Fabrication of superhydrophobic and oleophobic thin films with high stability and self-healing property

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Abstract. We fabricated the superhydrophobic and oleophobic thin film via layer-by-layer assembling of three kinds of silica nanoparticles and chemical vapor depositing of 1H,1H,2H,2H-perfluorooctyl trichlorosilane (PFTS). The water contact angle of the thin film could reach to 170°, and the contact angle of ethylene glycol was 140°. The thin film could recover the superhydrophobic property after the oxygen plasma treatment. Meanwhile, the thin film could endure the xenon lamp irradiation and water impact experiments.

1. Introduction
Self-cleaning thin films show excellent potential applications in our society, which could clean themselves with the help of the rain. Two types of self-cleaning thin films had been provided in the recent researches, which were superhydrophilic and superhydrophobic thin films. For superhydrophilic thin films, the water contact angles were smaller than 5°, and for superhydrophobic thin films, the water contact angles were larger than 150°. Both of these two thin films could realize self-cleaning, however, the superhydrophilic thin films would easily loss this property if they were contaminated by the oil in the environment. Superhydrophobic thin films, which possess micro-nano surface morphologies and low surface energy, were proved to have much better self-cleaning stability than superhydrophilic thin films 1-4.

In the practical applications, two problems would restrict the using of superhydrophobic thin films. First of all, the superhydrophobic thin films could not avoid contacting with oils. Such oils with low surface energy might penetrate into the micro-nano structure and lead to the losing of superhydrophobicity. Fabricating the thin films which possess both superhydrophobicity and oleophobicity could solve the problem. Such thin films would make oil slide away from the thin films with water and remain the self-cleaning property. The oleophobic thin films require higher surface roughness than superhydrophobic thin films 3,5-8.

Another problem that restrict the practical applications of superhydrophobic thin films is the loss of the low energy surface. The decorated low surface energy materials on the surface would keep consuming in daily application, which might lead to the loss of superhydrophobicity. Introducing self-healing property into the superhydrophobic thin films would supply the low surface energy materials continuously and improve the self-cleaning stability 9,11.
In the current work, we fabricated self-healing superhydrophobic and oleophobic thin films. Three kinds of silica nanoparticles were coated on glass substrate via layer-by-layer assembly. The 1H,1H,2H,2H-perfluorooctyl trichlorosilane (PFTS) with low surface energy was chemical vapor deposited on the thin films. Large amount of PFTS and long CVD treated time was carried out to store the PFTS in the mesoporous silica nanoparticles. The water contact angle of the thin film could reach to 170°, and the contact angle of ethylene glycol was 140°. The thin film could recover the superhydrophobic property after the oxygen plasma treatment. Meanwhile, the thin film could endure the xenon lamp irradiation and water impact experiments. The achievement would provide an effective method for the practical applications of superhydrophobic thin films.

2. Results and Discussions
For fabricating the self-healing superhydrophobic and oleophobic thin film, we synthesised silica hollow sphere, silica mesoporous nanosphere and silica nanosheet. The Transmission Electron Microscope (TEM) images of these nanoparticles were shown in Figure 1. Obviously, mesoporous were occurred in the silica mesoporous sphere and silica nanosheet, which could be used to store the 1H,1H,2H,2H-perfluorooctyl trichlorosilane (PFTS).

![Figure 1 TEM images of silica hollow spheres (a), silica mesoporous nanospheres (b) and silica nanosheets (c).](image)

We used layer-by-layer assembling to fabricate the thin films. Driven by the electrostatic force between the PDDA and silica nanoparticles, various silica nanoparticles could be assembled on the glass substrates layer by layer. We assembled 2 layers of silica hollow spheres, 8 layers of silica mesoporous nanospheres and 3 layers of silica nanosheets to fabricate the thin film. The Scanning Electron Microscope (SEM) images of the thin films were shown in Figure 2. Obviously, we had achieved homogeneous thin films. Figure 2b showed the amplified images of the thin films. Micro and nano dual surface structures could be observed, which suited the demand for superhydrophobic and oleophobic thin films. We could also notice some mesoporous on the thin film, which could be used to store the 1H,1H,2H,2H-perfluorooctyl trichlorosilane (PFTS).

![Figure 2 SEM images of prepared thin films](image)

After the assembling, we used the chemical vapor deposition to decorate the PFTS on the thin film. Large amount of PFTS and long CVD treated time was carried out to store the PFTS in the mesoporous silica nanoparticles. After that, we measured the water contact angle and contact angles of ethylene glycol for the thin film. As shown in Figure 3 a and d, the water contact angle was 170° and the contact angle for ethylene glycol was 140°. The thin films showed excellent superhydrophobicity and oleophobicity. The thin film also possessed self-healing properties. After oxygen plasma treatment, the thin film lost its superhydrophobicity, and the water contact angle was decreased to 33° (Figure 3 b). However, after treated the thin film in hygrothermal environment (50 °C, 95% humidity) for 6
hours, the water contact angle of the thin film was recovered to 166° (Figure 3c). The reason for the self-healing properties might because the stored PFTS in the mesoporous of the thin film would turn to the surface in such hygrothermal environment.

Figure 3 Water contact angles of the thin film (a), after oxygen plasma treatment (b), after treating hygrothermal environment for 6 h (c) and contact angle of ethylene glycol for the thin film (d).

The achieved thin film also showed good stability. We put the thin film under the Xenon lamp, the intensity of the lamp was 80000 μW/cm². After exposure for 10 hours, we measured the water contact angles of the thin film. As shown in Figure 4a and b, the water contact angle only decreased 1° after the experiment, indicating the thin film could endure the long-term light irradiation. Meanwhile, we also used the water impact test to characterize the mechanical stability. 100mL water (about 4500 drops) was dropped from the burette 45cm higher than the thin films in 37 minutes. The water contact angle of the thin film did not show obvious decreasing after the experiment, as shown in Figure 4c, d.

Figure 4 Water contact angles of the thin film before (a) and after (b) Xenon lamp exposure experiment. Water contact angles of the thin film before (c) and after (d) water drop impact test.

3. Experimental Section

3.1 Materials.
Tetraethyl orthosilicate (TEOS, 99+ %), sodium poly(4-styrenesulfonate) (PSS, Mw=70000) and 1H,1H,2H,2H-perfluorooctyltrichlorosilane (CF3(CF2)5CH2 CH2SiCl3, PFTS) were obtained from Alfa Aesar. Poly (diallyldimethylammonium chloride) (PDDA, Mw=200000 350000, 20wt%) was purchased from Aldrich. Cetyltrimethylammonium bromide (CTAB, ≥ 99%), aqueous ammonia
(25%), absolute ethanol (99.5%) and ethyl ether (≥99.5%) were purchased from Beihua Fine Chemicals. Poly (acrylic acid) (PAA, 30wt% in water, Mw=5000) was purchased from Shandong Heli water treatment company. Ultrapure water with a resistivity higher than 18.2 MΩ·cm was used in all experiments and was obtained from a three-stage Millipore Mill-Q Plus 185 purification system (Academic).

3.2 Preparation of varied silica nanoparticles.

Synthesis of hollow silica nanoparticles: 0.98 g PAA dissolved in 4.5 mL aqueous ammonia was mixed with 90 mL absolute ethanol, followed by injection of 5 aliquots of TEOS totalling 2.25 mL over a time interval of 50 min under vigorous magnetic stirring at room temperature. After 10 h, 80 nm hollow silica nanoparticles formed.

Synthesis of silica nanosheets: 0.5 g CTAB was dissolved in a mixture composed of 70 mL water, 0.8 mL aqueous ammonia, and 20 mL ethyl ether. After the emulsion system was vigorously stirred at room temperature for 0.5 h, 2.5 mL of TEOS was quickly dripped into the mixture. The resulting mixture was vigorously stirred at room temperature for 4 h, and a white precipitate was obtained, filtered, washed with pure water, and dried in air at 60°C for 24 h. After centrifugation, the nanoparticles precipitated under the liquid were collected and calcinated in air at 550°C for 5 h to remove CTAB and other organic components.

3.3 Thin film assembly.

Slide glass was used as substrate. First, the substrate was washed with ultrapure water and cleaned by oxygen plasma for 5 min. Second, the cleaned substrate was alternately dipped in PDDA and PSS solutions for 5 min, and redundant polyelectrolytes were removed by shaking in pure water for 2 min and rinsing for 1 min, followed by drying with N2 flow. The concentrations of PDDA and PSS aqueous solutions were 2 mg mL-1. A multilayers thin film of (PDDA/PSS)5/PDDA was prepared, and was used as a primer in all experiments. Third, the (PDDA/PSS)5/PDDA-covered substrate was alternately dipped in varied silica nanoparticles suspensions and a PDDA solution by the same procedure for an appropriate number of cycles. Finally, the as-prepared coatings were calcinated (heating rate: 1 K min⁻¹) at 550°C for 3 h to remove the polyelectrolytes and other organic components.

3.4 Surface modification of thin films.

Surface modification of the coatings surface was carried out by a simple chemical vapor deposition (CVD) of PFTS. The glass substrate with assembled silica nanoparticles coatings on both sides was treated by oxygen plasma for 10 min, placed in a Teflon container, on the bottom of which was dispensed 200μL of PFTS, and sealed by stainless steel autoclave. There was no direct contact between the substrate and the PFTS droplets. The autoclave was put in an oven at 120°C for 8 h to enable the vapor of PFTS to react with the hydroxyl groups on the coating surface. Finally, the autoclave was opened and placed in an oven at 150°C for an additional 1.5 h to volatilize unreacted PFTS molecules on the coating.

3.5 Characterization.

For transmission electron microscopy (TEM) observations, powder samples were added on carbon-coated copper grids and observed on a JEOL JEM-2100F transmission electron microscope at an acceleration voltage of 200 kV. Freshly fabricated coatings were examined by scanning electron
microscopy (SEM) on a Hitachi S-4300 scanning electron microscope operated at 10 kV. Contact angles of different liquids on fabricated coatings were measured at ambient temperature on a Kino SL200B3 automatic contact angle meter.

4. Conclusions
In this work, we used layer-by-layer assembling to fabricate the thin films, which contained three kinds of silica nanoparticles. After decorating PFTS via chemical vapor deposition, the thin film shower superhydrophobicity and oleophobicity. The water contact angle was 170°, and the contact angle of ethylene glycol was 140°. The thin film could recover the superhydrophobic property after the oxygen plasma treatment. Meanwhile, the thin film could endure the xenon lamp irradiation and water impact experiments. The achieved thin film could provide a new method for the applications of superhydrophobic thin films.

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