (COF) with abrasion time. (d) Relationship between the surface roughness, water contact angle and sliding angle. SEM images of the wear tracks after different grits of sandpaper friction: (e)-(f) 320 Cw; (g)-(h) 600 Cw; (i)-(j) 800 Cw; (k)-(l) 1200 Cw.

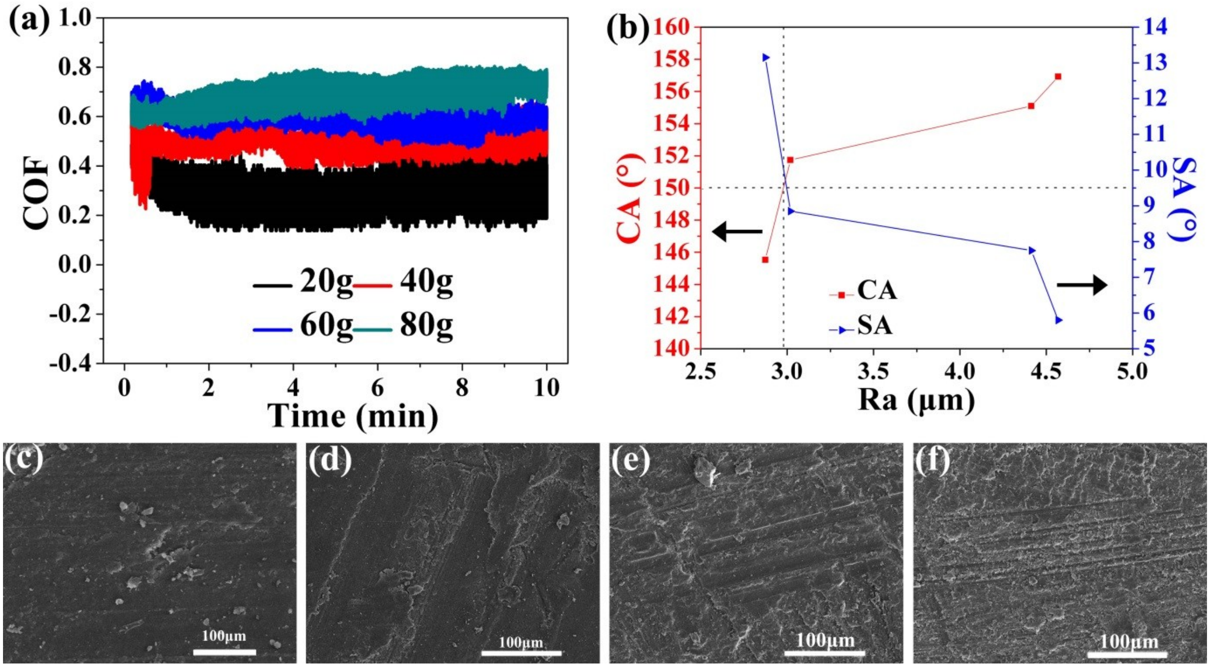

Figure S4. Friction test of SiO_2/PS blocks on the pin-on-disk tribotester using sandpaper (Grit 800 Cw) under loading weights of 20, 40, 60, and 80 g, respectively. (a) Plot of the coefficient of friction (COF) and the abrasion time. (b) Relationship between the surface roughness, water contact angle and sliding angle. SEM images of the wear tracks after different loading weights friction: (c) 20 g; (d) 40 g; (e) 60 g; (f) 80 g.

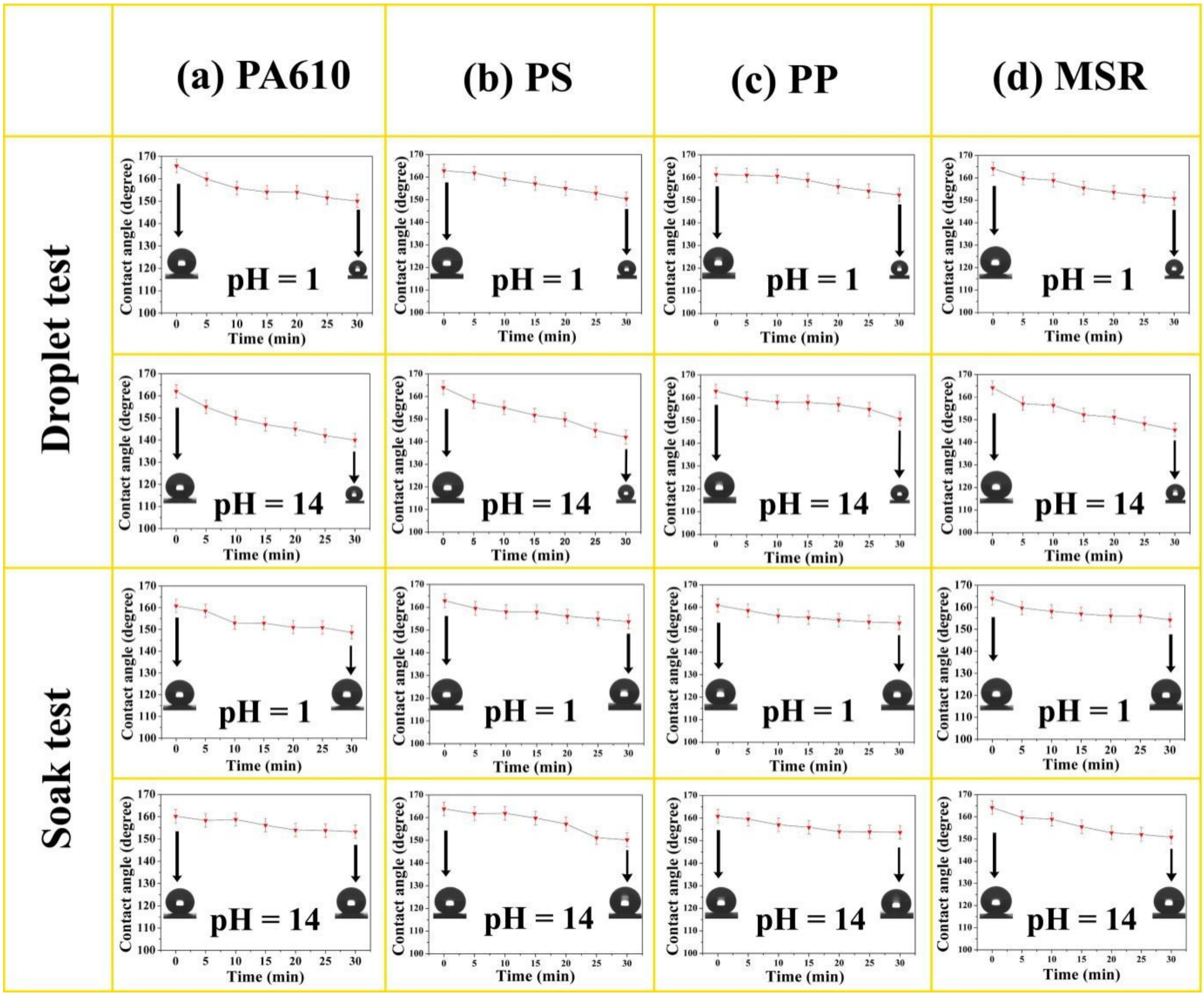

Figure S5. Contact angle as a function of time in acidic/alkali droplet contact tests and acidic/alkali sock tests on SiO_2/polymer blocks. The polymers are polyhexamethylene adipamide (PA610), polystyrene (PS), polypropylene (PP), and methyl silicone resin (MSR), respectively.

Table S1. Classification system for radar diagram.

Radar diagram point	**WCA θ [deg]**	**WSA α [deg]**	**Retention ratio η [%]**	**Hardness H_A [deg]**
1	$\theta \le 120$	$\alpha > 33$	$\eta \le 80$	$H_A \le 92$
2	$120 < \theta \le 125$	$29 < \alpha \le 33$	$80 < \eta \le 82$	$92 < H_A \le 92.5$
3	$125 < \theta \le 130$	$25 < \alpha \le 29$	$82 < \eta \le 84$	$92.5 < H_A \le 93$
4	$130 < \theta \le 135$	$21 < \alpha \le 25$	$84 < \eta \le 86$	$93 < H_A \le 93.5$
5	$135 < \theta \le 140$	$17 < \alpha \le 21$	$86 < \eta \le 88$	$93.5 < H_A \le 94$
6	$140 < \theta \le 145$	$13 < \alpha \le 17$	$88 < \eta \le 90$	$94 < H_A \le 94.5$
7	$145 < \theta \le 150$	$9 < \alpha \le 13$	$90 < \eta \le 92$	$94.5 < H_A \le 95$
8	$150 < \theta \le 155$	$5 < \alpha \le 9$	$92 < \eta \le 94$	$95 < H_A \le 95.5$
9	$155 < \theta \le 160$	$1 < \alpha \le 5$	$94 < \eta \le 96$	$95.5 < H_A \le 96$
10	$\theta > 160$	$\alpha \le 1$	$\eta > 96$	$H_A > 96$

Table S2. Average values and errors of performance characteristics and their corresponding points on radar diagram in brackets. The samples were SiO_2/PA610 blocks that were fabricated under 5, 10, 30 and 40 MPa.

Property	**5 MPa**	**10 MPa**	**30 MPa**	**40 MPa**
WCA initial [deg]	152.5±2.8 (8)	155.5±2.1 (9)	162.5±1.8 (10)	163.8±2.0 (10)
WSA initial [deg]	6.8±2.4 (8)	5.5±2.2 (8)	3.5±2.1 (9)	1.2±1.8 (9)
WCA after abrasion [deg]	150.0±2.1 (7)	151.5±2.7 (8)	152.8±1.7 (8)	154.2±1.9 (8)
WSA after abrasion [deg]	12.5±2.2 (7)	9.2±1.6 (7)	6.6±1.5 (8)	3.2±1.3 (9)
Retention ratio [%]	85.8±2.3 (4)	88.4±2.2 (6)	96.0±0.8 (9)	96.6±0.5 (10)
Hardness [deg]	91.2±0.6 (1)	93.3±0.7 (4)	94.2±0.3 (6)	95.3±0.2 (8)
WCA pH=1 [deg]	140.0±2.2 (5)	142.5±1.3 (6)	150.0±1.8 (7)	152.5±2.0 (8)
WCA pH=14 [deg]	130.5±3.1 (4)	132.7±3.3 (4)	135.5±2.6 (5)	140.5±3.5 (6)

Table S3. Average values and errors of performance characteristics and their corresponding points on radar diagram in brackets. The samples were SiO_2/PS blocks that were fabricated under 5, 10, 30 and 40 MPa.

Property	**5 MPa**	**10 MPa**	**30 MPa**	**40 MPa**
WCA initial [deg]	152.2±3.1 (8)	155.0±2.5 (8)	159.3±2.3 (9)	162.5±2.8 (10)
WSA initial [deg]	4.7±2.1 (9)	4.7±2.3 (9)	3.5±2.0 (9)	1.85±1.5 (9)
WCA after abrasion [deg]	149.5±3.6 (7)	152.3±2.6 (8)	154.5±1.8 (8)	156.8±1.5 (9)
WSA after abrasion [deg]	33.2±2.2 (1)	27.3±2.0 (3)	17.2±1.9 (5)	5.8±1.5 (8)
Retention ratio [%]	85.1±3.9 (4)	92.3±2.3 (8)	96.0±1.3 (9)	96.4±1.0 (10)
Hardness [deg]	93.1±0.5 (4)	94.0±0.6 (5)	94.8±0.4 (7)	95.5±0.4 (8)
WCA pH=1 [deg]	140.0±2.0 (5)	145.2±1.8 (7)	150.5±2.5 (8)	152.3±3.8 (8)
WCA pH=14 [deg]	135.5±3.5 (5)	137.2±2.2 (5)	143.5±2.8 (6)	145.5±2.5 (7)

Table S4. Average values and errors of performance characteristics and their corresponding points on radar diagram in brackets. The samples were SiO_2/PP blocks that were fabricated under 5, 10, 30 and 40 MPa.

Property	**5 MPa**	**10 MPa**	**30 MPa**	**40 MPa**
WCA initial [deg]	154.2±3.3 (8)	157.1±2.8 (9)	162.3±2.5 (10)	163.2±2.6 (10)

WSA initial [deg]	7.3±1.9 (8)	3.5±2.0 (9)	2.6±1.6 (9)	1.0±1.3 (10)
WCA after abrasion [deg]	152.3±2.7 (8)	155.2±2.5 (9)	159.1±2.0 (9)	160.5±1.6 (10)
WSA after abrasion [deg]	18.2±2.1 (5)	13.5±1.8 (6)	6.6±1.9 (8)	2.3±1.4 (9)
Retention ratio [%]	81.5±3.7 (2)	86.4±3.4 (5)	91.8±1.0 (7)	96.1±0.8 (10)
Hardness [deg]	93.2±0.7 (4)	94.1±0.5 (6)	94.8±0.4 (7)	95.5±0.3 (8)
WCA pH=1 [deg]	143.5±3.5 (6)	146.5±3.0 (7)	152.9±2.6 (8)	155.0±1.8 (8)
WCA pH=14 [deg]	128.2±2.3 (3)	139.8±2.1 (5)	150.0±2.9 (7)	151.5±2.5 (8)

Table S5. Average values and errors of performance characteristics and their corresponding points on radar diagram in brackets. The samples were SiO_2/MSR blocks that were fabricated under 5, 10, 30 and 40 MPa.

Property	**5 MPa**	**10 MPa**	**30 MPa**	**40 MPa**
WCA initial [deg]	153.2±2.5 (8)	154.5±3.0 (8)	162.6±2.8 (10)	164.5±2.0 (10)
WSA initial [deg]	7.5±3.2 (8)	5.5±1.4 (8)	3.3±1.8 (9)	1.5±1.2 (9)
WCA after abrasion [deg]	150.0±2.2 (7)	151.5±2.7 (8)	155.0±2.2 (8)	156.2±2.8 (9)
WSA after abrasion [deg]	20.2±3.5 (5)	16.8±2.9 (6)	6.5±2.5 (8)	2.6±1.4 (9)
Retention ratio [%]	92.1±2.1 (8)	93.1±2.8 (8)	94.2±1.2 (9)	95.3±0.7 (9)
Hardness [deg]	91.5±0.5 (1)	92.5±0.7 (2)	94.5±0.4 (6)	96.2±0.2 (10)
WCA pH=1 [deg]	145.0±1.5 (6)	148.0±3.0 (7)	150.0±1.9 (7)	152.5±2.1 (8)
WCA pH=14 [deg]	127.5±3.8 (3)	130.5±2.4 (4)	139.5±2.6 (5)	142.2±3.0 (6)

Table S6. Average values and errors of performance characteristics and their corresponding points on radar diagram in brackets. The samples were a brick (A), Never wet superhydrophobic coating (B) and the Never wet spray coated brick (C).

Property	**A**	**B**	**C**
WCA initial [deg]	0 (1)	160.5±2.7 (10)	156.5±3.0 (9)
WSA initial [deg]	N/A (1)	2.8±1.8 (9)	5.6±2.0 (8)
WCA after abrasion [deg]	0 (1)	134.5±3.0 (4)	117.5±2.5 (1)
WSA after abrasion [deg]	N/A (1)	38.5±3.3 (1)	85±5.8 (1)
Retention ratio [%]	92.8±2.6 (8)	68.8±4.1 (1)	94.2±1.8 (9)
Hardness [deg]	91.5±1.2 (3)	N/A (1)	89±0.9 (1)
WCA pH=1 [deg]	0 (1)	143.5±2.9 (6)	140.0±2.3 (5)
WCA pH=14 [deg]	0 (1)	132.5±3.5 (4)	129.8±3.8 (3)

Movie Captions

Movie S1

Knife was used to scratch on the SiO_2/PP block, followed by finger print and tape peeling tests. Water dropping tests were performed after each mechanical test.

Movie S2

The SiO_2/PP block was scratched by a knife in water, and then removed. Water was dropped onto the sample to test the wettability.

Movie S3

The SiO_2/PP block was abraded by a file in air, and then water was dropped onto the sample.

Movie S4

The SiO_2/PP block was abraded by a file in water, and then removed. Water was dropped onto the sample in air.

Movie S5

Liquid nitrogen test on the SiO_2/PP block. The sample was dipped into liquid nitrogen for ~10 s, and then removed. Water was then dropped onto the frozen sample. The sample was then heated by a hair dryer followed by water dropping tests.

Movie S6

The SiO_2/PA610 block was pressed by a Newton meter at ~200 N, followed by water dropping tests.

Movie S7

The SiO_2/PA610 block was broken by hammer beat. Water was then dropped onto the cross-sectional crack to test the superhydrophobicity inside the block.

Movie S8

The SiO_2/PA610 block was impacted strongly by running sand, followed by running water.

References

[S1] D. Zhi, Y. Lu, S. Sathasivam, I. P. Parkin, X. Zhang, *Journal of Materials Chemistry A* **2017**, 5, 10622.