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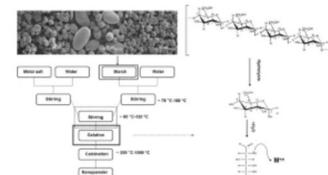
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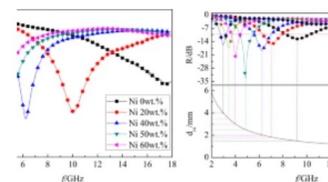


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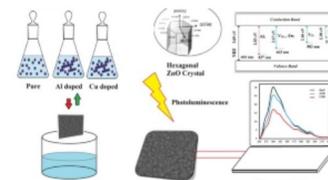


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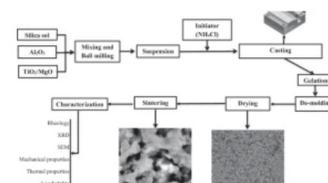
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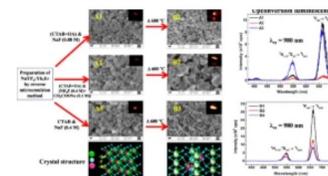


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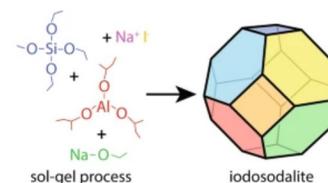


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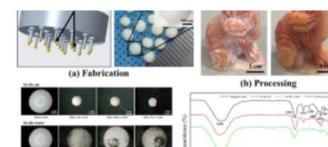


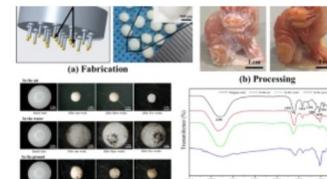
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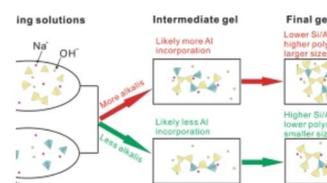


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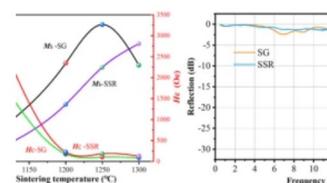


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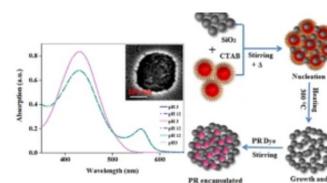
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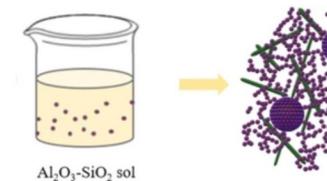


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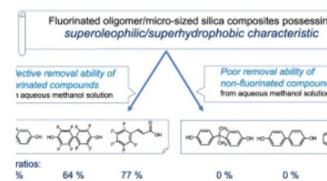


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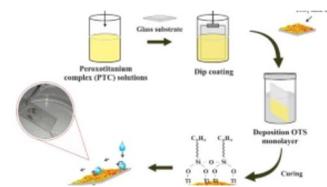


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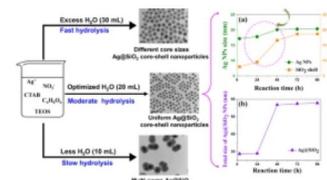
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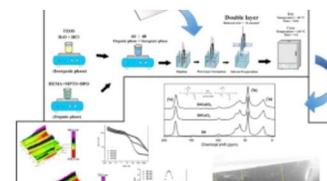


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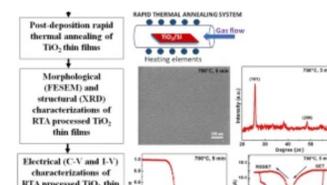
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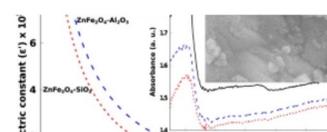
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*Self-cleaning material based on
superhydrophobic coatings through an
environmentally friendly sol–gel method*

**Nurul Pratiwi, Zulhadjri, Syukri Arief,
Admi & Diana Vanda Wellia**

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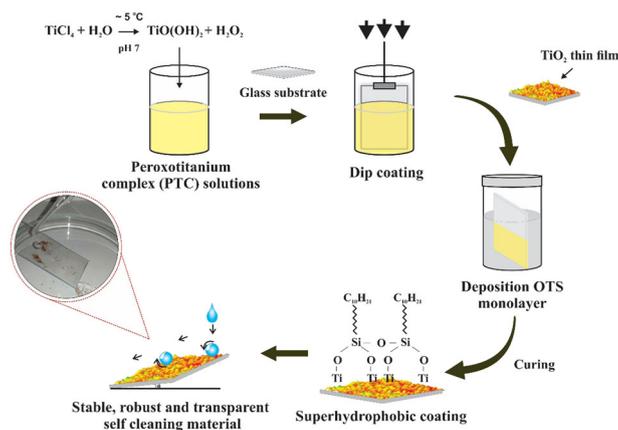
Self-cleaning material based on superhydrophobic coatings through an environmentally friendly sol-gel method

Nurul Pratiwi¹ · Zulhadjri¹ · Syukri Arief¹ · Admi¹ · Diana Vanda Wellia¹ Received: 27 April 2020 / Accepted: 12 August 2020 / Published online: 21 August 2020
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Abstract

Recently, there has been increasing interest in developing artificial superhydrophobic surfaces, especially in the field of self-cleaning application. However, the poor robustness and high-cost preparation of these surfaces have always been some issues for their industrial development. Herein, we describe an environmentally friendly way to prepare stable, robust, and transparent superhydrophobic coatings through the deposition of a rough substructure of TiO₂ film followed by chemical modification using octadecyltrichlorosilane (OTS), a fluorine-free organic silane. The as-prepared coatings exhibited a great superhydrophobic property and ultralow adhesion (with a static water contact angle of $158 \pm 2^\circ$ and sliding angle of $4 \pm 1^\circ$). It was found that the superhydrophobic coatings can still maintain good performance after UV irradiation, chemical immersion, and physical abrasion. More importantly, the coated surfaces showed an excellent self-cleaning ability against dirt particles after rinsed with water droplets.

Graphical Abstract

**Keywords** Superhydrophobic · Octadecyltrichlorosilane · TiO₂ · Transparent glass · Self-cleaning

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Highlights

- Environmentally friendly and low-cost method to prepare superhydrophobic coatings using TiO₂ thin film and monolayer octadecyltrichlorosilane (OTS).
- High transparency of the as-prepared superhydrophobic coatings.
- The superhydrophobic coatings exhibited good chemical and mechanical stability.
- The surface of superhydrophobic glass showed an excellent self-cleaning property.

1 Introduction

The super-wettability feature on the surface and interface of solid material has become one of the essential aspects of surface chemistry development [1]. Over the last decades, superhydrophobic surfaces, an excellent nonwetting systems, have gained remarkable attention due to their tremendous applications in self-cleaning [2], antifouling [3], heat exchangers [4], oil-water separation [5], smart sensing [6], and thermal insulation [7]. Inspired by nature, superhydrophobic surfaces, which have static water contact angle (CA) > 150° and sliding angle (SA) < 10°, are constructed by two main factors, hierarchically micro-/nanoscale surface structure (for trapping air) and surface chemical compositions (for lowering the surface energy) [8].

Various methods have been used to prepare artificial superhydrophobic coatings, such as chemical vapor deposition [9], photolithography [10, 11], RF magnetron sputtering [12], and electrospinning [13]. Even though superhydrophobic surfaces could be produced, most of all these reported methods still involve complicated procedures, high energy consumption and difficulty in scaling-up [14]. Therefore, a low-cost and simple method for preparing superhydrophobic coatings, such as wet-chemical methods have been considered as an alternative method [15].

The sol-gel method assisted with the dip-/spray-/spin-coating technique was one of the favored method to create the surface roughness by incorporating the micro/nano of inorganic particles [16]. Following by chemical surface modification with low surface energy materials, the artificial superhydrophobic surfaces could be successfully achieved [17]. There are several studies that have been reported on developing superhydrophobic coating through this combination method. Kong et al. have prepared superhydrophobic coating on glass substrate by fabricated a micro-/nanos-structured TiO₂ film via the sol-gel dip-coating method and then modified by fluoroalkylsilane molecules [18]. The as-prepared coatings not only showed a high static water CA up to 165.6° but also enhanced the reversible wettability conversion between hydrophobicity and hydrophilicity. However, the transparency and stability of coatings were not clearly mentioned. As an improvement to avoid the use of fluorine compound, Zhang et al. prepared superhydrophobic SiO₂-based coating onto the glass substrate by

a sol-gel spin-coating technique at low temperature and then followed by surface modification of trimethylchlorosilane [19]. As the results, the obtained coatings exhibited high transparency, good robustness, and excellent antiwetting behavior with a static water CA of 164 ± 2°. However, the use of a large amount of organic solvent in this work may potentially be a harmful pollutant for the environmental.

Based on all of these drawbacks, the fabrication of superhydrophobic coatings is quite limited for some reasons: first, methods that widely used to fabricate superhydrophobic coatings are costly and tricky [20]. Second, some chemicals that involved in the fabrication of superhydrophobic coatings such as fluorinated compounds are very hazardous due to their nondegradable and high toxic properties [21]. Third, the high surface roughness that is needed to give the superhydrophobic coatings is always contradictory with the transparency properties [22]. Forth, the robustness and stability of artificial superhydrophobic coatings are still limited in the practical application [23]. Therefore, the development of a coating with sustainable superhydrophobicity and good coating integrity through an environmentally safe method is highly desirable.

In our previous work, we discussed the optimum parameters in fabricating hydrophobic coatings on the glass surface by using a facile and environmentally friendly method [24]. The high surface roughness of TiO₂ film was obtained through a simple peroxy sol-gel dip-coating method. The effect of wettability with different concentrations of silane compounds was also investigated. Even though showing a high transparency, the static water CA was found of 146°, which was categorized as “ultra-hydrophobic.” In this study, an environmentally friendly and cost-effective method to prepare stable, robust, and transparent superhydrophobic coatings were developed to improve the previous work. The coating was prepared by chemical deposition of TiO₂ films through a simple peroxy sol-gel method on glass substrates and its subsequent dipping modification with octadecyltrichlorosilane (OTS), fluorine-free compounds. This approach is considered as a green technology since the use of water solvent and neutral pH without any hazardous chemicals. Moreover, this paper describes the morphological, mechanical, and chemical stability as well as the self-cleaning ability of the as-prepared coatings.

2 Materials and methods

2.1 Materials

Titanium tetrachloride (TiCl_4 0.09 M in 20% HCl), ammonium hydroxide (NH_4H 25%), and OTS ($\text{C}_{18}\text{H}_{37}\text{Cl}_3\text{Si} \geq 90\%$) were purchased from Aldrich. Hydrogen peroxide (H_2O_2 30%) and anhydrous ethanol ($\text{C}_2\text{H}_6\text{O} \geq 99.5\%$) were purchased from Merck. All chemicals were analytical reagent grade and used without any further purification. The sodalime glass slides (CAT. No. 7101) with a thickness of 1 mm were purchased from Sail brand.

2.2 Preparation of TiO_2 sol

TiO_2 sol was synthesized with the typical peroxy sol–gel method [24, 25]. At the temperature condition of 5 °C, the drop-wise of 36 mL TiCl_4 was dissolved in 300 mL deionized water under strong magnetic stirring for 30 min and then the solution was neutralized by the drop-wise addition of ammonia solution. This solution was kept stirring vigorously for 24 h to obtain the fine white precipitates. These precipitates were washed repeatedly with deionized water until no Cl^- ions were detected. Finally, the obtained precipitates were dissolved in 80 mL deionized water at ambient temperature. Then 28 mL H_2O_2 was added drop-wise into the mixture under constant stirring for 4 h to form an aqueous transparent yellowish peroxotitanium complex (PTC) solutions.

2.3 Fabrication of TiO_2 films on the glass substrate

The cleaning treatment procedures of glass slide were adopted from the previous work [24, 25]. The precleaned glass slide was dipped in PTC solutions for 30 s and was withdrawn using a dip-coater with a speed rate of 0.1 cm/s. Then, the coated glass was dried in vacuum at 80 °C for 5 min. This coating procedure was repeated five times. Finally, the coated glass was cured at 120 °C in vacuum for 1 h.

2.4 Preparation of superhydrophobic surfaces

The TiO_2 coated glass was placed into the OTS/ethanol solution (2%, v/v) at room temperature for 6 h. The obtained coatings were rinsed with ethanol and dried at 60 °C for 3 h in a vacuum oven. Monolayer OTS-coated glass was prepared as well for comparison.

2.5 Characterization

Surface morphologies and topographies of the coatings were observed by field emission scanning electron microscopy (FESEM, FEI Inspect F50) and atomic force

microscopy (AFM, Bruker nanoscan 9). The chemical compositions of coated and uncoated glass slides were investigated by Fourier-transform infrared spectroscopy (FTIR, PerkinElmer) and energy dispersive spectroscopy (EDS, EDAX Apollo X). Water CA and SA were measured at ambient condition by CA analyzer (SEO Phoenix 300) with 5 μL of water droplets. The CA measurements were taken at five different positions, and an average of total measurement was used to determine the final CA value. The SA value was measured by tilting the sample until the water droplet roll-off. An average of five times measurement on each sample was applied as the final SA value.

2.6 Mechanical test

The robustness of the as-prepared superhydrophobic coatings was investigated by the conventional abrasion tests. The as-prepared coated glass slide was placed face down on standard sandpaper (1500 mesh), and the pressure was set up by placing a weight (100 g) on top of it. Then, the average of CA and SA values were measured after dragging the coated glass slide horizontally with the speed rate of 0.16 cm/s for 100 cm.

2.7 Chemical test

The CA and SA values of the as-prepared coated glass slide were measured after varying the pH value of the drops with a pH range of 1–13. Moreover, to find out the durability of the coated glass slide to extreme environments, the CA and SA values of this coating were measured after being dipped in neutral (pH 7), acid (H_2SO_4 , pH 4), and base (NaOH, pH 10) solutions for 20 h.

2.8 UV exposure test

The coated glass slide was placed horizontally in a close reactor with UV A blacklight blue ($\lambda = 352$ nm, Camag). The distance between the substrate and the UV lamp was set up for 13 cm. Then, these coating was irradiated by UV light for 5 h. At interval 60 min, the average CA and SA values of this irradiated coating were measured.

2.9 Self-cleaning test

Carborundum particles (with sizes in the range of 37–44 μm) were used as a model pollutant. The procedure of the self-cleaning test was carried out by setting up the coated glass slide in a clean petri dish at an angle of $\sim 10^\circ$, and the carborundum particles were placed on top of it. Then, the cleaning process was evaluated after the water droplets were dropped onto the polluted coated glass slide. The uncoated glass was used as a comparison.

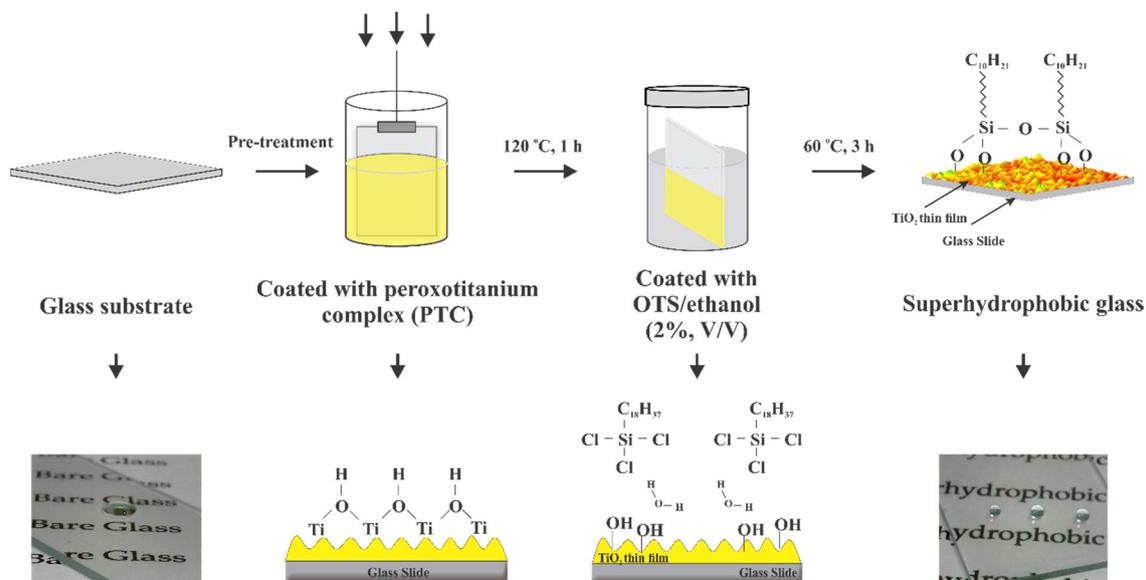


Fig. 1 The fabrication procedure of the superhydrophobic surface

3 Results and discussion

3.1 Morphology, composition, and wettability of as-prepared superhydrophobic coatings

The schematic illustration of the superhydrophobic coatings fabrication on a glass substrate was shown in Fig. 1. Herein, the TiO₂ films were used to construct the sub-rough structure on the hydrophilic glass surface. It is found that the chemical interaction occurs after the hydroxyl group =Ti–OH on TiO₂ film and ≡Si–OH on the pretreated glass slide condense, forming cross-linked chains of ≡Si–O–Ti≡ [24, 25]. As a result, the TiO₂ films were coated on the glass surface with a good surface roughness. However, in order to decrease the surface energy on the roughened surface of TiO₂-coated glass, the OTS monolayer was grafted on it. The main reaction occurs when the head of OTS (–SiCl₃) physisorbs and then react with the adsorbed water layer on the surface of the TiO₂-coated glass to form a silanol group (–Si(OH)₃). After that, this hydrolyzed head of OTS (–Si(OH)₃) condenses with OH-groups on the surface of TiO₂ films and then forms a strong chemical interaction of ≡Si–O–Ti≡. Consequently, the OTS molecules are firmly grafted on the surface of TiO₂-coated glass [26, 27]. As the condensation reaction occurs among the neighboring OTS molecules, a densely long-chain alkyl groups (–C₁₈H₃₇) of OTS tail are arranged and finally decreased the surface energy of the as-prepared coated glass [24, 28]. Through this fabrication mechanism, the as-prepared coated glass not only showed superhydrophobic property but also exhibited transparent and stable coatings.

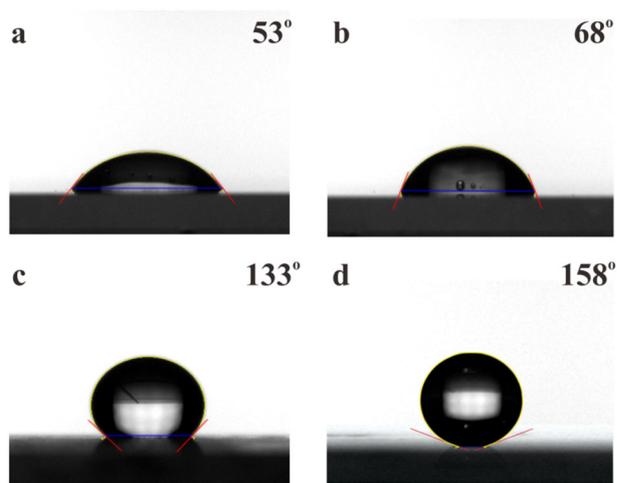


Fig. 2 Images of water droplets on (a) uncoated glass, (b) TiO₂-coated glass, (c) OTS-coated glass, and (d) superhydrophobic glass

Figure 2 presents the shapes of static waterdrops on the uncoated, TiO₂-coated, OTS-coated, and superhydrophobic glass, respectively. As shown in Fig. 2a and b, both the uncoated glass and the TiO₂-coated glass exhibit hydrophilic property with CAs < 90° which are mostly attributed by surface roughness and high surface energy from these surfaces [29, 30]. Contradictory, the glass slide that coated with OTS monolayer shows the hydrophobic property with CA of 133 ± 3° (Fig. 2c) due to the nonpolar long alkyl chain of OTS that arranged in the layer to lower the surface energy of the glass slide [31]. However, after the TiO₂-coated glass slide was subsequently treated by OTS, the

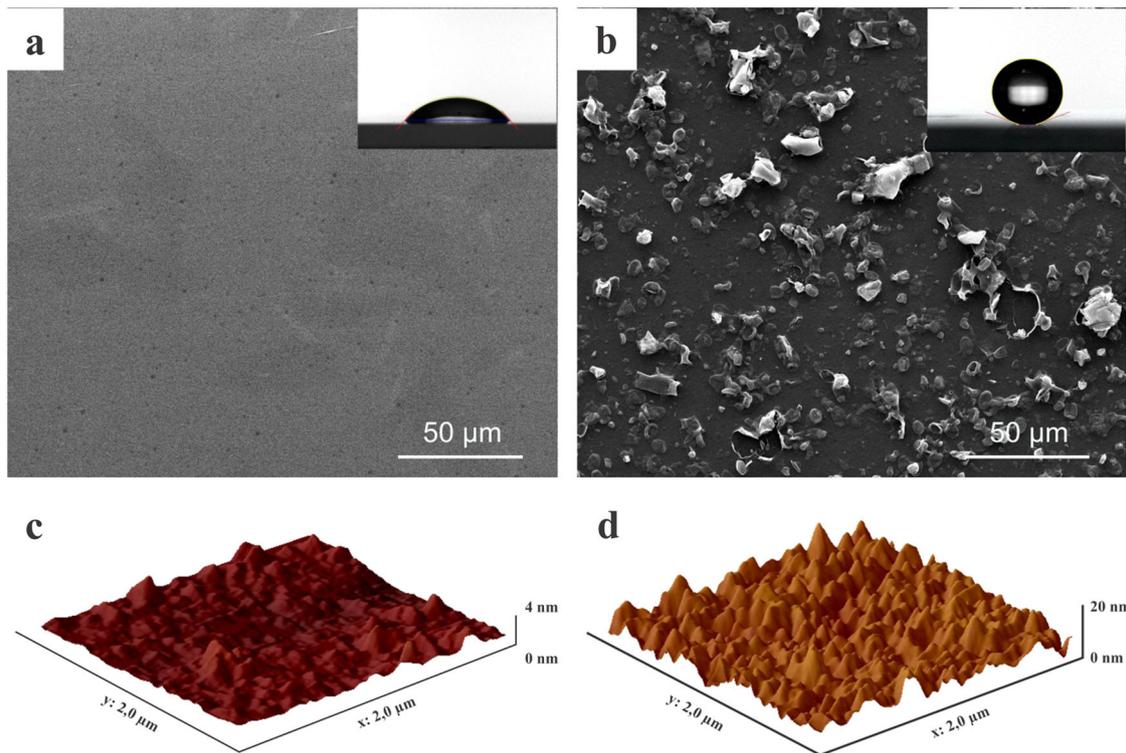
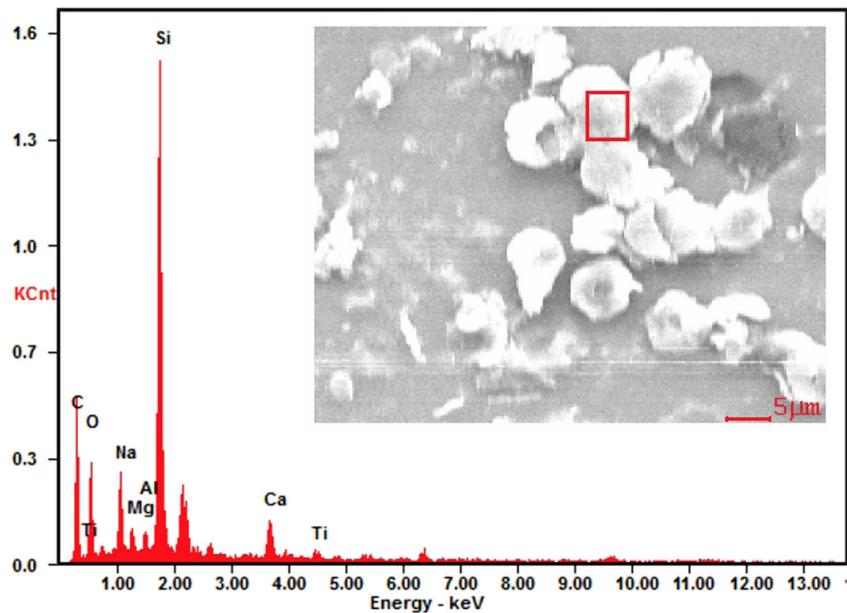


Fig. 3 FESEM images of (a) uncoated glass and (b) superhydrophobic glass (insets are images of water droplets). AFM images of (c) uncoated glass, and (d) superhydrophobic glass

Fig. 4 EDX spectra of superhydrophobic glass (inset is region analysis)



glass slide exhibited a good superhydrophobic property with CA as high as $158 \pm 2^\circ$ (Fig. 2d). Here, through the combination of the roughened surface of TiO_2 film and the low-surface-energy of OTS, the superhydrophobicity of the as-prepared coated glass surface can be explained according

to Cassie–Baxter model [32]. In this model, it is presumed that the water droplet is situated on solid–vapor–liquid interfaces since there is a large amount of trapped air in the grooves within the surface rough structure forming a low adhesion composite surface and significantly causes an

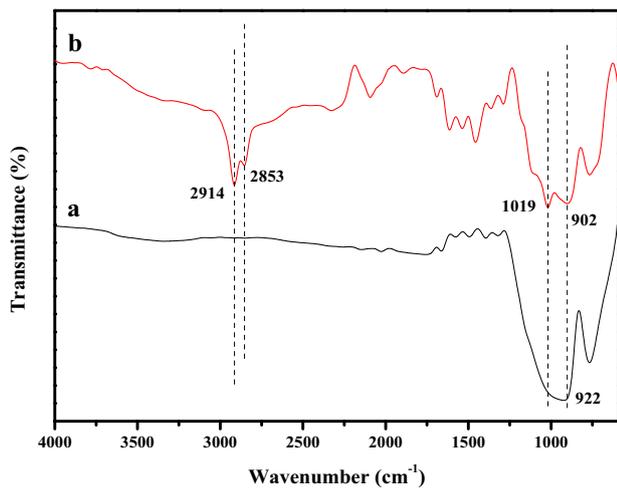


Fig. 5 FTIR spectra of (a) uncoated glass and (b) superhydrophobic glass

increase of CA as well as a decrease of SA [15, 33, 34]. Thus, a high quality of superhydrophobic surface could be successfully fabricated [14, 15].

As mentioned before, one of the most important factors needed in fabricating the super-wetting system is high surface roughness. Therefore, the surface morphologies and topographies of the as-prepared coating were further studied. Figure 3 shows the FESEM images of uncoated and superhydrophobic glass. It can be seen that the uncoated glass exhibits smooth surface (Fig. 3a), whereas the superhydrophobic glass surfaces are covered by uneven hierarchical structures, which is attributed to the deposition of TiO₂ and OTS layer (Fig. 3b). The topographies of this coated glass were further confirmed by AFM analysis (Fig. 3c, d). It is found that the mean roughness (R_a) of uncoated glass, and superhydrophobic glass is 2 and 4 nm, respectively.

Figure 4 shows the EDX spectra and the regional analysis of superhydrophobic glass. It was observed that the high spectra of Si and C represent the composition of OTS layer. In contrast, the detected low spectra of Ti and O, which is attributed to the existence of TiO₂ compounds on the coated glass surface, confirming that the surface of TiO₂ film was mostly grafted by OTS monolayer. Furthermore, the signal of Si, Al, Na, Ca, and Mg elements could be also attributed to the dominant elements of sodalime glass [5].

To investigate the interpretation of chemical structure as well as the chemical interactions, the uncoated and superhydrophobic glass were characterized by FTIR. Figure 5 presents the FTIR spectra of the samples in the range of 4000–400 cm⁻¹. As shown in Fig. 5a, it is observed that the absorption peaks at 922 cm⁻¹ is attributed to the Si–O–Si bend vibration on the sodalime glass. However, after the glass consecutively being coated with TiO₂ film and OTS (Fig. 5b), this absorption peak is shifted to the 1019 cm⁻¹,

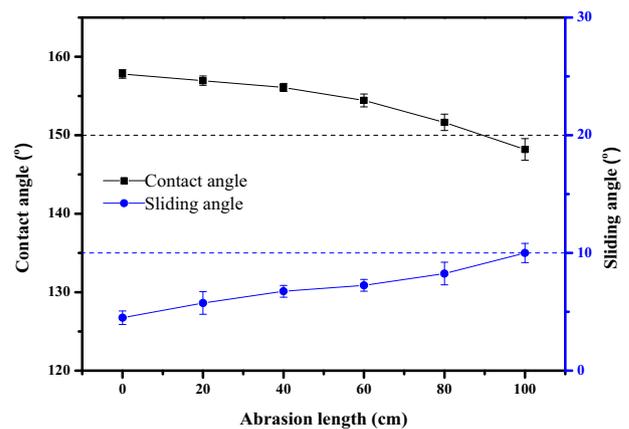


Fig. 6 CAs and SAs of the superhydrophobic glass as a function of the abrasion length

which assigning to asymmetric Si–O–Si stretching vibration as a result of the cross-linked interaction of OTS [35, 36] and to the 902 cm⁻¹, which indicating the interaction of Si–O–Ti groups, confirming the covalent interaction between TiO₂ layer with OTS layer and/or TiO₂ layer with glass substrate [25, 26, 37]. Besides, the characteristic absorption peaks that only could be found on the coated glass (Fig. 5b) are exhibited at 2914 and 2853 cm⁻¹, which respectively assigned to asymmetrical –CH₃– and symmetrical –CH₂– strain vibrations confirming the presence of the long-chain alkyl groups of OTS compounds [38].

3.2 Mechanical and chemical stability

In order to evaluate the ability of the coated glass in maintaining its superhydrophobic properties against abrasion from the external environment, the abrasion test was carried out by adapting the previously reported analogical procedures [39, 40]. Figure 6 shows the CA and SA of superhydrophobic glass after dragged for 100 cm on 1500 mesh sandpaper. It is observed that the CA of the coated glass surface, after dragged for 80 cm, decrease from 158 ± 1° to 152 ± 1° and the value of the SA increase from 4 ± 1° to 8 ± 1°. However, after being dragged for 100 cm, the CA of coated glass remains 148 ± 1° with SA of 10 ± 1°. It can be concluded that the as-prepared coated glass has good mechanical stability because it can still maintain superhydrophobic surfaces (CA > 150°, SA < 10°) after 80 cm of abrasion and exhibit ultrahydrophobic surfaces after further abrasion.

Besides the mechanical robustness, the chemical stability is also an important feature in the artificial superhydrophobic coatings so that this material can be used in harsh environments. Figure 7a shows the CA and SA of the as-prepared superhydrophobic glass with different pH value. Here, we use sulfuric acid and sodium hydroxide for

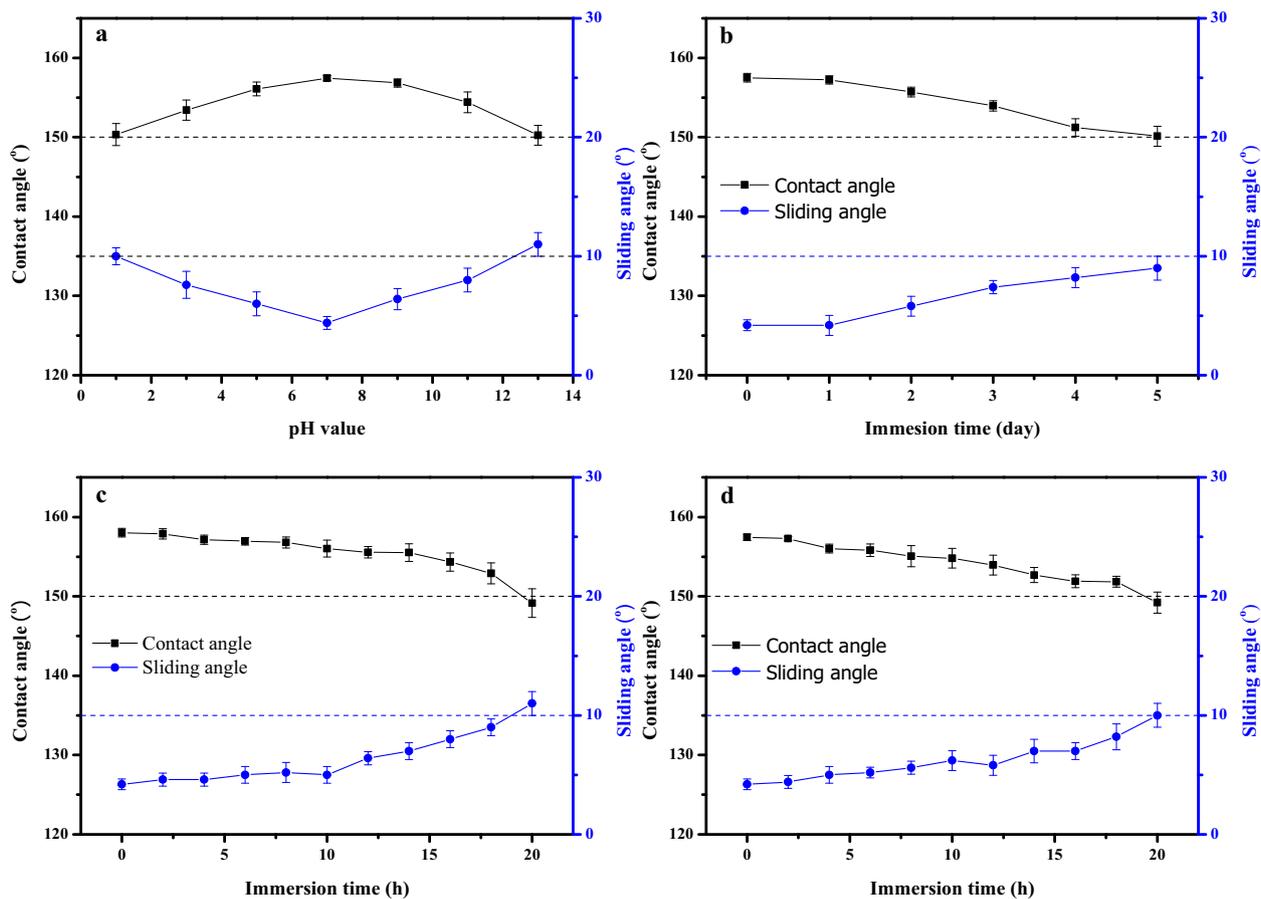


Fig. 7 CAs and SAs of the superhydrophobic glass as a function of (a) different pH value of liquid droplets, (b) immersion time in water (pH 7), (c) immersion time in acid solution (pH 4), and (d) immersion time in alkaline solution (pH 10)

ranging the pH values of the liquid droplet. The CA of a liquid droplet on the surface of superhydrophobic glass decreases slightly when the liquid droplet at acid point or base point, but still perform the superhydrophobic property ($CA > 150^\circ$). On the contrary, the SA increases at the acid and base point, with the average SA value $< 10^\circ$. As the superhydrophobic glass perform high CA of the liquid droplet at pH 7, we further investigate the durability of this coating at this condition. Figure 7b shows the CA and SA of the superhydrophobic surface that immersed in water (pH ~7–8) for 5 days. After the superhydrophobic surface was immersed in water, the CA slightly decreased from $158 \pm 1^\circ$ to $150 \pm 1^\circ$, and the SA slightly increased from 4° to $9 \pm 1^\circ$ in the last day. These results assert that the as-prepared superhydrophobic glass has good durability in maintaining its superhydrophobicity even though in environment with high relative humidity. The CA and SA of the as-prepared superhydrophobic glass as a function of immersion time in the acid (pH 4) and base (pH 10) solution are present in Fig. 7c and d, respectively. It is found that, as the immersion time increase, the CA of superhydrophobic glass gradually decrease to $153 \pm 1^\circ$ and $152 \pm 1^\circ$ after 18 h immersed in

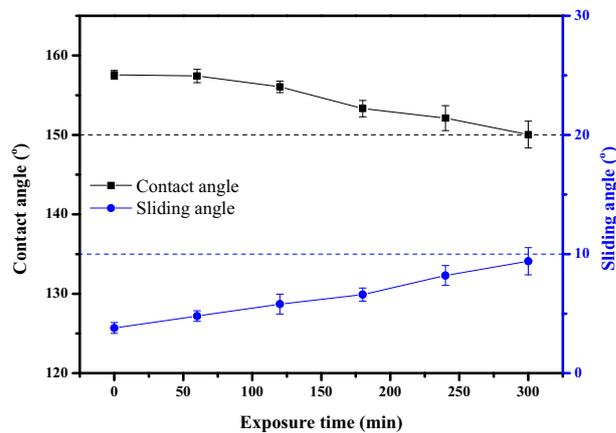
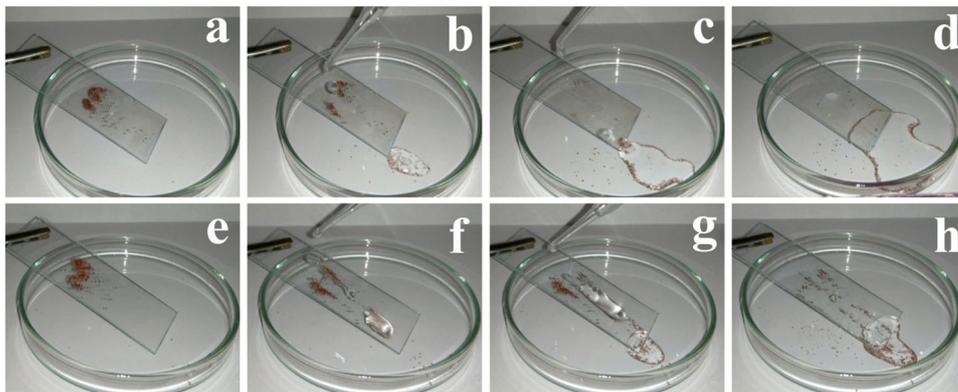


Fig. 8 CAs and SAs of the superhydrophobic glass as a function of UV exposure time

acid and base solution, successively. Meanwhile, the SA of superhydrophobic glass slightly increases to $9 \pm 1^\circ$ and $8 \pm 1^\circ$ after respectively immersing in acid and base solution for 18 h. Here, the acid and base solution could initiate a

Fig. 9 Self-cleaning simulation of the (a–d) superhydrophobic glass and (e–h) uncoated glass



hydrolysis and condensation reaction with silane compound, which further could damage the interaction between the OTS layer and TiO_2 film resulting in a decrease of CA and increase of SA value, gradually [41, 42]. However, the strong interaction between the interlayer of OTS and TiO_2 film on the coated glass surface is believed could slow down this devastation. Therefore, it can be concluded that the as-prepared superhydrophobic glass has good long-term stability in a neutral, acidic and alkaline environment.

To further evaluate the stability of the as-prepared coated glass in outdoor applications, the CA and SA of these coatings after UV exposure were measured. In Fig. 8, the CA of the superhydrophobic glass only slightly decrease to $150 \pm 2^\circ$ from $158 \pm 1^\circ$ and SA gradually increase to $8 \pm 3^\circ$ from $3 \pm 1^\circ$ after UV exposure for 300 min, exhibiting a good stability and durability of the coatings. Generally, when exposed to UV light, the TiO_2 films could easily trigger the hydrophilic properties by creating the oxygen vacancies, which further could decrease the CA value. However, the obtained results confirm that the presence of TiO_2 layers on the surface of coated glass, after being irradiated by UV light, did not have a significant effect on decreasing the CA value. It is due to the presence of oxygen atoms from OTS molecules can gradually replace the oxygen vacancies on TiO_2 film to maintain the hydrophobicity [21].

3.3 Self-cleaning ability

Even though self-cleaning properties generally could be performed in both super-wetting system (superhydrophilic and superhydrophobic) by using water, but the cleaning process for both of these surfaces is entirely different. Herein, the self-cleaning ability on the superhydrophobic surface that we fabricated and applied on the glass substrate will be described. Figure 9 shows the self-cleaning simulation of uncoated and superhydrophobic glass. The cleaning process was observed by capturing the ability of water droplets in removing the carborundum particles, which were placed on the glass

surface. As shown in Fig. 9a–d, the carborundum particles on the coated glass surface were removed as quickly as the water droplets rolled-off, obtained a clean surface. In contrary, the carborundum particles on the uncoated glass were quite difficult to remove with the same procedure (Fig. 9e–h). Generally, the cleaning process performed on the superhydrophobic surface was employed by physical interaction between the water droplets and the contaminant that rolling-off from this surface [43]. To make this happen, high surface roughness and low surface energy must be presented. In this work, TiO_2 film was used to increase the surface roughness by creating the hierarchical rough structure. This surface roughness traps a large amount of air between its grooves, meanwhile, the OTS layer was used to decrease the surface energy [14, 38]. Together, those features could maintain the water droplet in the solid–vapor–liquid phase forming a high-water CA and a low-water SA. This explained that the two mentioned features on the as-prepared superhydrophobic glass caused the water droplets easily rolling-off over the modified surface without wetting the surface so that contaminants will be easier to remove [38].

4 Conclusions

Superhydrophobic glass has been successfully prepared through an environmentally friendly and low-cost strategy to prepare mechanically robust, UV stable, chemically resistance, and transparent superhydrophobic coatings by depositing TiO_2 film on the glass substrate, followed by surface modification of fluorine-free compound of OTS. The coated glass exhibited excellent superhydrophobic property with CA of $158 \pm 2^\circ$ and ultralow adhesion with an SA of $4 \pm 1^\circ$. The coated glass has been shown to have good mechanical and chemical stability while maintaining its superhydrophobic surface after 80 cm of abrasion against 1500 mesh sandpaper, and after being immersed in acidic (pH 4) and alkaline (pH 10) solutions for 18 h. Moreover, this modified glass substrate has also been shown to have

good durability while maintaining its superhydrophobic surface after soaking in water for 5 days and UV irradiation for 300 min. Importantly, the as-prepared superhydrophobic glass has a good self-cleaning property, which can be employed to clean contaminants (SiC particles) on its surface quickly compared to uncoated glass. The study showed that this feasible strategy can be used to fabricate the remarkably nonwetting system on various substrate.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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