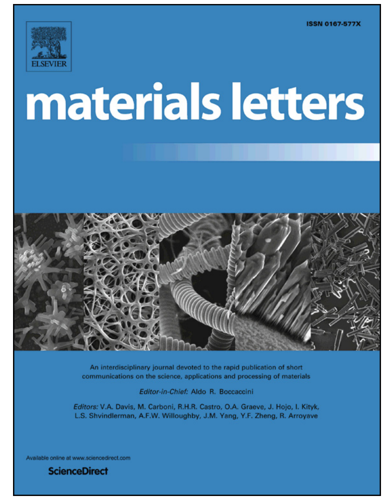

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Fabrication of Self-healing Waterbased Superhydrophobic Coatings from POSS modified Silica Nanoparticles

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Abstract:

The preparation of waterborne superhydrophobic coatings with self-healing ability is reported. These coatings were environment-friendly water-based system and could be easily deposited on many different substrates. And most of all, it could repair the damaged surfaces and recover its superhydrophobicity and self-cleaning ability via heating even after O_2-plasma etching or immersing with amphiphiles aqueous solution. This simple and practical method provides a new approach to make durable superhydrophobic materials in the spirit of green.

Keywords: Nanoparticles; Waterborne; Superhydrophobicity; Surfaces; Self-healing

1. Introduction

Due to self-cleaning ability and water repellency, superhydrophobic coatings can be used in many important potential applications [1–5]. Currently, special attention has been focused on their mechanical durability, especially in the outdoor [6–10]. From a practical standpoint, endowing a superhydrophobic coating with the self-repairing ability may be the best strategy to realize the long service of superhydrophobic coatings [11–16]. Some works about self-healing superhydrophobic coatings have been developed lately. Sun group prepared spray-coated self-repairing superhydrophobic coatings. Once the top layers of coatings were scratched or destroyed, the stored healing agents fluoroalkyl silane in the inner of coating could migrate onto the scratched surface and repair their superhydrophobicity [17]. Esteves *et al.* also prepared a superhydrophobic coating with self-replenishing ability. Through re-orientating the dangling chains onto the surfaces, the chemical compositions of damaged surface could be spontaneously replenished, and it restored its superhydrophobicity [18]. However, to date, usually adding pungent or volatile solvents to disperse the hydrophobic substance in artificial superhydrophobic surfaces applications, therefore it easily caused environmental issues. The ideal thing is to use a water-based system, and it can avoid the environmental impact of the solvent-based coatings [19, 20]. Thus, preparation of long-lived water-based superhydrophobic coatings is a recent research endeavor.

Herein, we fabricated self-healing waterborne superhydrophobic coatings from the polysiloxane emulsion combining POSS modified SiO_2 nanoparticles. The obtained coatings can be easily coated on some different substrates to form robust surperhydrophobic surfaces. Although the coatings lost their superhydrophobicity after O_2-plasma etching or immersing with amphiphiles aqueous solution, the coatings could restore their superhydrophobicity via simply heating treatment. The approach meets the requirements of the industrial coatings as it uses environmentally-benign waterborne polymer dispersions that can be produced in high tonnage.

2. Experimental Section

2.1. Materials

3-Mercaptopropyltrimethoxysilane (MPTMS) and 1H,1H,2H,2H-perfluorodecanethiol (PFDT) were purchased from Shanghai Macklin Biochemical Technology *Co., Ltd.* (China). Octavinyloctasilsesquioxane (POSS-V8) was obtained from Zhengzhou Alfa Chemical *Co., Ltd.* (China). Hydrophilic silica nanoparticles were obtained from Degussa Chemical *Co., Ltd.* (Germany). Polysiloxane latex (BS-45, solid content: 55 wt%) was obtained from Wacker Chemicals (Germany).

2.2. Modification of SiO_2 nanoparticles

MPTMS-POSS-PFDT was synthesized according to previous literatures [21]. Briefly, POSS-V8 (3.17 g, 0.005 mol), AIBN (0.007 g) and toluene (20 mL) were placed in a 50 mL glass reactor equipped with a magnetic stirrer and purged with a pure argon. MPTMS (0.98 g, 0.005 mol) and PFDT (2.4 g, 0.005 mol) were successively added into the mixture by drop at 40 ^{o}C, and then the stirring was continued at 60 ^{o}C for 3 h.

Silica nanoparticles (3 g), ammonia (0.3 g) and water (100 ml) were mixed and added to a 250 mL single-necked flask, and then ultrasonic dispersed for 10 min. Then the mixed solution including 20 g tetrahydrofuran and 0.5 g MPTMS-POSS-PFDT added into the as-obtained SiO_2 nanoparticles dispersion, and the stirring was continued at 50 °C for 12 h. The MPTMS-POSS-PFDT modified silica (MS) nanoparticles were collected through centrifuging (5000 rpm, 8 min). Then MS nanoparticles were washed with water and tetrahydrofuran for 3 times, and redispersed in deionized water for further use.

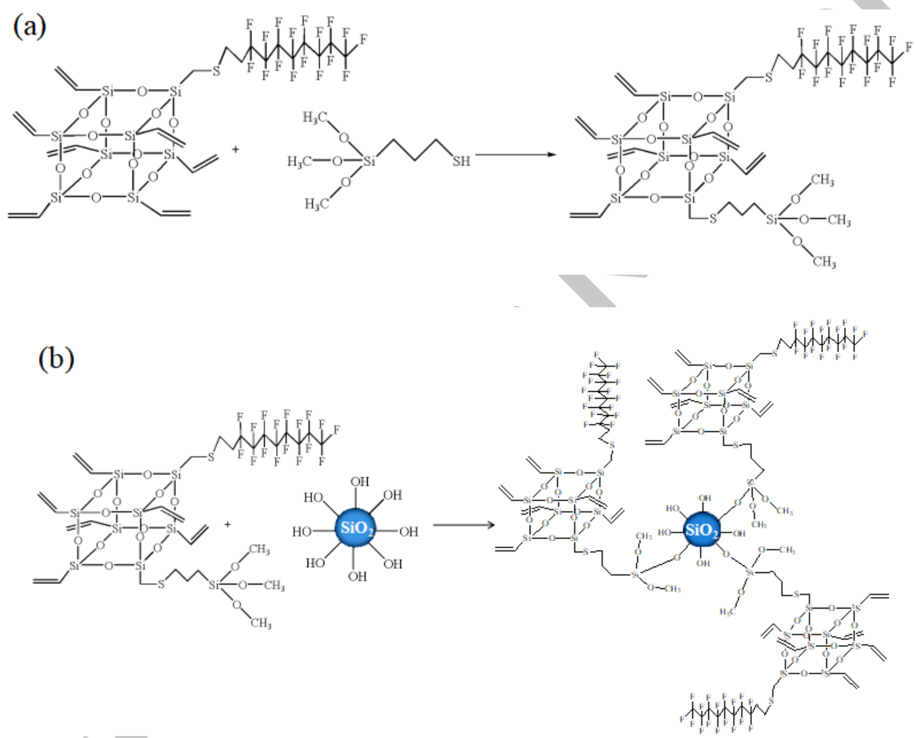


Fig. 1. Synthetic route of MPTMS-POSS-PFDT modified silica nanoparticles.

2.3. Preparation of water-based superhydrophobic coatings

In a typical preparation process, 10g MS aqueous dispersion (solid content: 65 wt%), 17.5g polysiloxane latex (BS-45, solid content: 55 wt%) and 25g deionized water were added into a 150ml plastic beaker, and were stirred at 1000 rpm for 5 min. And subsequently sprayed on the substrates and dried at 80 °C for 15 min.

2.4. Characterization

Infrared spectra was recorded on a FT-IR spectrometer (NICOLET, Thermo Fisher Scientific, China) with the wavenumber range from 500 to 3500 cm^{-1} at room temperature. The morphologies of surfaces were carried out with a scanning electron microscope (SEM, SU1510, HITACHI, Japan) at an accelerating voltage of 5 KV. The wettability of surfaces was measured by optical contact angle measuring instrument (Dataphysics, Germany) with a 5 μL deionized water droplet at room temperature (five values were measured for each specimen). The UV irradiation stability of specimens was evaluated using a QUV accelerated weathering tester (QUV/se, USA) with 310 nm wavelength UV lamps. The specimens were exposed to the UV-irradiation (irradiation intensity : 0.71 W m^{-2}) at 60 °C for 4 h, and next condensation at 50 °C for 4 h. O_2 plasma etchings were conducted using a plasma instrument (DT-01, China) at ambient temperature for 3 min.

2. Results and discussion

Fig. 1a shows FT-IR analyses of MPTMS-POSS-PFDT and MS nanoparticles. After the modification of silica nanoparticles, these nanoparticles still leaved some hydroxyl groups for water dispersion. A new peak at 1200 cm^{-1} was assigned to the C-F stretching vibrations of the fluorinated alkyl chains. Meanwhile new peaks at 2989 and 2943cm^{-1} contradiction emerged, which respectively assigned to the carbonyl stretching band, CH_3 and CH_2 of MPTMS-POSS-PFDT. These results indicated that MPTMS-POSS-PFDT have successfully grafted on the silica. When the MS nanoparticles were gradually added into the polysiloxane latex, because the surface roughness and hydrophobic substances of surface was increased, the wettability of corresponding coating turned from hydrophilicity to superhydrophobicity with 40wt% MS nanoparticles (Fig. 1b), and continuing to increase MS amount could not cause any substantial increase in water contact angle (WCA). And that is, the critical total nanoparticle load is 40 wt%. From Fig.1c,d, the surface showed a hierarchical roughness with a mass of micrometric aggregates and nanometric bulges compared with smooth surface without nanoparticles (Fig. S1), which was mostly consisted of MS nanoparticles. Besides, this coating can be applied on many different substrates, such as aluminum plate, cotton fabric, glass and wood. (Fig. 2e). Further, these surfaces are also not wetted by other aqueous liquids such as soy, milk, orange juice, coffee and tea (Fig. 2f).

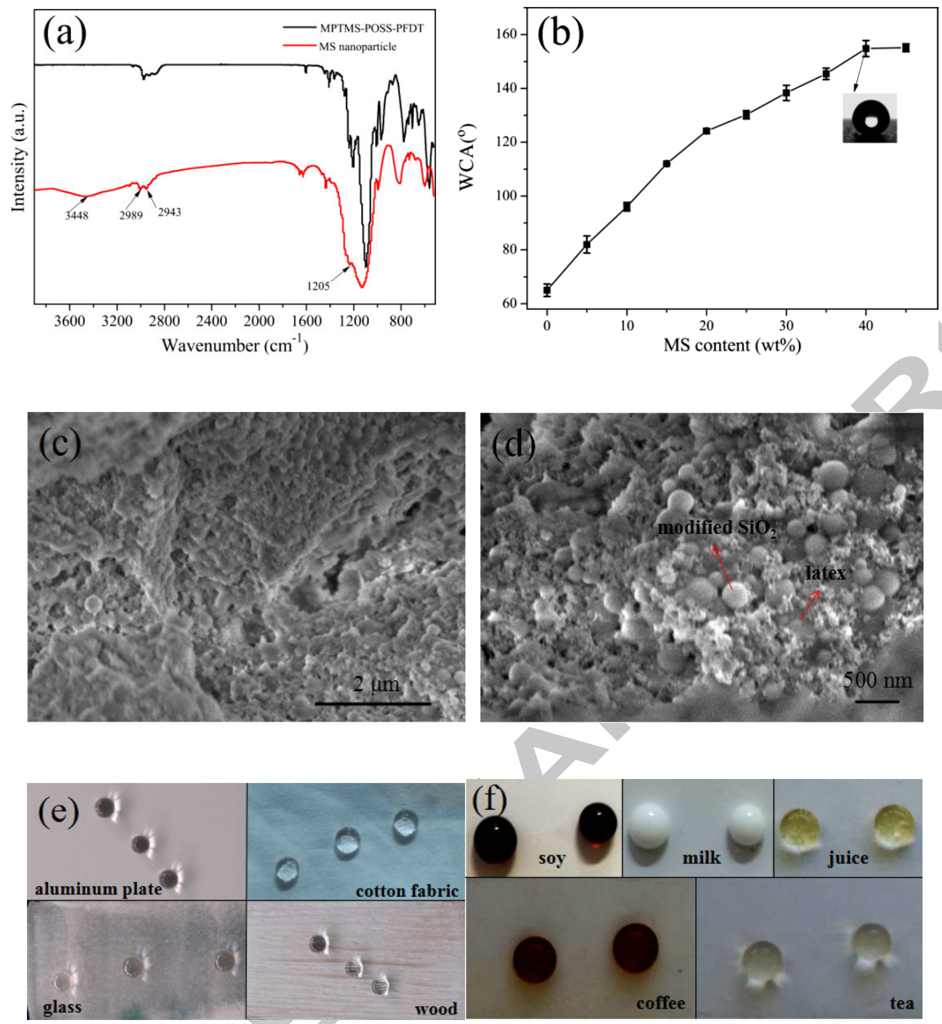
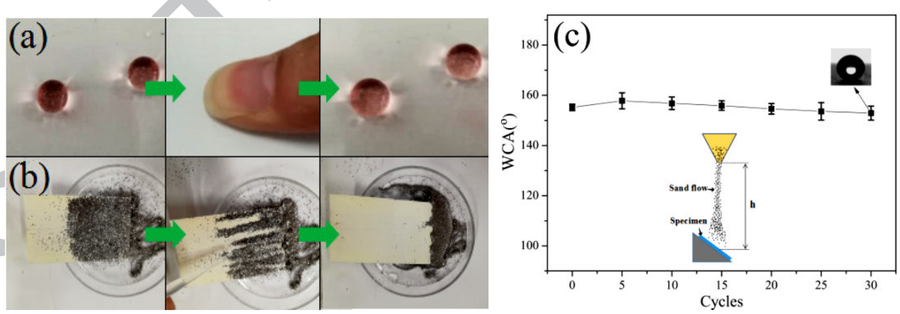


Fig. 2. (a) FT-IR spectra of MPTMS-POSS-PFDT and MS. (b) Changes of WCA with the different content of MS nanoparticles in the polysiloxane latex. (c) SEM images of the coating with 40 wt% of MS nanoparticles; (d) the enlarged image of (c). (e) Photos of the superhydrophobic surfaces formed on the different substrates. (f) Images of different liquids droplets on superhydrophobic surfaces.

From Fig. 3a, powdered dusts on the surface can be easily washed down by water, indicating it has a good self-cleaning ability. Although the superhydrophobic coating was pressed by a thumb, the surface still sustained the superhydrophobicity (Fig. 3b). Moreover, when sand gains with 300 to 600 μm diameter impacted the surface from a height of 30 cm, the surface remained the superhydrophobicity even after 30 cycles abrasion of the sand (Fig. 3c). After 360 h accelerated ageing test, the surface was still the superhydrophobic (154.8^{o}), and no distinct changes in the contact angle values of the acid/alkali solution droplets with pH ranging from 2 to 12 was observed (Fig. 3d,e). All these results indicate that this coating possesses a good durability for mechanical damage or chemical erosion.

We further investigated the self-healing ability of this superhydrophobic coating. As shown in Fig. 3f and 3g, the superhydrophobic surface changed into the superhydrophilicity after O_2 plasma treatment [22,23]. However, due to the easily rotation and movement of fluorinated alkyl chains, the damaged surface may be restored its superhydrophobicity (155.6°) under room temperature for several hours or more, and higher temperature could accelerate the recovery efficiency. Using this plasma/heating healing process could repair the damaged surface for about ten cycles. Additionally, the coated aluminum plate was immersed into 50 mL Triton X-100 aqueous solution (3 wt%) for 1 h, followed by ethanol washing and drying. The immersed surface turned into the hydrophobicity (66.3°), but after heating at 80 °C for 15 min, the WCA of surface was back to above 150° again. And after seven immersing/heating cycles, the surface sustained the superhydrophobicity. When the surface was chemically damaged, the introduction of polar groups would increase surface free energy. Whereas the heating could increase the mobility of the fluorinated alkyl chains, and the polar groups tended to be hidden inside the coating layer, and thus more fluorinated alkyl chains were migrated on the surface to minimize the surface free energy.



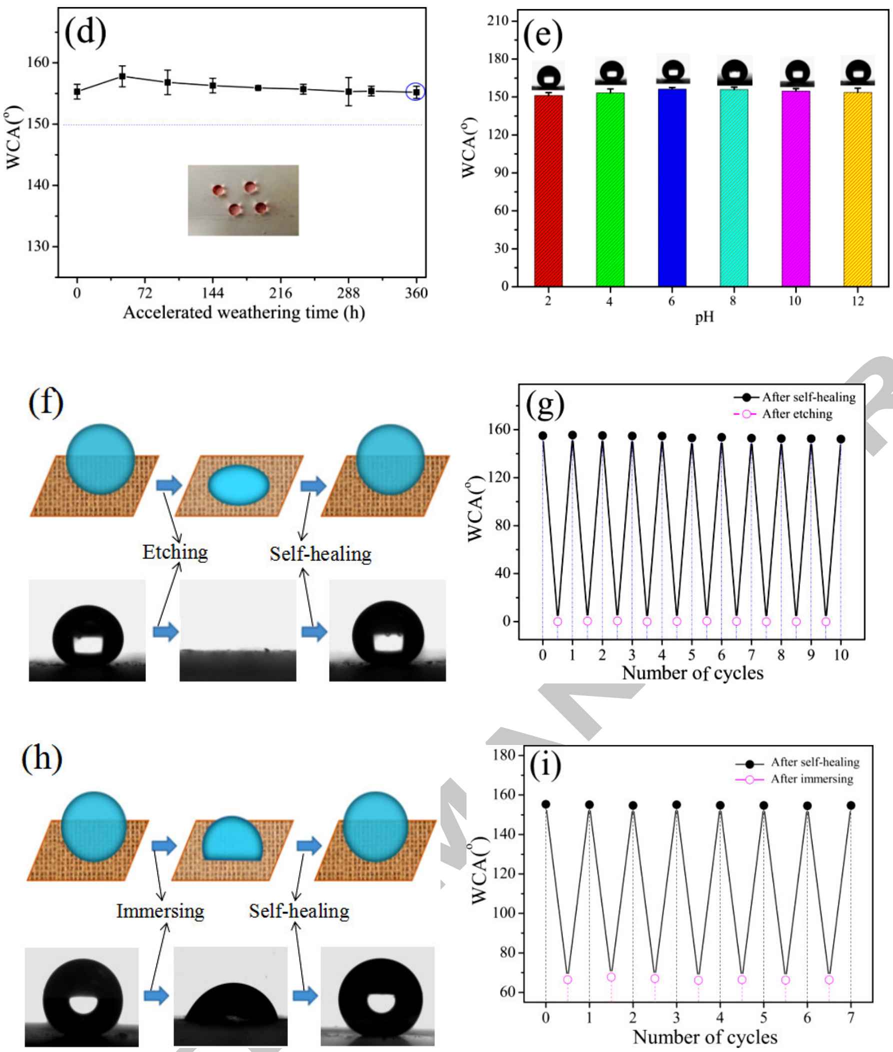


Fig. 3. (a) Photos of water droplets on the superhydrophobic coating before and after the finger pressing. (b) Self-cleaning function of the superhydrophobic coating. (c) Mechanical stability of the superhydrophobic coating. (d) The WCA of superhydrophobic coating with different accelerated weathering time. (e) The CAs of water droplets with different pH value on the superhydrophobic coating. (f and g) The process of O_2-plasma etching and high temperature repairing. (h and i) The process of amphiphilic solution and high temperature repairing.

3. Conclusion

In conclusion, we have successfully developed a waterborne superhydrophobic coating with self-healing ability from MS nanoparticles. These coatings could be readily sprayed on different substrates to obtain superhydrophobic surfaces, and they demonstrated durable superhydrophobicity against sands rubbing and UV light. Additionally, the surfaces could restore their superhydrophobicity under heating even after O_2-plasma treating or water immersing. We believe that the self-healing ability combining with the waterborne character assured their practical applications in the outdoors.

Acknowledgement

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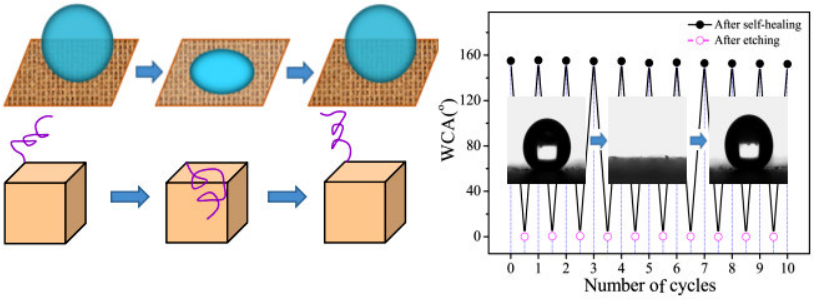
Graphical Abstract:



Highlights

- A self-healing waterborne superhydrophobic coating was developed.
- This durable coating can be easily deposited on many different substrates.
- The surface of coating possesses the self-healing superhydrophobic ability.