Creation of a multifunctional superhydrophobic coating for composite insulators

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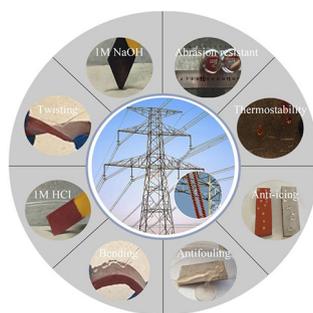[c] State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People's Republic of China

HIGHLIGHTS

- The coating exhibits great mechanical durability, and excellent super-hydrophobicity.
- The as-prepared coating still remains superhydrophobicity after 300 °C high temperature treatment.
- The coating of composite insulators for power system is extremely suitable.

GRAPHICAL ABSTRACT

Multifunctional micro-nanoscale SiO_2/epoxy resin superhydrophobic coating created by a simple and low-cost method. Moreover, the coating exhibits great mechanical durability and excellent chemical stability and properties of anti-icing and self-cleaning, which makes the composite insulator run normally under extreme conditions and satisfies a completely need of power system.

ARTICLE INFO

ABSTRACT

Composite insulators with a superhydrophobic coating can tremendously improve the reliability and stability of transmission line systems and railway systems; thus, they play a crucial role in global electricity issues and power systems. However, the majority of superhydrophobic coatings for composite insulators suffer from weaknesses, such as poor mechanical stability and complicated and toxic preparation processes. To improve these defects, a multifunctional, micro-nanoscale SiO_2/epoxy resin superhydrophobic coating for composite insulators was created. The coating maintained excellent superhydrophobicity through a bending experiment, a twisting test, a knife-scratch, a durability test, a pH test and UV light treatment. Moreover, it also performed well in the areas of anti-icing, high thermal stability (300 °C), self-cleaning and antifouling. In view of above-mentioned advantages, composite insulators with the proposed superhydrophobic coating show great potential for the national economy and power industry.

1. Introduction

Composite insulators, as an important component in transmission lines and railway systems, are usually used to support the conductor and prevent current return in global electricity issues [1]. However, it has been demonstrated that the power system suffers from various issues, including conductor shaking, environmental pollution and insulator icing, which could lead to insulator failures, insulation performance degradation and even tower collapse [2]. Therefore, it is necessary to endow composite insulators with desirable performance characteristics, from the point of view of safety and stability operation.

Inspired by natural superhydrophobic surfaces, such as lotus leaves [3], butterfly and dragonfly wings [4] and the water strider [5], a variety of superhydrophobic coatings were developed with a focus on the roughness and low surface energy of the material [6–8]. They were employed in many areas, including self-cleaning, anti-icing, antibacterial applications, oil-water separation and corrosion prevention [9–15]. In a word, a superhydrophobic coating is a suitable candidate for protecting the composite insulators from damages generated during practical applications [16–17]. Accordingly, Liao et al. reported a superhydrophobic coating for insulators [18]. The surface showed anti-icing and self-cleaning properties based on superhydrophobicity, contact angles (CAs) larger than 150° and sliding angles (SAs) less than 5°. Compared with room temperature vulcanized silicone rubber (RTV) coated glass slide, it could effectively reduce the freezing area. In addition, they [19] also fabricated a ZnO/SiO$_2$/PTFE (Polytetrafluoroethylene) sandwich-nanostructure superhydrophobic coating for composite insulators, which showed good corrosion resistance and insulating performance. Superhydrophobic coatings for insulators, however, are limited by poor mechanical stability, troublesome chemical processes and toxic substances. Taking practical applications and simple methods into account, global power systems urgently require a superhydrophobic coating with excellent anti-icing properties and mechanical durability. The coating is designed using a facile and environmentally friendly strategy, which continues to be a challenge for us.

The fabrication of a multifunctional, micro-nanoscale SiO$_2$/epoxy resin superhydrophobic coating for composite insulators in power systems is reported in this paper. The various substrates such as composite insulators, glass, wood and fabric were coated with micro-nanoscale SiO$_2$ particles using an epoxy resin, curing agent and PVDF. The results showed that the coatings possess superhydrophobicity, self-cleaning and anti-icing properties, high thermal stability and chemical durability. After a knife-scratch test, a UV light test, and even 500 abrasion cycles using sandpaper with a 400 g load, the coating maintained its superhydrophobicity on account of its low-energy stability and micro/nano structures. This method was proven to be more simple and efficient than other methods reported. Importantly, the SiO$_2$/epoxy coating can prevent liquid from contacting the surface of composite insulators, which indicates great potential for applications in the reduction of electricity loss, as well as safeguarding transmission line systems and railway systems.

2. Experimental section

2.1. Materials

Tetraethoxysilane (TEOS) (AR) was purchased from Shantou XILONG Chemical Reagent Co. Inc, China. Ammonium hydroxide (NH$_3$·H$_2$O) (AR 97%) was obtained from Henan Xinxiang ZHONGYUAN organic chemical Co. Ltd., Chain. 3-hydroxytyramine hydrochloride (dopamine hydrochloride, 99.5%) was purchased from Sigma-Aldrich. 1,1,1,3,3,3-hexamethyl disilazane (HMDS, 98%) was obtained from Shanghai KEFENG Chemical Reagent Co. Lnc. Epoxy resin and curing agent were purchased from Beijing Yuhong Waterproof Technology Co. Ltd. Sudan red IV, orange II sodium salt and methylene blue were
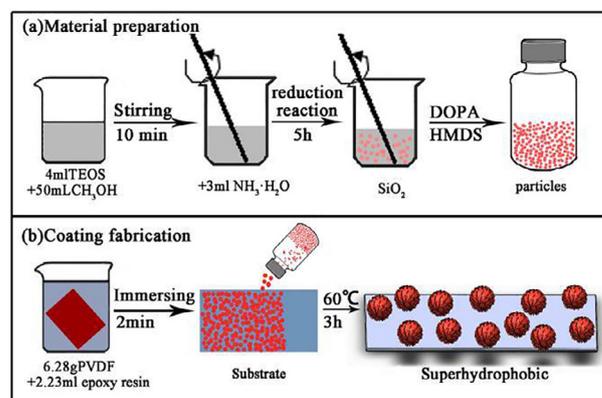

Fig. 1. (a) Preparation procedure of the superhydrophobic HMDS-DOPA SiO$_2$ powders and (b) coating fabrication.

obtained from Aldrich. In addition, all other chemicals were analytical-grade reagents and were used as received.

2.2. Preparation of superhydrophobic powder

Schematic Fig. 1 shows the preparation procedure for the superhydrophobic coating. First, 4 mL of tetraethoxysilane (TEOS) was mixed with 50 mL of ethanol and stirred for 10 min. Next, 3 mL of NH$_3$·H$_2$O was added to the above mixture and stirred for 5 h at room temperature. Subsequently, 0.03 g of 3-hydroxytyramine hydrochloride (DOPA) and 8 mL of 1,1,1,3,3,3-hexamethyl disilazane (HMDS) were added into this solution while stirring. After the hydrolysis reaction (TEOS and HDMS) was down, the mixture was then dried in a vacuum oven at 100 °C for 3 h. The brown HMDS-DOPA particles were collected through filtration and washed with ethanol twice. Finally, the superhydrophobic powders were obtained and harvested for the subsequent experiment.

2.3. Characterization

To characterize the morphologies of the original SiO$_2$ powders and superhydrophobic HMDS-DOPA powders, field emission scanning electron microscopy (FESEM) images were obtained on JSM-6701F, using Au-sputtered specimens. Transmission electron microscopy (TEM) measurements were carried out with a TechnaiG20 (FEI) operating at 300 kV. X-ray photoelectron spectroscopy (XPS) (ESCALAB 250Xi, Thermo Scientific) measurements were performed using Al-Kα radiation and used to analyse elements and functional groups. Fourier transform infrared spectroscopy (FTIR), Nicolet iS10, and Thermo Scientific were used to record the spectra. Three-dimensional surface imaging was carried out using Surface Imaging System atomic force microscopy (AFM, CSPM 5500). The size distribution of particles was measured with Zetasizer Nano ZS ZEN 3600. The water CAs and SAs were measured (JC2000D) with a 5 μL distilled water droplet at ambient temperature. The average water contact angle and sliding angle values were obtained by measuring the same sample at five different positions. All photographs were obtained by a Sony camera (DSCHX200).

3. Results and discussion

3.1. Structure and characterization of superhydrophobic HMDS-DOPA SiO$_2$/epoxy powders

The micro/nano structure and morphologies of the original SiO$_2$ powders and superhydrophobic HMDS-DOPA SiO$_2$ powders were investigated by SEM and TEM, respectively, in Fig. 2. It is clearly shown that the radii of pristine SiO$_2$ particles were less than 100 nm, and the
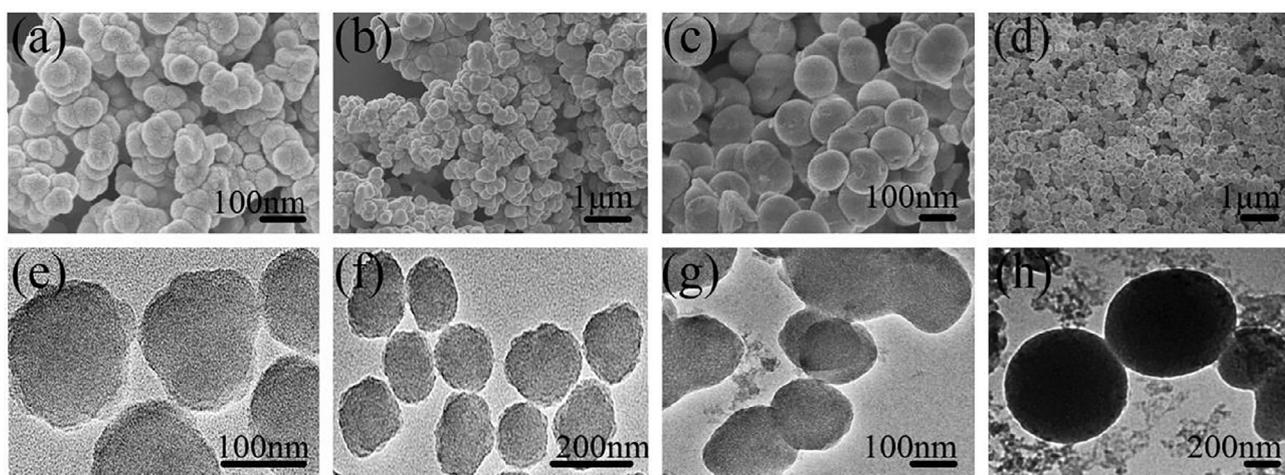
Fig. 2. SEM images of the original SiO$_2$ reacted by NH$_3$·H$_2$O and TEOS (a and b), SEM images of superhydrophobic HMDS-DOPA SiO$_2$ powders (c and d). TEM images of the original SiO$_2$ reacted by NH$_3$·H$_2$O and TEOS (e and f), TEM images of superhydrophobic HMDS-DOPA SiO$_2$ powders (g and h).
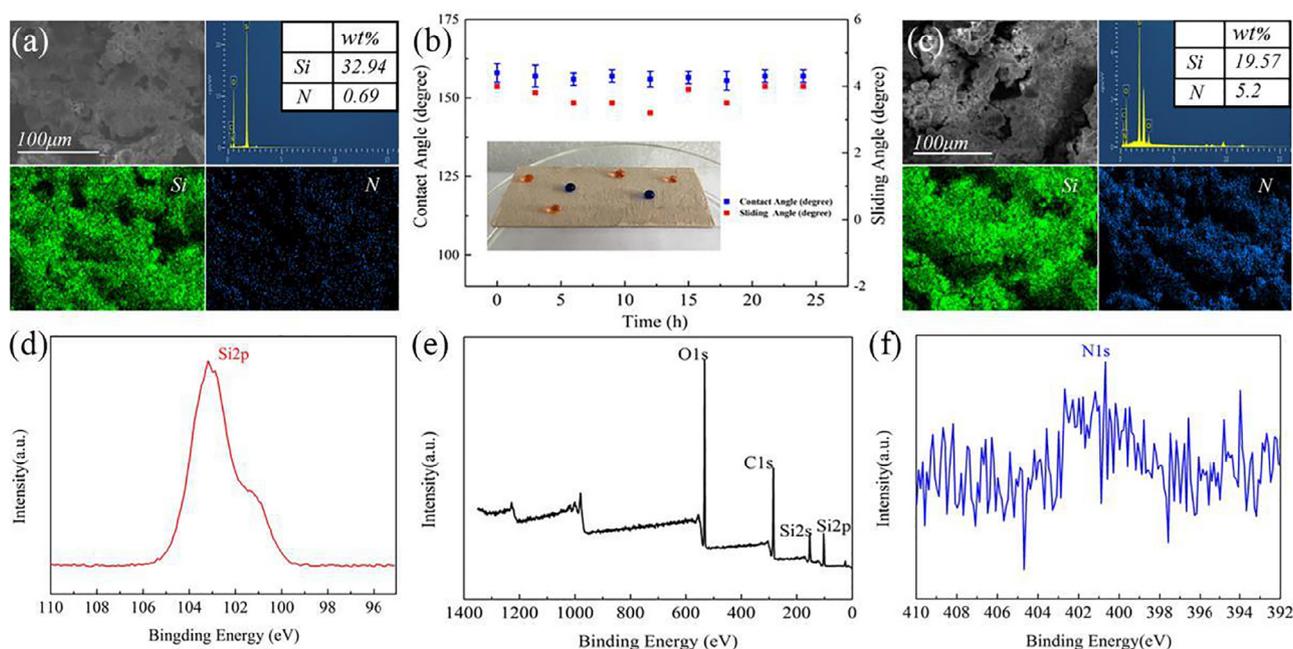

Fig. 3. (a) EDS spectrum and EDS maps of Si and N elements of the original SiO$_2$ surface (Scale: 100 μm). (b) The images of superhydrophobic HMDS-DOPA SiO$_2$ and its water contact angles and sliding angles. (c) EDS spectrum and EDS maps of Si and N elements of superhydrophobic HMDS-DOPA SiO$_2$ surface (Scale: 100 μm). (d–f) Si2p, XPS survey spectra and N1s spectra of superhydrophobic HMDS-DOPA SiO$_2$ coating.

SiO$_2$ particles modified by HMDS-DOPA were larger than 100 nm in diameter. The modified particles homogeneously covered the surface and formed a micro/nano-scale roughness. At the same time, the highly hydrophobic −CH$_3$ groups of HMDS provided the modified DOPA with lower surface energy [20]. Because of the HDMS added in the system, the rest of the −OH groups on the surface of the −OSi(CH$_3$)$_3$ were converted. The highly hydrophobic −CH$_3$ group gives the system a lower surface energy, resulting in a superhydrophobic nanocoating. TEOS and HDMS hydrolytic reactions generate ≡Si−O−Si(CH$_3$)$_3$ on the surface, which leads to the superhydrophobicity of the particles. [21] Therefore, these conditions offered the coating outstanding super-hydrophobicity, as shown in Movie S1 and Fig. 3a. The brown coating displayed extraordinary superhydrophobic properties with CAs larger than 155° and SAs less than 5°. According to the XPS and EDS patterns of the original SiO$_2$ particles and superhydrophobic HMDS-DOPA SiO$_2$ (Fig. 3b and c), proportions of the element of Si and N in the original SiO$_2$ were 32.94% and 0.69%, respectively. After they were modified

by DOPA and HMDS, the element of N increased to 5.2%, which illustrated the successful introduction of DOPA and HMDS onto the surface. In addition, four main characteristic peaks, appearing at 532.61 eV, 400.63 eV, 284.44 eV and 103.1 eV, which attributed to the existence of O, N, C and Si, respectively, as shown in Fig. 3d–f.

Similarly, Fig. 4 exhibited the FTIR of the samples. The peaks at 1672 cm^{-1} and 961 cm^{-1} were classified as the gap of H$_2$O and −Si−OH, and the peak at 1087 cm^{-1} was the symmetric stretching gap of the Si−O−Si bond, which belonged to hydroxyl groups of SiO$_2$. The bonds of modified SiO$_2$ increased significantly at 3148 cm^{-1}, 2963 cm^{-1}, 1407 cm^{-1} and 1255 cm^{-1} compared to the original SiO$_2$ because they were wrapped by the hydrophobic group or hydrophobic bond (−OH, −CH$_3$, C−C and Si−C).

Fig. 5 demonstrates the micro/nano dual roughness of the super-hydrophobic SiO$_2$. It is of great importance to explain why the coating maintained a nano structure. From Fig. 5a and b, it can be observed that superhydrophobic SiO$_2$ was larger than the original SiO$_2$. Clearly, it was
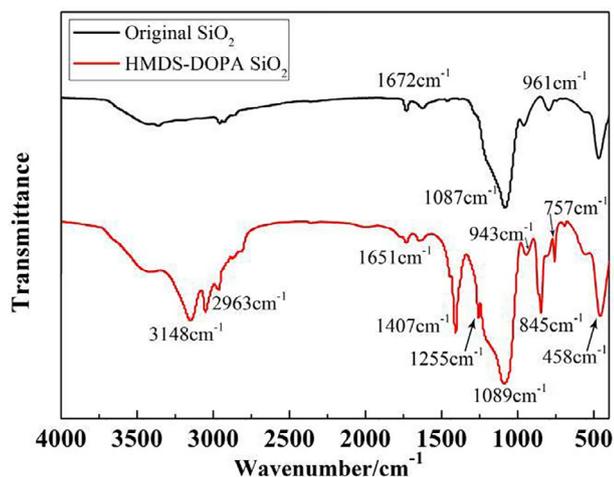
Fig. 4. FTIR spectra of the SiO_2 coating and the micro-nanoscale SiO_2/epoxy resin superhydrophobic coating.

completely constituted by nanowires and exhibited a morphology with an average surface roughness (Ra) of approximately 92 nm (Fig. 5d). The main reason is that the particles were modified by DOPA and HMDS as a result of roughness.

3.2. Fabrication of superhydrophobic coatings on various materials

As presented in Fig. 6, the brown HMDS-DOPA particles were applied to various substrates (hard, soft, elastic and cotton materials). For the curing reaction of epoxy resin, the particles were immersed in a mixture of 6.28 g PVDF, 0.74 mL of curing agent and 2.23 mL of epoxy resin for 2 min at room temperature to form solution A. Then, the various substrates, such as fabric, composite insulator, wood and glass, were immersed in solution A for 2 min to be completely infiltrated. Next, the coatings were covered with modified SiO_2 particles via dip-coating and sieve-deposition. Then, the coating covered with brown particles was dried at 60 °C for 3 h. Finally, the samples deposited by powders were pressed by glass in order to improve bonding strength. Thus, the obtained SiO_2/epoxy resin coating showed superhydrophobic properties.
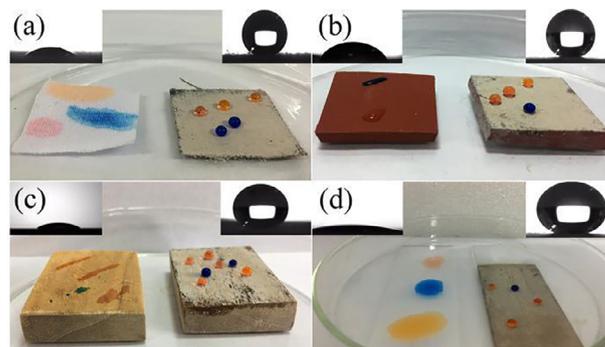

Fig. 6. Photographs of water droplets on four different original substrates (left) and coated substrates (right) (a) fabric, (b) composite insulator, (c) wood, and (d) glass, respectively. Shown in the insets are the optical images of the static water droplets (5 μL).

3.3. Mechanical durability of superhydrophobic SiO_2/epoxy resin coating.

It is well known that micro/nano structures are vital for the construction of superhydrophobic surfaces and that the corresponding the structure could be easily destroyed or removed due to its fine structure and weak mechanics. Some attempts have been made to increase the mechanical stability of superhydrophobic surfaces [22–25]. For instance, Zhang et al. [26] introduced a robust superhydrophobic coating which possessed a rapid healing ability after ultra-abrasion. In this paper, a simple abrasion test was performed to demonstrate that the proposed coating could maintain superhydrophobicity even after undergoing thirty abrasions. Moreover, it could be easily repaired within one minute if the coating lost superhydrophobicity under ultra-abrasion.

Herein, a simple sandpaper-abrasion test was carried out to evaluate the mechanical stability of the prepared superhydrophobic glass coating (7.5 cm × 2.5 cm). Fig. 7 and Movie S2 show that the variation of contact angle and mass with the increase of friction cycles that with a distance of 10 cm under 400 g weight. The results showed that the superhydrophobic coating could maintain superhydrophobicity even after large cycles (Fig. 5). The CA reached its maximum value (158°) after a slight decrease, and there was no obvious damage on the coating. It is surprising that a comparatively stable value (150°) was maintained
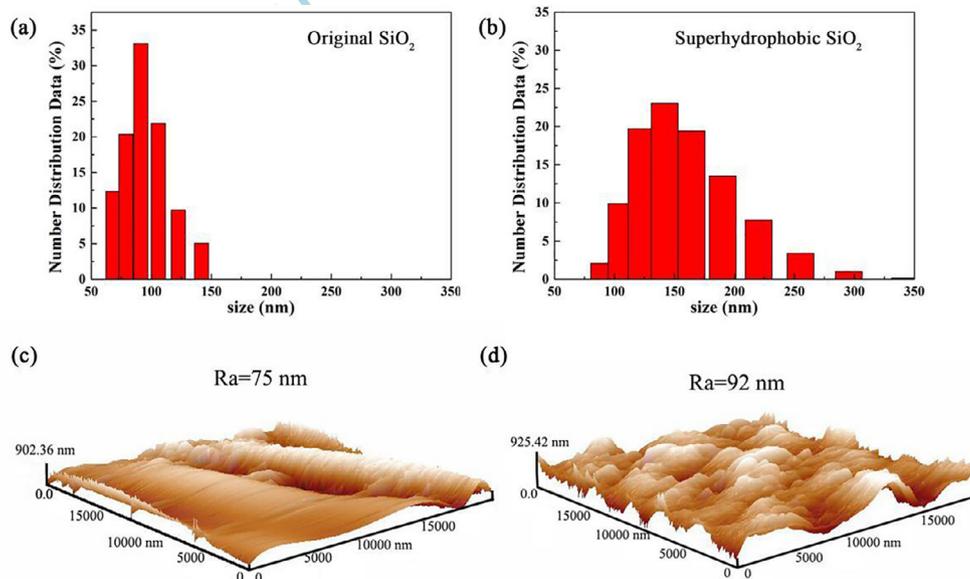

Fig. 5. The particle size distribution of original SiO_2 (a), the AFM of the original SiO_2 (c). The particle size distribution of superhydrophobic SiO_2 (b), the AFM of superhydrophobic SiO_2 (d).
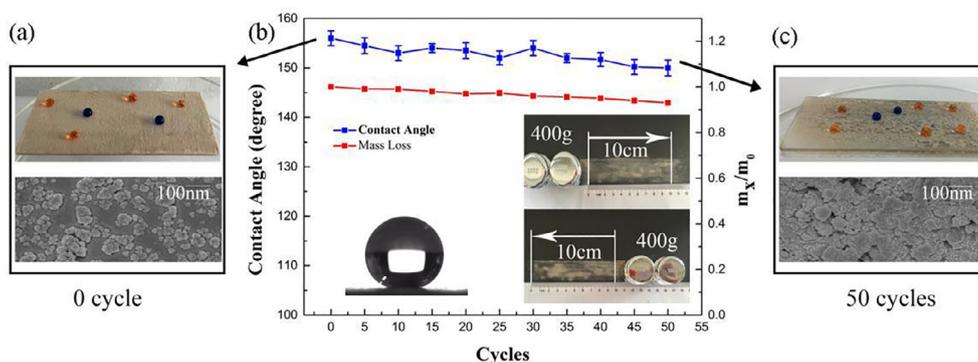
Fig. 7. (a) and (c) Photographs of the SEM before and after 50 abrasion cycles respectively. (b) Contact angle and mass loss (m_0 and m_x are the mass of the superhydrophobic coating before and after cycles with sandpaper) under 400 g weight.

through 50 abrasion cycles, and the loss of quantity was approximately 15.6%, which indicated a satisfactory wear-resisting performance of micro-nanoscale SiO_2/epoxy resin coating. The contact angles of the micro-nano coating remained stable after abrasion. It is clear that there is no apparent change to the coating before and after 50 abrasion cycles, according to a comparison with the SEM images (Fig. 7a and c). As shown in Fig. S3, when the composition was analysed by EDS, elemental Si decreased from 19.57% to 16.45%, and elemental N decreased from 5.2% to 1.43%, which indicates that the surface was modified by DOPA and HMDS, and the coating retained favourable superhydrophobicity.

Importantly, the coating was immersed in water for 20 days, and the wetting behavior was measured every 5 days, and all the contact angles were higher than 150° as shown in Fig. S1, indicating the stability of the superhydrophobic coating. Furthermore, a bending experiment, a twisting test and a knife-scratch were also performed to prove the mechanical stability and robustness of the coating, as shown in Fig. S2. There is no distinct change in superhydrophobicity, and excellent mechanical durability was maintained even after extreme treatment, which suggested that the mechanically durable micro-nanoscale SiO_2/epoxy resin superhydrophobic coating could be applied to composite insulators for power systems.

3.4. Chemical stability, self-cleaning and antifouling properties of superhydrophobic SiO_2/epoxy resin coating

Many composite insulators were installed in large-span, long-distance transmission lines through plateaus, mountains or other high-altitude areas. Due to the thin atmosphere, UV radiation in high altitude areas is comparably intense, and high-intensity UV light treatment could increase accident rates among high altitude transmission lines. Not only may the mechanical durability and chemical stability be influenced, but the low-surface-energy may also be damaged by UV light treatment, which is a significant factor for chemical durability. Therefore, a simple UV light test was necessary. In this work, a coated glass test (7.5 cm × 2.5 cm) was conducted under UV light irradiation from an artificial light source (20 W, 254 nm), as exhibited in Fig. S4. It is clear that the contact angles were greater than 150° under strong UV-light exposure, and it is worth noting that the coating can maintain its superhydrophobic property for 24 h. The hydrophobicity has a tendency to decrease as a result of irradiation. Elemental Si decreased from 19.57% to 13.14%, and elemental N decreased from 5.2% to 2.99%, implying that the surface had been modified by DOPA and HMDS under strong UV light treatment. The transmission results of the superhydrophobic coating are shown in Fig. S5. While the wavelengths ranged from 200 nm to 380 nm, the transmittance was close to 0, SiO_2 particles were relatively small and evenly dispersed on the surface; therefore, they had more favorable interface reflection performance. When the UV light hit the coating it contacted with the new interface,

leading to completely diffused reflection and enhanced reflective properties. Thus, it can shield and resist UV radiation. In addition, in this test, the intensity of UV radiation used was approximately 2% that of sunlight; therefore, the coating of composite insulators is extremely suitable for power systems.

However, the acid or alkaline liquid produced by industrial pollution can corrode the surface of the composite insulator, causing it to fail. The chemical durability of the superhydrophobic SiO_2/epoxy resin coating was evaluated by placing strong acid (1 M HCl) and alkaline (1 M NaOH) droplets onto its surface. After that, the surfaces were measured by pH test papers, as shown in Fig. 8af. The coating was not sensitive to them and exhibited distinguished acid and alkali repellence. In addition, the coating showed low adhesion. Therefore, the coating of composite insulators has satisfactory acid-and-alkali resistant abilities under natural conditions.

The line composite insulator could be under protracted operation and may suffer from natural disasters, such as high winds, dust storms and so on. The superhydrophobic coating has the special property of easily dissolving pollutants on its into liquid, and dirt on the superhydrophobic coating's surface can always be removed by water to reduce surface energy [27–28]. It is well known that lotus leaves can always stay clean in dirty environments thanks to their great superhydrophobicity [29–35]. In this paper, self-cleaning experiments and antifouling experiments were carried out to display that this same property can be applied in composite insulators for power systems. As Fig. 8h–j and Movie S3 exhibited, some sand and dust were spread randomly on the coating, after which clean water was poured on it, causing the sand and dust to wash away easily. Muddy water was also poured to demonstrate the superhydrophobic coating's antifouling ability. As shown in Fig. 8k–m and Movie S4, muddy water was poured directly on the coating, and the coating still remained clean. The adhesion of dust on the superhydrophobic surface was very weak. In consideration of this ability of the superhydrophobic SiO_2/epoxy resin coating, it is suitable for composite insulators.

3.5. Anti-icing and thermal durability properties of superhydrophobic SiO_2/epoxy resin coating

Affected by climate and terrain, transmission lines could suffer from ice accumulation, causing tower collapse as the result of electric power, telecommunication interruptions and wire shaking accidents [36], all of which cause great losses to the national economy and power industry. Numerous studies have attempted to explore anti-icing surfaces applied to many fields [37–41]. Consequently, an anti-icing test was conducted, and both coated and uncoated composite insulators were placed in a temperature of -10 °C, as Fig. 9 showed, water could roll down the coated surface even at -10 °C. Although the uncoated composite insulators had been frozen for 300 s, the coated composite insulators still retained their superhydrophobicity, as shown in Fig. 9a. The water
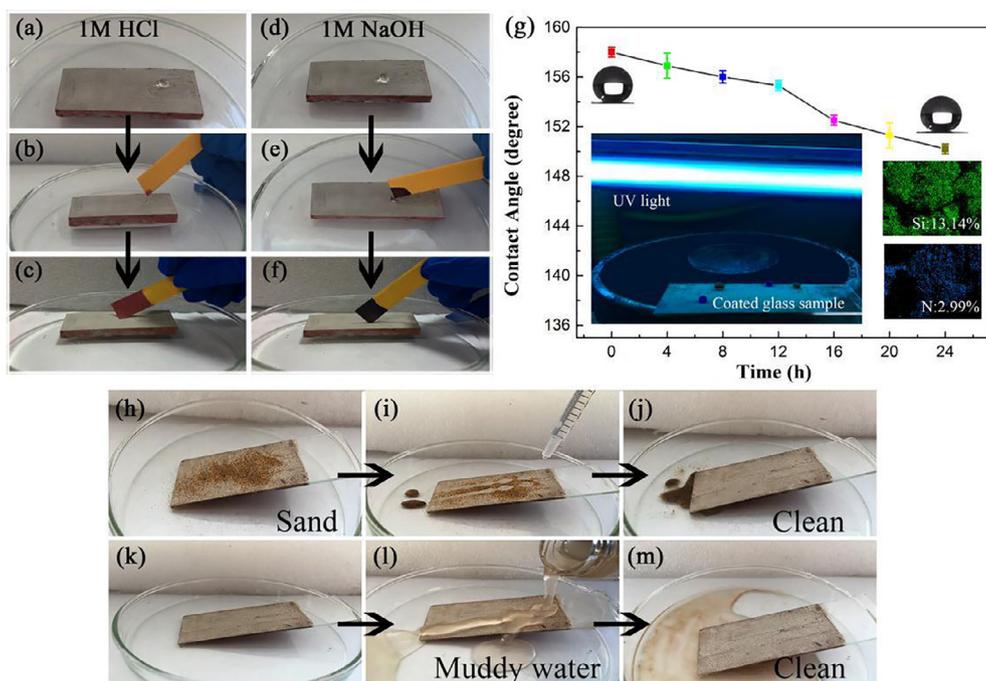
Fig. 8. 1 M HCl (a–c) and 1 M NaOH (d–f) droplets on the superhydrophobic SiO₂/epoxy resin coating absorbed by pH test papers. (g) The contact angle of superhydrophobic SiO₂/epoxy resin coating after 0–24 h strong UV-light exposure treatment. Self-cleaning experiment (h–j) and anti-fouling experiment (k–m) process of the SiO₂/epoxy resin coating.

droplet on the coated composite insulator took 960 s to partially freeze and approximately 1740 s to completely freeze as shown in Fig. 9b and c, which also proved that the surfaces had low adhesion. With icing delay and low adhesive properties, the superhydrophobic coating can prevent composite insulators from suffering a freezing disaster in hostile environments.

Recently, there has been an increasing number of investigations focusing on the thermal durability of superhydrophobic coating [42–48]. Some composite insulators have to endure high-temperature environments such as plateaus, deserts and so on. The contact angles were measured at several temperatures (0 °C–300 °C), and the EDS maps of Si and N elements before and after 300 °C were drawn, as shown in Fig. 10. It can be clearly observed that all contact angles were greater than 150° when the temperature increased from 0 °C to 300 °C, showing thermal stability (Fig. 10b). It can be seen from SEM and EDS images (Fig. 10a and c), that the tested surface was coated with a number of small particles, forming a suitable roughness, which can

enhance water wettability according to the equation of Cassie. From the EDS survey of the heat-treated HMDS-DOPA particles, the elemental Si decreased from 19.57% to 16.45% and the elemental N decreased from 5.2% to 1.43%, which proved that the modified surface remained stable even after 300 °C. More importantly, although the coating could be damaged slightly by the high temperature, the surface still possessed its superhydrophobic property, as Fig. 10d–f displayed. It is certain that the fabricated coated surface is competent to protect composite insulators in high temperatures.

4. Conclusions

In summary, a simple and green method for fabricating the SiO₂/epoxy resin coating for composite insulators via dip-coating and sieve-deposition was employed in this study. Through a bending experiment, a twisting test, a knife-scratch and even after 50 abrasion cycles under 400 g weight, the coating still retained excellent superhydrophobicity.
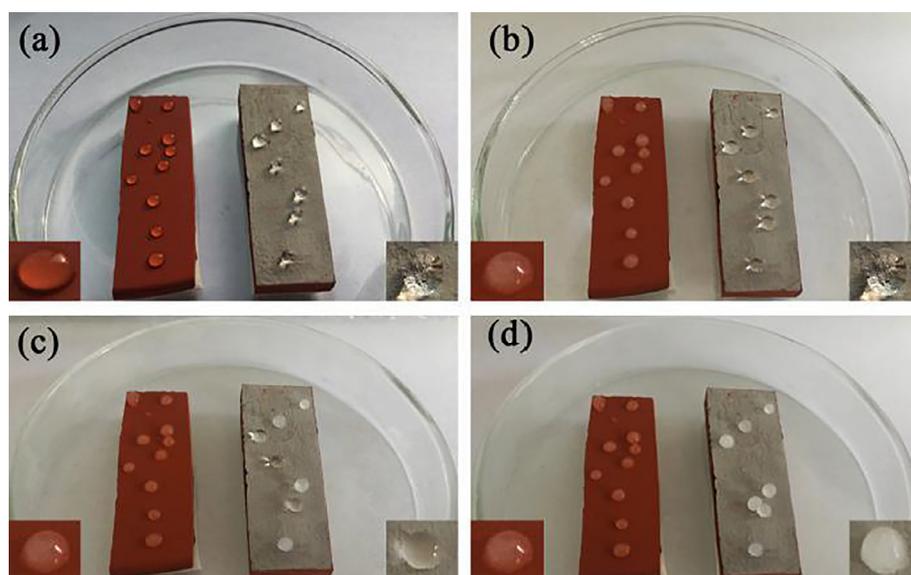

Fig. 9. Anti-icing test of coated and uncoated composite insulators: (a) t = 0 s (b) t = 300 s (c) t = 960 s (d) t = 1740 s.
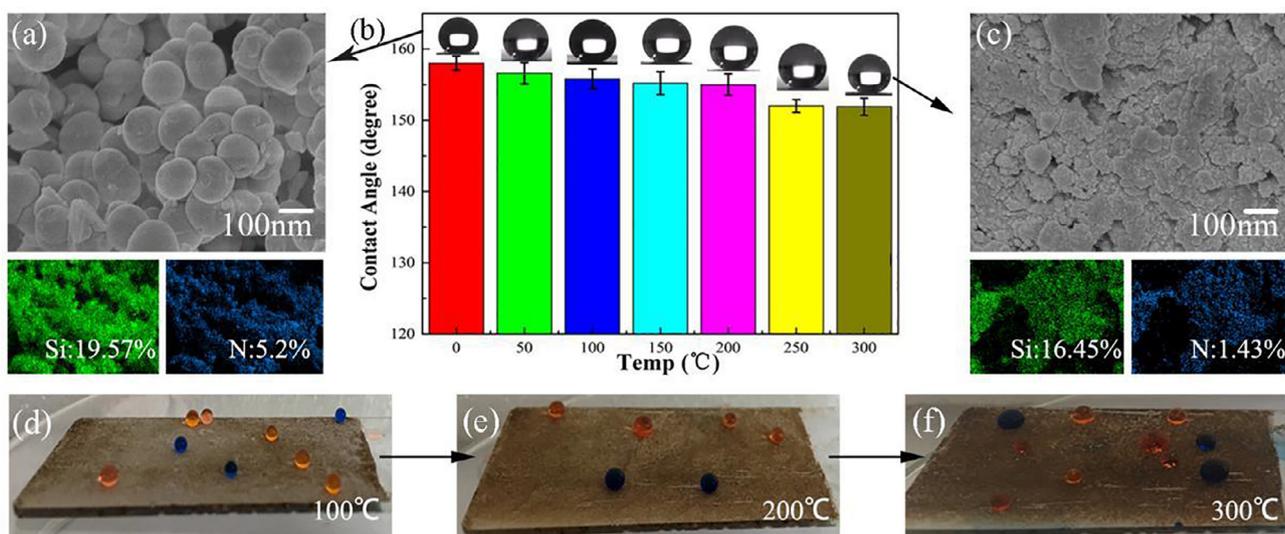
Fig. 10. (a) and (c) Photographs of the SEM and EDS maps of Si and N elements before and after 300 °C, respectively. (b) Photographs of the contact angles at different temperatures (0 °C–300 °C). (d–f) Photographs of the SiO$_2$/epoxy resin superhydrophobic coating at high temperature (100 °C, 200 °C, 300 °C).

Meanwhile, the coating on composite insulators could maintain its superhydrophobicity for 24 h under strong acid (1 M HCl), alkaline (1 M NaOH) or UV light treatment. Compared with other coatings, the as-prepared coating possesses multiple features including robust mechanical stability, superb anti-icing performances, high thermal stability (300 °C), and excellent antifouling and self-cleaning characteristics. In consideration of the abovementioned advantages, such superior properties will endow the superhydrophobic coating with a promising application value in power systems, which is of great benefit to global electricity issues.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.cej.2018.07.095.

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