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Feasible fabrication of durable superhydrophobic SiO₂ coatings with translucency and self-cleaning performance

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Abstract

In this work, a versatile strategy was proposed to fabricate translucent superhydrophobic coatings by spraying the suspension of modified SiO₂/polydimethylsiloxane (PDMS) on various substrates. The wettability can be adjusted by changing the mass ratio of modified SiO₂ nanoparticles in the suspension. By optimizing the parameters in the spraying process, a superhydrophobic surface with a water contact angle of 164.1° ± 3.4° and a sliding angle of 4.2° ± 0.4° was achieved. As prepared translucent superhydrophobic SiO₂/PDMS coatings show good mechanical durability, chemical stability, and self-cleaning performances.

1. Introduction

In nature, there exist many plants and animals possessing special non-wettability, such as the unsullied lotus leaf from mud and agile dancers of water strider. Inspired by these, superhydrophobic surface, which is firstly discovered in 1997 by Barthlott and Neinhuis [1] and featured by the super-large water contact angle (CA, larger than 150°) and very small sliding angle (CA, less than 10°), has drawn much attention in both academic and industrial communities [2]. Till now, this special surface has found considerable potential application in areas of oil/water separation [3], anti-icing [4], corrosion protection [5], drag reduction [6], self-cleaning [7], etc. Recent studies demonstrate that both low surface energy and rough microstructure are two indispensable contributors to synergistically dominate the final wettability [8]. According to above mentioned principles, two strategies are developed to construct artificial superhydrophobic surface. The first method is to modify rough textures with low surface energy compound, and the second one is to rough the intrinsic hydrophobic materials. On the basis of this, various approaches, e.g., electrodeposition [9], lay-by-lay (LBL) assembly [10], and etching [11], are developed to achieve this excellent water-repellency. However, it is worthy to note that most of the reported methods are limited in large-scale fabrication due to the intricate process and sophisticated instruments.

Recently, a promising method, i.e. spraying technique, has been given much focus in preparing superhydrophobic coatings (or films) due to its merits of low-cost equipment, easy operation, and substrate-independence [12–14]. Through spraying lay-by-lay (LBL) assembled materials, Li et al developed durable and selfcleaning superhydrophobic coatings [15]. By using one-step spraying inorganic particles, Li et al fabricated colorful superhydrophobic coatings on metal surfaces [16]. With the same method, Wang et al used dual-scale silica micro/nano particles as well as 1H, 1H, 2H, 2H-perfluoroctyltriethoxysilane, a kind of low surface energy component, to construct protective superhydrophobic coatings on Mg alloy surfaces [17]. The water-proof character of above coatings prepared by the spraying technique is mainly attributed to the aggregation of intrinsic hydrophobic or low surface energy material modified particles, which determines the weak binding force between the substrates and coatings from another perspective [18]. Accordingly, it is imperative to address the poor mechanical durability of these superhydrophobic coatings. It is well known that robustness and superhydrophobicity are two conflicting performances, that is, increasing hydrophobicity will decrease the durability, and vice versa. Therefore, it is still a challenge to fabricate robust superhydrophobic coatings by a feasible and cost-effective method. To improve the durability of superhydrophobic materials, one effective
strategy is to construct self-healing superhydrophobic surfaces by preserving low surface energy compound in the porous micro-/nanostructures. Once the superhydrophobicity is lost, the entrapped healing agent, i.e. low surface energy modifier, has a strong motivation to migrate to the upper layer to lessen the system surface energy. Such a healing process always requires external stimulations, such as heating [19] and applying voltage [20], to recovery the superhydrophobicity, which limits the practical use in large-scale. For this, Lu et al groundbreakingly proposed to promote the superhydrophobic robustness by using commercial adhesives on the substrate surface before dip-coating TiO₂ particle-based coatings [21]. Enlightened by this idea, Liu sprayed fluoroalkyl silane-modified CaCO₃ nanoparticles on the 3M organic adhesive coated substrates surface to prepare durable superhydrophobic coatings [22]. Recently, inorganic binder of aluminum phosphate was also reported to be acted as the adhesive to enhance the robustness of superhydrophobic TiO₂ coatings [23]. It is worthy to note that above superhydrophobic coatings prepared by the thought of ‘paint + adhesive’ usually require two steps, i.e. preparatory treatment with the adhesive is necessary before coating the final paint. Thence, it is more tempting to construct durable superhydrophobic coatings in one step. Moreover, single-performance superhydrophobic surfaces can no longer meet people’s needs, and the development of a non-wettable surface that integrates versatile functions is becoming a new trend [24].

Inspired by above mentioned investigations, in this work, we developed a one-step spraying process to fabricate durable superhydrophobic coatings with translucency, chemical durability, and self-cleaning functions. SiO₂ nanoparticle, a widely used material in fabricating superhydrophobic surfaces [25, 26] due to its merits of low-cost, low toxicity, environmental friendliness, and chemical stability, was chosen as the bulk substrate before the spraying process. Commercially available soft substrates, such as silicon dioxide (SiO₂, 99.5%) before the spraying process. Commercially available soft substrates, such as silicon dioxide (SiO₂, 99.5%) and ethanol (EtOH, $\geq$ 99.7%) were purchased from Aladdin Biochemical Technology Co., Ltd (China). Dodecyltrimethoxysilane (DTMS, $\geq$ 93.0%) was purchased from Tokyo Chemical Industry Co., Ltd (Japan). Polydimethylsiloxane (PDMS) prepolymer (Sylgard 184A) and its corresponding curing agent (Sylgard 184B) was purchased from Dow Corning Corporation (USA). All the chemical agents were used with no further purification.

2. Experimental section

2.1 Materials and chemical agents

Two kinds of commercially available hard substrates including aluminum alloy (AA2024-T3) and glass were used as the models. The aluminum alloy substrate was polished with SiC sandpaper to 800 grit to remove the surface oxide layer. Both the hard substrates were degreased in absolute ethanol for 15 min followed by sequentially washing again with deionized water and ethanol. The substrates were dried with flowing cold air before the spraying process. Commercially available soft substrates, such as filter paper, medical absorbent cotton, paper, and fabric, were used directly. Silicon dioxide (SiO₂, 99.5%) nanoparticles with a grain size of 15 nm, acetate (HAc, 99.5%), sodium hydroxide (NaOH, 96%), ammonia solution (NH₄OH, n-hexane (97%) and ethanol (EtOH, $\geq$ 99.7%) were purchased from Aladdin Biochemical Technology Co., Ltd (China). Dodecyltrimethoxysilane (DTMS, $\geq$ 93.0%) was purchased from Tokyo Chemical Industry Co., Ltd (Japan). Polydimethylsiloxane (PDMS) prepolymer (Sylgard 184A) and its corresponding curing agent (Sylgard 184B) was purchased from Dow Corning Corporation (USA). All the chemical agents were used with no further purification.

2.2 Fabrication of superhydrophobic SiO₂ (SH-SiO₂) nanoparticles

The preparation of SH-SiO₂ nanoparticles is mainly referred to our previous work [18]. All in all, the modified SiO₂ nanoparticles were obtained through the dehydration condensation, as depicted in the upper part of figure 1. Specifically speaking, 2.00 g of DTMS was dissolved in 60.00 ml of EtOH, and 1.00 g of SiO₂ nanoparticles were added into 20.00 ml of alkaline aqueous solution (pH 7 ~ 8). Then the DTMS and SiO₂ solution was, respectively, magnetically stirred for 30 min before mixing together and further stirring for another 30 min. After that, the mixture was aged for 12 h at room temperature before centrifugalized at 10000 r min⁻¹ for 5 min. Finally, the superhydrophobic SiO₂ (SH-SiO₂) nanoparticles were obtained after desiccation at 80°C for 6 h.

2.3 One-step spraying of superhydrophobic coatings

The spraying process was depicted in the lower part of figure 1. The suspension used for spraying was prepared by mixing the following A and B solutions. Different weight percentage of SH-SiO₂ nanoparticles was added in solution A which consisted of 6.00 ml hexane and 1.00 g of PDMS prepolymer. Solution B contained 0.10 g of curing agent (1/10 of PDMS weight) and 6.00 ml of hexane. Both above two solutions were stirred for 15 min separately. Then the spraying suspension containing various mass ratio of SH-SiO₂/PDMS (the content of
PDMS was set to be 1.00 g/12 ml of hexane), was obtained by mixing solution A and solution B. Before use, the suspension was stirred for another 15 min to ensure homogeneous component. After that, the resulting mixture was sprayed on the substrates at 3.0 bar by using an airbrush whose nozzle diameter is 0.30 mm. The distance between the airbrush nozzle and the substrates was kept at 15 ~ 20 cm. The coated samples were cured at 80 °C for 2 h. In addition, the hexane suspension without PDMS and curing agent added was also used to spray on the substrates for comparison.

2.4 Characterization
The chemical compositions and the size distribution of silica before and after DTMS modification were determined on the fourier transform infrared (FT-IR) spectroscopy (Nicolet 470, Thermo Nicolet, USA) and transmission electron microscope (TEM, HT-7700, HITACHI, Japan), respectively. The microstructure was observed on the scanning electron microscopy (SEM, S-3700N, HITACHI, Japan). The element composition and content were determined by the energy dispersive spectrometer (EDS, e-FLASH, Bruker, German). The static water contact angle (CA) and sliding angle (SA) values were investigated on the contact angle instrument (SZ-CAMD33, Shanghai Sunzern Instrument Co., Ltd., China) equipped with a high-speed camera. The volume of waterdrop used for wettability evaluation was set as 5 μl. The reported CA and SA values in this research were the average at five different positions on the substrate surface. Optical transparency of the coated glass was carried out on an ultraviolet and visible (UV–vis) double beam spectrophotometer (AUV-1900, Macy Instrument, China). Sandpaper abrasion test was performed on a home-made scratch tester. In detail, the superhydrophobic surface coated glass with a load of 50 g of weight was put on the 1200 grit sandpaper. Then the samples were moved at a rate of 2.0 cm s⁻¹ in each abrasion cycle (10.0 cm of length). Both CA and SA values were measured after each abrasion cycle. Water shock test was conducted by an airbrush with a nozzle diameter of 0.30 mm at 3.0 bar. The samples were placed vertically to the airbrush nozzle and the distance between them was kept at ~3.0 cm. In each cycle, the duration of water shock was set to 10 s, and the CA and SA values of the samples were measured after drying at 80 °C for 10 min to ensure the water on them was completely evaporated.

3. Results and discussion

3.1 Characterization of raw and superhydrophobic SiO₂ nanoparticle
In this research, long chain alkyl silane of DTMS was chosen as the low surface energy compound modifier, which effectively avoids the hazards of previously reported fluoroalkyl silane, which is known for bioaccumulation and poor degradation. The superhydrophobic SiO₂ nanoparticles were synthesized by the
dehydration condensation between the hydroxyl groups on the hydrophilic SiO₂ and hydrolyzed DTMS. As shown in figure 2, raw SiO₂ nanoparticles are completely wetted by the dyed water (figure 2(a)), indicating the hydrophilicity of the un-modified nanoparticles. Contrastingly, the water droplet on the DTMS-modified powders is nearly spherical (figure 2(d)), demonstrating the super water-repellency. To further examine the stability of modified SiO₂ nanoparticles, both raw and DTMS-grafted SiO₂ nanoparticles were placed into deionized water. For the former, it is because of the hydrophilic characteristics of SiO₂ that generates the final suspension (figures 2(b) and (c)). Interestingly, the modified nanoparticles sit firmly on the water surface (figure 2(e)). Even after 7 d of immersion, no particles are found in the water solution (figure 2(f)), demonstrating the excellent stability of as-prepared superhydrophobic SiO₂ (SH-SiO₂) nanoparticles. Actually, it is difficult to measure the CA and SA values of as-prepared superhydrophobic SiO₂ nanoparticles. In regards to this, we used a high-speed camera to record the whole dynamic movement process of 5 μl of water droplet on the only SH-SiO₂-containing coatings. As shown in figure 2(g), the water droplet bounces immediately once contacting the coating surface. After several bounce cycles, the water droplet rolls off the only SH-SiO₂-containing coatings surface without no contamination left, implying the low adhesion of water to as-prepared samples surface.

Figure 2. The water wettability images of raw SiO₂ powders (a)–(c) before and (d)–(f) after DTMS modification. (g) The dynamic process of 5 μl water droplet from contacting to leaving the surface of superhydrophobic SiO₂ films coated substrates.

The morphology of both SiO₂ and SH-SiO₂ particles was observed on the TEM. As displayed in figures 3(a) and (b), there is no obvious change in the particle size for both raw and modified SiO₂ nanoparticles (~15 nm). The excellent superhydrophobicity of as-prepared SH-SiO₂ nanoparticles is closely related with their chemical structure, for which FT-IR spectroscopy was performed. As shown in figure 3(c), the broad absorption band centered at 3410 cm⁻¹ and the peak at 1634 cm⁻¹ correspond to the stretching vibration and bending vibration of O–H and Si–OH groups, respectively, which is a sign of hydrated SiO₂ and also explains the hydrophilicity characteristic of raw SiO₂. Above two peaks are greatly depressed when SiO₂ nanoparticles are modified by DTMS due to the substitution of –OH by long alkyl silanol. The Si–O–Si asymmetric stretching vibration and symmetric stretching vibration are observed at 1064 cm⁻¹ and 805 cm⁻¹, respectively. The Si–OH stretching vibration can be detected in the spectroscopy of both raw and modified SiO₂ nanoparticles, and the strength in
the latter ones is much weaker than the former ones. Three peaks at 2960 cm\(^{-1}\), 2929 cm\(^{-1}\) and 2855 cm\(^{-1}\), as indicated in the yellow box, can only be detected in the spectrum of SH-SiO\(_2\) nanoparticles. This suggests the successful grafting of DTMS to the SiO\(_2\) surface, which explains the excellent superhydrophobicity observed in figures 2(d)–(g).

Fabrication of translucent superhydrophobic SiO\(_2\)/PDMS coatings

As mentioned above, the bonding force of superhydrophobic SiO\(_2\) nanoparticles with the substrate is poor due to the weak interaction among them. Therefore, the adhesive is introduced to promote the robustness of coatings. PDMS, a commonly used binder, has won much favor in areas of cosmetics, food, and pharmaceutical due to its virtues such as innocuity, good biocompatibility, and chemical stability [27–30]. The influence of mass ratio of SH-SiO\(_2\)/PDMS in the spraying solution on the CA and SA values of derived films is shown in figure 4(a), and the deviation is also given. It is worth noting that compared with the large SA range (0 ~ 180°), the deviation of SA value is so smaller that it could not be obviously observed from figure 4(a). To make it easy to investigate the relationship as above-mentioned, the content of PDMS in the final spraying suspension is kept as a constant value of 1.00 g per 12 ml of hexane in this research. For comparison, the wettability of bare substrate (using glass as the substrate here) is also given. The CA and SA values for bare substrate are 67.69 ± 1.02° and 180.00 ± 0.00°, respectively, indicating the inherent hydrophilicity of glass. After spraying PDMS, the wettability changes from hydrophilic to hydrophobic with CA values of 113.09 ± 1.64°. Meanwhile, the water droplet shows high adhesive to the PDMS with the SA value of 180.00 ± 0.00° indicating a Wenzel state. It is noteworthy that although the wettability has changed, the transmittance of PDMS-coated matrix is not affected as its overlapped transmittance curve with the bare one (figure 4(b)). With an increase in the mass ratio of SH-SiO\(_2\) nanoparticles/PDMS, the water contact angle increases, demonstrating the positive effect of modified
SiO2 nanoparticles on the composite coatings. Particularly, when the mass ratio of SH-SiO2 nanoparticles reaches up to 30%, the CA value is determined to be 161.11 ± 3.24°, and the SA one is reduced to 4.17 ± 0.42° showing a Cassie-Baxter state. At this time, the water droplet on the surface is almost spherical, which illustrates the implementation of superhydrophobicity. No obvious changes happen when further increasing the mass ratio of SH-SiO2 nanoparticles in PDMS. As most reported SiO2-based superhydrophobic surfaces are opaque, it will be interesting to construct translucent or transparent superhydrophobic coatings. Accordingly, the optical transmittance of some representative specimens in the visible range is recorded. As shown in figure 4(b), the increased mass ratio of modified SiO2 in PDMS results in decreased transmittance, which is also confirmed by the insets in figure 4(b). The reason for that is attributed to the increased coverage of rough scattering centers for light when more concentration of modified silica nanoparticles is incorporated in the derived coatings. Especially, the transmittance values of superhydrophobic samples prepared by spraying the suspension containing 30% and 40% mass ratio of SH-SiO2 are ∼42% and ∼14%, respectively. To balance the performances of superhydrophobicity and transmittance, the mass ratio of SH-SiO2 in the spraying suspension is kept as 30% in the followed research.

Surface microstructure of superhydrophobic SiO2/PDMS coatings
To better observe the microstructures, aluminum alloy was chosen as the substrate. Representative morphologies of bare and different coatings coated specimens are depicted in figure 5. Obvious polishing scratches can be observed for the bare Al alloy substrate (figure 5(a)). After spraying PDMS polymer, the scratches become relatively vague (figure 5(b)) due to the deposition of PDMS in the pit of scratches. Meanwhile, the corresponding mass ratio of Si/Al for only PDMS coated samples, which is determined by EDS, increases from 0 (for bare substrate) to 16.49% (data not given). When 10% mass ratio of modified nanoparticles is introduced in the suspension, micro-scale island-sea structures appear due to the aggregation of nanoparticles (figure 5(c)) [24]. Combined with figure 5(b), it is reasonable to speculate that the island parts mean the superhydrophobic SiO2 particles, and the sea ones represent the PDMS adhesive. However, it is worth to note that such microscale structure is not uniform and continuous so that the water dropping onto it is easy to be entrapped, which results in a large sliding angle of 180° (Wenzel state). In contrast, the water droplet on the superhydrophobic SiO2/PDMS surface (figure 5(d), with 30% of SH-SiO2 nanoparticles incorporated in the suspension) can easily roll off with SA values of only ∼4.17° (Cassie-Baxter state) because of the increased coverage of SH-SiO2 nanoparticles, which is also confirmed by the increased mass ratio of Si/Al (41.06%) for superhydrophobic coatings compared with samples that with less modified particles incorporation (figure 4(c, 26.62%)). Compared the morphology of sample in figure 5(d) with that in figure 5(c), one can see that the microstructure becomes rougher when increasing the SH-SiO2 nanoparticles content in the spraying suspension. For PDMS, an intrinsically hydrophobic material, it is the increased roughness that leads to the wettability transition from Wenzel to Cassie-Baxter state [31, 32].
Durability measurement
Mechanical durability is a key factor limiting the practical use of superhydrophobic coatings. In this research, the mechanical durability of superhydrophobic SiO₂/PDMS coatings was investigated by water shock and sandpaper abrasion, and glass and filter paper were chosen as the hard and soft substrates, respectively. For the former, the mechanical durability of superhydrophobic coating was evaluated by water shock to simulate the rain in nature. As expected, only SH-SiO₂ nanoparticles contained coatings are prone to be destroyed when exposed to an external force. As indicated in figure 6(a), after one shock cycle, the CA value of only SH-SiO₂-contained superhydrophobic surface decreases from 162.02 ± 2.76° to 86.75 ± 1.90°, suggesting the loss of superhydrophobicity. Impressively, after PDMS incorporation, the resistance of superhydrophobic coatings to water shock is greatly improved. As shown in figure 6(b), extending the water shock cycles results in gradually decreased CA values and increased SA values. When the water shock cycle increases to 12, the SA values increase to 41.41 ± 3.40°, implying the relatively strong adhesion of water on the surface. The SA value reaches up to 180.00 ± 0.00° when further increasing the cycle number to 13, which means that the water droplet will not roll away even if the substrate is turned 180°. It is worth noting that during the whole test cycles, the CA values of superhydrophobic SiO₂/PDMS samples are always greater than 150°, illustrating the obviously improved mechanical durability compared with the coatings with only SH-SiO₂ nanoparticles contained. In addition, sandpaper abrasion resistance is also used to evaluate the mechanical durability of aforementioned superhydrophobic coatings. During the first abrasion cycle, the only SH-SiO₂-containing superhydrophobic coating was rubbing off, exposing the underlying substrate (data not given). This phenomenon was also observed in our previous report work [18]. In contrast, after PDMS incorporation, the superhydrophobic coatings could endure 5 abrasion cycles, during which the CA values remain larger than 150° (data not given). This abrasion resistance is significantly amplified if permeable materials such as filter paper are used as substrates, for which only sandpaper abrasion test was conducted because the wetted substrate will be uneven after heating, resulting in the difficulty in wettability measurements. It is of worth noting that during the whole test cycles, the CA values of superhydrophobic SiO₂/PDMS samples are always greater than 150°, illustrating the obviously improved mechanical durability compared with the coatings with only SH-SiO₂ nanoparticles contained. In addition, sandpaper abrasion resistance is also used to evaluate the mechanical durability of aforementioned superhydrophobic coatings. During the first abrasion cycle, the only SH-SiO₂-containing superhydrophobic coating was rubbing off, exposing the underlying substrate (data not given). This phenomenon was also observed in our previous report work [18]. In contrast, after PDMS incorporation, the superhydrophobic coatings could endure 5 abrasion cycles, during which the CA values remain larger than 150° (data not given). This abrasion resistance is significantly amplified if permeable materials such as filter paper are used as substrates, for which only sandpaper abrasion test was conducted because the wetted substrate will be uneven after heating, resulting in the difficulty in wettability measurements. It is of worth noting that during the whole test cycles, the CA values of superhydrophobic SiO₂/PDMS samples are always greater than 150°, illustrating the obviously improved mechanical durability compared with the coatings with only SH-SiO₂ nanoparticles contained. In addition, sandpaper abrasion resistance is also used to evaluate the mechanical durability of aforementioned superhydrophobic coatings. During the first abrasion cycle, the only SH-SiO₂-containing superhydrophobic coating was rubbing off, exposing the underlying substrate (data not given). This phenomenon was also observed in our previous report work [18]. In contrast, after PDMS incorporation, the superhydrophobic coatings could endure 5 abrasion cycles, during which the CA values remain larger than 150° (data not given). This abrasion resistance is significantly amplified if permeable materials such as filter paper are used as substrates, for which only sandpaper abrasion test was conducted because the wetted substrate will be uneven after heating, resulting in the difficulty in wettability measurements. It is of worth noting that during the whole test cycles, the CA values of superhydrophobic SiO₂/PDMS samples are always greater than 150°, illustrating the obviously improved mechanical durability compared with the coatings with only SH-SiO₂ nanoparticles contained.

Figure 5. Typical SEM images of Al alloy (a) before and (b)–(d) after spraying different weight percentage of SH-SiO₂ powder: (b) 0%, (c) 10%, (d) 30%.
mechanical resistance between the coated glass and filter paper can be understood from the following two aspects. On one hand, the liquid PDMS polymer could fully cover the interspace of permeable filter paper making the whole bulk superhydrophobic, which endows the superhydrophobic coatings on filter paper with better mechanical abrasion resistance than that on flat glass. On the other hand, strong chemical bonds can be formed between the filter paper and PDMS, which makes the superhydrophobic coatings adhere firmly to the substrate [34, 35].

The chemical stability of as-prepared superhydrophobic SiO2/PDMS is summarized in figure 7(a). Obviously, a small fluctuation is observed with regard to the variation of CA and SA values with pH values of water droplet. It is worthy to notice that all CA values are larger than 155°, and the SA values are all less than 10°, demonstrating the good chemical stability. Therefore, such superhydrophobic coatings are expected to show the potential application in the fields of corrosion protection. Inspiringly, after 14 d of storage indoor, the composite coatings still remain stable superhydrophobicity (figure 7(b)).

**Waterproofing**

Figure 8 exhibits the waterproofing performance of superhydrophobic SiO2/PDMS coatings. As shown in figure 8(a), it is difficult to immerse the sample into the water. When the water bulk was opened a crack by the coated samples, a silver mirrorlike appearance occurs, which is ascribed to the large amount of entrapped air bubble that exists at the interface of water and coatings. Due to the excellent non-wettability property of superhydrophobic SiO2/PDMS coatings, above mentioned phenomenon can be understood from the well-known Cassie-Baxter model (equation (1)) [36, 37]:

\[
 \cos \theta = f_1 \cos \theta_1 - f_2 
\]

in which \( \theta \) and \( \theta_1 \) are the CA values on the smooth and rough surfaces, respectively, and \( f_1 \) and \( f_2 \) are, respectively, the area fractions of coatings in contact with the water droplet and entrapped air (\( f_1 + f_2 = 1 \)).

Here, \( \theta \), the CA values of smooth PDMS, is measured to be 113.09°, and \( \theta_1 \), for the superhydrophobic SiO2/PDMS coatings is 161.11°. After plugged the relative values into equation (1), the parameters of \( f_1 \) and \( f_2 \) are calculated to be 8.86% and 91.14%, respectively. Such a high amount of entrapped air pockets (91.14%) explains well for the above-mentioned mirrorlike appearance and the difficulty of the samples being wetted by
water. Similar mirrorlike phenomenon can also be observed at the interface between the dropped drink, such as milky tea, coffee, tea, coke and juice, and the superhydrophobic SiO$_2$/PDMS coatings (figure 8(b)). Actually, when the water droplet was jetted on the superhydrophobic coating surface, it immediately bounced off the coated surface, showing excellent water-repellency (figure 8(c)).

To inspect the versatility of as-prepared superhydrophobic composite coatings, both hard and soft substrates, such as metal, filter paper, cotton, paper, and fabric, are used. In comparison, the optical images of water droplet on these un-coated substrates are also given in the upper part of figure 9. As depicted in figure 9(a), the dyed water spreads and pins on the bare aluminum alloy surface, indicating the hydrophilic characteristic of Al alloy. In contrast, a spherical water droplet appears on the coated metal. Similar phenomenon is also observed on other hydrophilic substrates, such as paper and fabric (figures 9(d) and (e)). Actually, for superhydrophobic
coatings covered substrates, the water droplet on them immediately rolled away from where it was originally dropped, as shown in the lower part of image in figure 9(d). For substrates like filter paper and cotton, which are intrinsic superhydrophilic, the dropped water completely wets the un-treated substrates, showing CA values of 0° (the upper images in figures 9(b) and (c)). After coated with composite films, aforesaid superhydrophilic substrates show excellent water repellency (the lower images in figures 9(b) and (c)). The successful preparation of superhydrophobic surface on various substrates will give prominence to the versatility of spraying SiO₂/PDMS coatings.

Self-cleaning performance
Lotus leaves possess the capability to grow out of the mud but with dye, which is a vivid description of self-cleaning. During that process, water droplets could pick up the dust along their rolling away from the surface. For artificial superhydrophobic surfaces, it is also a desirable performance due to their potential application in areas such as the paints industry. In this research, self-cleaning property was evaluated by using dried dust as the model contamination on the substrates, and all the substrates were tilted ∼12° before performance evaluation. For comparison, the water behavior on the bare glass is also given. As shown in figure 10(a), some dust was firstly deposited on the substrate before water was dropped. For bare substrate, as expected, the dyed water droplets are attached to the substrate and mixed with the dust, resulting in a dustier surface. Excitingly, when the substrate was coated with superhydrophobic SiO₂/PDMS films, the dropped water could easily roll off the surface due to the small sliding angles of superhydrophobic SiO₂/PDMS coatings (figure 10(b)). It is during the rolling process that the dust was picked up by the water droplets, leaving a clean surface.

4. Conclusions

In summary, a feasible fabrication of durable and semitransparent superhydrophobic coatings was reported by spraying the mixture of modified SiO₂ nanoparticles and PDMS binder on both hard and soft substrates. The final superhydrophobicity is mainly attributed to the modified SiO₂ nanoparticles and the PDMS adhesive is used to anchor the coatings on the substrates to promote the coatings' robustness. Results show that the mass ratio of modified SiO₂ in PDMS plays an important role in adjusting the wettability of final coatings, and the superhydrophobic surface with a water contact angle of 161.11° and sliding angle of 4.17° was achieved when 30% of SH-SiO₂ was introduced. As a result, this superhydrophobic coating exhibits good mechanical durability, chemical stability, and self-cleaning performances. For that, as prepared superhydrophobic SiO₂/PDMS coatings with multifunction are expected to be used in the practical application of corrosion protection, oil-water separation, and so on due to its merits of low-cost and scalable fabrication.

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