Preparation of superhydrophobic surface with tunable adhesion on glass substrate

Jiyuan Zhu and Kaijin Liao
College of Mechanical and Control Engineering, Guilin University of Technology, Guilin 541004, People’s Republic of China
E-mail: zhuji@glut.edu.cn

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Abstract
Superhydrophobic coatings help to reduce the surface contamination of glass and improve its performance. A SiO2 nanoparticles superhydrophobic surface with tunable adhesion is obtained on a glass substrate after modifying with PDMS. With the water contact angle of 155.1 ± 3°, the superhydrophobic surface also shows excellent self-cleaning property, good durability and thermal stability. This method is facile, cost-effective and easy to operate and will expand the potential applications of glass materials in different fields.

1. Introduction

Glass has broad applications in many fields such as architecture, chemistry, optical and biomedical devices for its advantages of transparency, rigidity, bio-compatibility, and ease of surface modification [1, 2]. But its efficiency and performance are often degraded or restricted by surrounding environment. Surface contamination can be detrimental to the application of glass materials [1, 3] and it takes great manpower and costs for their cleaning. Superhydrophobic surfaces have obtained widespread attention both in academic researches and industrial applications due to their special self-cleaning [4, 5], corrosion resistance [6, 7], anti-icing [8, 9] and antibacterial properties [10, 11]. Preparation of superhydrophobic coatings with excellent self-cleaning properties and high stability on glass substrate will reduce the accumulation of dirt or dust on glass with time and improve its performance. So far, many researchers have investigated the fabrication of superhydrophobic coatings on glass substrate by means of different methods such as spin coating [1], deposition [12], sol–gel [13] and laser etching [14] etc, of which the use of cost-effective, environment-friendly materials, facile operation as well as the high quality multifunctional products have become the growing trend of research.

In recent years, transparent superhydrophobic surfaces on glass have aroused great attentations for their various applications including smart windows, safety glasses [15]. Low surface free energy and rough structure are two important contributing factors to the fabrication of superhydrophobic surfaces [16]. However, to superhydrophobic glass, transparency can be an elusive problem as the transparency of surface is intrinsically in conflict with the required rough structures because the textured part is light scattering [17]. So surface roughness can be a hinder to optical transparency due to surface inhomogeneity. Previous researches have concluded that to minimize optical loss and uphold efficient superhydrobicity, roughness dimension under certain micro/nanoscale is necessary, a higher requirement for technology [3, 18, 19]. So to obtain transparent and durable superhydrophobic coatings on glass substrate poses a challenge and makes the research a meaningful topic.

Adhesion is an important property for superhydrophobic surfaces. As the switchability in adhesion will allow the manipulation of the water droplet [20], superhydrophobic surfaces with tunable adhesion would broadly expand applications of the surfaces. Superhydrophobic coatings with low-adhesion have potential applications for self-cleaning and anti-fogging coatings [21]. Meanwhile, the high adhesive superhydrophobic surfaces can be potentially used in applications such as microfluidic devices and chemical microreactors [22]. The preparation of superhydrophobic surface with low adhesion on glass can keep the glass clean and transparent as the self-cleaning property of the surface will remove the dirt and greatly save labor. On the other hand, to a superhydrophobic coating with high adhesion, as the liquid can be controlled by the microstructure of...
the surface, it can be used for non-destructive transportation of liquids and biotechnology. It is no doubt that the adhesion-adjusting function of superhydrophobic glass will provide a better improvement for the performance and a wide range of applications in industrial and commercial fields.

In this work, we reported a facile method to successfully prepare a superhydrophobic surface on glass. The microstructure was generated by the deposition of Silica (SiO$_2$) nanoparticles on the glass surface. After the modification with a hydrophobic polydimethylsiloxane (PDMS) coating, a superhydrophobic SiO$_2$ coating was prepared. This superhydrophobic surface prepared by this approach has shown a high transparency and significant tunable adhesion. The surface also has excellent self-cleaning superhydrophobicity, good bouncing power and thermal stability. The method has great advantages in cost and operation. It also involves no complicated equipment and severe production conditions, which helps to promote the potential application of glass surfaces.

2. Material and methods

2.1. Materials

SiO$_2$ nanoparticles (~40 nm diameter), glass slide (76 × 26 mm), absolute ethanol, n-hexane, polydimethylsiloxane (PDMS) were obtained for the experiment. The water used was deionized water.

2.2. Methods

In the experiment, the samples were prepared by the following procedure: 0.5 g of SiO$_2$ nanoparticles and 99.5 g of ethanol were ultrasonicated in a beaker for 30 min to obtain a 0.5 wt% suspension. Then 1 g of PDMS and 50 ml of n-hexane were added to the suspension and stirred for 10 min to obtain solution A. And 0.1 g of curing agent and 50 ml of n-hexane were added to another beaker and kept for a 10 min stirring to get solution B. The mixture of solution A and B was stirred for 10 min to obtain a homogeneous solution. A clean glass slide was immersed in the SiO$_2$ nanoparticles suspension for 30 s and then dried at 50 °C for 5 min. The glass slide deposited with SiO$_2$ nanoparticles was soaked in the PDMS solution for 30 s and dried at 50 °C for 20 min. A typical experiment cycle is then formed. The same experiment was repeated several times, namely 1, 2, 3, 4, 5, and 6 cycles. The as-prepared samples were then respectively cured in the air for 48 h.

2.3. Sample characterization

Surface morphologies of the prepared samples were observed by scanning electron microscope (SEM, KYKY-EM6900, Tiantest Optical Equipment Co., Ltd, Dongguan). The transmittance of the sample surface was measured by an ultraviolet-visible spectrophotometer (721N, INESA ANALYTICAL INSTRUMENT Co., LTD, China). Wettability of the samples was measured with 6 μl droplets of deionized water using a contact angle measurement instrument (SDC-200, Sindin Precision Instrument Co., Ltd, Dongguan). The contact angles were measured at six different positions for each sample.

3. Results and discussion

3.1. Wettability and adhesion

Results of the contact angle measurement after each cycle are shown in figure 1(a). It is found that the water contact angles of samples gradually increase with the increase of cycle number. After 1 cycle, the contact angle of the sample was 77 ± 5°, exhibiting hydrophilicity. After 2 cycles, the contact angle of the sample increases to 103 ± 10°, and the sample shows hydrophobicity. After 4 cycles, the contact angle is 145 ± 9°, remaining hydrophobicity. After 5 cycles, the contact angle of the sample is 155.3 ± 7°, indicating the superhydrophobic nature. After 6 cycles, the contact angle is 155.1 ± 3°, suggesting the superhydrophobicity of the sample remains stable. As shown in figure 1(b), the 6 μl water droplet maintains a spherical shape on the sample surface after 6 cycles. In figure 1(c), it can be seen that even overturned 180°, the droplet remains still on the surface. This shows the excellent superhydrophobicity and high adhesion of the as-prepared sample. When the volume of droplet adds to 26 μl, the water droplet still maintains stable on the inverted surface because of the adhesion force as shown in figure 1(d). But if the volume exceeds 26 μl, the water will fall to the ground. Kept drying at 200 °C for 1 h, the adhesion of the sample surface will change. With a significant decrease in the adhesion, the sliding angle is about 3° (figure 1(e)).

A mixture of ink and water is used to test the bouncing behavior of the droplet on a dry glass slide. Figure 2(a–h) shows the process. When dripping 5 cm above the sample, the droplet soon spreads like a pie cake after striking the surface. It then aggregates due to surface tension but soon bounces off for the reacting force. The gravity causes it to drop again. It bounces repeatedly until it leaves the slide. The good bouncing performance indicates the excellent self-cleaning effect of the as-prepared superhydrophobic surface.
3.2. Surface morphologies

To study the effect of cycle number on the surface morphologies of the samples, we compared the SEM images of each sample after 0 (bare) and 2, 4, and 6 cycles. As shown in figure 3(a), surface of the bare slide is very smooth. Figure 3(b) is the SEM image of the sample surface after 2 cycles. Then the surface of the sample is much rougher than that of the bare glass slide. Due to agglomeration and precipitation, SiO$_2$ nanoparticle agglomerates of different shapes appear on the glass slide, but still many areas of the sample surface are not covered by SiO$_2$ nanoparticles. When the agglomerates become relatively dense, they join together to form a strip-like structure. Figure 3(c) shows the SEM image of the sample surface after 4 cycles. Compared with the sample after 2 cycles, the uncovered areas after 4 cycles are significantly reduced. With the increasing of SiO$_2$ nanoparticles, the former strip-like structure changes into flake shape with few agglomerates stacking on the surface. The transition is conducive to the hydrophobic microstructure and explains the significant increase of water contact angle of the sample after 4 cycles. Figure 3(d) is an SEM image of the sample surface after 6 cycles. Then, there are fewer uncovered areas of SiO$_2$ nanoparticles but more stacking agglomerates. By comparing the samples after 6 cycles with that after 2 cycles, it can be detected that the number of SiO$_2$ nanoparticles grows and the sample surface becomes much rougher, which is highly significant to the superhydrophobicity of surface.

SEM images of the heated samples at different magnification were analyzed. In figures 4(a)–(b), it can be found that after heating the sample for 6 cycles, the SiO$_2$ aggregates on the sample surface are decomposed into a large number of smaller aggregates. By further observing the SEM image of figures 4(c)–(d) with high magnification, the size of the decomposed aggregates is about 200 nm–500 nm. The aggregates stack with each other to form a micro-nano structure, which could trap air on the surface of the sample.

3.3. Adhesion mechanism

The wetting state of superhydrophobic surfaces generally falls into two states. One is the Wenzel state with high adhesion, and the other is the Cassie state with low adhesion. The change of the state can be achieved through changing the chemical composition of a surface or its microstructure. The mechanism for the change of surface adhesion of the sample is shown in figure 5. Before heating water fully enters into the grooves of the surface and
the droplet is pinned on the surface, suggesting the high adhesion and Wenzel state of the superhydrophobic surface. By heating the microstructure of the surface is of micro/nanoscale hierarchical structures, which is accepted as a prerequisite for Cassie state \[23\]. The hierarchical structure composed of the nanostructures on the surface of the micron structure was reported to be responsible for low sliding angle of the surface \[24\]. Then water can contact only the peak of the rough surface, trapping air pockets in the cavities of the rough surface. The droplet is suspended above the superhydrophobic surface, which is ascribed to the Cassie state.
3.4. Transparency
To study the transparency of the as-prepared samples, the samples after 0, 2, 4, and 6 cycles were compared respectively on a paper with letters. Compared with that of the bare glass, the sample after 2 cycles still has good transparency. Letters can still be seen very clearly as shown in figures 6(a–b). After 4 cycles, a transparent film is formed on the sample surface, but the letters in figure 6(c) are still clearly visible. After 6 cycles, the surface of the sample becomes more blurring, but there is no problem in seeing the letters clearly as shown in figures 6(d–e). In order to further study the optical properties of the samples, a UV-visible spectrophotometer was used to test the transmittance of the samples after different cycles in a visible wavelength range (770–390 nm). As shown in table 1, the transmittance of the sample decreases with the increasing number of cycles. As the cycle’s number increases, the light scattering effect caused by the hierarchical structure will intensify.

3.5. Durability
To study the real durability of the sample under ambient condition, the sample was placed outside and a daily contact angle measurement was carried out at regular daytime, but after 10:00 pm on the ninth and tenth days.

Figure 5. Schematic illustration of the surface structure altered by heating.

Figure 6. (a)–(d) Transparency of sample surface after 0, 2, 4 and 6 cycles. (e) Water droplet on the sample surface after 6 cycles.
As shown in figure 7, except for day 9 and 10, the contact angles of all the other days are above 150°, suggesting the superhydrophobic nature of the surface. The slight decrease on the two days, 149.5 ± 2° and 149.6 ± 6°, respectively, can be due to the increase of the humidity at night. However, on the eleventh day, after being exposed to the sun for a day, the contact angle of the sample also increases significantly and reaches 154 ± 3°. In order to further study the durability of the samples, the unheated samples and the heated samples were placed in the atmosphere for 6 months, and the wettability of the sample surface was studied. As shown in figures 7(b)–(c), after 6 months in the atmosphere, the CA of the unheated sample surface is 157°, and the droplets (26 μl) can be well pinned on the inverted surface, indicating good stability of the unheated sample. In figures 7(d–e), the CA of the droplets on the surface of the heated sample placed in the atmosphere for 6 months is 163.7° and the SA is 5.5°, indicating that the sample maintains a good superhydrophobicity.
3.6. Self-cleaning effect
To study the self-cleaning behavior of the treated sample, dry soil was spread on the surface. The process is shown in figures 8(a–h). Dripping 5cm above the sample, the droplet mixes with the soil and it soon rolls forward under the action of gravity. Another droplet is added and similar process repeats. This indicates the good self-cleaning nature of the as-prepared superhydrophobic surface.

3.7. Thermal stability
The sample was heated at different temperatures in a dry box to test its thermal stability. Figure 9 shows the contact angles of the sample after heating at different temperatures for 1 h. It can be seen that at the temperature of 100 °C–300 °C, no significant variation occurs to the water contact angle of the sample, which are still above 150°. The result confirms that the as-prepared superhydrophobic surface possesses excellent superhydrophobicity and good thermal stability.

4. Conclusion
A transparent and tunable SiO₂ nanoparticles superhydrophobic coating was successfully prepared on the glass substrate by modification with PDMS, and the water contact angle was 155.1 ± 3°. A transition of adhesion can be obtained on the prepared surface by heating at different temperatures. The superhydrophobic glass surface also shows excellent self-cleaning property, good durability and thermal stability. With these excellent properties, this superhydrophobic surface can have a potential application in different fields and will expand the application range of glass materials.

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ORCID iDs
Jiyuan Zhu @ https://orcid.org/0000-0001-9048-6355

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