

# Combining hierarchical surface roughness with fluorinated surface chemistry to preserve superhydrophobicity after organic contamination



Chih-Feng Wang<sup>a,\*</sup>, Shih-Wei Hung<sup>a</sup>, Shiao-Wei Kuo<sup>b</sup>, Chi-Jung Chang<sup>c</sup>

<sup>a</sup> Department of Materials Science and Engineering, I-Shou University, Kaohsiung 840, Taiwan

<sup>b</sup> Department of Materials and Optoelectronic Science, Center for Nanoscience and Nanotechnology, National Sun Yat-Sen University, Kaohsiung 804, Taiwan

<sup>c</sup> Department of Chemical Engineering, Feng Chia University, Taichung 407, Taiwan

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## ABSTRACT

Surfaces exhibiting superhydrophobicity are attracting commercial and academic attention because of their potential applications in, for example, self-cleaning utensils, microfluidic systems, and microelectronic devices. In this study, we prepared a fluorinated superhydrophobic surface displaying nanoscale roughness, a superhydrophobic surface possessing a micro- and nanoscale binary structure, and a fluorinated superhydrophobic surface possessing such a binary structure. We investigated the effects of the (i) hierarchy of the surface topography and (ii) the surface chemical composition of the superhydrophobic carbon nanotube/polybenzoxazine coatings on their ability to retain superhydrophobicity upon contamination with particles and organic matter, an important characteristic for maintaining non-wetting properties under outdoor conditions. We have found that the topographical microstructure and the surface chemical composition are both important factors for preservation of the non-wetting properties of such superhydrophobic surfaces upon contamination with organic matter.

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## 1. Introduction

The liquid repellency of a solid surface is one of the most important characteristics affecting its industrial applications. The wettability of a solid surface is determined by a combination of its chemical properties and its topographical microstructure. Surface roughness increases the surface area of a solid and, thereby, enhances its hydrophobicity (Wenzel model) [1]; in addition, air trapped within the grooves beneath the liquid leads to superhydrophobic behavior because the drop sits partially on air (Cassie–Baxter model) [2]. For example, the water contact angle of a natural lotus leaf is greater than 160° because (i) its waxy coating has a rough surface and (ii) air trapped between the water droplets and the wax crystals at the plant surface minimizes the contact area, causing water drops to bead and roll off the surface, thereby generating extreme water repellency and self-cleaning characteristics [3]. Such surface properties are applicable in many fields, including self-cleaning utensils, microfluidic systems, and microelectronic devices [4–14].

Durability is a fundamental issue for a superhydrophobic surface developed for industrial applications. Several strategies have been proposed recently to improve the wetting robustness of superhydrophobic surfaces [15–22]. For example, in a previous study we prepared a stable polybenzoxazine surface that displayed superhydrophobicity not only for pure water but also for corrosive water under both acidic and basic conditions [15]. More recently, we realized pressure-proof superhydrophobic films from flexible carbon nanotube (CNT)/polymer coatings, which maintained their superhydrophobicity after bending or pressing and displayed excellent environmental stability [16]. In addition, we have used microwave irradiation to prepare a durable superhydrophobic CNT/polybenzoxazine nanocomposite that retained its superhydrophobicity after a tape test [17]. Deng et al. used a porous deposit of candle soot as a template to prepare a superamphiphobic silica film that resisted impingement with sand [18]. Xu and coworkers used a colloid assembly method to fabricate superhydrophobic coatings exhibiting strong adhesion strength, high chemical stability, and good self-cleaning ability [19]. Yao et al. developed a water-repellent material decorated with ribbed, conical nanoneedles; it was sufficiently robust that compression experiments did not affect its superhydrophobicity [20]. Jin and coworkers demonstrated a superamphiphobic silica aerogel

\* Corresponding author. Tel.: +886 7 6577711 3129; fax: +886 7 6578444.  
E-mail address: [cfwang@isu.edu.tw](mailto:cfwang@isu.edu.tw) (C.-F. Wang).

that preserved its non-wetting properties upon wear damage [21].

In most practical applications, superhydrophobic surfaces are likely to encounter organic contaminants through continuous exposure to outdoor environments. To the best of our knowledge, superhydrophobic surfaces that preserve their non-wetting properties after contamination with organic matter have been reported only in a few studies [23]. In this present study, we developed three types of CNT/polybenzoxazine coatings: (i) a fluorinated superhydrophobic surface exhibiting nanoscale roughness; (ii) a superhydrophobic surface possessing a micro- and nanoscale binary structure; and (iii) a fluorinated superhydrophobic surface possessing such a binary structure. Herein, we report the results of our investigation into the influences of the morphology and the surface chemistry on the ability of these CNT/polybenzoxazine coatings to preserve their superhydrophobicity upon contamination with organic matter.

## 2. Experimental section

### 2.1. Materials

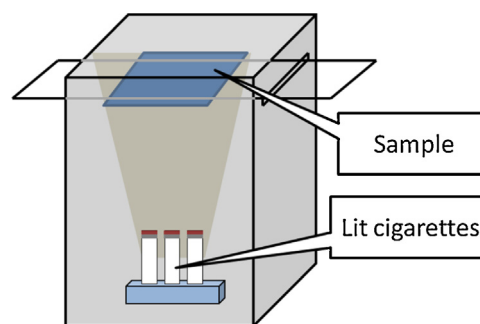
2,2-Bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl)propane (BA-a benzoxazine; Shikoku Chemicals), multiwalled CNTs (average diameter: 10–20 nm; length: 5–15  $\mu\text{m}$ ; Centron Biochemistry Technology), and 1H,1H,2H,2H-perfluorooctyltriethoxysilane (PTES; Sigma-Aldrich) were used as received. Water that had been purified through reverse osmosis was further purified using a Millipore Milli-Q system.

### 2.2. Sample fabrication

A solution of BA-a benzoxazine (0.5 g) in tetrahydrofuran (THF, 10 mL) was spin-coated (1500 rpm, 45 s) onto a glass slide using a photoresist spinner and then cured in an oven at 220 °C for 1 h to form a polybenzoxazine film. Two kinds of CNT/polybenzoxazine coating were prepared, using deposition and spray methods, respectively. In the deposition process, the CNT/THF suspension (1 mg/mL, sonicated for 2 h prior to use) was poured onto a polybenzoxazine-modified glass slide in an aluminium container and then the sample was dried at room temperature for 8 h before being cured in an oven (220 °C, 1 h). In the spray process, a CNT/EtOH suspension (1 mg/mL, sonicated for 2 h prior to use) was sprayed onto a polybenzoxazine-modified glass slide that was positioned on a heating plate (ca. 130 °C) and then the sample was cured in an oven (220 °C, 1 h). Surface modification of CNT/polybenzoxazine coating was performed by soaking the sample in a methanolic solution of PTES (1 wt%) for 2 h and subsequently baking it at 140 °C for 1 h. The film's durability toward organic contaminants was tested by following the experimental procedures detailed in Scheme 1. The superhydrophobic CNT/polybenzoxazine coatings were placed, in an iron box, facing three lit cigarettes at a distance of approximately 40 cm for various periods of time. In this test, nine cigarettes were consumed in whole experiment process.

### 2.3. Characterization

The microstructures of the CNT/polybenzoxazine coatings were characterized using a HITACHI-S-4700 scanning electron microscope (acceleration voltage: 15 kV); each specimen was coated with a thin layer of Pt/Pd prior to observation. The static contact angle and the sliding angle were measured, for a 5- $\mu\text{L}$  droplet, using an FDSA MagicDroplet-100 contact angle goniometer. Each reported contact angle is the average from six measurements.



**Scheme 1.** Cartoon representation of the organic contamination test on the superhydrophobic CNT/polybenzoxazine coatings.

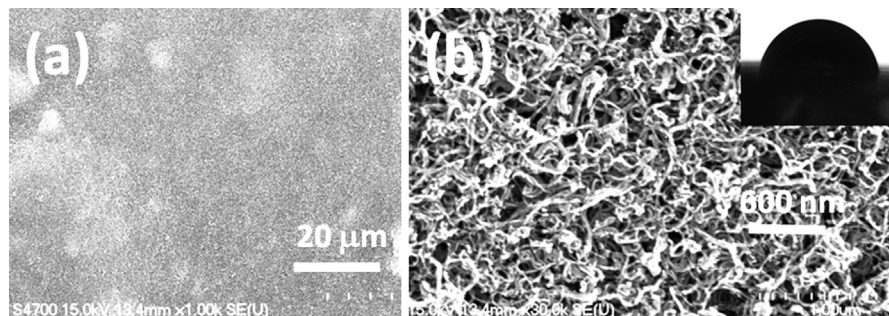
## 3. Results and discussion

We obtained smooth polybenzoxazine thin films through spin-coating of BA-a benzoxazine onto glass slides and then curing them at 220 °C for 1 h. We used either a deposition strategy or a spray method to prepare the CNT/polybenzoxazine coatings; Table 1 lists the conditions for these fabrication processes.

Fig. 1a and b displays top-view scanning electron microscopy (SEM) images of Sample 1, prepared using the deposition method, recorded at different magnifications. This substrate possessed a nanoscale structure, but no microscale texture. Its water contact angle was approximately 80°. Previous studies have indicated that nanostructured aligned carbon nanotubes (ACNTs) can exhibit hydrophilicity, which can be enhanced by changing either the surface free energy or the geometric structure, or both [24]. In this study we prepared three types of superhydrophobic CNT/polybenzoxazine coatings: the first in which we changed the surface chemical composition, the second in which we adjusted the topographical microstructures, and the third in which we applied both of these methods. We produced the superhydrophobic CNT/polybenzoxazine coating, Sample 2, through surface modification of Sample 1. The SEM images of Sample 2 (Fig. 2a and b) reveal that it retained the nanoscale structure of Sample 1. Relative to Sample 1, however, Sample 2 possessed a high water contact angle ( $162 \pm 1^\circ$ ) and a low sliding angle ( $4^\circ$ ). On this superhydrophobic surface, water droplets possessed near-spherical shapes and rolled off easily. We also prepared another superhydrophobic CNT/polybenzoxazine coating, Sample 3, using a spray method; Fig. 2c–e presents its SEM images. This superhydrophobic surface featured a rough surface possessing both micro- and nanoscale binary structures. Each micro-island (5–25  $\mu\text{m}$ ) on the superhydrophobic CNT/polybenzoxazine coating (Fig. 2c) was covered with branch-like nanostructures (diameters: 20–60 nm; Fig. 2d). Nanostructures were also present on the lower surface of the superhydrophobic film (Fig. 2e). Such a structure increased the surface roughness dramatically, leading to a composite interface in which air could become trapped within the grooves beneath the liquid, thereby inducing superhydrophobicity (the Cassie–Baxter model) [2]. Water droplets on Sample 3 also possessed high contact angles ( $161 \pm 1^\circ$ ) and readily moved upon the surface when tilted slightly (sliding angle:  $4^\circ$ ). We produced our third kind of superhydrophobic CNT/polybenzoxazine coating, Sample 4, through surface modification of Sample 3. Fig. 2f–h presents SEM images of this modified CNT/polybenzoxazine coating (Sample 4), which retained the micro-/nanoscale binary structure and superhydrophobicity (contact angle:  $163 \pm 1^\circ$ ; sliding angle:  $3^\circ$ ) of Sample 3. We evaluated the time-dependence of the wettability of these surfaces in terms of the contact angles of pure water; droplets positioned on our three superhydrophobic surfaces possessed near-spherical shapes for at least 30 min (the water droplets could still be

**Table 1**  
Preparation parameters, contact angles, and sliding angles of CNT/polybenzoxazine coatings.

Sample	Preparation method	Surface roughness scale	Fluorinated modification	Static contact angle (°)	Sliding angle (°)
1	Deposition	Nano	No	80 ± 5	>90
2	Deposition	Nano	Yes	162 ± 1	4
3	Spray	Micro- and nano	No	161 ± 1	4
4	Spray	Micro- and nano	Yes	163 ± 1	3

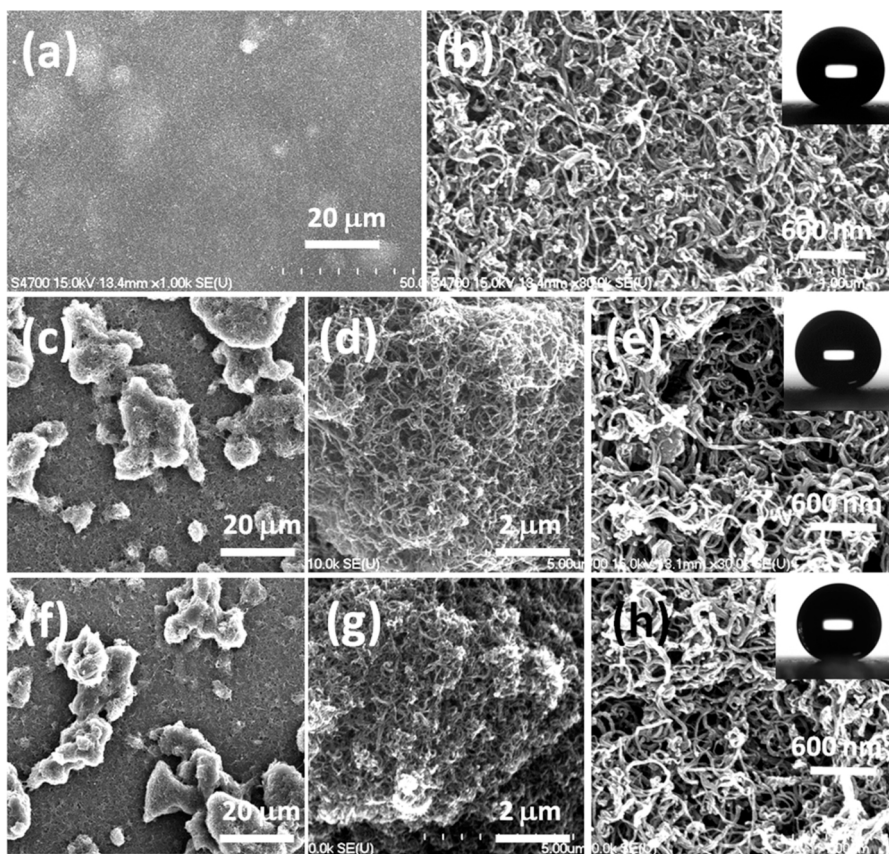


**Fig. 1.** (a) SEM image of the surface of Sample 1 on a glass slide. (b) Enlarged view of a microstructure in (a); inset: photograph of a water droplet on Sample 1.

moved with ease at that time), suggesting stable superhydrophobicity.

We examined the self-cleaning functions of our prepared superhydrophobic CNT/polybenzoxazine coatings when using  $\text{CaCO}_3$  powder as a contaminant. Fig. 3 presents the self-cleaning process of Sample 2. We sprinkled a sparse layer of contaminant powder on the surface and then placed a water droplet upon the

contaminated surface. Fig. 3a reveals that the water droplet maintained a spherical shape. When the particles of the contaminant powder contacted a moving water droplet, they were instantly adsorbed upon its surface, with the adsorbed particles thereafter remaining on the water droplet such that they did not contaminate the surface again (Fig. 3b). A small water droplet could clean a long distance until most of the water droplet surface was covered with



**Fig. 2.** (a) SEM image of the surface of Sample 2 on a glass slide. (b) Enlarged view of a microstructure in (a); inset: photograph of a water droplet on Sample 2. (c) SEM image of the surface of Sample 3 on a glass slide. (d) Enlarged view of a micro-island in (c). (e) SEM image of the lower surface of Sample 3; inset: photograph of a water droplet on Sample 3. (f) SEM image of the surface of Sample 4 on a glass slide. (g) Enlarged view of a micro-island in (f). (h) SEM image of the lower surface of Sample 4; inset: photograph of a water droplet on Sample 4.

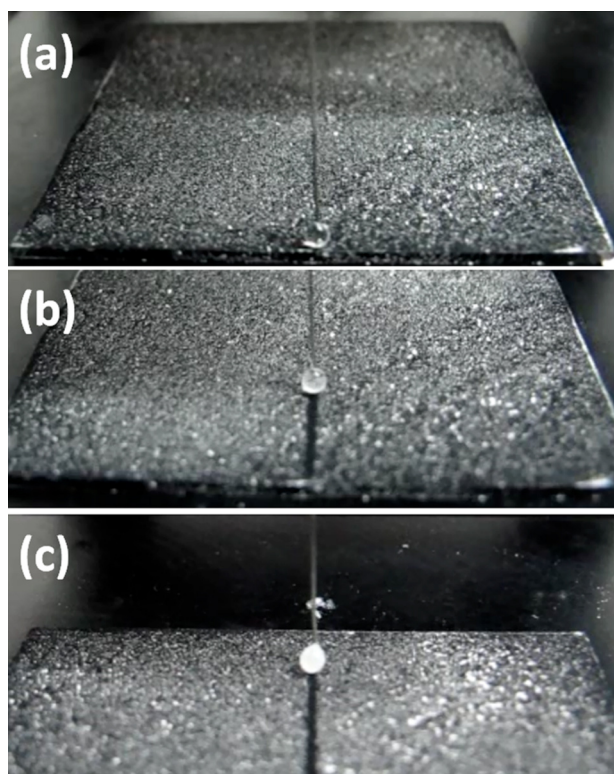


Fig. 3. Self-cleaning process on Sample 2.

the contaminant particles (Fig. 3c). Samples 3 and 4 possessed similar self-cleaning properties; indeed, all of the superhydrophobic CNT/polybenzoxazine coatings retained their superhydrophobicity after five cycles of contamination with  $\text{CaCO}_3$  powder and self-cleaning with water droplets. Thus, the different surface morphologies and chemical compositions of these superhydrophobic CNT/polybenzoxazine coatings did not have any obvious influence on the self-cleaning properties.

In real applications, exposure to organic contaminants might impair the superhydrophobicity as well as destroy the self-cleaning properties of such superhydrophobic surfaces. Therefore, we investigated the robustness of superhydrophobic CNT/polybenzoxazine coatings, featuring different structural hierarchies and surface chemical compositions, by subjecting our three types of superhydrophobic CNT/polybenzoxazine coatings (Samples 2–4) to an organic contaminant and then comparing their resultant superhydrophobicities. Fig. 4 displays photographs of water droplets on the superhydrophobic CNT/polybenzoxazine coatings after performing the organic contamination test. The presence of contaminant organic matter on Sample 2 decreased its hydrophobicity: the water contact angle decreased from  $160^\circ$  to  $136^\circ$  (Fig. 4a) and the sliding angle increased from  $4^\circ$  to  $90^\circ$ . In contrast, Samples 3 and 4 retained their superhydrophobicities (contact angles:  $160^\circ$  and

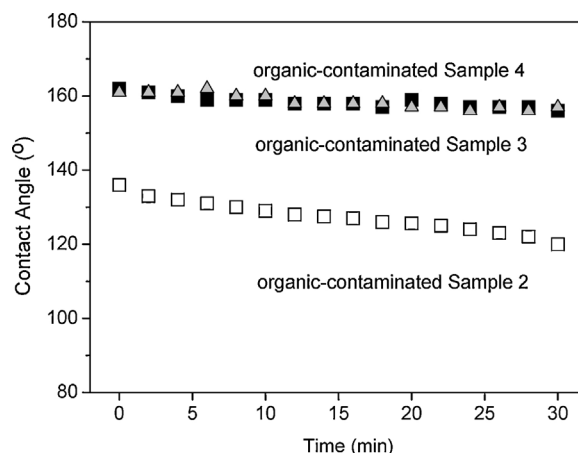


Fig. 5. Time-dependence of the water contact angles of the superhydrophobic CNT/polybenzoxazine coatings after contamination with organic matter.

$161^\circ$ , respectively) after performing the organic contamination test. Fig. 5 displays the time-dependence of the water contact angles for our superhydrophobic CNT/polybenzoxazine coatings after performing the organic contamination tests. The water contact angle of the contaminated Sample 2 decreased linearly over time, from an initial value of  $136^\circ$  to  $120^\circ$  within 30 min. In contrast, the water droplets on the surfaces of the contaminated Samples 3 and 4 retained their near-spherical shapes over the same period of time (and they could still be moved readily at that time), suggesting stable superhydrophobicity. In general, surface superhydrophobicity is evaluated using a combination of static contact angles and sliding angles. Notably, however, superhydrophobic surfaces, including those of lotus leaves and artificial materials, often lose their functionality when droplets are squeezed or impacted upon them. To further explore the effects of organic contaminants on our superhydrophobic CNT/polybenzoxazine coatings, we performed compression experiments in which we squeezed  $4\text{-}\mu\text{L}$  water droplets between a pristine superhydrophobic substrate (upper side) and another superhydrophobic substrate or a contaminated superhydrophobic substrate (lower side) and then slowly released the pressure, until the initial distance between the plates was restored [20,25]. We evaluated the internal pressure using the Laplace equation [26],

$$p = 2\gamma |\cos\theta| x^{-1} \quad (1)$$

where  $\gamma$  is the water surface tension,  $\theta$  is the contact angle under compression, and  $x$  is the distance between the Samples. For the system featuring the pristine Sample 3, the sequence of photographs in Fig. 6a reveals that the droplet flattened, with the contact angle gradually decreasing from  $160^\circ$  to  $146^\circ$ , upon increasing the drop's internal pressure from 85 to 140 Pa. Remarkably, the droplet recovered its original shape when we released the pressure, revealing robust superhydrophobicity over an extended range of compression. For the system featuring pristine Sample

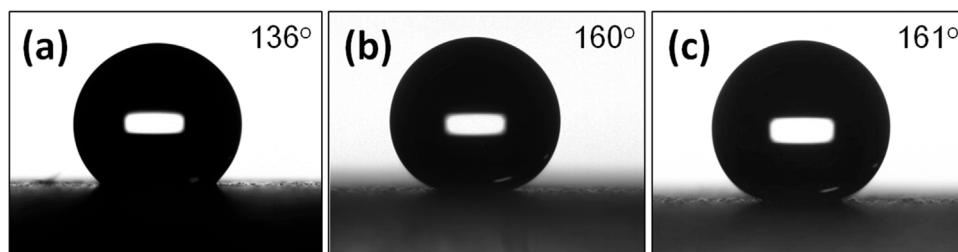
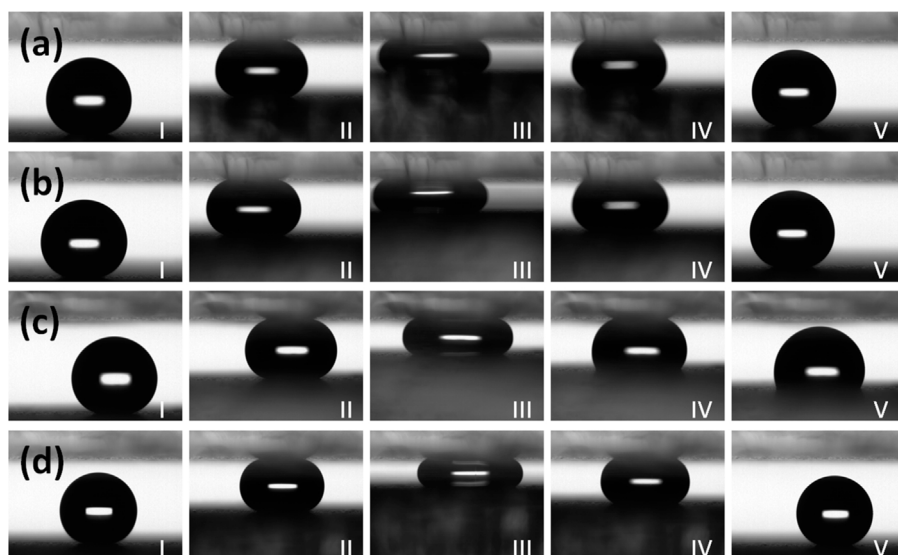


Fig. 4. Profile of a water drop on (a) Sample 2, (b) Sample 3, and (c) Sample 4 after contamination with organic matter.



**Fig. 6.** Behavior of a 4- $\mu$ L water droplet positioned between a pristine superhydrophobic substrate (upper side) and (a) Sample 3, (b) Sample 4, (c) organic-contaminated Sample 3, and (d) organic-contaminated Sample 4.

4, the behavior of the water droplet during the compression and relaxation process (Fig. 6b) was similar to that in the system containing pristine Sample 3. A water droplet that had been compressed under a pressure of 143 Pa readily rolled off the surface of Sample 4 when tilted at an angle of  $8^\circ$ . In contrast, for the system of photographs in Fig. 6c reveals that the water contact angle did not recover its initial value: the compressed droplet partially wetted the surface of the contaminated Sample 3, leading to a decrease in contact angle (from  $157$  to  $110^\circ$ ) and strong adhesion, highlighting the fragile superhydrophobicity of this contaminated surface. For the system containing the contaminated Sample 4, the droplet recovered its original shape when we released the pressure, revealing robust superhydrophobicity over an extended range of compression (Fig. 6d). Thus, our findings suggest that Sample 4 (a superhydrophobic surface featuring a micro-/nanoscale binary structure and a fluorinated surface chemical composition) possessed robust superhydrophobicity, even after contaminating it with  $\text{CaCO}_3$  powder or organic matter.

#### 4. Conclusions

Preserving superhydrophobicity in the face of organic contamination is one of the most important characteristics of a superhydrophobic surface aimed at outdoor applications. In this study we prepared three kinds of superhydrophobic CNT/polybenzoxazine coatings: Sample 2 possessing a nanoscale rough structure and a fluorinated surface chemical composition, Sample 3 possessing a micro-/nanoscale binary structure, and Sample 4 possessing both a micro-/nanoscale binary structure and a fluorinated surface chemical composition. Although each of these as-prepared superhydrophobic CNT/polybenzoxazine coatings exhibited stable superhydrophobicity and self-cleaning properties, the robustness of the superhydrophobicities of Samples 2 and 3 was diminished after contaminating them with organic matter. Notably, however, Sample 4 – the superhydrophobic CNT/polybenzoxazine coating possessing both a hierarchical structure and a low-surface-free-energy chemical composition – exhibited preserved superhydrophobicity upon contamination with both  $\text{CaCO}_3$  particles and organic matter. Such a structure could, therefore, serve as a guide for the preparation of superhydrophobic materials for outdoor use.

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#### References

- [1] R.N. Wenzel, Resistance of solid surfaces to wetting by water, *Ind. Eng. Chem.* 28 (1936) 988–994.
- [2] A.B.D. Cassie, S. Baxter, Wettability of porous surfaces, *Trans. Faraday Soc.* 40 (1944) 546–550.
- [3] L. Feng, S.H. Li, Y.S. Li, H.J. Li, L.J. Zhang, J. Zhai, Y.L. Song, B.Q. Liu, L. Jiang, D.B. Zhu, Super-hydrophobic surfaces: from natural to artificial, *Adv. Mater.* 14 (2002) 1857–1860.
- [4] H. Bellanger, T. Darmanin, E.T. de Givenchy, F. Guittard, Chemical and physical pathways for the preparation of superoleophobic surfaces and related wetting theories, *Chem. Rev.* 114 (2014) 2694–2716.
- [5] Z.L. Chu, S. Seeger, Superamphiphobic surfaces, *Chem. Soc. Rev.* 43 (2014) 2784–2798.
- [6] K.S. Liu, Y. Tian, L. Jiang, Bio-inspired superoleophobic and smart materials: design, fabrication, and application, *Prog. Mater. Sci.* 58 (2013) 503–564.
- [7] L. Yao, J.H. He, Recent progress in antireflection and self-cleaning technology—from surface engineering to functional surfaces, *Prog. Mater. Sci.* 61 (2014) 94–143.
- [8] J.Y. Lv, Y.L. Song, L. Jiang, J.J. Wang, Bio-inspired strategies for anti-icing, *ACS Nano* 8 (2014) 3152–3169.
- [9] C.P. Hsu, L.Y. Chang, C.W. Chiu, P.T.C. Lee, J.J. Lin, Facile fabrication of robust superhydrophobic epoxy film with polyamine dispersed carbon nanotubes, *ACS Appl. Mater. Interfaces* 5 (2013) 538–545.
- [10] S. Nagappan, S.S. Park, C.S. Ha, Recent advances in superhydrophobic nanomaterials and nanoscale systems, *J. Nanosci. Nanotechnol.* 14 (2014) 1441–1462.
- [11] H. Yao, C.C. Chu, H.J. Sue, R. Nishimura, Electrically conductive superhydrophobic octadecylamine-functionalized multiwall carbon nanotube films, *Carbon* 53 (2013) 366–373.
- [12] C.F. Wang, C.S. Liao, S.W. Kuo, H.C. Lin, Tunable wettability of carbon nanotube/poly (epsilon-caprolactone) hybrid films, *Appl. Surf. Sci.* 257 (2011) 9152–9157.
- [13] L. Shen, H.L. Ding, W. Wang, Q.P. Guo, Fabrication of Ketjen black-polybenzoxazine superhydrophobic conductive composite coatings, *Appl. Surf. Sci.* 268 (2013) 297–301.
- [14] T. Zhang, H.Q. Yan, Z.P. Fang, Y.P.F. E., T. Wu, F. Chen, Superhydrophobic and conductive properties of carbon nanotubes/polybenzoxazine nanocomposites coated ramie fabric prepared by solution-immersion process, *Appl. Surf. Sci.* 309 (2014) 218–224.
- [15] C.F. Wang, Y.T. Wang, P.H. Tung, S.W. Kuo, C.H. Lin, Y.C. Sheen, F.C. Chang, Stable superhydrophobic polybenzoxazine surfaces over a wide pH range, *Langmuir* 22 (2006) 8289–8292.
- [16] C.F. Wang, W.Y. Chen, H.Z. Cheng, S.L. Fu, Pressure-proof superhydrophobic films from flexible carbon nanotube/polymer coatings, *J. Phys. Chem. C* 114 (2010) 15607–15611.

- [17] C.F. Wang, H.Y. Chen, S.W. Kuo, Y.S. Lai, P.F. Yang, Rapid, low temperature microwave synthesis of durable, superhydrophobic carbon nanotube-polybenzoxazine nanocomposites, *RSC Adv.* 3 (2013) 9764–9769.
- [18] X. Deng, L. Mammen, H.J. Butt, D. Vollmer, Candle soot as a template for a transparent robust superamphiphobic coating, *Science* 335 (2012) 67–70.
- [19] Q.F. Xu, J.N. Wang, K.D. Sanderson, A general approach for superhydrophobic coating with strong adhesion strength, *J. Mater. Chem.* 20 (2010) 5961–5966.
- [20] X. Yao, Q.W. Chen, L. Xu, Q.K. Li, Y.L. Song, X.F. Gao, D. Quere, L. Jiang, Bioinspired ribbed nanoneedles with robust superhydrophobicity, *Adv. Funct. Mater.* 20 (2010) 656–662.
- [21] H. Jin, X.L. Tian, O. Ikkala, R.H.A. Ras, Preservation of superhydrophobic and superoleophobic properties upon wear damage, *ACS Appl. Mater. Interfaces* 5 (2013) 485–488.
- [22] X.T. Zhu, Z.Z. Zhang, X.H. Men, J. Yang, K. Wang, X.H. Xu, X.Y. Zhou, Q.J. Xue, Robust superhydrophobic surfaces with mechanical durability and easy repairability, *J. Mater. Chem.* 21 (2011) 15793–15797.
- [23] J.L. Zhang, G. Pu, S.J. Severtson, Fabrication of zinc oxide/polydimethylsiloxane composite surfaces demonstrating oil-fouling-resistant superhydrophobicity, *ACS Appl. Mater. Interfaces* 2 (2010) 2880–2883.
- [24] H. Liu, J. Zhai, L. Jiang, Wetting and anti-wetting on aligned carbon nanotube films, *Soft Matter* 2 (2006) 811–821.
- [25] J. Shieh, F.J. Hou, Y.C. Chen, H.M. Chen, S.P. Yang, C.C. Cheng, H.L. Chen, Robust airlike superhydrophobic surfaces, *Adv. Mater.* 22 (2010) 597–601.
- [26] A. Lafuma, D. Quere, Superhydrophobic states, *Nat. Mater.* 2 (2003) 457–460.