Electronic Supplementary Material (ESI) for Materials Advances.

Supplementary data

Self-assembly of hierarchical porous structure for stretchable superhydrophobic films by delicately controlling the surface energy

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KEYWORDS: Superhydrophobic, silica, hierarchical porous structure, surface energy, stretchable

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Materials and Methods

Materials

Silica nanoparticles (R974 type) were purchased from Shaoxing Lijie Chemical Co., Ltd. FS-3100 was obtained from Guangzhou Jieluhua Biotechnology Co., Ltd. Thermoplastic polyurethane was provided by Wanhua Chemical Group Co., Ltd. Trimethoxy(1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl)silane ($C_{13}H_{13}F_{17}SiO_3$, FAS-17), *p*-phenylenediamine (p-PDA, 97%), 1-methyl-2-pyrrolidinone (NMP, analytical pure), triphenyl phosphite (TPP, 98%), pyridine (Py, analytical pure), *m*-cresol (analytical pure), ethanol (analytical pure), trifluoroacetic acid-*d* (*d*-TFA, 99.5%), 1-aminoundecanoic acid (AU, 99.7%), 4,4′-oxydiphthalic anhydride (ODPA, 97%), calcium chloride ($CaCl_2$, 99.99%), lithium chloride (LiCl, 99.98%) were obtained from Aladdin Industrial Corporation.

Preparation of fluorinated silica dispersion

FAS-17 (1.5 mL) was added into anhydrous ethanol (50 mL). Acetic acid was slowly dropped into FAS-17 solution to adjust pH to 3. Silica nanoparticles (1 g) and anhydrous ethanol (50 mL) were added into the acid solution, and ultrasonically oscillated for 0.5 h. The suspension was stirred at 50 °C for 6 h. After that, the suspension was concentrated, and dried at 90 °C for 12 h to get the white powder (m-SiO_2).

m-SiO_2 (2 g), FS-3100 (1 g), and TPU (0.2 g) were added into ethyl acetate (100 mL). The suspension was vigorously shaken by sonication shaker for 20 min and ultrasonic cell crusher for 30 min, respectively. Finally, FAS-17 (2 mL) was slowly added to the suspension. The mixture was vigorously stirred for 24 h to obtain m-SiO_2 dispersion.

Fabrication of stretchable superhydrophobic surfaces

PAI (0.15 g) and TPU (0.05 g) were completely dissolved in NMP (5 mL), and the solution was cast onto the glass plate, the PAI-TPU stretchable substrate was dried at 80 °C for 3 h. m-SiO_2 dispersion was sprayed on PAI-TPU wet surface before NMP was completely evaporated (Pressure was 0.7 MPa and the distance between the gun and the substrate was 20 cm). Finally, the samples were placed in an oven at 90 °C for 5 h to get PAI-TPU/m-SiO_2 stretchable superhydrophobic surfaces.

Materials characterization

Fourier-transform infrared (FTIR) spectra of the samples were measured by FTIR spectrometer (Avatar 370, Thermo Nicolet). KBr pellet technique was applied to monitoring changes in the range of 400–4000 cm^{-1} with a resolution of 0.1 cm^{-1}. The proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded by Bruker 500 MHz instrument with trifluoroacetic acid (TFA) containing tetramethylsilane as the internal reference. Thermogravimetric analysis (TGA) was carried out by instrument (TGA 4000, PerkinElmer) at a heating rate of 10 °C min^{-1} in the temperature range from 30 to 700 °C under nitrogen atmosphere. The samples for tensile test were prepared with a size of 20 mm long and 10 mm wide, and they were measured on tensile apparatus (WDT-10, KaiQiangLi) at room temperature with a drawing rate of 5 mm min^{-1}, an average of at least five individual determinations was used. X-ray photoelectron spectroscopy (XPS) was collected on an ESCALAB 250XI system (Thermo Fischer, Waltham, MA, USA) using Al-Kα radiation ($h\nu$ = 1486.6 eV). The atomic force microscope (AFM) surface images were collected in contact mode (SPM-9700, Shimadzu) with an Au-coated silicon probe (Nanosensors, PPP-CONT Au, a tip radius of curvature <10 nm, and a spring constant of 0.2 N m^{-1}). Root-mean-square roughness (R_q) was analyzed automatically using the NanoScope v1.5 software, and the R_q

was determined from the average of five measurements at various positions on the surfaces of the samples. Scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) was carried out by field emission scanning electron microscope (Zeiss SUPRA55, Jena, Germany) and X-ray energy spectrum (X-Max, Oxford, UK). The microstructures of specimen were observed at an acceleration voltage of 5 kV after gold-spraying and elemental analysis. The contact and sliding angles were measured using a JC2000D1 at ambient temperature. Water droplets (about 5 μL) were carefully dropped onto the surfaces of the samples, the contact and sliding angles were determined from the average of five measurements at various positions on the surfaces of the samples.

Synthetic procedure of DIDA and PAI

As shown in the Fig. S1, the diimide-diacid (DIDA) was synthesized by the condensation of ODPA with 11-aminoundecanoic acid through dehydration cyclization, then PAI was prepared from 1,4-diaminobenzene and DIDA monomers through Yamazaki–Higashi phosphorylation reaction. The detailed synthetic procedure was described as below.

Synthesis of DIDA monomer. ODPA (20.15 g, 0.065 mol), AU (26.13 g, 0.13 mol) and acetic acid (140 mL) were mixed. The mixture was vigorously stirred for 6 h at room temperature. Then the mixture was slowly heated to reflux for another 10 h. The solution was cooled to room temperature, and washed by deionized water until the filtrate became neutral. The product was dried at 90 °C for overnight (yield: 91%). FTIR (KBr, *v*, cm^{-1}): 3462, 1772, 1706, 1400, 1367, 1073, 745. Proton nuclear magnetic resonance (^{1}H-NMR, δ/ppm, *d*-TFA): 11.60 (broad, COOH), 8.038 (d, 2 H), 7.64 (d, 2 H), 7.55 (dd, 2 H), 3.84(t, 4 H), 2.56 (t, 4 H), 1.78 (m, 8 H), and 1.39 (m, 24 H).

Synthesis of poly(amide–imide) (PAI). DIDA (3.38 g, 0.005 mol), LiCl (1 g, 0.024 mol), and $CaCl_2$ (2 g, 0.018mol) were added into a three-mouth flask. TPP (6 mL), Py (6 mL), NMP (13 mL), and p-PDA (0.55 g, 0.005 mol) were successively added into the flask. The mixture was heated to reflux for 8 h. The solution was poured into anhydrous ethanol, and the crude product was washed by ethanol and distilled water in sequence to remove $CaCl_2$ and LiCl. Finally, the product was placed in a vacuum drying oven at 80 °C for 8 h (yield: 86%). FTIR (KBr, *v*, cm^{-1}): 3295, 1769, 1708, 1551, 1398, 746. ^{1}H-NMR (δ/ppm, *d*-TFA): 7.89 (d, 2H), 7.47 (s, 2H), 7.43(s, 2H), 7.37 (t, 4H), 7.48 (d, 4H), 7.22 (s, 2H), 3.69 (t, 4H), 2.57 (t, 4H), 1.64 (m, 8H), 1.28 (m, 24H).

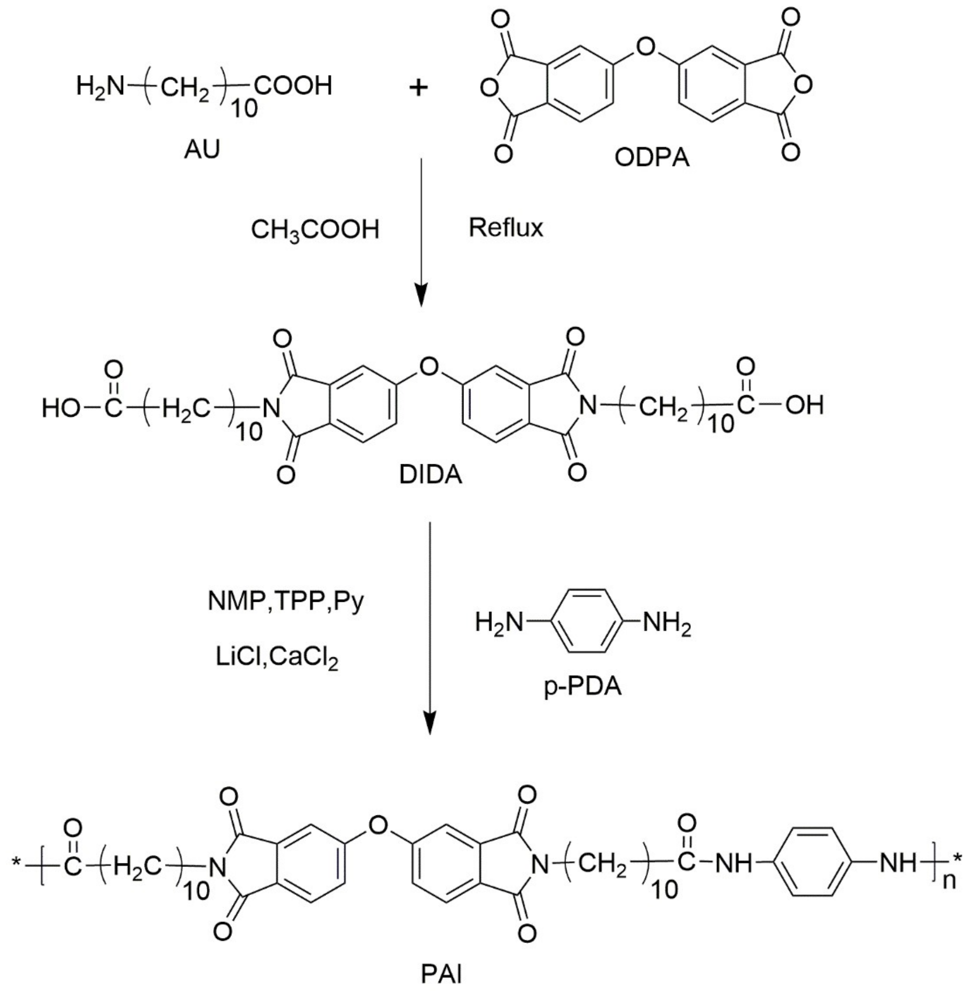

Fig. S1 Synthetic procedure of DIDA and PAI.

The proton nuclear magnetic resonance (^{1}H-NMR) spectra

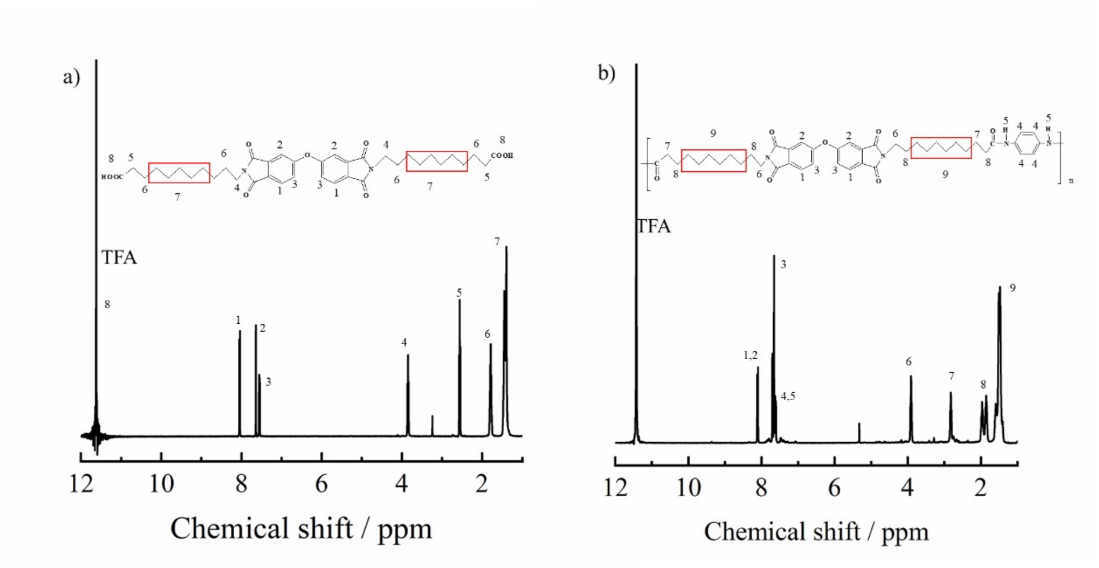

Fig. S2 The ^{1}H NMR spectra of DIDA (a) and PAI (b).

The Fourier-transform infrared (FTIR) spectra

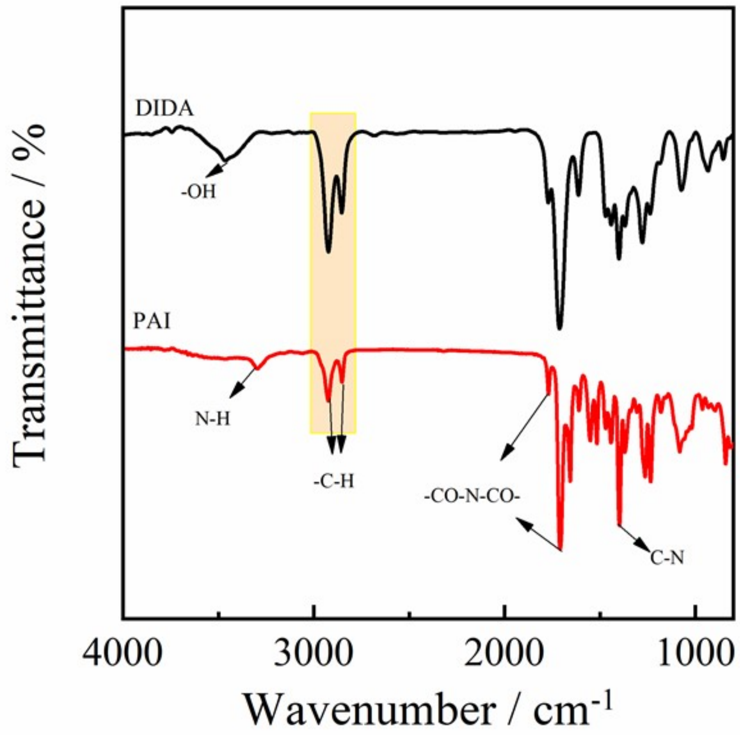

Fig. S3 The FTIR spectra of DIDA (black line) and PAI (red line).

Thermal weight analysis of SiO_2 and m-SiO_2

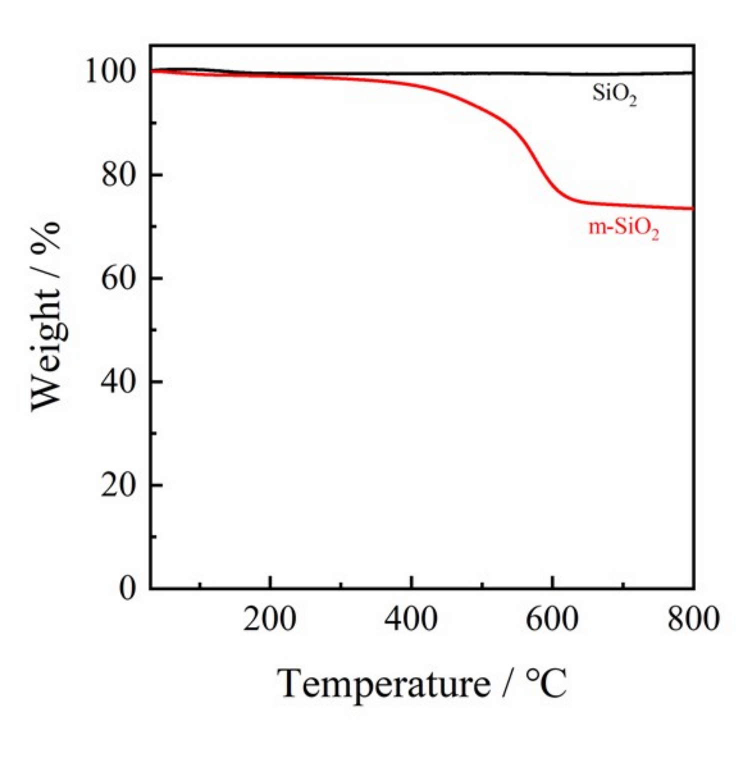

Fig. S4 TGA curves of SiO_2 (black line) and m-SiO_2 (red line).

EDS mapping of PAI-TPU/m-SiO_2 superhydrophobic surface

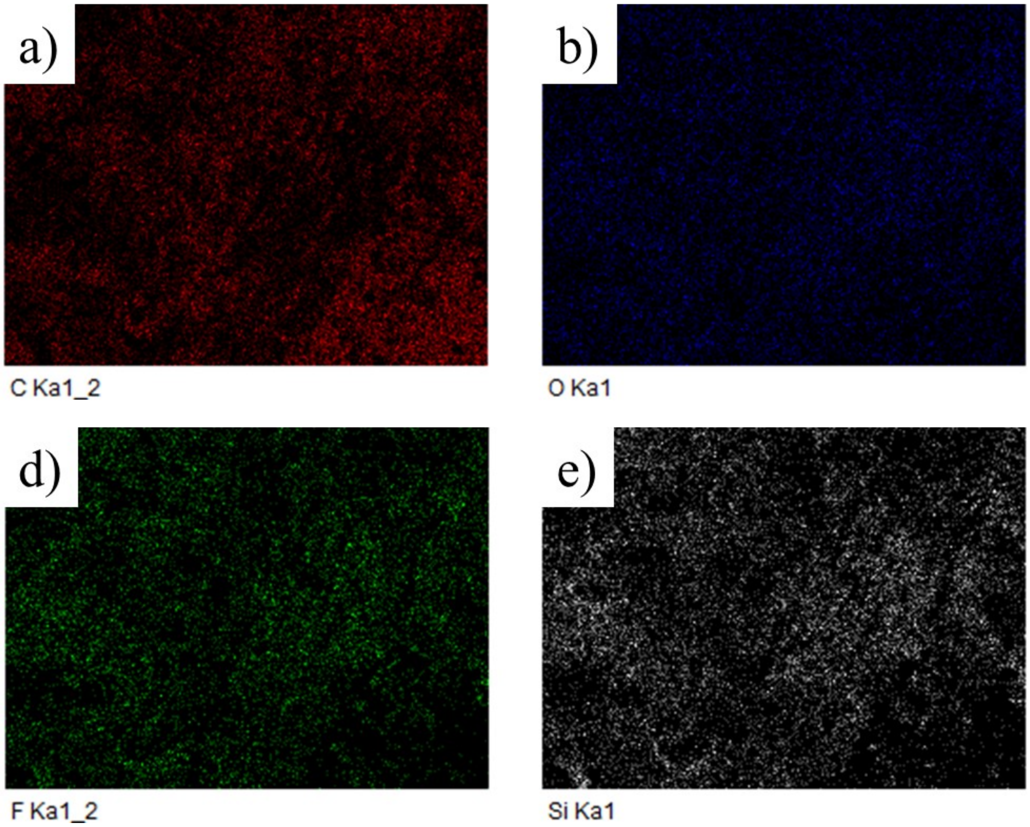

Fig. S5 EDS mapping of C (a), O (b), F (c) and Si (d) elements of PAI-TPU/m-SiO_2 superhydrophobic surface.

Mechanical property of PAI-TPU/m-SiO_2 superhydrophobic surface

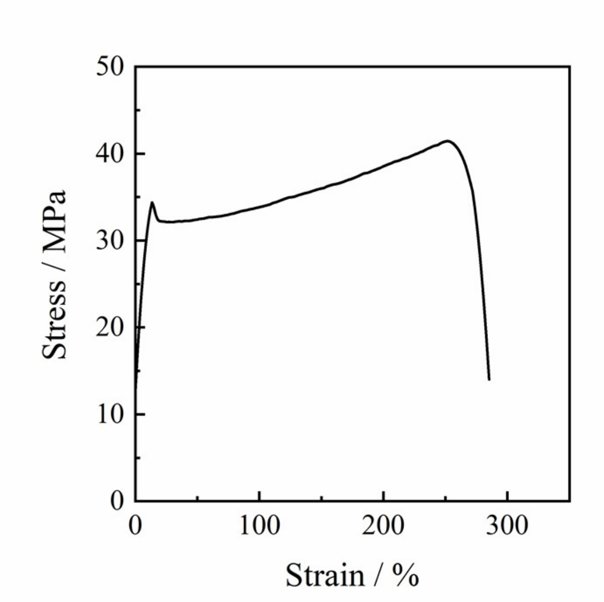

Fig. S6 Stress–strain curve of PAI-TPU/m-SiO_2 superhydrophobic surface.

Wetting behavior of PAI-TPU/m-SiO_2 surfaces under different strains

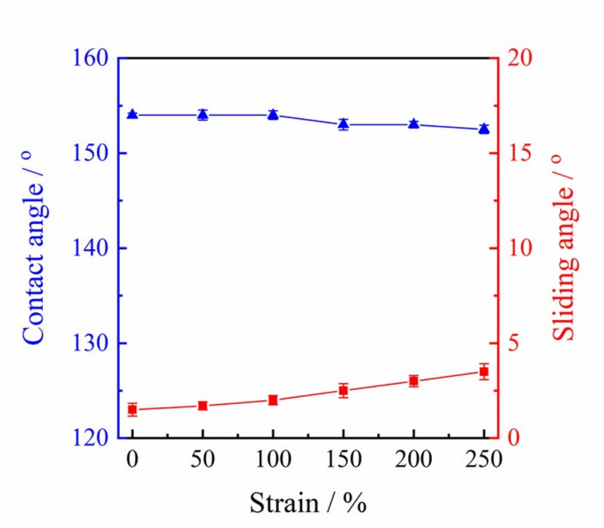

Fig. S7 The wetting behavior of PAI-TPU/m-SiO_2 surfaces under different strains.

Thermal stability of PAI pristine, TPU pristine, and PAI-TPU substrate films

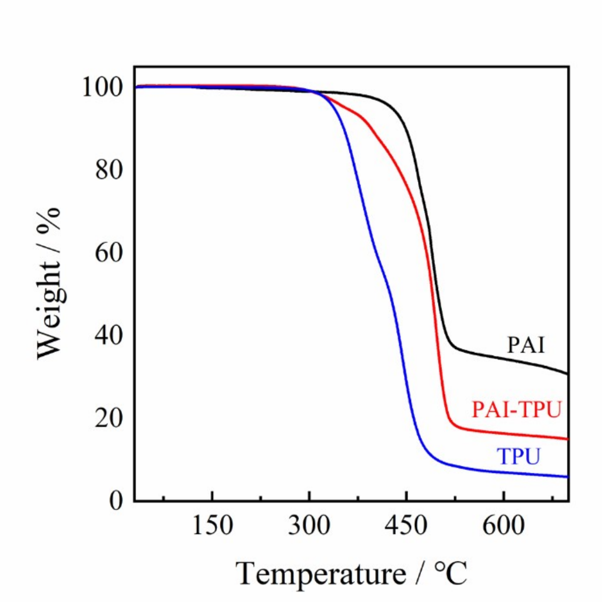

Fig. S8 TGA curves of PAI pristine (black line), TPU pristine (blue line), and PAI-TPU substrate (red line) films.