Fabrication of superhydrophobic surface with different particle size SiO2 by layer-by-layer assembly method

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Abstract. Surface coarse structure is one of key factors affecting the superhydrophobicity, yet it’s not very clear that what kind of structure is the best for hydrophobicity. Herein in order to study the effect of surface coarse structure, eight kinds of spherical SiO2 (20 nm, 60 nm, 200 nm, 500 nm, 1 μm, 2 μm, 5 μm and 10 μm) were taken as raw material respectively to explore the effect of particle size on the hydrophobic performance. SiO2 was deposited on the glass substrate layer by layer using the electrostatic assembly method based on the reaction of amino and epoxy groups. The sample’s structure and properties were characterized respectively by scanning electron microscopy and contact angle measuring instrument. The relationship between SiO2 particle size and surface hydrophobicity was explored and the superhydrophobic stability were tested. The results show that the surface of SiO2 film layers are stacked together and arranged tightly, and when SiO2 particle size is the closer to 200 nm, surface hydrophobic property is the better. 200 nm SiO2 owns the best hydrophobicity, whose contact angle is 154.3 ° and sliding angle is 7.58 °.

1. Introduction
The superhydrophobic surface usually refers to the surface [1] whose water contact angle (CA) greater than 150 ° and sliding angle (SA) less than 5 °. Superhydrophobic surface has wide application prospects in self-cleaning [2-4], anti-icing and anti-fog [5-6], fluid drag reduction [7-8], corrosion protection [9-10], oil-water separation [11-13] and other fields.

At present, it is commonly recognized that the surface coarse structure and surface chemical composition are two main factors affecting the superhydrophobic surface. The research indicates that even for the material with the lowest surface at present, its smooth surface can only obtain 119 ° contact angle [14]. Although the construction of micro/nano rough structure is necessary for obtaining superhydrophobic property, there is no definite conclusion that what surface microstructure owns the best superhydrophobic performance. In order to study the influence of surface microstructure on hydrophobic properties, many scholars have done a lot of meaningful work from thermodynamic analysis and experimental point of view. Zhang calculated the wetting properties of cylindrical, conical, pyramid shaped, sinusoidal surface morphology in the theory under composite state, and found sinusoidal microstructures had the best hydrophobic properties [15]. Hazlett thought that the best structure of superhydrophobic surface is fractal structure [16], but Nakajima et al. thought rough degree of different grades is the main factor affecting the superhydrophobic surface, and the fractal structure not be [17]. Ren et al. suggested superhydrophobic surface mainly depends on the solid-liquid contact area, rather than the roughness factor [18].

Besides theory research, some scholars also try to study how the structure affects the hydrophobicity by preparing the surface of different structures and sizes [19-24]. Tamesue S et al. [19]
fabricated micron square column using polydimethylsiloxane (PDMS) and adjusted the column height and width, finding that the wider the column, the better the hydrophobic performance independent of the height. Duan Zongfan et al. [22] prepared the protrusions array through the interference fringes etching on the silicon, and then deposited a layer of hydrophobic TiO2, finding when the interval is 3.3, 1.67, 1.11 and 0.83 μm, corresponding CA were 145°, 153°, 157° and 163°, namely the smaller the interval, the greater the CA. Huang ChenYu [24] used magnetic fluid to make cone array with different tilt angle (0°, 25°, 50°, 70° and 90°), and then deposited nickel on the top to obtain micro/nano structure, finding that the surface with 90° tilt angle owned the best hydrophobicity (CA 163.1).

Unfortunately, both the experimental and theoretical studies have not obtained the quantitative relationship between the surface microstructure and the surface wettability. The electrostatic assembly method is a method of combining the opposite charges with each other or the interaction of the surface groups to make the micro/nanoscale particles together, which is applied frequently to fabricate superhydrophobic surface due to its convenience and effectiveness [25-30]. To study the influence of different surface microstructure on the surface hydrophobic properties, the spherical SiO2 with different particle size was selected as raw material, and electrostatic assembly was applied to construct different roughness structure. The surface microstructure and wettability were characterized and analyzed, and the change of hydrophobic properties with the particle size was discussed.

2. Experimental section

2.1. Materials
Anhydrous ethanol, hydrochloric acid, sulfuric acid, potassium hydroxide, hydrogen peroxide and nitric acid was supplied by Sinopharm Chemical Reagent Co., Ltd. Aminopropyl triethoxysilane (KH-550), epoxypropyl trimethoxy silane (KH-560) was obtained from Gezhou hengda chemical Co., Ltd. Trifluoroocetyl triethoxysilane (F8261) was purchased from Alfa Aesar Chemical Co., Ltd. 500 nm, 20 nm, 2 μm, 5 μm, 10 μm SiO2 was supplied by Nanjing Haitai nano materials Co., Ltd, and 60 nm, 200 nm, 1 μm SiO2 was obtained from Xuan Cheng Jing Rui New Material Co., Ltd. The water used in all experiments was purified with a resistivity greater than 18 MΩ cm (PCR-20, China).

2.2. Modification of amine or epoxy and layer-by-layer assembly of SiO2
At first 1g KH-560 or KH-550 was added to 150mL ethanol, and experienced the ultrasonic oscillation about 5 min. Then add SiO2 to the solution under magnetic stirring for 12 h. The modified SiO2 ethanol solution was separated by centrifugation, and the sediment drying under 100 °C for 24 h.

The glass slides were treated with Piranha solution at 70 °C for 2 h to increase the hydroxyl content on the surface. Then, it was soaked in 1vol% KH-550 ethanol solution 30 min, and the amino was loaded onto the substrate surface.

Firstly, the treated slides were immersed in the SiO2 ethanol solution with amino groups on the surface. The solution was heated to 80 °C for 1h in oil bath, so that SiO2 with amino groups on the surface was loaded onto the glass slide. Secondly, the same process was carried out in the SiO2 ethanol solution with epoxy group in order to covering SiO2 with epoxy group on the above treated slides. Thirdly, repeat first and second step seven cycles to increase the coverage rate. At last, the coated slides were immersed in the ethanol solution of 1wt% F8261, heated in water bath to 70 C reacting 30min, then the glass slides were heated at 120 °C 2h to lower surface energy.

2.3. Characterization
Chemical composition was characterized via Fourier transform infrared spectroscopy in the wave number range of 4000-400cm⁻¹ with KBr compression method (FT-IR, Bruker, Vertex70).The morphology of the samples was observed by scanning electron microscopy (SEM, Hitachi, S-4800) . Contact angle and sliding angle were measured on contact angle system (KRUSS, Germany, DSA30) at room temperature with a droplet of 5 μL. An average of five measurements taken at different positions on each sample was applied to calculate the average value.
3. Results and discussion

The surface of micro/nano SiO₂ is generally rich in silicon hydroxyl groups. The hydrolysis products of silane coupling agent KH-560 and KH-550 can react with silicon hydroxyl groups, so that grafting amine and epoxy groups on SiO₂. Through the reaction of amine group and epoxy group SiO₂ was assembled together layer-by-layer and finally modified with fluoro silane. The general process of the experiment is shown in Figure 1.

![Figure 1. Flow chart of layer-by-layer assembly](image)

In order to increase the content of the hydroxyl group of SiO₂, it was treated with the Piranha solution. When SiO₂ was modified by amino or epoxy groups, the ratio of SiO₂ to silane coupling agent should be controlled to retain some hydroxyl groups for the last hydrophobic modification.

3.1. Modification of amine or epoxy of SiO₂

Figure 2 shows that the absorption peak of epoxy group near 810 cm⁻¹-940 cm⁻¹ can be covered by the Si-O bond absorption band of SiO₂ in the infrared spectrum of 20 nm SiO₂ modified by KH-560. As shown in Figure 2a, when the mass ratio of SiO₂ to KH-560 is 1:1, the absorption peak of -OH near 3430 cm⁻¹ is very strong, indicating that the hydroxyl group on the SiO₂ surface remains a lot. The infrared spectrum of 1:4 is displayed in figure 2c, the absorption peak of –OH is very weak compared with that in Figure 2a, implying the less –OH. As the mass ratio is 1:2, SiO₂ owns the moderate –OH, making it clear that some hydroxyl groups on SiO₂ surface react with silane coupling agent KH-560, and there are still some abundant hydroxyl groups on the surface, which provides a premise for subsequent low surface modification. To sum up, when the mass ratio of SiO₂ and silane coupling agent KH-560 is 1:2, the effect is best. When applying KH-550, it comes to the same conclusion.

![Figure 2. FTIR spectra of SiO₂ modified by KH-560: (a) 1:1, (b) 1:2, (c) 1:4](image)

3.2. Morphologies and wettability

The surface of unmodified surface is selected to prevent the modified organic substance to influence the effect of observation. Figure 3 exhibits SEM images for the micro surface morphology of each size. From figure 3a, it can be seen that arrangement of 10 μm ball is uniform, and basically covers the entire glass substrate. As shown in figure 3b, 5 μm ball stack together but out of order, and there exists other sizes SiO₂ ball implying that the particle size distribution is not uniform. Figure 3c, 3d is respectively the surface morphology of 2 μm and 1 μm SiO₂, which exhibits that particle size distribution of SiO₂ is not very uniform but relatively consistent; in the figure 3e, 3f, 3g, 3h, 3i, 3j it
can also be found the similar things, that is SiO$_2$ balls stack together, although not a neat arrangement in theory, but the arrangement is relatively compact and the particle size distribution is also uniform, basically covering the whole base.

![Figure 3. SEM images of surface morphology of different particle SiO$_2$: (a) 10 μm, (b) 5 μm, (c) 2 μm, (d) 1 μm, (e) 500 nm, (f) 200 nm, (g) 60 nm, (h) 40 nm.](image)

The hydrophobicity of eight kinds of microstructures constructed above is tested, and contact angle and sliding angle are obtained before and after the modification. It is found before the modification all are superhydrophilic, namely CA< 5 °. The contact angle between the water droplet and the surface is shown in figure 4. From figure 4a it can be seen that before the modification the water droplets are completely wetted on the surface, and water droplet can’t be seen in the horizontal direction. The microstructures of other SiO$_2$ before modification are the same as above. Except the microstructure of 20 nm particle size, contact angle of others after modification is more than 150 °, and the difference is not very great. Figure 4b displayed images of 5μl water droplet on 200 nm SiO$_2$ surface. The water on the surface of films are nearly spherical even though experiencing a long time contact with the sample surface, indicating excellent superhydrophobicity. The contact angle is 154.3 °, and the sliding angle is 7.68 °. Figure 4c shows the contact angle on 20 nm SiO$_2$ surface, which clearly shows that contact area between the droplet and the surface is obviously larger than that of other particle SiO$_2$. The droplets are spherical corona, no longer spherical, and are completely adhered to the surface of the sample and cannot be rolled. Its contact angle is 138.4 °, which can only be considered as a hydrophobic state.

![Figure 4. Contact angle before and after the modification: (a) 200 nm before modification, (b) 200 nm after modification, (c) 20 nm after modification.](image)

The hydrophobic properties of the microstructures are very different before and after the modification. Before modification, all the surface is superhydrophilic. The reason is that the hydroxyl groups and amino groups or epoxy groups on the surface of SiO$_2$ particles belong to hydrophilic groups. The surface rough structure is not enough to counteract the influence of hydrophilic groups.
So the microstructure surfaces before modification are superhydrophilic, and their contact angles are less than 10 °, or even less than 5 °. After modification, due to the graft of fluothane chain hydrophobic properties is greatly improved, contact angles basically more than 150 °. Water can roll on most surfaces indicating the importance of low surface energy material on superhydrophobicity, especially when surface rough structure is in worse condition.

![Figure 5. The change of the hydrophobicity with SiO2 particle size](image)

Figure 5 shows the change of the surface hydrophobicity following with the particle size of SiO2. It is found that the contact angle and sliding angle are changed regularly with the change of the particle size. From 20 nm to 200 nm, with the larger of particle size, the contact angle becomes larger, and then smaller from 200 nm to 10 μm. That means that when the particle size is smaller or larger than 200 nm, the hydrophobic property decreases. The surface constructed by 200 nm SiO2 have the best hydrophobic property, whose contact angle and sliding angle is respectively 154.3 ° and 7.58 °. The results tell us the rough structure usually has an optimal value, and here 200 nm is the best for spherical SiO2.

4. Conclusions

Surface morphology of eight kinds of spherical SiO2 microstructures is characterized and relationship between hydrophobicity and particle size is studied. It is found that SiO2 particles on the surface are stacked together tightly, which basically cover the whole glass substrate and form a compact structure. All the microstructures surface are superhydrophilic before modified, and after modification the hydrophobicity increases significantly and the contact angles are basically above 150 °. The 200 nm SiO2 microstructure surface owns the best hydrophobic properties, whose contact angle and sliding angle is respectively 154.3 ° and 7.58 °. The closer the particle size is to 200 nm, the better the surface hydrophobicity is, and vice versa.

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