

## Fabrication of superhydrophobic films with robust adhesion and dual pinning state via in situ polymerization

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### ABSTRACT

Superhydrophobic films on glass substrate with robust adhesion and dual pinning to the water droplets were fabricated utilizing a novel in situ polymerized fluorinated polybenzoxazine (F-PBZ) having drooping aliphatic chains and incorporated SiO<sub>2</sub> nanoparticles (SiO<sub>2</sub> NPs). By employing the F-PBZ/SiO<sub>2</sub> NPs modification, the as-prepared composite films possess the robust adhesion to the glass substrate and superhydrophobic pinned state with water contact angle (WCA) of 150° and the non-pinned state with WCA approaching to 165°. Surface morphological studies have indicated that the wettability of the resultant films could be controlled by tuning the surface composition as well as the hierarchical structures. The key role of micro and sub-micro-sized structures and the nanometer sized voids is discussed by the investigation into static contact angle, contact angle hysteresis, droplet evaporation, and propensity for air pocket formation. The as-prepared films exhibited high adhesion toward the glass substrate with considerable durability in corrosive water and proved their simultaneous use in the transportation of micro-droplets, which could be helpful to design large-area and highly scalable superhydrophobic films.

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### 1. Introduction

Extremely water-repellent surfaces, often called superhydrophobics, are attractive in numerous applications for example in non-wetting, non-fogging, non-icing, and self-cleaning surfaces or in droplet transportation and in micro- and macro-fluidic devices [1–5]. Superhydrophobic surfaces are categorized into a non-pinned surface (the lotus effect) and a pinned surface (the petal effect) where water droplet gets stuck to the surface [6–9]. Two distinct theoretical models (Wenzel and Cassie-Baxter) have been developed to explain the wetting of surfaces and to guide the development of superhydrophobic techniques [10,11]. Such fascinating wetting and adhesion properties have sparked much research and have been attributed to a combination of the chemical nature of the surface and hierarchical nano- and microscale surface topography.

Several fabrication methods like, inorganic particle deposition, sol-gel techniques, plasma treatments, electrospinning, and casting techniques were used to prepare the non-pinned superhydrophobic films [12–18]. On contrary to mimicking the pinned surfaces, vertical aligned multi-walled carbon nanotubes with strong shear binding, hard nanopillars of poly(dimethylsiloxane)

(h-PDMS), and an aligned superhydrophobic polystyrene (PS) nanotube films were designed [19–21]. Heptadecafluorodecyltrimethoxysilane modified square-pillar-structured on silicon substrate using photolithography were also obtained [22,23]. Thus far, the fabrication of dual superhydrophobic surfaces is quite challenging, due to requirement of high-resolution photolithographic steps along with spatially tailored wet-chemical experimental conditions with limited scalability and high cost.

The polybenzoxazine (PBZ), a newly developed class of low surface free energy (SFE) materials with a wide range of interesting features including near-zero volumetric change upon curing, good UV and chemical resistance, and higher glass-transition temperature [24–26]. In the past few years, 2,2-bis(3,4-dihydro-3-methyl-2H-1,3-benzoxazine) propane (BA-m), 2,2-bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl)propane (BA-a), and recently 2,2-bis(3-fluorophenyl-3,4-dihydro-2H-1,3-benzoxazinyl)hexafluoro propane (BAF-fa) were reported as low surface energy materials [27–29]. Conversion of films of bis(3-allyl-3,4-dihydro-2H-1,3-benzoxazinyl)-isopropane (B-ala) from hydrophobic to hydrophilic by UV-exposure has been also reported [30]. However, the poor adhesion strength to the substrate to some extent limits their role for practical applications. Therefore, the objective here is to synthesize a novel benzoxazine monomer with comparable low SFE, which can incorporate SiO<sub>2</sub> nanoparticles (SiO<sub>2</sub> NPs) with high adhesion to the substrate.

In this contribution, we present the fabrication of highly durable superhydrophobic films on the glass substrate by in situ

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polymerization of fluorinated polybenzoxazine (F-PBZ) incorporated SiO<sub>2</sub> NPs (F-PBZ/SNP) functional layer (Scheme 1). We used a novel bifunctional fluorinated benzoxazine, namely 2,2-bis(3-octadecyl 1-3,4-dihydro-2H-1,3-benzoxazinyl)hexafluoro propane (BAF-oda) as a starting monomer with outwardly projected drooping aliphatic hydrocarbon chains that could directly form a hydrophobic cross-linked thermosetting polymer incorporated with SiO<sub>2</sub> NPs through in situ polymerization. By controlling the F-PBZ/SNP modification, the superhydrophobic films with dual pinning to the water droplet were described by the investigation into static water contact angle (WCA), water contact angle hysteresis (WCAH), droplet evaporation, and propensity for air pocket formation. Additionally, the film adhesion to the substrate and durability in corrosive environment is also discussed.

## 2. Experimental

### 2.1. Materials

4,4'-(Hexafluoroisopropylidene) diphenol (BAF, 98%), octadecylamine (oda), aniline, bisphenol-A, paraformaldehyde, anhydrous calcium chloride, and SiO<sub>2</sub> nanoparticles (diameter of particles, 7–40 nm, specific surface area, 120 m<sup>2</sup> g<sup>-1</sup>) were supplied by Aladdin Chemistry Co. Ltd. Hydrochloric acid, sodium hydroxide, ethyl alcohol, and trichloromethane were supplied by Shanghai Chemical Reagents Co. Ltd. China. Glass slides (25.4 × 76.2 × 1 mm) used as coating substrate were supplied by Shanghai Machinery Imp. & Exp. corporation). Milli-Q water with a resistance of 18.2 MΩ was obtained from a Millipore system. All chemicals were of analytical grade and were used as supplied.

### 2.2. Synthesis of BA-a and BAF-oda benzoxazine monomers

The BA-a and BAF-oda were synthesized using bisphenol-A, aniline, BAF, oda, and paraformaldehyde via Mannich reaction (Scheme S1 and S2). The detail of chemical synthesis and structural confirmation by <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectroscopy of BAF-oda and BA-a are presented in ESI (Figs. S1 and S2).

### 2.3. Preparation of F-PBZ/SNP films

F-PBZ/SNP films were deposited on the glass substrate by spray coating the dichloromethane solution of 3 wt.% of BAF-oda monomer with varying concentration of SiO<sub>2</sub> NPs (0.1, 0.3, 0.5, 0.8, 1, 2, and 3 wt.%). For comparison, the BA-a films with same concentrations of SiO<sub>2</sub> NPs were also deposited. The coated films were firstly

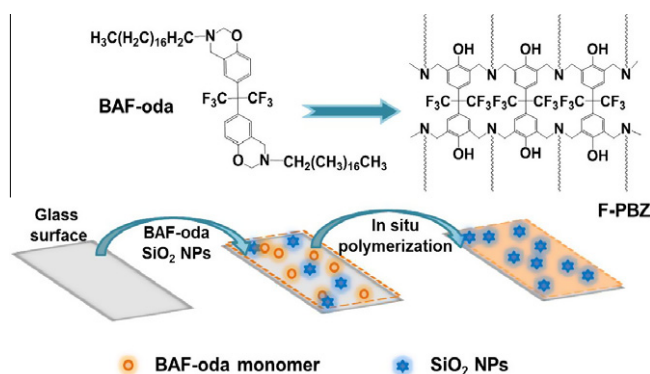
dried at 60 °C in vacuum for 20 min for complete solvent evaporation and then cured at 200 °C for 1 h (Scheme 1). The relevant F-PBZ/SiO<sub>2</sub> NPs coated glass films were denoted as BF-x/SNP-y, where *x* is the concentration BAF-oda (*x* wt.%), and *y* is the concentration of SiO<sub>2</sub> NPs (*y* wt.%), e.g., BF-3/SNP-2.

### 2.4. Characterization

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance 400 (resonance frequency of 400 MHz for <sup>1</sup>H), and *d*-CH<sub>2</sub>Cl<sub>2</sub> was used as the solvent. Fourier transform infrared (FT-IR) spectrographs were recorded by a Nicolet 870FT-IR spectrometer. Differential scanning calorimetry (DSC) was carried out at a heating rate of 5 °C min<sup>-1</sup> under a nitrogen atmosphere using an Auto Q20 Differential Scanning Calorimeter, TA Instruments, USA. The morphology of films was observed by field emission scanning electron microscopy (FE-SEM) (S-4800, Hitachi Ltd., Japan). The topographic roughness parameter (Ra) was measured by a non-contact optical profilometry using an interferometer profiler (WykoVeeco, model NT9100, USA). WCA (3 μL), WCAH, and sliding angle (SA) (10 μL) measurements were performed by a contact angle goniometer Kino SL200B equipped with tilting base. WCA measurements were performed using circle fitting model, while WCAH was measured using increment decrement method. Advancing and receding contact angles were measured by adding and removing 1 μL water from the droplet that is in contact with the testing sample. WCA, water contact length (WCL), and water droplet diameter (WD) were also measured on two types of superhydrophobic surfaces (superhydrophobic surface with pinned and with non-pinned state), and for each type, three different samples were used.

## 3. Results and discussion

The F-PBZ film formed on the surface of glass substrate has presented the WCA of 112° with SFE of 15.8 mJ/m<sup>2</sup>, indicated the formation of cross-linking structure within the PBZ (Fig. S3). The lower SFE of F-PBZ compared to non-fluorinated PBZ (P(BA-a), 19.2 mJ/m<sup>2</sup>) is attributed to the presence of fluorine groups in the benzoxazine molecules as well as to the strong intramolecular hydrogen bonding among the hydroxyl groups of PBZ cross-linking chains [28]. In order to demonstrate the existence of intramolecular hydrogen bonding in the F-PBZ, we compared the FT-IR spectra of the BAF-oda monomer and the F-PBZ, as presented in Fig. 1a. The typical distinguishing bands for the oxazine ring at 723 cm<sup>-1</sup> and for CH<sub>2</sub> wagging appeared at 1261 cm<sup>-1</sup>. The trisubstituted benzoxazine ring is characterized by the stretching vibration band at 878 cm<sup>-1</sup> in BAF-oda curve, which disappeared in the F-PBZ curve, indicated the complete curing of monomer into the polymeric structure [31]. At the same time, a broad absorption band around 3400 cm<sup>-1</sup> has confirmed the presence bonded hydroxyl group [32]. The curve for BF-3/SNP-2 in the Fig. 1a has appeared with the characteristic adsorption peaks at 1100 cm<sup>-1</sup> for Si–O–Si and at 929 cm<sup>-1</sup> for Si–OH bond have confirmed the incorporation of SiO<sub>2</sub> NPs within the composite BF-3/SNP-2 films. Additionally, to determine the degree of hydrogen bonding, we performed curve-resolving of the FT-IR spectra (Fig. 1b). The network structure of polybenzoxazine is supported by strong hydrogen bonding interactions, which consisted of (i) O···H<sup>+</sup>N intramolecular hydrogen bonding, (ii) OH···N intramolecular hydrogen bonding, and (iii) OH···O intermolecular hydrogen bonding [33]. The chemical cross-links in the F-PBZ consists largely of OH···N and O<sup>-</sup>···H<sup>+</sup>N intramolecular hydrogen bonds (proton-transfer equilibrium), which is clear from Fig. 1b. The presence of long chain alkyl groups has reduced the strength of OH···O intermolecular hydrogen bond-



**Scheme 1.** Schematic for the strategy using the in situ polymerization approach to the synthesis of F-PBZ/SiO<sub>2</sub> NPs coated on the glass surfaces.

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