

Facile fabrication of flexible superhydrophobic surfaces with high durability and good mechanical strength through embedding silica nanoparticle into polymer substrate by spraying method

Shuhan Hou^a, Insub Noh^b, Xinlu Shi^a, Yanbin Wang^{a}, Hyung Do Kim^{b*}, Hideo Ohkita^{b*},
Biaobing Wang^{a*}*

^aJiangsu Key Laboratory of Environmentally Friendly Polymeric Materials, Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, School of Materials Science and Engineering, Changzhou University, Changzhou 213164, People's Republic of China

^bDepartment of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo, Kyoto 615-8510, Japan

*Corresponding Authors:

wangyanbin@cczu.edu.cn (Y. Wang); hyungdokim@photo.polym.kyoto-u.ac.jp (H.D. Kim);
ohkita@photo.polym.kyoto-u.ac.jp (H. Ohkita); biaobing@cczu.edu.cn (B. Wang).

Abstract: Flexible superhydrophobic surfaces have been attracting more and more attention due to their foldable property. However, the superhydrophobic structure was easily damaged or destroyed owing to their poor interfacial force between substrate and superhydrophobic coating. Herein, fluorinated silica nanoparticles (F-SiO₂) were sprayed onto the wet poly(amide-imide) (PAI) surface, which made F-SiO₂ easily went into PAI substrate to enhance the durability of superhydrophobic surface. The PAI/F-SiO₂ flexible surface exhibited a water contact angle (CA) of beyond 160 ° and a sliding angle (SA) of as low as 3 °, while the tensile strength (34 MPa) was comparable to that of PAI substrate (35.8 MPa). Encouragingly, the superhydrophobicity and hierarchical porous structure of PAI/F-SiO₂ surface were maintained even they were folded by 5000 times or underwent sandpaper abrasion test (500 cm of wear on a 1200 grit sandpaper under 50 g load), while the nanocomposites failed the sandpaper abrasion test when F-SiO₂ were sprayed onto completely dried PAI surface. More importantly, the CA and SA just slightly decreased when PAI/F-SiO₂ surfaces were heated at 300 °C for 24 h due to the unique surface morphology and high thermal stability of PAI, which is one of the highest thermal stabilities for flexible superhydrophobic films. In addition, PAI/F-SiO₂ surfaces maintained superhydrophobic after hot water jet impact, acid-base immersing, UV irradiation, and ultrasonic treatment, indicating the fabricated surfaces could be used for practical application especially under harsh conditions. Furthermore, the superhydrophobic surfaces possessed icephobic properties. It should be noted that PAI/F-SiO₂ surfaces showed such excellent properties, although their fabricating procedure did not undergo any optimization. This wet spraying method was also used to fabricate flexible superhydrophobic surfaces with other polymers as substrates such as poly(acrylic acid) (PAA), thermoplastic polyurethane (TPU), polystyrene (PS), and poly(vinyl alcohol) (PVA). Therefore,

the simple strategy provided a general route to prepare flexible superhydrophobic films with high durability.

KEYWORDS: Superhydrophobic, silica, durability, spray, flexible

1. Introduction

Surface wettability is a significant characteristic of polymer films. For example, poly(amide-imide) (PAI) as one kind of high-performance polymers has been widely utilized in our daily life and industries owing to its unique properties such as excellent thermal stability, high mechanical property, and good processability [1-3]. Just like other commercial polymer materials, PAI films are also easily contaminated by liquids and attached onto their surfaces, which impacts adverse effects on their properties. It is well known that when the water contact angle (CA) is higher than 150° and sliding angle (SA) is lower than 10° , the surface can be considered as superhydrophobicity. Superhydrophobicity, as a special state of wettability, can make the water droplets quickly roll off from polymer surface, and decreases the negative impact on the performances of polymer films. In addition, because of its rough structure and low surface energy, superhydrophobic surface also played a very important role in other fields such as anti-icing [4], drag reduction [5], anti-corrosion [6], self-cleaning [7], oil/water separation [8], and so forth. Therefore, developing flexible superhydrophobic surfaces have been attracting more and more attention.

Various methodologies have been proposed to prepare superhydrophobic surface including sol-gel method [9], chemical vapor deposition (CVD) [10], template method [11], laser etching [12], electrospinning [13], brush-painting [14], and spin-coating [15]. However, these methods

always went with some common limitations involving strict requirements on manufacturing equipment and environment, or complicated manufacturing process. Spraying method also has been used to fabricate superhydrophobic surface [16-23], it just only needs a pump and a spray gun. Furthermore, this method is not sensitive to the environmental condition. Thus, spraying method is considered as an ideal way for industrial applications. For example, Allahdini et al. sprayed methoxy-functional silicone resin, fumed silica nanoparticles, and methyltriethoxysilane on various substrates such as glass and metals [19]. The spray-coated surfaces superhydrophobic characteristic with water CA of about 160 °. Furthermore, the superhydrophobic surfaces could shed various contaminants in both wet and dry conditions, and improve the freezing delay times. Despite these advantages, it remained a challenge to prepare flexible superhydrophobic materials with high durability. For example, Kim et al. chemically modified silicon dioxide (SiO₂) with perfluorooctyltriethoxysilane (PFOTES), and sprayed poly(vinylidene fluoride) (PVDF) and PFOTES-SiO₂ nanoparticles on poly(methyl methacrylate) (PMMA) substrate [24]. The prepared FSM-PMMA surface showed a high CA of 163 ° and low SA of 7 °, but CA significantly decreased to below 150 ° and SA sharply increased to far beyond 10 ° after moving for 110 cm on the sandpaper.

To strength the interfacial adhesion between the coating and substrate, lots of binders were incorporated into the spraying suspensions [25-29]. For example, Zhang et al. used epoxy resin (EP) and polydimethylsiloxane (PDMS) as binders to prepare robust superhydrophobic surfaces [26]. With the synergistic effect of PDMS and EP, SiO₂ particles were firmly attached to the substrate, and the coating remained superhydrophobic even after 7.5 m abrasion on a sandpaper (800 Cw) under 50 g of weight or exposed to harsh environments (strong UV irradiation for 2 h and chemical solution corrosion for 1 h). Another strategy is to construct double or multilayer

structures [30-34]. For example, Yu et al. adopted two-step spraying method to fabricate superhydrophobic surfaces with polydopamine (PDA) as intermediate layer [32]. Compared to the superhydrophobic materials without PDA intermediate layer, the superhydrophobic materials with PDA intermediate layer exhibited improved water repellence, durability, and mechanical stability. It is obvious that although the performances of superhydrophobic materials were improved, these approaches also made the low-cost and simple spraying method expensive and complicated.

In this study, spraying approach has been used to fabricate flexible superhydrophobic surface with high durability. Firstly, nano-SiO₂ particles were fluorinated by trimethoxy(1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl) silane (FAS-17) to decrease the surface energy of coating. Then, the fluorinated silica (F-SiO₂) nanoparticles were sprayed onto the wet PAI surface to fabricate PAI/F-SiO₂ flexible superhydrophobic films. This made F-SiO₂ tightly embedded into PAI substrate. In addition, the control samples (Spraying F-SiO₂ onto the completely dried PAI surfaces) were also prepared. The surface wettability, mechanical, and icephobic properties were investigated. Moreover, the durability of the fabricated flexible superhydrophobic films were investigated using sandpaper abrasion tests, hot water jet impact, acid-base immersing, UV irradiation, and ultrasonic treatment. To find out the origin of the excellent properties of PAI/F-SiO₂ flexible superhydrophobic films, surface chemistry was investigated by Fourier-transform infrared spectra (FTIR), X-ray photoelectron spectroscopy (XPS) and energy dispersive spectroscopy (EDS). Morphologies were researched by atomic force microscopy (AFM) and scanning electron microscopy (SEM). Another purpose is to develop a universal strategy for fabricating flexible superhydrophobic surface with good durability, and thus the surface wettability of composites with other polymers as substrate such as poly(acrylic acid) (PAA), thermoplastic polyurethane (TPU), polystyrene (PS), and poly(vinyl alcohol) (PVA) were also researched.

2. Materials and Methods

2.1. Materials

Silica nanoparticles (R974 type, ~12 nm) were purchased from Shaoxing Lijie Chemical Co., Ltd. 4,4'-Diaminodiphenylmethane (DCP) was obtained from Tokyo Chemical Industry (TCI) Co., Ltd. FS-3100 was obtained from Guangzhou Jieluhua Biotechnology Co., Ltd. Trimethoxy(1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl)silane (C₁₃H₁₃F₁₇SiO₃, FAS-17), 1-methyl-2-pyrrolidinone (NMP), ethanol, trifluoroacetic acid-*d* (*d*-TFA), triphenyl phosphite (TPP), 1-aminoundecanoic acid (AU), pyridine (Py), 4,4'-oxydiphthalic anhydride (ODPA), calcium chloride (CaCl₂), lithium chloride (LiCl) were obtained from Aladdin Industrial Corporation.

2.2. Synthesis of flexible polymer substrate

Diimide diacid (DIDA) monomer was obtained by the condensation reaction of ODPA and AU through dehydration cyclization as shown in the Fig. 1. The target polymer PAI was prepared through Yamazaki–Higashi phosphorylation reaction between DIDA and 4,4'-diaminodiphenylmethane (DCP) [35-39]. The detailed synthetic procedure was offered in the Supplementary Information. The FTIR and proton nuclear magnetic resonance (¹H-NMR) spectra of DIDA and PAI are collected in the Fig. S1 and Fig. S2, respectively.

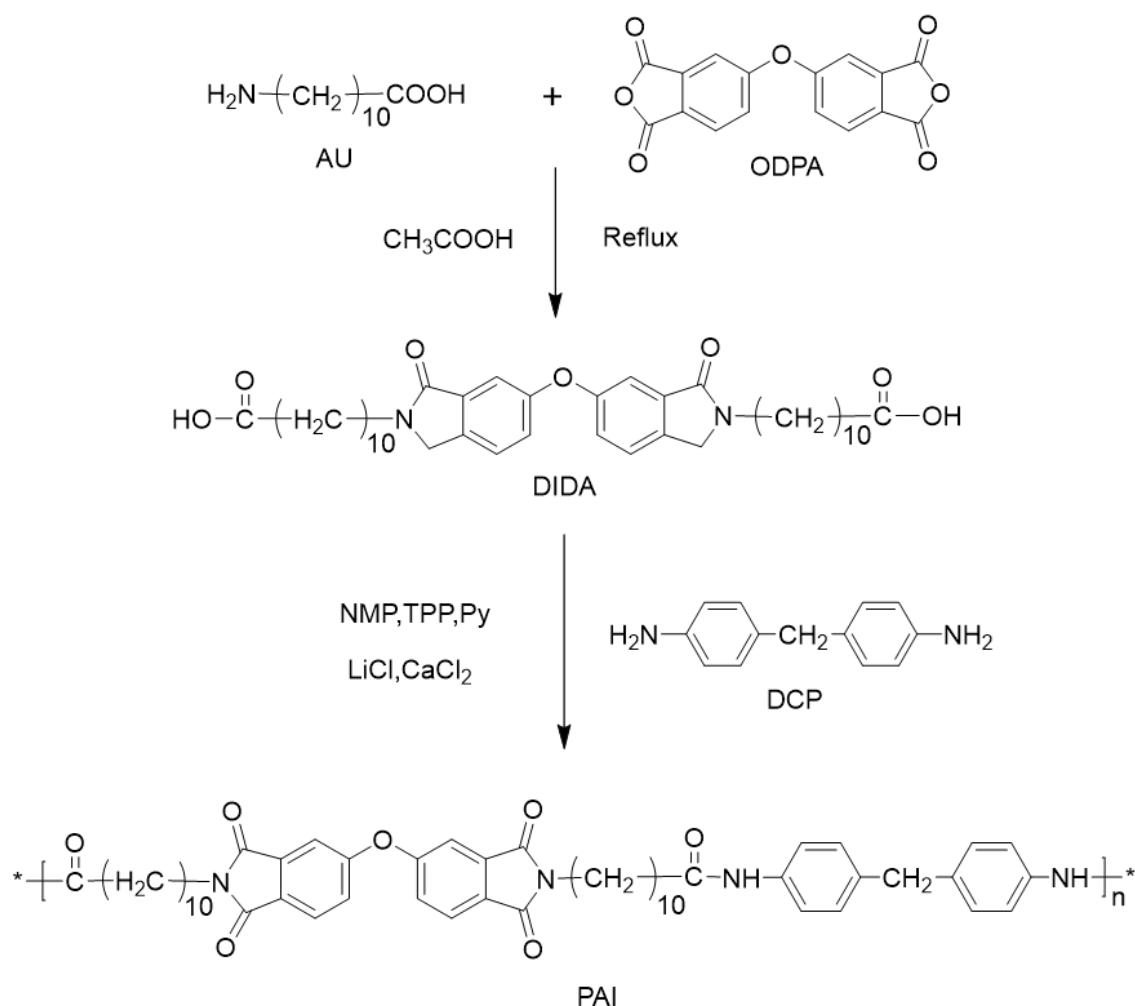


Fig. 1. Synthetic route of DIDA monomer and PAI polymer.

2.3 Preparation of fluorinated silica dispersion

Silica nanoparticle (1 g) and nonionic fluorinated surfactant (FS-3100, 0.4 g) were added into distilled water (60 mL). The silica suspension was vigorously shaken by sonication shaker for 20 min and ultrasonic cell crusher for 30 min, respectively. Finally, FAS-17 (1 mL) was added into silica suspension, and then vigorously stirred for 24 h to obtain fluorinated silica dispersion.

2.4 Fabrication of PAI/F-SiO₂ surfaces and control samples

PAI (0.2 g) was added into NMP (5 mL). The solution was cast onto the glass plate, and dried at 90 °C for 3 h. The superhydrophobic F-SiO₂ dispersion was sprayed on PAI wet surface before NMP was completely evaporated (distance between polymer substrate and gun was 15 cm, pressure was 0.7 MPa). Finally, the samples were dried at 80 °C for 6 h to obtain PAI/F-SiO₂ flexible superhydrophobic films. The control samples were prepared with similar method of PAI/F-SiO₂ surfaces, except that F-SiO₂ dispersion was sprayed onto the completely dried PAI surfaces.

2.5 Materials characterization

Samples for FTIR spectra were measured with a spectrometer (Avatar 370, Thermo Nicolet) in the range of 500–4000 cm⁻¹ with resolution of 0.1 cm⁻¹. The ¹H-NMR spectra were measured with a Bruker 500-MHz instrument by using TFA containing tetramethylsilane (TMS) as internal reference. The thermal stability of samples was researched by thermogravimetric analysis (TGA 4000, PerkinElmer) in the temperature range from 30 to 700 °C with a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. The mechanical property of samples was investigated with a tensile apparatus (WDT-10, KaiQiangLi) at a drawing rate of 5 mm min⁻¹, the size of samples was 20 mm long and 10 mm wide, and an average of at least five individual data was used to determinate the mechanical property. XPS was performed on an ESCALAB 250XI system using Al-K α radiation ($h\nu = 1486.6$ eV). The AFM (SPM-9700, Shimadzu) surface images were researched using contact mode with Au-coated silicon probe. SEM with EDS was performed with a field emission scanning electron microscope (SUPRA55, Zeiss) and X-ray energy spectrum. The contact and sliding angles of samples were evaluated by a contact angle meter (JC2000D1 Shanghai Auto-Lab Technology), and the contact and sliding angles were calculated from the average of five values at different positions.

3. Results and Discussion

3.1 Design and preparation of flexible superhydrophobic surfaces

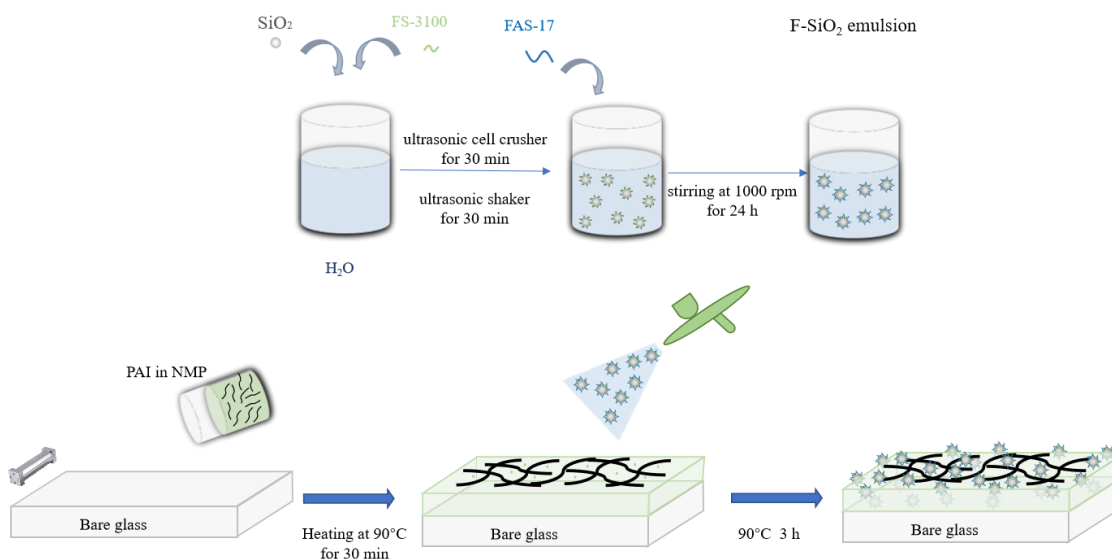


Fig. 2. Schematic representation of the fabrication of flexible superhydrophobic surfaces.

Fig. 2 shows the key steps of fabrication of PAI/F-SiO₂ flexible superhydrophobic surfaces.

For the preparation of F-SiO₂ dispersion, a nonionic surfactant (FS-3100) was used, which played a very important role in fabricating homogeneous dispersion of silica nanoparticles in water. Then, a fluorine containing silane coupling agent (FAS-17) was added into the silica dispersion to bind the adjacent SiO₂ nanoparticles together. More importantly, FAS-17 can be grafted on the surface of silica nanoparticles to decrease the surface energy of SiO₂ nanoparticles. The successful modification of SiO₂ was confirmed by FTIR spectra (Fig. S3), in which the band at 1208 cm⁻¹ is ascribed from the C–F stretching vibration of FAS-17 [40]. Because of the similar structure of FS-3100 and FAS-17, they can be intertwined to form a network structure, which is helpful for further lowering the surface energy of the particles. For the flexible polymer substrate, a high-performance polymer (PAI) was designed, in which the repeating unit contains imide ring and suitable aliphatic

chain, and simultaneously was endowed with good thermal stability, mechanical property, and solubility. A selective solvent (*N*-methylpyrrolidone, NMP) with high boiling point was used to prepare PAI solution, although many other solvents such as tetrahydrofuran (THF), and chloroform also can dissolve PAI. This is because the solvent is evaporated slowly, and gives enough time for F-SiO₂ going into polymer substrate, which is the key to successful preparation of flexible superhydrophobic surfaces. Finally, F-SiO₂ dispersion was sprayed on the wet surface of PAI substrate before the solvent was totally evaporated. In order to discuss the advantages of this method, control samples (Spraying F-SiO₂ onto the completely dried PAI surfaces) were also prepared.

3.2 Surface wettability

Surface wettability was determined by water contact angle measuring equipment with 5-μL of water droplets on the different surfaces. As shown in the Fig. 3a, CA on the surface of PAI neat film was 76 °, and water droplets wet the pristine material surface completely owing to the polar amide group in the PAI main chain. After spraying F-SiO₂ coating, CA of PAI/F-SiO₂ surface obviously increased up to 154 ° as shown in the Fig. 3b. In order to investigate the adhesion of the flexible surfaces, SA was also measured, it was found that the SA of PAI/F-SiO₂ surface (3 °) sharply decreased compared to PAI substrate (90 °), suggesting a much lower adhesion between water and PAI/F-SiO₂ surface. For control samples, they showed similar surface wettability with a CA of 154 ° and SA of 4 ° as shown in the Fig. S4. In addition, wettability in various environments is also very important for the application of superhydrophobic materials. Encouragingly, PAI/F-SiO₂ superhydrophobic films also had good resistance to wetting by various liquids in our daily life including coffee, milk, and tea as shown in the Figure 3c. On the other hand, other polymers

195 were also chose as substrates to fabricate flexible superhydrophobic surfaces, such as TPU, PS,
196 PVA, and PAA. Like PAI/F-SiO₂ superhydrophobic surface, the wettability of TPU/F-SiO₂, PS/F-
197 SiO₂, and PVA/F-SiO₂ surfaces was also significantly improved and satisfied the
198 superhydrophobic requirement as shown in the Fig. 3b, although TPU, PS, and PVA neat films
199 showed different polarity. More interestingly, PAA as one kind of strong water absorbing polymers
200 also can be used as flexible substrate to prepare superhydrophobic surface as shown in the Fig. S5.
201 These results suggested that the wet spraying method was a universal strategy for fabricating
202 flexible superhydrophobic surface in spite of the polarity of polymer substrate.

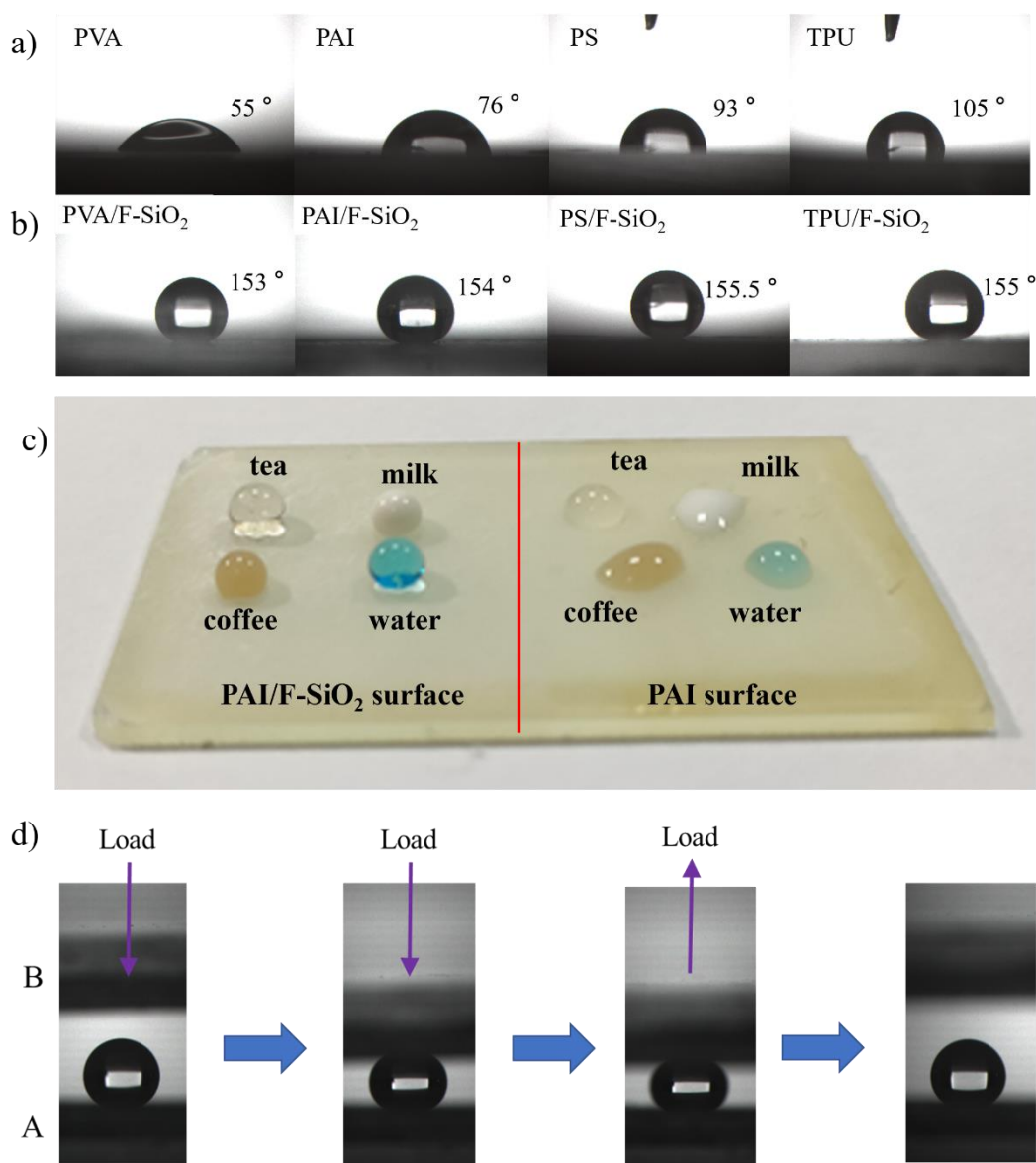


Fig. 3. Digital photographs of water droplets on the surface of polymer substrates (a) and flexible superhydrophobic films (b). Digital photographs of different liquids on the PAI/F-SiO₂ and PAI surfaces (c). Schematic illustration of the wetting state of PAI/F-SiO₂ superhydrophobic surface (d).

In order to describe the wetting behavior of droplets on the superhydrophobic surfaces, squeezing experiment was conducted. Firstly, a water droplet was laid on the PAI/F-SiO₂ surface (surface A), and the water droplet showed a spherical shape as shown in the Fig. 3d. Then, another superhydrophobic surface B squeezed the water droplet, the droplet became ellipsoid from spherical shape rather than wetting surface A. When surface B moved away, the water droplet

returned to its original spherical shape. This phenomenon suggested that the contact between PAI/F-SiO₂ superhydrophobic surface and water droplet was Cassie's state rather than Wenzel's state [41].

3.3 Surface chemistry and morphology

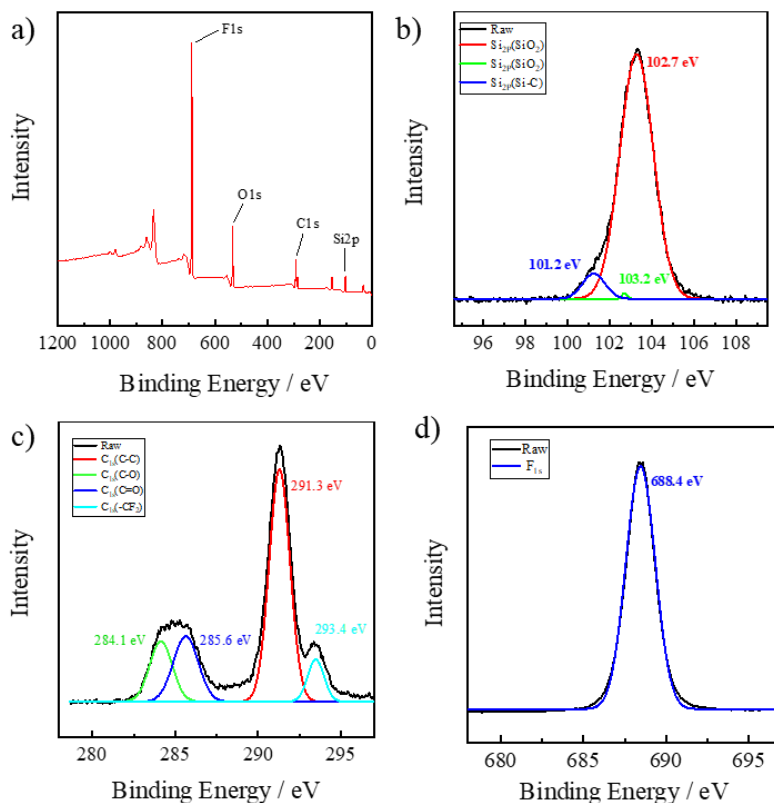


Fig. 4. XPS survey (a) and high resolution Si_{2p} (b), C_{1s} (c), and F_{1s} (d) spectra of PAI/F-SiO₂ flexible superhydrophobic surfaces.

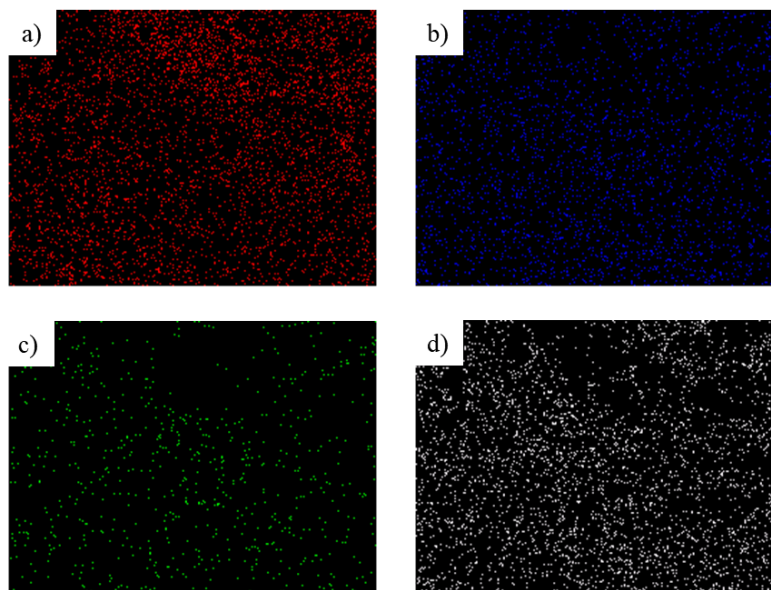


Fig. 5. EDS mapping of C (a), O (b), F (c) and Si (d) elements of PAI/F-SiO₂ superhydrophobic surface.

In general, superhydrophobic surface can be obtained by the combination of chemical composition with low surface energy and micro/nano scale roughness. Micro/nano scale roughness structure with low surface energy can decrease the liquid–solid contact area by forming trapped air pockets, resulted in increase of CA and decrease of SA [42]. For the surface chemistry, XPS was used to research the chemical components of flexible superhydrophobic surfaces. Fig. 4a shows the overview scan of photoelectron peaks from Si_{2p}, C_{1s} and F_{1s}. In more detail, as shown in the Fig. 4b, peaks at 103.2 eV and 101.2 eV in the Si_{2p} spectra were attributed to hydrophobic SiO₂ nanoparticles and the peak at 102.7 eV was ascribed from Si–C group of FAS-17. As shown in the Fig. 4c, peaks at 285.6 eV and 284.1 eV in the C_{1s} spectra were respectively derived from C–O and C–C groups of FS-3100 and FAS-17. Moreover, the peaks at 293.4 eV and 291.3 eV were originated from –CF₃ and –CF₂ groups. The –CF₃ and –CF₂ groups were confirmed again by the peak at 688.4 eV in the F_{1s} spectrum as shown in the Fig. 4d [21], which played a very important role in achieving superhydrophobic property. On the other hand, the elemental distribution of PAI/F-SiO₂ superhydrophobic surface was investigated by EDS elemental mapping as shown in

the Fig. 5. It was found that C, F, O, and Si elements were uniformly located on the PAI/F-SiO₂ superhydrophobic surface, suggesting F-SiO₂ nanoparticles were uniformly distributed in the superhydrophobic surface, and the whole surface can be expected to possess the same superhydrophobic behavior.

The surface morphology was firstly researched by SEM. As shown in the Fig. 6a, PAI/F-SiO₂ superhydrophobic surface exhibits a hierarchical porous and clustered-like structure. Such structures favor the entrapment of air pockets and production of a layer of air cushion underneath the water droplets, which is in charge of the superhydrophobic behavior of PAI/F-SiO₂ surface. For control samples, they showed similar surface morphology as shown in the Fig. S6. Fig. 6b shows that F-SiO₂ nanoparticles are bound to each other, and many nanoparticles are partially embedded in the flexible PAI substrate, since the F-SiO₂ was sprayed on the wet PAI surface under positive pressure, which is vital for the durability of superhydrophobic surface. In order to quantitatively investigate the surface roughness and visualize the surface texture, PAI/F-SiO₂ superhydrophobic surfaces were observed by AFM. It is well known that arithmetic average roughness (R_a) representatives the average roughness between peaks and valleys while the root mean square roughness (R_q) means the standard deviation of the distribution of surface roughness height. As shown in the Fig. 6c and 6d, PAI pristine film showed relatively smoother surface with R_q and R_a values of 4.8 and 4.0 nm, respectively. After spraying F-SiO₂ on the surface of PAI, R_q and R_a values of PAI/F-SiO₂ flexible superhydrophobic surfaces sharply increased to 187.6 and 138.4 nm as shown in the Fig. 6e. Moreover, AFM 3D image of PAI/F-SiO₂ superhydrophobic surface exhibits an uneven mountain-like structure as shown in the Fig. 6f. The unique structure is helpful for facilitating air pockets located under the water droplets, and formation of liquid–air–

solid interface, which is beneficial for decreasing the contact area between PAI/F-SiO₂ superhydrophobic surfaces and water droplets [43].

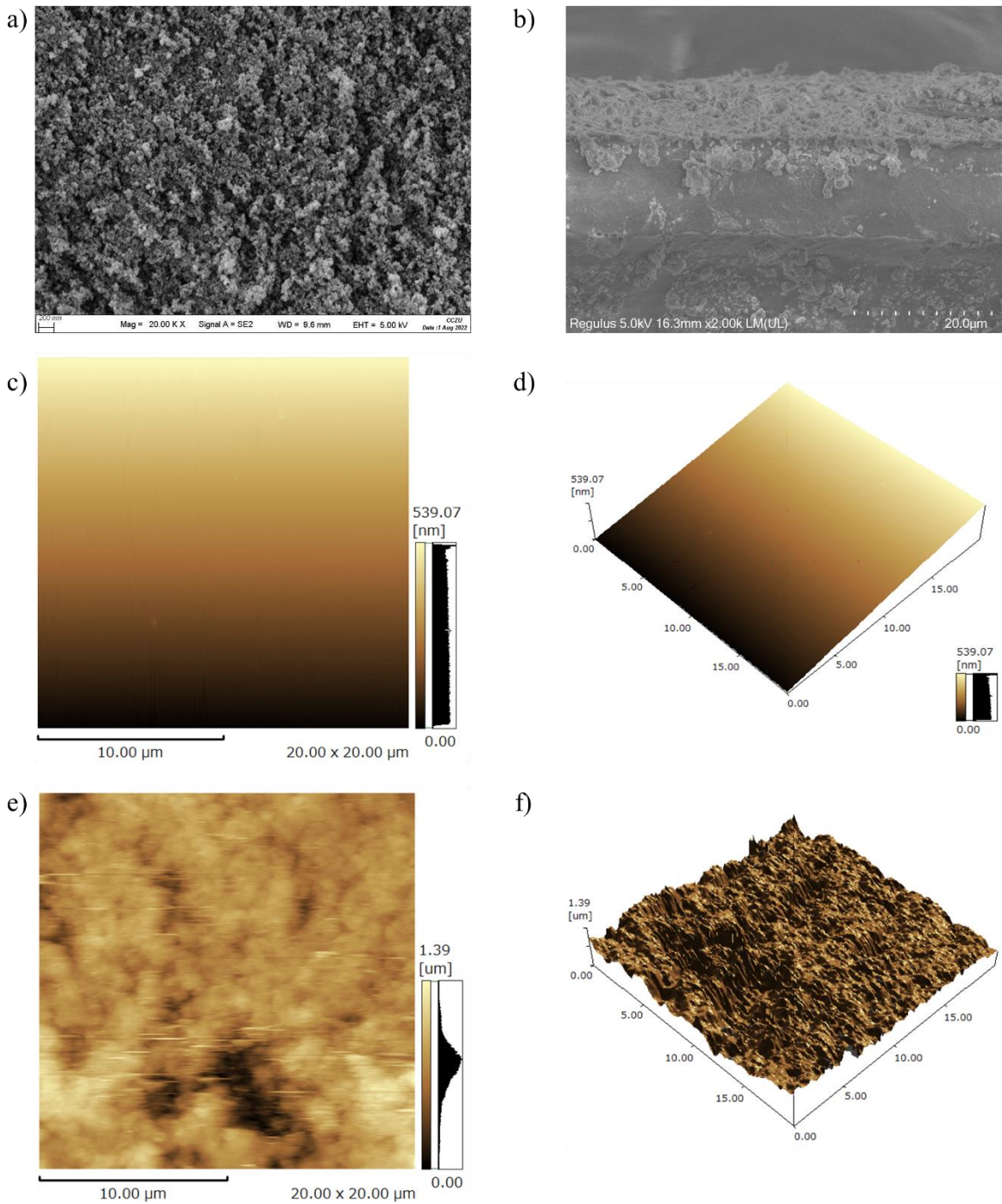


Fig.6. SEM images of surface (a) and cross section (b) of PAI/F-SiO₂ superhydrophobic material. AFM 2D (c, e) and 3D (d, f) images of PAI pristine surface (c, d) and PAI/F-SiO₂ superhydrophobic surface (e, f).

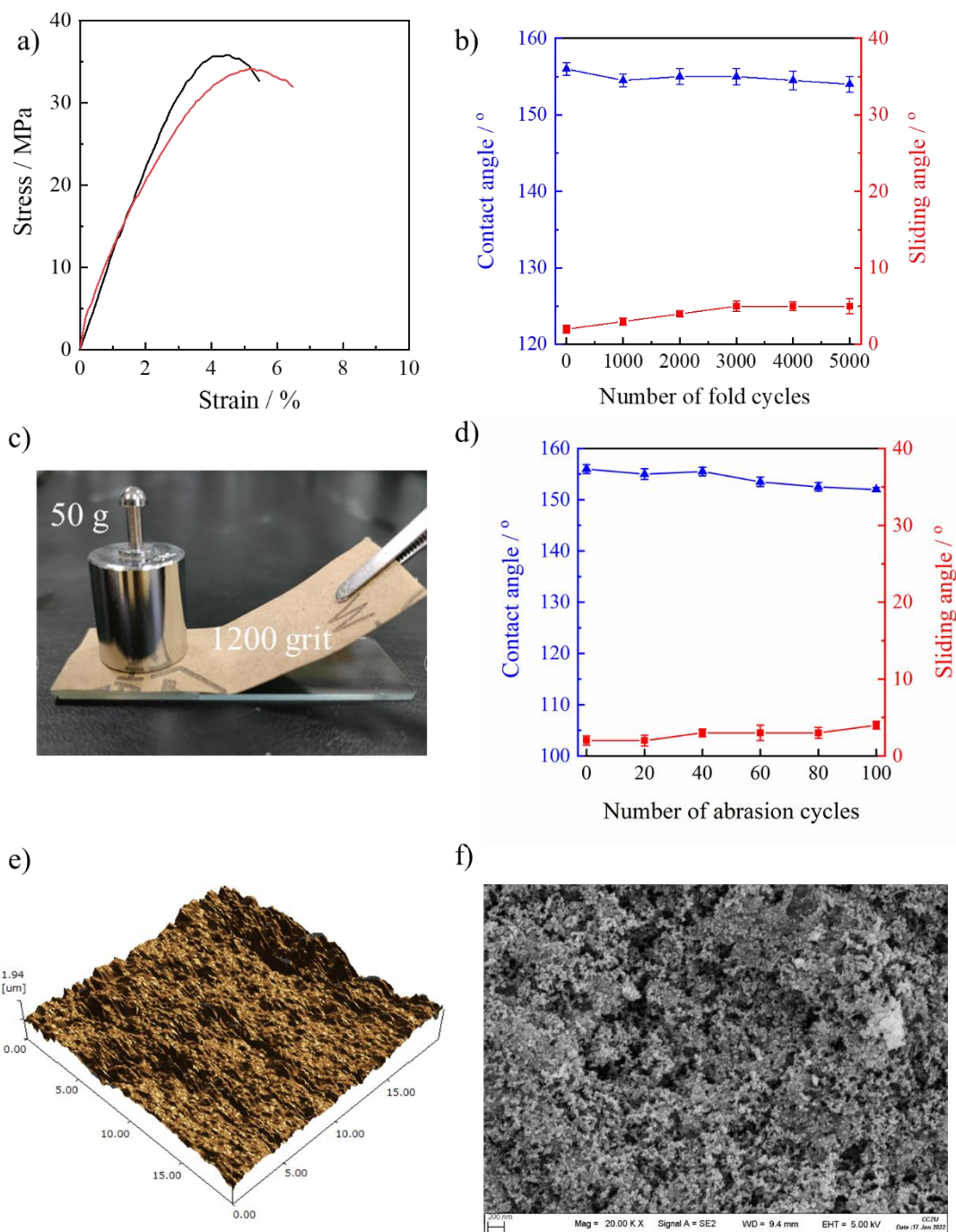


Fig.7. Stress–strain curves of PAI pristine (black line) and PAI/F-SiO₂ superhydrophobic (red line) films (a). CA and SA as a function of fold times (b). Photograph illustrating the sandpaper abrasion test (c). CA and SA as a function of mechanical abrasion cycle number (d). AFM 3D (e) and SEM (f) images after sandpaper abrasion test.

The mechanical property of PAI pristine and PAI/F-SiO₂ superhydrophobic films was investigated in terms of tensile testing. The tensile strength of PAI/F-SiO₂ superhydrophobic film (34.1 MPa) is comparable to that of PAI pristine film (35.8 MPa) as shown in the Fig. 7a, suggesting that the high mechanical property of flexible polymer substrate was not effected using this wet spraying method. On the other hand, the flexible superhydrophobic surfaces for practical applications should maintain a high water-repellency even after severe mechanical deformation. In order to investigate flexibility of the fabricated superhydrophobic surfaces, PAI/F-SiO₂ films were peeled from glass substrate for bending test. As shown in the Fig. 7b, PAI/F-SiO₂ flexible surface still shows superhydrophobic property with a CA of 156 ° and SA of 5 ° even after it was folded by up to 5000 times with a bending angle of 180 °, suggesting that PAI/F-SiO₂ superhydrophobic films possesses excellent flexibility. Moreover, crease was not observed after this severe mechanical treatment, indicating interface adhesion between PAI substrate and the superhydrophobic coating was high enough to prevent F-SiO₂ from peeling from PAI. For further researching mechanical robustness, PAI/F-SiO₂ superhydrophobic films were adhered to the glass substrate, and evaluated by sandpaper abrasion test using 1200-grit sandpaper and a load of 50 g, and the superhydrophobic films as shown in the Fig. 7c. The wettability of the PAI/F-SiO₂ surface was recorded after every 20 abrasion cycles (each cycle is 50 cm). It is found that CA and SA of PAI/F-SiO₂ surface were nearly unchanged after 100 abrasion cycles (500 cm) as shown in the Fig. 7d while CA of control samples obviously decreased to 134 ° and their CA significantly increased to 15 ° even after one abrasion cycle (50 cm) as shown in the Fig. S7. These results demonstrated that this wet spraying method did effectively improve the mechanical robustness of superhydrophobic surface. Furthermore, even if F-SiO₂ nanoparticles on the outer surface was rubbed off, the F-SiO₂ nanoparticles embedded in the polymer substrate would form a much

stronger protective layer to prevent the surface from being damaged. Therefore, as shown in the Fig. 7e and 7f, the roughness (R_q : 186.1 nm, R_a : 136.6 nm) and micro-clusters structure were kept when it was rubbed many times. The excellent mechanical robustness of PAI/F-SiO₂ superhydrophobic surface was also investigated by ultrasonic treatment (50 W, 40 kHz). It was found that the surface morphology exhibited no obvious change after 30-min shaking as shown in the Fig. S8, and the superhydrophobicity was still kept after the flexible surfaces suffered from 10 cycles treatment.

3.5 Thermal/cooling stability

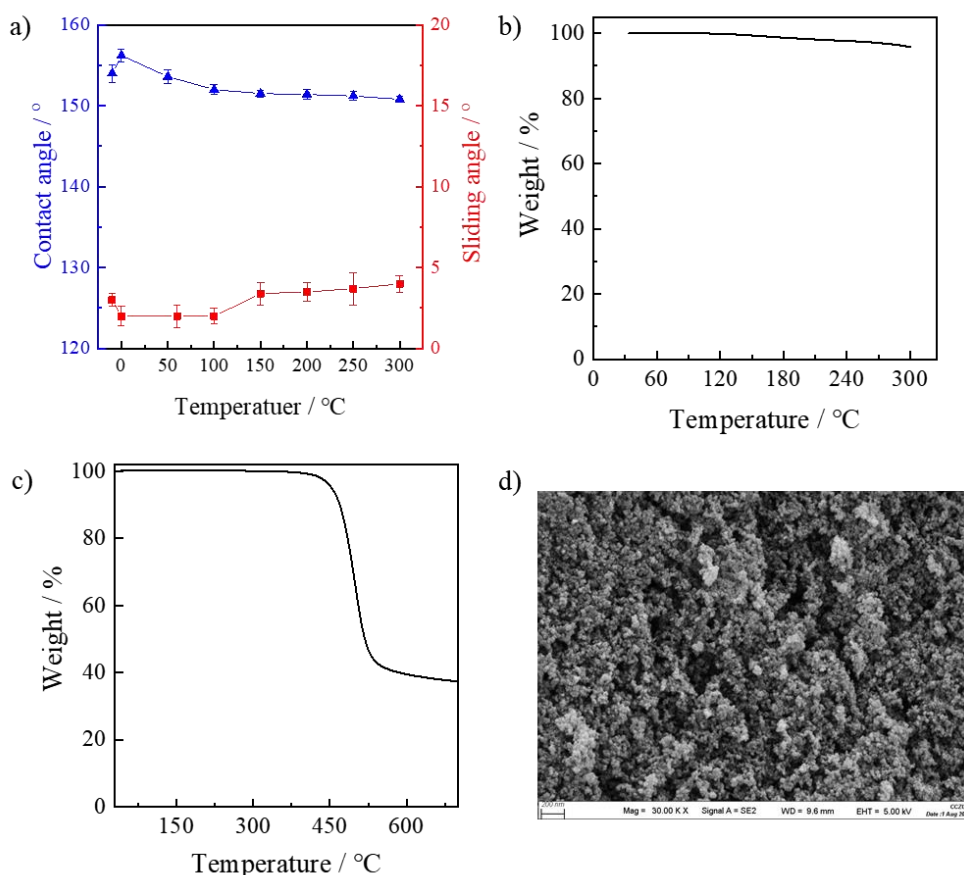


Fig. 8. CA and SA as a function of temperature (a). The TGA curves of PAI/F-SiO₂ superhydrophobic (b) and PAI pristine (c) films. The morphology of PAI/F-SiO₂ surface after thermal treatment under 300 °C for 24 h (d).

Fig. 8a shows the wettability change with varying temperature. Encouragingly, PAI/F-SiO₂ surfaces exhibited CA > 150 ° and SA < 10 ° even after they were treated at a wide temperature for 24 h ranging from -10 to 300 °C. It is worth pointing out that thermal stability of PAI/F-SiO₂ films at 300 °C with such a long time is one of the highest values for flexible superhydrophobic film as we know [44-46]. With further increasing temperature to 350 °C, although the superhydrophobicity was sustained, PAI/F-SiO₂ film became yellow. In order to disclose origin of the excellent thermal stability, thermogravimetric analysis (TGA) was performed. As shown in the Fig. 8b, the weight of PAI/F-SiO₂ superhydrophobic film is nearly unchanged with increasing temperature from 30 to 300 °C owing to the unique thermal stability of PAI. Indeed, as shown in the Fig. 8c, the initial decomposition temperature (temperature at 5 wt% loss) of PAI is as high as 453.6 °C. In other words, the substrate polymer played a key role in the thermal stability of superhydrophobic film. Combining advantages of the excellent thermal stability of PAI and silica nanoparticles, no obvious morphology changes were found after the extreme thermal treatment as shown in the Fig. 8d.

3.6 Chemical and UV durability

Chemical stability is an important characteristic of flexible superhydrophobic surfaces, particularly when they are applied in extreme conditions. Herein, the flexible superhydrophobic coating was completely immersed in various acid/base for 6 h, and the wettability was tested to discuss its chemical resistance. As shown in the Fig. 9a, the change in CA and SA of PAI/F-SiO₂ flexible surface is not large even it was exposed to such extreme conditions of pH = 1 or 13. CA is still beyond 150 °, and SA is lower than 5 °. In addition, the water droplets on the PAI/F-SiO₂ surface retained their spherical shape after strong acid or strong alkali corrosion. These results

suggested that PAI/F-SiO₂ flexible superhydrophobic surface was able to resist strong acid and strong alkali. This is because that low surface energy coating with the air pocket structure can prevent acid–base solution immersing into the superhydrophobic surface [47].

It is well known that large quantities of organic components in superhydrophobic materials would be oxidized, and facilitate formation of some hydrophilic groups when they are subjected to UV-light exposure. Therefore, another focus of the PAI/F-SiO₂ flexible superhydrophobic surface is its UV resistance. In this study, the CA and SA just slightly decreased even UV irradiation time extended to 175 h as shown in the Fig. 9b, suggesting that PAI/F-SiO₂ surface still met superhydrophobic requirement owing to the UV-resistance of C–F and Si–O groups in F-SiO₂ nanoparticles [48].

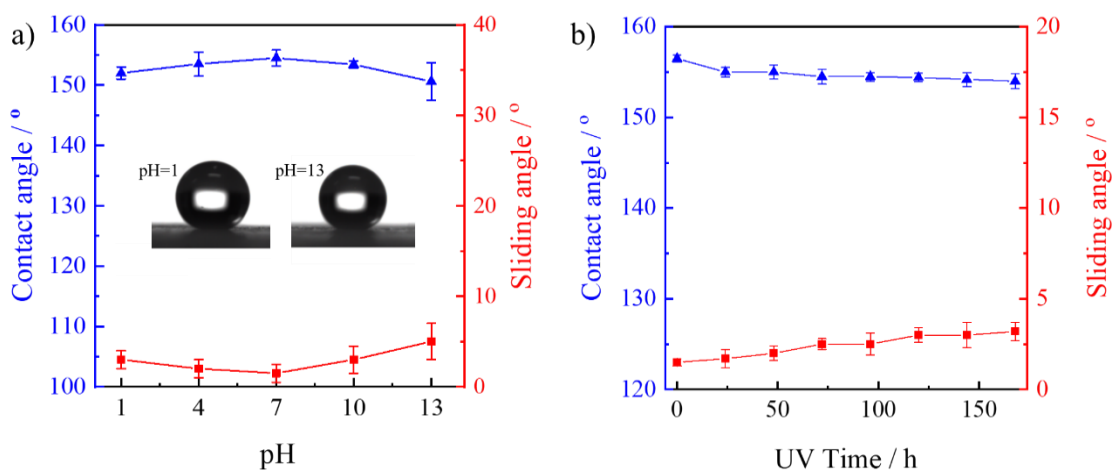


Fig. 9. CA and SA as a function of pH value (a) and UV irradiation time (b).

3.7 Dynamic impalement resistance

Superhydrophobic surfaces those can effectively repel hot water jet impacting is a special characteristic for many usages including heat exchange, and hot-fluid transportation [49]. Unfortunately, most of traditional superhydrophobic surfaces are not able to resist hot water, since

the delicate air pockets are easy to be destroyed owing to the fast evaporation and the reduced surface tension [50]. To research this durability, an impact experiment was designed. As shown in the Fig. 10a, boiling water was pour on the PAI/F-SiO₂ superhydrophobic surface from a height of 15 cm by using a beaker, and the angle between superhydrophobic surface and horizontal base line is 20 °. CA and SA were recorded after pouring every 200 mL boiling water as shown in the Fig. 10b. It was found that with increasing amount of splashing water, CA just slightly decreased while SA increased, but the superhydrophobicity was still kept even the volume of splashing water increased up to 1600 mL. Moreover, the morphology after hot water jet impacting was researched. As shown in the Fig. 10c and 10d, the roughness (R_q : 208 nm) and clustered-like structure with hierarchical porous were remained. These results suggest the fabricated PAI/F-SiO₂ flexible superhydrophobic surface possesses good dynamic impalement resistance.

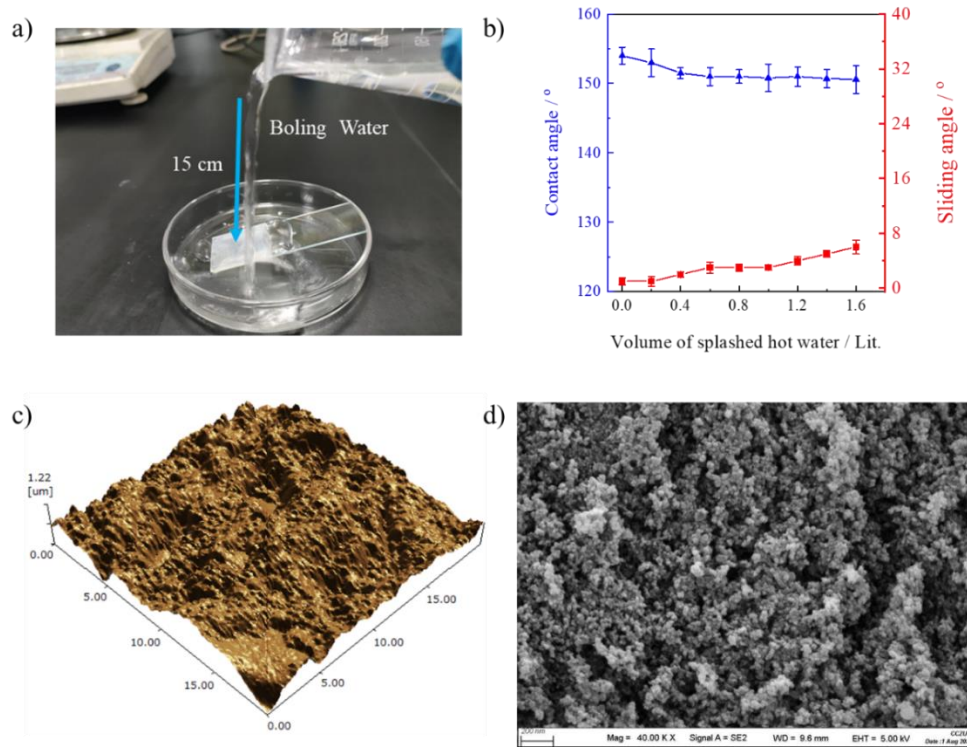


Fig. 10. Photograph illustrating hot water jet impacting onto superhydrophobic surface (a). CA and SA as a function of volume of hot water jet impact (b). The AFM 3D (c) and SEM (d) images after hot water jet impact.

3.8 Icephobic properties

Icing is a serious problem around the world, especially for cold regions, which can cause disasters in many fields including power line, aircrafts and so on. Therefore, prevention or delay of ice formation has been attracting more and more attention [51]. It is well known that the time that freezes water droplet on cold surface is mainly controlled by the heat transfer rate between water droplet and the surface. In general, the freezing process involves two steps: precooling and ice growth. From macroscopic viewpoint, the time that completes precooling process $\Delta t_{\text{precooling}}$ is expressed as shown in the equation 1 [4]:

$$\Delta t_{\text{precooling}} = (\rho_w C_w \Delta T) / q \quad (1)$$

where ρ_w and C_w are density and specific heat of water, ΔT is temperature change of water droplet, and q is heat transfer cooling rate per unit mass. The time that completes ice growth phases $\Delta t_{\text{ice growth}}$ can be expressed by the equation 2:

$$\Delta t_{\text{ice growth}} = (\rho_w \Delta H) / q \quad (2)$$

where ΔH is enthalpy change of droplet, which involves sensible and latent heat components. Therefore, it is obvious that decreasing heat transfer rate can delay the freezing process.

The icing delay test was performed by placing the water droplets on the cold surfaces of PAI pristine and PAI/F-SiO₂ flexible superhydrophobic films those were precooled and maintained at this subfreezing temperature. Firstly, precooling process started when the droplets were placed on the PAI and PAI/F-SiO₂ cold surfaces. Then, ice growth process started, and freezing front began to spread until it reached the tip of the droplets. It should be noted that although PAI pristine and PAI/F-SiO₂ superhydrophobic surfaces showed similar patterns, the duration of precooling process and the speed of freezing front were quite different. It is found that PAI/F-SiO₂ superhydrophobic

surface exhibited an obvious delay (~ 302 s) in the freezing process compared to PAI pristine surface (~ 30 s) at -20 °C. This is because that higher CA of PAI/F-SiO₂ superhydrophobic surface reduced the contact area between the droplet and solid surface, and reduced the heat transfer rate [52]. Moreover, hierarchical porous and clustered-like structures of PAI/F-SiO₂ superhydrophobic surface further reduced the heat transfer rate owing to the lower thermal conductivity of air [53].

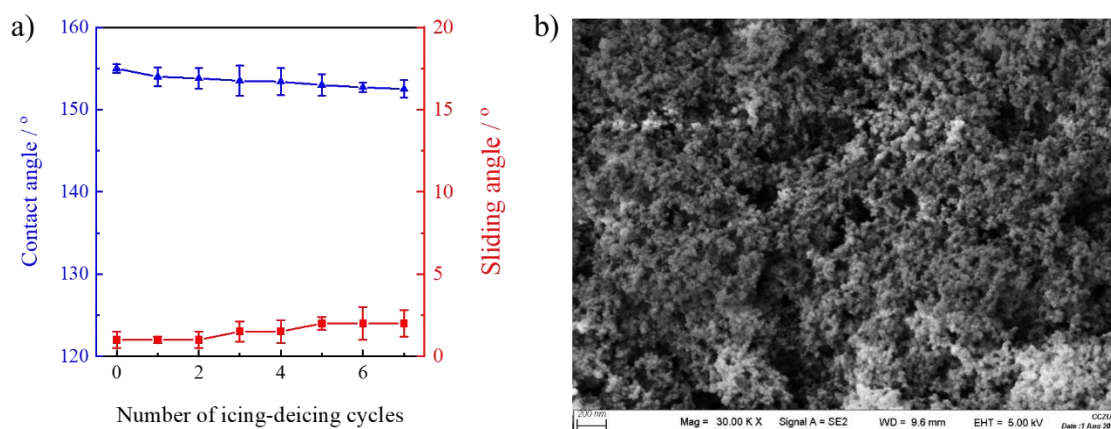


Fig. 11. CA and SA as a function of icing/deicing cycles (a). The SEM surface image after seven cycles of icing/deicing.

The cyclic process of icing/deicing may damage the surface morphology, leading into a loss of superhydrophobicity. In this study, the wettability of PAI/F-SiO₂ superhydrophobic surface was evaluated after icing/deicing process as shown in the Fig. 11a. It is found that CA and SA were evaluated to be 152.5 ° and 2 ° respectively, suggesting the superhydrophobicity of PAI/F-SiO₂ flexible surface is not affected even after seven cycles of icing/deicing process. In addition, the surface morphology after icing/deicing treatment was also investigated. As shown in the Fig. 11b, the hierarchical porous and clustered-like structures were still observed. These results further confirmed the effectiveness of the wet spraying method to fabricate superhydrophobic surface with high robustness.

4. Conclusion

In summary, this study demonstrated a simple and effective method for fabricating superhydrophobic surfaces with high mechanical flexibility and excellent durability. Comparing with directly spraying F-SiO₂ on the completely dried PAI surface, this wet spraying method made F-SiO₂ easily embedded PAI substrate to enhance the interfacial force between flexible substrate and nanoparticle coating. Therefore, the mechanical robust of PAI/F-SiO₂ surface was obviously improved compared to control samples. In addition, PAI/F-SiO₂ surface exhibited excellent durability during sand abrasion test, strong acid or strong alkali treatment, UV irradiation, and hot water jet impacting. Most importantly, the surface still kept superhydrophobic even after it was heated at 300 °C for 24 h, which is one of the highest values for flexible superhydrophobic films. Moreover, the surface also possessed good icephobic properties, which can obviously delay the icing process, and the unique superhydrophobic structure was nearly unaffected even after icing/deicing process. We also confirmed that this method was generally applicable to fabricate other flexible superhydrophobic surfaces. Therefore, this work provides a simple and universal route to prepare flexible superhydrophobic surfaces with versatile properties.

Acknowledgments

This work was partly supported by the Postgraduate Research & Practice Innovation Program of Jiangsu Province (SJCX22_1328), International Research Fellow of Japan Society for the Promotion of Science (S23012), and Iketani Science and Technology Foundation (0314001-D).

Author Contributions

Shuhan Hou fabricated samples, measured their wetting behavior, durability. Insub Noh investigated the morphology and analyzed the results. Shuhan Hou and Insub contributed equally to this work. Xinlu Shi synthesized and characterized polymer substrate. Yanbin Wang, Hyung Do Kim, Hideo Ohkita, and Biaobing Wang designed the research objective, wrote and revised the manuscript.

Appendix A. Supplementary Data

Supplementary data to this article can be found online at <https://www.sciencedirect.com/journal>.

References

1. T. Byun, S.J. Kim, S.Y. Kim, Soluble and transparent poly(amide-imide)s with ultra-low coefficients of thermal expansion, *Polymer* 247 (2022) 124813.
2. M. Zahra, S. Zulfiqar, M.F. Wahab, M.I. Sarwar, Exploring a novel family of poly(amide-imide)s as promising cationic sorbents for water remediation, *React. Funct. Polym.* 174 (2022) 105240.
3. Y.B. Wang, J.X. Chen, Y.P. Shen, T. Wang, Y.H. Ni, Z.H. Zhang, L.W. Sun, B.B. Ji, B.B. Wang, Control of conductive and mechanical performances of poly(amide-imide) composite films utilizing synergistic effect of polyaniline and multi-walled carbon nanotube, *Polym. Eng. Sci.* 59 (2019) E224–E230.
4. A. Elzaabalawy, S.A. Meguid, Development of novel icephobic surfaces using siloxane-modified epoxy nanocomposites, *Chem. Eng. J.* 433 (2022) 133637.
5. S.V. Rad, A. Moosavi, A. Nouri-Boroujerdi, H. Najafkhani, S. Najafpour, Drag reduction in internal turbulent flow by fabricating superhydrophobic Al₂O₃/waterborne polyurethane coatings, *Surf. Coat. Tech.* 421 (2021) 127406.
6. Z. Jin, H. Mei, L. Pan, H. Liu, and L. Cheng, Superhydrophobic self-cleaning hierarchical micro-/nanocomposite coating with high corrosion resistance and durability, *ACS Sustainable Chem. Eng.* 9 (2021) 4111–4121.
7. C. Lu, Y. Gao, S. Yu, H. Zhou, X. Wang, and L. Li, Non-fluorinated flexible superhydrophobic surface with excellent mechanical durability and self-cleaning performance, *ACS Appl. Mater. Interfaces* 14 (2022) 4750–4758.

- 452 8. G.B. Demirel, E. Aygöl, Robust and flexible superhydrophobic/superoleophilic melamine
453 sponges for oil-water separation, *Colloids and Surfaces A* 577 (2019) 613–621.
- 454 9. B.E. Fouhaili, A. Ibrahim, C. Dietlin, A. Chemtob, X. Allonas, C. Croutxé-Barghorn, Single-
455 step formation of superhydrophobic surfaces using photobase-catalyzed sol-gel process, *Prog. Org.*
456 *Coat.* 137 (2019) 105293.
- 457 10. C.R. Yu, A. Shanmugasundaram, D.W. Lee, Nanosilica coated polydimethylsiloxane
458 mushroom structure: A next generation flexible, transparent, and mechanically durable
459 superhydrophobic thin film, *Appl. Surf. Sci.* 583 (2022) 152500.
- 460 11. S. Rima, M. Lattuada, Protein amyloid fibrils as template for the synthesis of silica nanofibers,
461 and their use to prepare superhydrophobic, lotus-like surfaces, *Small* 14 (2018) 1802854.
- 462 12. Y. Tuo, H. Zhang, W. Rong, S. Jiang, W. Chen, and X. Liu, Drag reduction of anisotropic
463 superhydrophobic surfaces prepared by laser etching, *Langmuir* 35 (2019) 11016–11022.
- 464 13. L.C. Hu, C.H. Xue, B.Y. Liu, X.J. Guo, J.H. Wang, and F.Q. Deng, Scalable superhydrophobic
465 flexible nanofiber film for passive daytime radiative cooling, *ACS Appl. Polym. Mater.* 4 (2022)
466 3343–3351.
- 467 14. X. Zhang, W.Z. Zhu, G.J. He, P.Y. Zhang, Z.J. Zhang, I.P. Parkin, Flexible and mechanically
468 robust superhydrophobic silicone surfaces with stable Cassie-Baxter state, *J. Mater. Chem. A* 4
469 (2016) 14180–14186.
- 470 15. J. Ju, X. Yao, X. Hou, Q.H. Liu, Y.S. Zhang, A. Khademhosseini, A highly stretchable and
471 robust non-fluorinated superhydrophobic surface, *J. Mater. Chem. A* 5 (2017) 16273–16280.
- 472 16. S. Gupta, A. Babu, H.S. Arora, H.S. Grewal, High durability of non-fluorinated
473 superhydrophobic nanocomposite coatings, *Mater. Lett.* 270 (2020) 127717.

- 474 17. C. Ellis-Terrell, R. Wei, R. McKnight, X. Huang, K. Lin, Thermal stability of
475 superhydrophobic and oleophobic silica nanoparticle spray coating, *Mater. Today Commun.* 25
476 (2020) 101370.
- 477 18. V.T. Do, D.M. Chun, Fabrication of large-scale, flexible, and robust superhydrophobic
478 composite films using hydrophobic fumed silica nanoparticles and polydimethylsiloxane, *Polymer*
479 244 (2022) 124630.
- 480 19. A. Allahdini, R. Jafari, G. Momen, Transparent non-fluorinated superhydrophobic coating
481 with enhanced anti-icing performance, *Prog. Org. Coat.* 165 (2022) 106758.
- 482 20. S. Brown, J. Lengaigne, N. Sharifi, M. Pugh, C. Moreau, A. Dolatabadi, L. Martinu, J.E.
483 Klemberg-Sapieha, Durability of superhydrophobic duplex coating systems for aerospace
484 applications, *Surf. Coat. Tech.* 401 (2020) 126249
- 485 21. T. Yang, M. Wang, X. Wang, X. Di, C. Wang, and Y. Li, Fabrication of a waterborne,
486 superhydrophobic, self-cleaning, highly transparent and stable surface, *Soft Matter* 16 (2020)
487 3678-3685.
- 488 22. B. Swain, A.R. Pati, S.S. Mohapatra, and A. Behera, Interchanging characteristic of plasma
489 spray coating from superhydrophobic to hydrophilic under the applied electric field, *Surf. Eng.* 37
490 (2021) 1328-1337.
- 491 23. J.E. Mates, I.S. Bayer, J.M. Palumbo, P.J. Carroll, C.M. Megaridis, Extremely stretchable and
492 conductive water-repellent coatings for low-cost ultra-flexible electronics, *Nat. Commun.* 6 (2015)
493 8874.
- 494 24. M.K. Kim, W.H. Yao, Y.R. Cho, Fabrication of superhydrophobic surface with hierarchical
495 structure by thermal imprinting and spraying, *Colloids and Surfaces A* 634 (2022) 127973.

496 25. Y. Teng, Y. Wang, B. Shi, Y. Chen, Facile preparation of economical, eco-friendly
 497 superhydrophobic surface on paper substrate with excellent mechanical durability, *Prog. Org. Coat.*
 498 147 (2020) 105877.

499 26. J. Zhang, L. Zhang, and X. Gong, Large-scale spraying fabrication of robust fluorine-free
 500 superhydrophobic coatings based on dual-sized silica particles for effective antipollution and
 501 strong buoyancy. *Langmuir* 37 (2021) 6042–6051.

502 27. G. Ren, Y. Song, X. Li, B. Wang, Y. Zhou, Y. Wang, B. Ge, X. Zhu, A simple way to an ultra-
 503 robust superhydrophobic fabric with mechanical stability, UV durability, and UV shielding
 504 property, *J. Colloid Interf. Sci.* 522 (2018) 57–62.

505 28. D. Zhi, Y. Lu, S. Sathasivam, I.P. Parkin, and X. Zhang, Large-scale fabrication of translucent
 506 and repairable superhydrophobic spray coatings with remarkable mechanical, chemical durability
 507 and UV resistance, *J. Mater. Chem. A* 5 (2017) 10622–10631.

508 29. S.M. Lim, J. Ryu, E.H. Sohn, S.G. Lee, I.J. Park, J. Hong, and H.S. Kang, Flexible, elastic,
 509 and superhydrophobic/superoleophilic adhesive for reusable and durable water/oil separation
 510 coating, *ACS Appl. Mater. Interfaces* 14 (2022) 10825–10835.

511 30. A. Tripathy, A. Kumar, S. Sreedharan, G. Muralidharan, A. Pramanik, D. Nandi, and P. Sen,
 512 Fabrication of low-cost flexible superhydrophobic antibacterial surface with dual-scale roughness,
 513 *ACS Biomater. Sci. Eng.* 4 (2018) 2213–2223.

514 31. H. Daneshmand, A. Sazgar, M. Araghchi, Fabrication of robust and versatile superhydrophobic
 515 coating by two-step spray method: An experimental and molecular dynamics simulation study,
 516 *Appl. Surf. Sci.* 567 (2021) 150825.

32. X. Yu , X. Shi , F. Xue , W. Bai , Y. Li , Y. Liu , L. Feng, SiO₂ nanoparticle-containing superhydrophobic materials with enhanced durability via facile and scalable spray method, *Colloids and Surfaces A* 626 (2021) 127014.
33. S. Wang, X. Yu, and Y. Zhang, Large-scale fabrication of translucent, stretchable and durable superhydrophobic composite films, *J. Mater. Chem. A* 5 (2017) 23489–23496.
34. Z. Chen, G. Li, L. Wang, Y. Lin, W. Zhou, A strategy for constructing superhydrophobic multilayer coatings with self-cleaning properties and mechanical durability based on the anchoring effect of organopolysilazane, *Mater. Design* 141 (2018) 37–47.
35. Z. Fan, Y. Wang, J. Jeon, H.D. Kim, Y. Fang, X. Shi, Z. Luo, H. Ohkita, B. Wang, Enhancing multiwalled carbon nanotubes/poly(amide-imide) interfacial strength through grafting polar conjugated polymer on multiwalled carbon nanotubes, *Surf. Interfaces* 32 (2022) 102130.
36. C. Chang, Y. Wang, Y. Horiuchi, H.D. Kim, Y. Fang, H. Ohkita, B. Wang, Obvious improvement of dispersion of multiwall carbon nanotubes in polymer matrix through careful interface design, *Polym. Adv. Technol.* 2022, 33 (2022) 3350–3358.
37. Y.W. Fang, H. Yu, Y.B. Wang, Z.H. Zhang, C.L. Zhuang, G. Fang, Z.L. Luo, B. Zhang, B.B. Wang, Simultaneous improvement of mechanical and conductive properties of poly(amide-imide) composites using carbon nano-materials with different morphologies, *J. Polym. Eng.* 40 (2020) 806–814.
38. Y.B. Wang, H. Yu, Y.C. Li, T. Wang, T. Xu, J.X. Chen, Z.C. Fan, Y.F. Wang, B.B. Wang, Facile preparation of highly conductive poly(amide-imide) composite films beyond 1000 S m⁻¹ through ternary blend strategy, *Polymers* 11 (2019) 546.

538 39. Y.B. Wang, T. Wang, T.M. Wang, J.Y. Zhang, J.X. Chen, R. Yang, L.X. Ruan, B.B. Wang,
 539 Facile preparation of multifunctional poly(amide-imide)/polyaniline films: Combining self-
 540 cleaning, self-extinguishing, and conductive, *Polym. Eng. Sci.* 59 (2019) E33–E43.
 541 40. Y. Xie, W. Xiong, S. Kareem, C. Qiu, Y. Hu, I.P. Parkin, S. Wang, H. Wang, J. Chen, L. Li,
 542 Z. Chen, H. Sun, and X. Zhao, Robust superamphiphobic coatings with gradient and hierarchical
 543 architecture and excellent anti-flashover performances, *Nano Res.* 15 (2022) 7565–7576.
 544 41. H. Wang, M. He, H. Liu, and Y. Guan, One-step fabrication of robust superhydrophobic steel
 545 surfaces with mechanical durability, thermal stability, and anti-icing function, *ACS Appl. Mater.*
 546 *Interfaces* 11 (2019) 25586–25594.
 547 42. C. Schlaich, L. Yu, L.C. Camacho, Q. Wei, and R. Haag, Fluorine-free superwetting systems:
 548 construction of environmentally friendly superhydrophilic, superhydrophobic, and slippery
 549 surfaces on various substrates, *Polym. Chem.* 7 (2016) 7446–7454.
 550 43. Q. Yang, W. Su, J. Hu, Y. Xu, Z. Liu, and L. Hui, Synthesis of superhydrophobic cellulose
 551 stearoyl ester for oil/water separation, *Nanomaterials* 12 (2022) 1964.
 552 44. H. Huang, C. Wu, S. Wu, R. Pan, L. Yin, X. Jin, Y. Pan, H. Wang, X. Yan, C. Hong, W. Han,
 553 X. Zhang, Super-flexible, thermostable and superhydrophobic polyimide/silicone interpenetrating
 554 aerogels for conformal thermal insulating and strain sensing applications, *Chem. Eng. J.* 441 (2022)
 555 136032.
 556 45. S. Gao, H. Li, H. Guan, L. Zheng, X. Lai, W. Chen, X. Zeng, Facile fabrication of
 557 superhydrophobic, flame-retardant and conductive cotton fabric for human motion detection,
 558 *Cellulose* 29 (2022) 605–617.
 559 46. Z. Fang, Y. Qin, Y. He, and X. Cu, A facile method for preparing superhydrophobic and flame-
 560 retardant fabrics materials, *Adv. Eng. Mater.* 23 (2021) 2100502.

561 47. A.B. Gurav, H. Shi, M. Duan, X. Pang, X. Li, Highly transparent, hot water and scratch
562 resistant, lubricant-infused slippery surfaces developed from a mechanically-weak
563 superhydrophobic coating, *Chem. Eng. J.* 416 (2021) 127809.

564 48. Z. Ji, Y. Liu, F. Du, Rational design of superhydrophobic, transparent hybrid coating with
565 superior durability, *Prog. Org. Coat.* 157 (2021) 106294.

566 49. H. Zhou, X. Jing, and Z. Guo, Mechanically durable and long-term repairable flexible
567 lubricant-infused monomer for enhancing water collection efficiency by manipulating droplet
568 coalescence and sliding, *Nanoscale Adv.* 2 (2020) 1473–1482.

569 50. Y. Liu, X. Chen, and J.H. Xin, Can superhydrophobic surfaces repel hot water ?, *J. Mater.*
570 *Chem.* 19 (2009) 5602–5611.

571 51. S. Rabbani, E. Bakhshandeh, R. Jafari, G. Momen, Superhydrophobic and icephobic
572 polyurethane coatings: Fundamentals, progress, challenges and opportunities, *Prog. Org. Coat.* 165
573 (2022) 106715.

574 52. F.Z. Chen, Y.Q. Wang, Y.L. Tian, D.W. Zhang, J.L. Song, C.R. Crick, C.J. Carmalt, I.P. Parkin,
575 Y. Lu, Robust and durable liquid-repellent surfaces, *Chem. Soc. Rev.* 51 (2022) 8476–8583.

576 53. K. Maghsoudi, E. Vazirinasab, G. Momen, R. Jafari, Icephobicity and durability assessment
577 of superhydrophobic surfaces: The role of surface roughness and the ice adhesion measurement
578 technique, *J. Mater. Process. Tech.* 288 (2021) 116883.