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A stretchable superhydrophobic coating with electrothermal ability for anti-icing application

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Abstract

Surface icing in the transmission lines may cause serious accidents. Although the superhydrophobic/electrothermal synergistically anti-icing strategy has been introduced, most coatings tended to lose superhydrophobicity under large deformation. In this research, we prepared a kind of stretchable superhydrophobic coating by partially embedding the modified graphene into the Ecoflex elastomer. The excellent resilience of the Ecoflex elastomer together with the outstanding interfacial area of graphene results in the maintainment of superhydrophobicity even under 300% strain. Furthermore, this coating has outstanding superhydrophobic and electrothermal property simultaneously due to the introduction of graphene. After applying 20 V voltage, this coating could melt 2 mm thick ice layer within 115 s. Moreover, this superhydrophobic coating demonstrated excellent mechanical and chemical durability, and outstanding thermostability.

1. Introduction

Transmission lines are a key component of the power system, but they are vulnerable to ice accretion [1, 2]. The icing in the transmission lines will greatly increase the weight and wind resistance, which may even cause tower collapse in severe cases [3]. Therefore, the research on transmission line’s anti-icing technology is of great significance to ensure the safe operation of power system. The current de-icing technology can be mainly divided into two categories: active and passive de-icing methods. The active de-icing methods include ultrasonic method [4], photothermal method [5], electrothermal method [6, 7], and so on. In particular, electrothermal method has been widely used in industry because of its simplicity and high efficiency [8]. Nevertheless, the major drawback of the electrothermal method is the high energy consumption.

Compared with the active de-icing method, the passive method tried to prohibit the ice accretion without the extra energy consumption. A typical passive method is to construct superhydrophobic surfaces [9–12]. The superhydrophobic effect was inspired by the lotus leaves [13, 14]. As is well known, the water droplets on the lotus leaves exhibit a nearly ball-like shape and roll off easily. Thus, the superhydrophobic coatings are considered as ideal anti-icing materials. The further researches proved that the superhydrophobic materials could postpone the formation of ice crystals [15], or lower the ice adhesion strength [16] or both [17, 18]. However, most superhydrophobic materials can only delay the formation of icing to a certain extent. For the power transmission lines, the icing accident occurs only when bad weather lasts for several days. But now ice will form on the surface of superhydrophobic materials after one hour at the most. Nevertheless, it should be noted that some new icephobic coatings may prevent ice formation completely [19].

Recently, some researches suggested that the new generation of de-icing materials should have both active and passive functions. For instance, Shiratori et al. fabricated a conductive superhydrophobic coating by embedding conductive nanoparticles into ethyl cyanoacrylate, which could rapidly melt newly formed frosts due
to the Joule heat [20]. Zhang et al. introduced a synergistically de-icing strategy by putting a superhydrophobic surface on the electric heating plate superhydrophobic [21]. As previously shown, a new kind of anti-icing method based on the synergistical effect of superhydrophobicity and Joule heating using graphene was introduced [22]. However, this coating can’t retain superhydrophobicity under large deformation. The transmission lines tend to be continuously operated at various wind speeds, and then the according deformations will generate inevitably.

In order to achieve stretchable superhydrophobic/electrothermal synergistically anti-icing strategy, a new kind of coating was prepared in this research by partially embedding the modified graphene into the Ecoflex elastomer. The excellent resilience of the Ecoflex elastomer together with the outstanding interfacial area of graphene results in the retention of superhydrophobicity even under 300% strain. Furthermore, this coating has outstanding superhydrophobic and electrothermal property simultaneously due to the introduction of graphene. After applying 20 V voltage, this coating could melt 2.0 mm thick ice layer within 115 s. Moreover, this superhydrophobic coating demonstrated excellent mechanical and chemical durability.

2. Experimental section

2.1. Materials
The graphene nanosheets with grade M were bought from XG Science, USA. The two part crosslinkable polydimethylsiloxane resin (Ecoflex 0030, Smooth-On Co., USA) was bought from the local market. 1H, 1H, 2H, 2H-perfluorooctyltrithoxysilane (C₈F₁₃H₄Si(OCH₂CH₃)₃, FAS), ethanol and methyl blue was provided by Aladdin Reagent Co., Ltd, Shanghai, China. All chemicals were utilized as received.

2.2. Preparation of hydrophobic powders
The hydrophobic graphene powders were fabricated based on the previous research with some modification [10, 12, 22]. First, 0.2 g FAS and 8 g ethanol were mixed to form a solution. After 2 h stirring, we added 0.2 g graphene into the solution. Then, the solution was stirred for 8 h to ensure uniformity. We further painted the solution onto the glass slide by means of a Pasteur pipette (2 ml). After normal temperature drying for 24 h, the FAS modified graphene powders were obtained and collected.

2.3. Fabrication of the stretchable superhydrophobic sample
The schematic for preparing stretchable superhydrophobic sample can be found in figure 1. First, the Ecoflex polydimethylsiloxane film with a typical thickness of 2 mm was prepared by mixing the part A and part B at a weight ratio of 1:1 (figure 1(a)). After 4 h, the Ecoflex film was semi-cured. Then, the graphene powders were coated onto the Ecoflex film with the help of a stainless steel mesh, as shown in figure 1(b). The stainless steel mesh has a mesh size of 200μm, which means that the graphene powdwr with the particle size smaller than 75 μm could pass through the mesh. Due to the gravity force, the graphene powders tended to be partially embedded into the Ecoflex film (figure 1(c)). In this research, the graphene was poured with excess, and then anything that
Observe the surface morphology. As shown in figure 2, the special surface structure is crucial for preparing superhydrophobic materials. Here, the SEM was utilized to study the surface micro/nano structures of the samples.

3. Results and discussion

3.1. Characterization
The surface micro/nano structures of the samples were observed using the scanning electron microscope (SEM, FEI FEG 450). The surface chemical compositions of the samples were accessed by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250Xi, USA). We further measured the water contact angles (CAs) and roll-off angles (RAs) using a home-made contact angle meter. The average values were utilized in the research after measuring at least five positions for each sample.

2.4. Characterization
The surface micro/nano structures of the samples were observed using the scanning electron microscope (SEM, FEI FEG 450). The surface chemical compositions of the samples were accessed by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250Xi, USA). We further measured the water contact angles (CAs) and roll-off angles (RAs) using a home-made contact angle meter. The average values were utilized in the research after measuring at least five positions for each sample.

2.5. Icing/deicing test
The icing/deicing test was performed based on previous research with mini modifications [22]. Briefly, we utilized a digital microscope to record the freezing process, and utilized an infrared imager to measure the surface temperature. For recording how a droplet was frozen, we placed the sample onto a Peltier stage. The surface temperature of the Peltier stage was set to −15 °C. Then, a water droplet (~5 µl) was carefully placed onto the surface of the sample.

To form a thick ice layer (~2 mm thickness) on the surface, we put the sample into a climate chamber which simulating the old rain environment (temperature: −5 °C, relatively humidity: 30%). In the next step, a large amount of microscale droplets were produced by the commercial moisturizer to simulate the rain droplets. Then, the ice layer would slowly form on the surface of the sample. In the further electrothermal de-icing test, we applied a DC voltage to generate Joule heating.

3. Results and discussion

The special surface structure is crucial for preparing superhydrophobic materials. Here, the SEM was utilized to observe the surface morphology. As shown in figure 2(a), many microscale bulges with irregularly shape were found. The size of bulges ranged from several micrometers to hundreds of micrometers. From the high magnification SEM image (figures 2(b) and (c)), it can be deduced that the bulges were composed of graphene from the thickness and nanoscale wrinkles. As a typical two-dimensional material, graphene is prone to agglomeration. In this research, the graphene were aggregated into micron bulges. Then the micro structure of bulges together with the nanostructure of graphene (figure 2(c)) tended to form a hierarchical structure, which is crucial for superhydrophobicity [13, 23].

Furthermore, the surface chemical composition is another key factor for superhydrophobicity. Here, the XPS test was utilized. From the survey spectra (figure 3(a)), the F 1s, O 1s, Si 2p, and C 1s peaks were detected. For the F 1s XPS spectrum (figure 3(b)), the total peaks were composed of one main component due to the CF₃ (689.32 eV) species and one minor components arising from the Si-Fₓ interaction (689.75 eV). It should be noted the CF₃ came from the FAS chain which played a key role in lowering the surface energy [24]. For Si 2p spectrum (figure 3(c)), the dominant peaks located at 104.15 eV were attributed to Si-OH or Si-Fₓ species, and the other peaks at 102.64 eV were ascribed to SiO₂-based network [25]. The C 1s (figure 3(d)) spectrum can be deconvoluted to three peaks at 284.50, 284.78, 285.60, 292.00 and 294.27 eV, which were assigned to C-Si, C-C, C-O, CF₂ and CF₃, respectively [26, 27].

In our daily life, the deformation is inevitable since the object is inevitably acted upon by a force. Particularly, the transmission line tended to gallope under air flow. In this research, the sample retained superhydrophobicity even under large deformation. From figures 4(a)–(d), it can be found that the water droplets maintained nearly round shape with increasing strain and even up to ~300%. From figure 4(e), the water CAs gradually became lower and RAs gradually became larger as the strain increases. However, the contact angles were still higher than [26, 27].

![Figure 2. SEM images of the graphene composite at (a) low and (b and c) high magnifications, respectively.](image-url)
Figure 3. (a) Survey XPS spectrum of the graphene composite; (b) F 1s, (c) Si 2p and (d) C 1s XPS spectrum of the graphene composite.

Figure 4. The water droplets on graphene composite at strain of 0% (a), 100% (b), 200% (c) and 300% (d). (e) CAs and RAs of graphene composite at various stretching strains. (f) The CAs and RAs of graphene composite after cyclic stretching-releasing cycles.
150° and the RAs were still lower than 10° under 300% strain, suggesting excellent superhydrophobicity. It should be noted that many white parts can be found when the strain is 300%, indicating that the Ecoflex substrate tended to expose under large deformation. The retainment of superhydrophobicity can be attributed to the hierarchical structure (figure 2). The stability of the sample under cyclic stretch was further investigated. As shown in figure 4(f), the sample maintained superhydrophobicity of the sample even after being pulled to 100% strain for 1000 times.

Although superhydrophobic materials have shown many fascinating properties, durability is an essential element from the viewpoint of practical applications. In this research, we utilized both physical and chemical methods to access the durability. For the physical test, the most widely used sandpaper-abrasion test was adapted. According to reference [28], the abrasion distance and applied normal pressure are two essential factors for the convenience of comparison. Here, a 200 g weight (∼5 KPa pressure) was utilized, and the 150 grid SiC sandpaper was used to abrade the sample (figure 5(a)). We further define that every 20 cm of abrasion distance as one cycle. The further CA and RA datas can be found in figure 5(b). It can be found that the water contact angles gradually get lower and RAs gradually get higher. However, the water CAs and RAs are still in the range of superhydrophobicity, suggesting the excellent mechanical durability of the stretchable superhydrophobic materials in this research.

In addition to the potential mechanical damage, superhydrophobic materials would inevitably meet the erosion of the corrosive liquids in engineering practice. In this research, we tested the chemical durability of the superhydrophobic samples. Six kinds of liquids were used, and they are 3.5 wt% NaCl and aqueous solution with the pH adjusted to 1, 4, 7, 10 and 14. This test was performed by first immersing the sample in liquid for 24 h and then rinsing with water. Figure 5(c) further demonstrated the surface wettability measurement. It can be found that the water contact angles were all higher than 150° and roll-off angles were all smaller than 10°, suggesting excellent chemical durability. To further demonstrate the broad applicability, we tested the thermostability of the stretchable superhydrophobic sample. The samples were heated at 200 °C, and the relationship between

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**Figure 5.** (a) the image of sandpaper-abrasion process; (b) the plot of CAs and RAs after each abrasion cycle; (c) the plot of CAs and RAs after being immersed in different corrosive liquids for 24h; (d) CAs and RAs of the as-prepared sample after 200 °C heat treatment for 0–24 h.
surface wettability and the heating time can be found in figure 5(d). The values of contact angles and roll-off angles showed that the heat treatment didn’t change the superhydrophobicity. Thus, this superhydrophobic sample has the potential to be used in the high temperature environment.

Based on the aforementioned stretchable and durable superhydrophobicity, we further investigated the potential application in anti-icing. First, the freezing time of water droplet was measured, and a bare glass slide was used for comparison. As shown in figure 6(a), a hemispherical shaped water droplet coated on the surface of bare glass, which was completely frozen after 122 s. On the other hand, a nearly round shaped water droplet was found on the superhydrophobic surface which was completely frozen after 394 s. Thus, the superhydrophobic surface should effectively delay the formation of ice. We attribute this phenomenon to the Cassie state. As the Cassie state described, the water droplet tended to trap air to form a gas cushion, which not only greatly reduced the contact area with the coating but also prevented the heat transfer [29, 30].

In this research, the graphene was used for preparing superhydrophobicity. As a typical 2D nanomaterial, graphene not only has outstanding interfacial area but also has excellent electrical conductivity. Here, the electrothermal property of the as-prepared superhydrophobic surface based on graphene was investigated. Here, the surface conductivity of the sample was measured to be 4.26 S m⁻¹ using the Keithley electrometer (Keithley 2450). Figure 6(b) demonstrated the relationship between the temperature and time after supplying different voltage. As shown in figure 6(b), the 10 V voltage could increase the surface temperature from −5 °C to the saturation temperature of 18.5 °C rapidly. Whereas after applying 25 V voltage, the surface temperature increased rapidly from −5 °C to 53.5 °C within 60 s and reached the high temperature of 89.1 °C after 180 s.

Although the superhydrophobic coating could greatly delay the formation of ice layer, it can not completely prohibit the ice accretion. In this research, we further put the superhydrophobic sample into climate chamber which simulating the old rain environment. After ~50 min, an ice layer (~2.0 mm) was formed on the surface of the sample. Here, we tried to use the electrothermal effect to rapidly melt the ice. A DC voltage of 20 V was applied. As shown in figure 7(b), the liquid water appeared after ~30 s which indicated that the ice started melting. After ~115 s, all the ice on the surface was melted. Furthermore, the melted ice rolled off easily. Finally a dry and clean surface was left, indicating the superhydrophobicity was retained (figure 7(d)). What is more, we further investigated the anti-icing stability in term of the cyclic icing/deicing test. The CA gradually became smaller from 162° to 154° and the RA gradually became larger from 4° to 7°, suggesting that superhydrophobicity was maintained (figure 8). Thus, it can be concluded the cyclic icing/deicing process didn’t seriously damage the surface structure. Therefore, our stretchable superhydrophobic surface has a bright future for the de-icing applications in the electric power system.

When the sample was used as electrothermal active anti-icing coating, the deterioration under external heating should be considered. In this research, we applied 20 V voltage onto the sample, and then measured the surface wettability and electrical conductivity. As shown in figure 9(a), the values of contact angles and roll-off angles were still in the range scope of the superhydrophobicity. Furthermore, the electrical conductivity was between 4.00 and 5.00 S/m (figure 9(b)). Therefore, this superhydrophobic coating is enough robust to withstand the deterioration of external heating.
Figure 7. The rapidly electrothermal de-icing process of graphene superhydrophobic composite.

Figure 8. The plot of CAs and RAs as a function of icing-deicing cycles.

Figure 9. (a) the CAs and RAs and (b) electrical conductivity of the as-prepared sample after being applied 20 V voltage for 0–24 h.
4. Conclusions

In summary, a new kind of superhydrophobic coating based on Ecoflex and graphene was prepared. As the ecoflex elastomer was used as the substrate, this coating exhibited high resilience and extensibility. Due to the high interfacial area of graphene, this coating retained superhydrophobicity even after being stretched to 300%. Furthermore, the graphene endowed excellent electrothermal performance to the composite, which could increase the surface temperature to 89.1 °C rapidly after applying 25 V. The combination of superhydrophobicity and electrothermal ability further led to excellent anti-icing property, which could melt 2.0 mm thick ice layer within 115 s. Moreover, this superhydrophobic coating demonstrated excellent mechanical and chemical durability, and outstanding thermostability.

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Data availability statement

All data that support the findings of this study are included with the article (and any supplementary files).

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