Article
Preparation of Transparent Sandwich-like Superhydrophobic Coating on Glass with High Stability and Self-Cleaning Properties

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Abstract: High stability and transparent superhydrophobic coating on a glass substrate that can effectively repel the wetting dust as a self-cleaning property are beneficial traits for solving the decrease in optical lens clarity in an unmanned underground mining environment. However, the transparent superhydrophobic coating has still not been applied due to the contradiction between visibility, hydrophobicity and durability. Herein, a sandwich-like superhydrophobic coating was designed and prepared on borosilicate glass, which consisted of a micro/nanostructure body of neutral silicone sealant (primer) and hydrophobic silica nanoparticles (interlayer), as well as a protective layer of ultraviolet (UV) gel. The coated glass exhibited excellent superhydrophobicity towards many aqueous solutions, and had highly visible light transparency of 80% at 4 wt.% primer mass content. Furthermore, significant tests including the droplet impact, hot water boiling, stirring in acetic acid aqueous solution and sandpaper abrasion were performed on our superhydrophobic coating, which indicated that the obtained transparent coating had good stability and excellent mechanical durability. The coated glass also showed a more wonderful self-cleaning property compared with that of the original glass. This superhydrophobic coating on glass substrate, fabricated by a facile and cost-effective layer-by-layer construction approach, has great potential for general and practical application in the unmanned mining environment under multiple dust and atomized water conditions.

Keywords: transparent superhydrophobic coating; sandwich-like; self-cleaning; stability; mechanical durability

1. Introduction

A dangerous amount of dust is always generated around the coal mining and anchor drilling face, which may lead to gas explosion and even seriously threaten production and safety [1–3]. Unmanned mining has thus attracted extensive attention from many experts and scholars, and despite being widely applied in the actual production process, it still suffers from significant issues which include the risk of a high concentration dust which can easily adhere to the glass lens and lower its visibility, especially under the high-pressure water atomization circumstances [4,5]. Inspired by the lotus leaf [6,7], artificial superhydrophobic surfaces with static contact angles (CAs) above 150° and sliding angles (SAs) below 10° have been successfully fabricated by various methods in recent years [8–14]. These functional surfaces have been proven to possess a self-cleaning property, demonstrating its potential application in coal production. This is because atomized water droplets falling on the superhydrophobic surface may be susceptible to capture, wrapping and taking away the hydrophilic pulverized coal dust particles. Thus, if further endowed with mechanical robustness, antireflection and transparency, the glass lens with superhydrophobicity may display good self-cleaning and high-resolution monitoring under harsh
atomization conditions, which would be beneficial for promoting the rapid development of intelligent mining technology.

From the publicly accessible literature, methods preparing the transparent superhydrophobic coating mainly include bottom–up (e.g., sol–gel, CVD and self-assembling); top–down (e.g., template-based and etching) and their combination (e.g., phase-separation) [15]. Based on the sol–gel process, Huang et al. [16] prepared spherical silica nanoparticles with a 40~50 nm diameter under acidic conditions and dip coated on the glass surface, which acquired the rough structure with the CAs above 160° and 95% transparency. Cai et al. [17] used candle ash as the template, chemically deposited methyltrimethoxysilane and prepared the rough nano spherical structure body on the glass surface, before removing it through high-temperature calcination to obtain transparent superhydrophobic coating. Chen et al. [18] proposed an effective theoretical model capable of predicting the coating surface roughness and CAs, and realized the self-assembling block polymer PS-b-PDMS body nanostructure and acquired the transparent superhydrophobic surface through annealing and plasma etching. Xu et al. [19] adopted the nickel plate etched by HNO3 solution as a template, based on the R2R technology, prepared the PDMS coating on the PET base materials and obtained excellent transparency and superhydrophobicity. Wang et al. [20] accurately etched a series of groove with a spacing of 50–75 µm on the glass surface, adopted a picosecond pulse laser, and successfully prepared the transparent superhydrophobic coating with a CA of 172° and average visible light transmittance of 87.28% through perfluorosilane modification. Based on the high temperature curing induced by the phase separation of silicon dioxide and PFA, Zhao et al. [21] created a stable rough transparent superhydrophobic structure on the glass surface. Although superhydrophobic coating transparency has now been successfully guaranteed, the contaminant media used and the reliance on advanced equipment, however, have limited the practical application of superhydrophobic material—which also provides a meaningful research topic.

Considerating the superhydrophobic coating instability mechanism under the thermal, mechanical, and chemical action, two strategies have been proposed to maintain the material durability and stability. On the one hand, one could protect the low surface energy material constructed on the coating surface integrity even under mechanical abrasion [22]. On the other hand, one could improve the micro/nanostructure body strength and its adhesion to substrates [23]. In order to realize the green and transparent superhydrophobic optical glass lens surface preparation with high stability and self-cleaning properties under the friction and adhesion of atomized wetted dust, in this work, we adopted the neutral silicone sealant, hydrophobic silica nanoparticles and UV gel as the primer, hydrophobic medium and protective layer, respectively, and we successfully constructed a sandwich-like structure body on the borosilicate glass surface with an easy and cost-effective spraying method. Moreover, based on the micro surface topography, 3D roughness, CAs, SAs and transmittance measurements clarified the influence of the primer mass content on wettability and transparency. Additionally, a series of stability and durability tests were creatively designed and conducted to accurately evaluate the impact of resistance, thermal and chemical stability and abrasive wear characteristic. Finally, the optical glass lens self-cleaning test was proposed to simulate the dense-pulverized coal dust and water atomizing environment under mining conditions to verify its excellent practical performance relevant to its self-cleaning ability and visibility. The success of the preparation of a facile and cost-effective green and robust transparent sandwich-like superhydrophobic coating and the application for unmanned coaling mining can expand the application field of superhydrophobic technology.

2. Materials and Methods

2.1. Materials

The hydrophobic silica nanoparticles with 20 nm diameter through sol–gel treatment used in the experiments were obtained from Juli metal material Co., Ltd. (Tianjin, China). Neutral silicone sealant mixed with PDMS, calcium carbonate, MTBS and KAT-245 (one of
the silane coupling agent), etc., was purchased from Longsun Silicon Material Technology Co., Ltd. (Dongguan, China). Ethyl acetate and ethanol of 99.7 wt.% were provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). UV gel composed of basic resin, active monomer and photoinitiator were provided by Heda new materials Co., Ltd. (Guangzhou, China). Borosilicate glass with average visible-light transmission above 92% were ordered from Guluo glass Co., Ltd. (Luoyang, China), whose surface performed hydrophilic properties and with an average CA of 27.4°.

2.2. Fabrication Process of the Superhydrophobic Coating and Protective Layer

Considering the silicone sealant’s strong bonding effect with nanoparticles and UV gel protective effect for the coating, the robust and transparent superhydrophobic glass coating fabrication include three procedures of pretreatment, superhydrophobic micro/nanostructure body preparation and protective layer construction, which are illustrated in Figure 1 [23].

Figure 1. Schematic illustration of preparing the sandwich-like superhydrophobic coating.

2.2.1. Pretreatment

In order to prevent the interference of the adhered pollutants, oil staining and other organic compounds on the superhydrophobic coating fabrication process, it is necessary to ultrasonically clean the glass surface with ethanol and deionized water for 20 min successively, before drying it for 1 h at 130 centigrade and reserved [24].

2.2.2. Fabrication of Superhydrophobic Micro/Nanostructure Body

Firstly, neutral silicone sealant needs to be fully dispersed in 20 mL ethyl acetate solution with different mass content levels (2 wt.%, 3 wt.%, 4 wt.%, 5 wt.%, 6 wt.%, 7 wt.%, 8 wt.%) through the treatment of 30 min ultrasonic vibration and 1 h magnetic stirring with 1500 rpm under ambient temperature conditions. We then adopted 20 mL ethyl acetate as the dispersant and 0.75 g silica nanoparticles as the hydrophobic medium, under the same dispersion process conditions, and prepared the superhydrophobic dispersion. Moreover,
we adjusted the distance between the spray pen atomizing nozzle to the glass surface to 150 mm, sequentially sprayed the superhydrophobic dispersion on the glass surface twice along one S-shaped trajectory and evenly under the 6 Bar air pressure, which was then then dried for 90 min at 130 centigrade.

2.2.3. Fabrication of UV Gel Protective Layer

Finally, in order to maintain the superhydrophobic micro/nanostructure body durability and stability, it is necessary to construct a protective layer coated on the superhydrophobic surface [25]. Sprayed the UV gel ethanol dispersant on the superhydrophobic layer then exposed the sample to ultraviolet irradiation for 1 h and solidification. Under the conditions of the primer layer preparation process, the coating mechanical firmness, transparency, facile, and cost-effective properties can be guaranteed.

2.3. Characterization

We adopted a JY-PHa contact angle meter (Suliang Instrument Technology Co., Ltd., Suzhou, China) to transfer a 10 µL deionized water droplet from a microsyringe to the borosilicate glass-coated surface and adjusted the platform to a certain inclination to slide the water droplet; randomly and evenly sampled five points on the glass surface to test the water CAs and SAs at ambient temperature conditions; and recorded the average values. The LH-221 transmittance tester (Lian huicheng Technology Co., Ltd., Shenzhen, China) with a measurement error below 1% and an adjustable illuminant wave length range was used to evaluate the visible, infrared, and ultraviolet light transmission of the superhydrophobic coating. In addition, the coating surface physical morphology, topography and roughness also can be tested, recorded and calculated with the LEXT OLS 4000 laser confocal microscope (OLYMPUS, Co., Ltd., Tokyo, Japan), PS50 surface profilometer (Nanovea Co., Ltd., Irvine, CA, America), and VHX5000 super field microscope (KEYENCE Co., Ltd., Osaka, Japan).

3. Results and Discussion

3.1. Wettability and Transparency of Coating

We adopted the CA and SA to evaluate the fabricated coating wettability and discussed the influence of the silicone sealant primer mass content, and the experimental results were recorded in Figure 2.

![Figure 2. Water CAs and SAs of the coated glasses with a different primer mass content.](image-url)
Due to the low surface roughness of the original glass smooth surface, the water droplet would spread on it and exhibited a low CA below 30°. However, when the primer mass content was 2 wt.%, the CA of the coated surface reached 149.6°. Due to the bonding effect between the primer and the hydrophobic silica nanoparticles, the coated surface became highly hydrophobic with a typical Wenzel state. This phenomenon illustrated that the proper rough structure is beneficial for the improvement of surface wettability [26]. However, the 43° SA was still at a high level and remained in the Wenzel state due to the loss of the air package. With the increase in primer content from 2 wt.% to 3 wt.%, superhydrophobicity was achieved; the water droplet pinning effect disappeared; the CA was significantly improved from 149.6° to 161.1°; and the SA decreased from 43° to 3°. In addition, by continually increasing the primer content in the range of 3 wt.%–6 wt.%, the large-scale fluctuations of CA and SA values did not occur, which illustrates that the prepared coating remained stably superhydrophobic in this interval. However, when the primer content exceeded 6 wt.%, the CA values of the coatings performed a slight reduction [27,28].

In addition to the water droplet, we also tested the as-prepared coating with other aqueous liquids such as fresh beer, pure milk, carbonated drinks and an aqueous solution of acid, alkali and salt, which all exhibited a spherical shape with high-level CAs and low-level SAs as shown in Figure 3.

![Figure 3](image_url)

**Figure 3.** Superhydrophobicity of the coated glass towards different aqueous solutions.

For a further explanation of the influence of the silicone sealant mass on the superhydrophobicity of the as-prepared coatings, it is necessary to examine the sandwich-like micro/nanostructural body morphological characteristics. The coating peak height distribution (Column 1 and 2, PS50 surface profilometer), 3D profile (Column 3, LEXT OLS 4000 laser confocal microscope) and surface morphology (Column 4, LEXT OLS 4000 laser confocal microscope) with a different primer content are presented in Figure 4, in which the 2 wt.% primer content is adopted, the hydrophobic silica nanoparticles covered on the silicone sealant surface are inhomogeneous and even some portions lack nanoparticle adhesion. From the surface topography, although the coating thickness distribution tends to be normal, the altitude difference of the peaks and valleys is small, which lowered the surface roughness to 155 nm. Because of this specific surface morphology characteristic, the air package is difficult to store and the coating is performed the Wenzel hydrophobic state. If the primer content is increased to 4 wt.%, despite the silica nanoparticles and silicone sealant agglomeration being more prone to occur, the surface coverage of nanoparticles and the coating surface roughness would all be increased and the coating surface profile height fluctuation would be smoother, so that the light cannot be scattered forwards and backwards. In addition, the increased primer content would lead to the enhanced bonding strength of the silica nanoparticles, which is beneficial for the formation of the micro/nanostructural body and the air package storage, and the coating surface hydrophobic state would convert from the Wenzel to Cassie, leading the coating to enter the superhydrophobic state and the water droplet pinning effect to disappeared. However, with the continuously increasing primer content, the CA rise and SA decline were all termi-
nated when the primer content exceeded 6 wt.%. To explore the termination mechanism, from the coating surface morphology optical pictures, there were two characterizations to be observed. Firstly, the coating surface thickness and height distribution peak value were more prone to the high level and the clustered structure body appeared. Secondly, the primer surface was almost completely covered with silica nanoparticles and still performed a uniform and consistent micro/nanostructure, even increasing the primer content to 8 wt.%, which illustrated that the termination of the CA and SA variation was mainly because of the saturation of the silica nanoparticles bonded and dispersed on the primer layer. However, it is worth noting that the CA values of the coatings performed a slight reduction in addition to an increase in the primer content when exceeding 6 wt.%, since massive nanoparticles were agglomerated and damaged its micro/nanostructure.

Figure 4. Surface morphology of the prepared coating with different primer amounts and no UV gel.

Then, the prepared transparent superhydrophobic borosilicate glass coating clarity was evaluated and characterized with ultraviolet–visible–infrared light transmission in the wavelengths of 365 nm, 380–760 nm and 940 nm, respectively. As plotted in Figure 5, the transmittance significantly varied with the different primer mass contents. In the visible light interval, the average transmittance of the original glass was 92.1%, which slightly decreased to 88.1% after constructing a layer of the micro and nanostructural body and a protective layer under the 2 wt.% primer content. From the optical pictures, the red school badge covered by the coated glass can be clearly seen if the primer content was lowered to 4 wt.%. In order to fabricate the transparent superhydrophobic coating, considering the Mie and Rayleigh scattering theory [29–31], it is necessary to ensure that the surface roughness is less than or approximately equal to the light source wavelength based on the coating surface morphology features and roughness measurement; the primer content increases from 2 wt.% to 5 wt.%; the coating surface roughness (Sa) ranges from 155 nm to 940 nm;
and when the primer content reaches 5 wt.%, the surface roughness value exceeds the visible spectrum range and the light can be scattered forwards and backwards (reflected), thus formatting a non-transparent surface.

![Figure 5. Light transparency of the coated glass with a different primer mass content.](image)

Based on the above analysis, the increase in the primer content will trigger the coating surface non-uniformization and increase the roughness, resulting in decreasing light transmittance. However, the low primer content will deteriorate the coating’s mechanical firmness and make the superhydrophobic layer prematurely fail. Therefore, 4 wt.% primer content can be chosen and provided for future studies.

3.2. Stability and Mechanical Durability

The prepared superhydrophobic coating stability and mechanical durability are essential for practical applications, especially for the unmanned operation in hazardous environments. In order to protect the coating to resist the external physical and chemical damage, the sandwich-like micro/nanostructural body fully utilized the silicone sealant strong bonding effect and UV gel protective effect under the consideration of the transparency requirements and colloid mutual solubility with the dispersant.

As illustrated in Figure 6a, in the water droplets’ impact test employed to evaluate the superhydrophobic coating’s mechanical durability, the distance between the injecting needle to the coated glass surface H was maintained as 0.5 m, and the gravitational acceleration g as 9.8 m/s². The velocity v of the droplet arriving at the glass surface can be calculated as 3.162 m/s, considering the free falling movement characteristic, which is shown in Equation (1). Additionally, the volume of the water jet in one impacting cycle can be set to 0.25 L:

\[ v^2 = 2gH \]  

(1)
Figure 6. The water droplets impacting test: (a) schematic diagrams; (b) micro-element division method of the water column; (c) water CAs versus the droplet amount; and (d) water SAs versus the droplet amount.

Considering the relationship between the water column impact strength and the falling height, it is necessary to discuss the calculation method of the pressure’s impact on the coated surface under the following assumptions:

1. The water column maintains a free falling movement and continuous flow;
2. The mechanical action mode of the coated surface and water column is inelastic vertical collision, and the rebound velocity \( v' \) is located between \( v \) and 0;
3. The water column mass distribution is uniform.

As shown in Figure 6b, the water column is divided across several mass elements in the flowing direction due to the \( \Delta L \) being infinitesimal, so these micro-elements can be simplified to standard cylinders. If the velocity is \( v \), the mass of this micro-element \( \Delta m \) can be calculated as Equation (2):

\[
\Delta m = \rho \Delta L S = \rho v \Delta t S
\]  

(2)

Based on the momentum theorem, assuming that the average impact force of the water column mass element and the coated surface is \( F \), and the reaction time is \( \Delta t \), the collision equation and the average impact pressure \( P \) can be expressed as Equation (3) and Equation (4)—while \( \rho \) and \( S \) represent the water column density and cross-sectional area, respectively:

\[
(F - \Delta mg) \Delta t = \Delta mv' - \Delta mv
\]

(3)

\[
P = \rho v (v' - v) + \rho v \Delta t
\]

(4)

As \( \Delta t \) approaches 0, the term of \( \rho v \Delta t \) can be ignored, and the average impact pressure can be acquired as 10 kPa and 20 kPa, respectively, if \( v' = 0 \text{ m/s} \) and \( v' = 3.162 \text{ m/s} \). Moreover, because of the inelastic vertical collision characteristic, the pressure values were located in the interval of 10 kPa–20 kPa. However, although under the high impact pressure level and 16 cycles impacting test, as the CAs and SAs are plotted in Figure 6c,d, the transparent glass coating maintained excellent stability, mechanical durability and superhydrophobicity.

Moreover, the thermal resistance, chemical stability and abrasive wear characteristic can be evaluated through the experiments of the hot water boiling test, acetic acid stirred test and sandpaper wear test.

As shown in Figure 7, the superhydrophobic coating thermal stability is extremely important in the application of hot-fluid transportation and heat-exchange; however, due to the fast evaporation and puncture of the air pockets entrapped within surface microstructures and the liquid surface tension reduced [32], the superhydrophobic coating surface state will convert from Cassie to Wenzel. As plotted in Figure 7b,c, the CAs and SAs were measured every 10 min under the 80 °C hot water boiling conditions, indicating that the water CAs fluctuated within a small range, from 157° to 141°. In addition, although the SAs performed within two zones with little amplitude fluctuation from 2.6° to 4.3°, this also exhibited a relatively stable and excellent superhydrophobic property.
In order to check the superhydrophobic coating chemical stability, we adjusted the ratio of the acetic acid to deionized water and prepared acetic acid aqueous solution with a pH of 2.4, performed an acid resistance test under the 1500 rpm magnetic stirring action, and examined the evolution of the CAs and SAs on borosilicate glass coating every 10–200 min, as shown in the results recorded in Figure 8a. Throughout the test, the CA maintained a similarly high level (above 155°), which illustrated that the fabricated coating resisted the acid corrosion and successfully retained its superhydrophobicity. In contrast, as illustrated in Figure 8c, the SA increased sharply to above 10° after 100 min and the water droplet pinning effect occurred, indicating that the air pockets entrapped in the micro/nanostructure body was fractured. This phenomenon also demonstrated that the damage of acid corrosion to the superhydrophobic surface seemed much more severe than that of high temperature.
an abrasive wear test was employed to evaluate the durability with a load pressure of 1 kPa on the #1000 sandpaper.

Figure 9. Sandpaper wear test under a pressure of 1 kPa (#1000 standard sandpaper) in the sandpaper abrasion test: (a) schematic diagram; and (b) water CAs versus the sandpaper abrasion distance.

Figure 9b presents the CAs’ evolution with the increase in the sandpaper abrasion distance and compared the morphology of the sandwich-like structure and single adhesive layer. It can be clearly seen that it consists of three zones. Zone I corresponds to the sliding distance between 0 m and 1.5 m if the sandwich-like micro/nanostructural body is successfully constructed on the original glass. Within this interval, the CAs remain substantially unchanged, meaning that the coating preserves relatively stable superhydrophobic properties because of the UV layer protection, which can also verify that there is no zone I if there is no protective layer. When the sliding distance exceeds 1.5 m, the CA begins to decrease sharply, implying that the UV protective layer is gradually destructive, and only the primer layer bonding effect played a mechanical role in adhering the silica nanoparticles. Significantly, the fitted curves are approximately parallel within this zone, which also confirmed the above conclusions. Finally, after the primer layer bonding effect failed, within zone III, the CA was maintained stable again with a low level below 110°, which meant the glass surface coating hydrophobicity failed. Moreover, the CA and the visible transmittance of the newly prepared coated glass surface all exceeded 150° (the sandwich-like structure was 158° and the single adhesive layer was 167°) and 75% (the sandwich structure was 75.4% and the single adhesive layer was 79.8%), but the superhydrophobicity and transparency of the coated glass surface with sandwich-like micro/nanostructures was slightly inferior to the surface of the single primer layer, which was because of the UV gel’s uneven spraying and the coverage effect on hydrophobic silica nanoparticles. Moreover, the performance comparison of the superhydrophobic transparent coating prepared in this paper and other recently published studies are listed in Table 1.

Table 1. The comparison of the superhydrophobic transparent coating prepared in this paper and in other recently published studies.

| Materials                     | Methods                              | CAs (°) | Transmittance (%) | Stability                                    |
|-------------------------------|--------------------------------------|---------|-------------------|----------------------------------------------|
| Modified SiO₂ [33]            | Self-assembly process                | 161.5   | 83.13             | Excellent sand, water jet and corrosive media resistance |
| Fluorinated silica multi-walled carbon nanotubes [34] | Spray-drying                        | 159     | 75                | Low                                          |
| SiO₂, PMMA [35]              | Sol–gel and Template-based method    | 152     | 93                | Low                                          |
| Silica nanowires [36]         | CVD                                  | 158     | 89                | Displayed antifogging properties, Exhibited a good resistance to acidic and basic solutions over a wide range of pH values |
| Silica nanoparticles, FAS [37]| Alkaline etching                      | 150     | 79                | Excellent sand and water jet and scratch resistance |
| Silicone oils, SiO₂ [38]      | LISS                                 | 110     | -                 | Highly hot water, pH liquids and scratch resistance |
| Silica glass [39]            | Femtosecond laser and modify         | 150     | 92                | Excellent sand and water jet resistance |
| SiO₂ and COP [40]             | Dip-coating                          | 150     | 87                | Excellent sand and water jet resistance |
3.3. The Self-Cleaning Performance Evaluation

Because of the coal measure mudstone hydrophilicity, atomized water droplets are easy to capture and the floating pulverized coal dust adheres to the optical glass lens surface, which deteriorates the unmanned operating environment’s visibility and triggers safety accidents. Fortunately, the micro/nanostructure body of the prepared transparent and robustness coating can repel the atomized water droplets’ adhesion and accelerate spheroidization with a small sliding angle. As shown in Figure 10a,e, we adopted pulverized coal with 80 nm particle size to simulate the floating dust under the mining conditions and spread over the prepared coated and original glass surface, respectively. The rolling water droplet with 1 mL volume supplied by a syringe can continuously carry away the dust on the coated surface and leave a self-cleaning channel after 40 water droplets, as plotted in Figure 10b–d. However, due to the original glass surface hydrophilicity, water droplets only can wet the dust and wrap it as illustrated in Figure 10f–h; once the droplets have evaporated, the dust will adhere and contaminate the glass surface, and deteriorate the machine vision.

Moreover, if the adhered powder or dust on the glass is water soluble, the self-cleaning process may vary. As illustrated in Figure 11a–d, the layer of sodium bicarbonate covered on the coated glass surface was soluble and rolled away along one self-cleaning channel in the spherical shape because of the large CA and low SA. In addition, after 20 water droplets, the channel is completely clean and no damage and water logging are observed. Despite the sodium bicarbonate covered on the original glass surface was also soluble and washed away after 50 water droplets as shown in Figure 11e,f, but the water logging remained on the glass surface throughout the experimental process due to the hydrophilic state, which will deteriorate the transparent glass visibility and fail the optical glass lens applicability.
Figure 11. Self-cleaning test on different substrates after sodium bicarbonate contaminations: (a–d) the coated glass; and (e–h) the original glass.

Moreover, in order to simulate the actual working circumstances of mines, in this work, the optical glass lens self-cleaning test was creatively designed under the dense-pulverized coal dust and water atomizing environment to verify the prepared superhydrophobic coating’s applicability. Figure 12a illustrated the experimental system, adopted a minimum quantity lubrication system to continuously provide atomizing water droplets and adjusted the water flow velocity and pressure to 250 mL/h and 0.5 Bar, respectively. Under the external vibration effect, the pulverized coal with 80 nm particle size fell into the spraying environmental field and floated around. A monocular lens was electronically assembled with 0.7 × 4.5 zoom and a Panasonic CMOS sensor with 38 megapixels, which treated the outermost layer of the lens with superhydrophobicity and performed the light filling operation once placed in the constructed environment.

Figure 12. Self-cleaning test under the simulated working circumstances: (a) device diagram; (b) the coated glass; and (c) the original glass.

Under the atomizing environment, continuous shooting was employed which recorded massive screenshots in 10 min and compared the optical clarity difference between the coated and original lens surface. As illustrated in Figure 12b,c, it can be seen that the clarity
of the newly prepared coated and original glass surface significantly varied due to the sandwich-like micro/nanostructural body overlap and the surface roughness rise. After 1 min atomization spray of water, a small amount of pulverized coal dust adhered to and covered the glass surface due to the hydrophilicity of the original glass and some water stains could be found, but its visible light transmittance was still higher than that of the coated glass. However, after 3 min, the uncoated glass surface had more dust adhered to it so that the red school badge was not clearly visible, and even after 10 min, the surface was completely covered and lost its visibility. Due to the superhydrophobicity, the increased surface tension made the water droplets contact the coating spheroidization and took away the pulverized coal dust adhering to the glass surface and achieved surface self-cleaning function. Therefore, although the coated glass surface gradually became vague because of the increased volume of atomized water around the experimental environment, but there was still no dust adhesion occurrence and acceptable levels of visible light transmittance and visibility were maintained. Moreover, we also repeated the experiments 10 times, and the optical glass lens maintained their clear visibility and self-cleaning ability if the ultrasonic cleaning was performed after each test.

4. Conclusions

A green, robust and transparent sandwich-like superhydrophobic coating was successfully prepared by the layer-by-layer spraying method. The increase in the primer amount will trigger the coating surface’s non-uniformization and increase the roughness, which results in decreased light transmittance. However, a low primer amount will deteriorate the coating mechanical firmness and make the superhydrophobic layer fail prematurely. Then, the impact resistance, thermal stability, chemical stability and abrasive wear characteristic were evaluated due to the silicone glass sealant’s strong bonding effect and UV gel protective effect, whilst the prepared coating maintained excellent stability and mechanical durability. Moreover, the optical glass lens self-cleaning test was creatively carried out under the dense-pulverized coal and water atomizing conditions; and the experimental results are available for expanding the superhydrophobic surface’s application range and resolving the machine vision’s inferior visibility during the unmanned mining process.

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References

1. Liu, T.; Liu, S. The impacts of coal dust on miners’ health: A review. Environ. Res. 2013, 190, 109849. [CrossRef] [PubMed]
2. Guo, C.; Shao, H.; Jiang, S.; Wang, Y.; Wang, K.; Wu, Z. Effect of low-concentration coal dust on gas explosion propagation law. Powder Technol. 2020, 367, 243–252. [CrossRef]
3. Li, B.; Li, M.; Gao, W.; Bi, M.; Ma, L.; Qin, Q.; Shu, C. Effects of particle size on the self-ignition behaviour of a coal dust layer on a hot plate. Fuels 2020, 260, 116269. [CrossRef]
4. Han, F.; Zhang, J.; Zhao, Y.; Li, J. Dynamic wetting characteristics of droplets on spherical dust surface. *J. China Coal. Soc.* 2021, 46, 2614–2622. [CrossRef]

5. Chai, Z.; Zhang, H.; Yang, P.; Yang, Z.; Zhang, B. Molecular dynamics simulation of the effect of temperature and pressure on water absorption characteristics of kaolinite. *J. China Coal. Soc.* 2021, 46, 2537–2564. [CrossRef]

6. Alshehri, A.; Champagnon, P.; Keirnsbuckl, L.; Dogheche, E.H. Nanotechnology to Improve the Performances of Hydrodynamic Surfaces. *Coatings* 2019, 9, 808. [CrossRef]

7. Lin, Y.; Chen, H.; Wang, G.; Liu, A. Recent Progress in Preparation and Anti-Icing Applications of Superhydrophobic Coatings. *Coatings* 2018, 8, 208. [CrossRef]

8. Wang, Z.; Song, J.; Wang, T.; Wang, H.; Wang, Q. Laser Texturing for Superwetting Titanium Alloy and Investigation of Its Erosion Resistance. *Coatings* 2021, 12, 1547. [CrossRef]

9. Xu, S.; Wang, Q.; Wang, N.; Zheng, X. Fabrication of superhydrophobic green surfaces with good self-cleaning, chemical stability and anti-corrosion properties. *J. Mater. Sci.* 2019, 54, 13006–13016. [CrossRef]

10. Yi, Z.; Zhao, B.; Liao, M.; Qin, Z. Fabrication of Superhydrophobic Wood Surface by Etching Polydopamine Coating with Sodium Hydroxide. *Coatings* 2020, 10, 847. [CrossRef]

11. Zhang, Z.; Shen, Z.; Wu, H.; Li, L.; Fu, X. Study on Preparation of Superhydrophobic Ni-Co Coating and Corrosion Resistance by Sandblasting–Electrodeposition. *Coatings* 2020, 12, 1164. [CrossRef]

12. Kim, M.K.; Yao, W.; Cho, Y.R. Fabrication of superhydrophobic surface with hierarchical structure by thermal imprinting and spraying. *Colloid Surf. A* 2022, 634, 694. [CrossRef]

13. Qu, J.E.; Xu, C.; Nie, C.; Wang, H.; Cao, Z.; Li, Y.; Wang, X. A new environmentally friendly approach to prepare superhydrophobic colored stainless steel surface for decoration, anti-corrosion and self-cleaning. *J. Mater. Sci.* 2020, 56, 854–869. [CrossRef]

14. Zheng, Z.; Liao, C.; Xia, Y.; Cai, W.; Xie, C.; Zhang, W.; Liu, Y. Facile fabrication of robust, biomimetic and superhydrophobic polymer/graphene-based coatings with self-cleaning, oil-water separation, anti-icing and corrosion resistance properties. *Colloid Surf. A* 2021, 627. [CrossRef]

15. Shen, K.; Ly, X.; Jia, Y.; Jin, G.; Huang, Y.; Hou, R.; Fu, J.; Shi, S. Research progress of transparent superhydrophobic surface. *Surf. Technol.* 2021, 50, 108–119. [CrossRef]

16. Huang, W.H.; Lin, C.S. Robust superhydrophobic transparent coatings fabricated by a low-temperature sol–gel process. *Appl. Surf. Sci.* 2014, 305, 702–709. [CrossRef]

17. Cai, Z.; Lin, J.; Hong, X. Transparent superhydrophobic hollow films (TSHFs) with superior thermal stability and moisture resistance. *RSC Adv.* 2018, 8, 491–498. [CrossRef]

18. Cheng, L.C.; Simonatis, J.W.; Gadelrab, K.R.; Tahir, M.; Ding, Y.; Alexander-Katz, A.; Ross, C.A. Imparting Superhydrophobicity with a Hierarchical Block Copolymer Coating. *Small* 2019, 16. [CrossRef] [PubMed]

19. Xu, W.; Yi, P.; Gao, J.; Deng, Y.; Peng, L.; Lai, X. Large-Area Stable Superhydrophobic Poly(dimethylsiloxane) Films Fabricated by Thermal Curing via a Chemically Etched Template. *ACS Appl. Mater. Interfaces* 2020, 12, 3042–3050. [CrossRef] [PubMed]

20. Wang, B.; Hua, Y.; Ye, Y.; Chen, R.; Li, Z. Transparent superhydrophobic solar glass prepared by fabricating groove-shaped arrays on the surface. *Appl. Surf. Sci.* 2017, 427, 957–964. [CrossRef]

21. Zhao, S.; Zhao, J.; Wen, M.; Yao, M.; Wang, F.; Huang, F.; Zhang, Q.; Cheng, Y.; Zhong, J. Sequentially Reinforced Additive Coating for Transparent and Durable Superhydrophobic Glass. *Langmuir* 2018, 34, 11316–11324. [CrossRef]

22. Zhu, G.; Zhao, Y.; Liu, L.; Wang, L.; Wang, J.; Yu, S. Facile fabrication and evaluation of self-healing Zn-Al layered double hydrogen superhydrophobic coating on aluminum alloy. *J. Mater. Sci.* 2021, 56, 14803–14820. [CrossRef]

23. Lu, Y.; Sathasivam, S.; Song, J.; Crick, C.R.; Carmalt, C.J.; Parkin, I.P. Robust self-cleaning surfaces that function when exposed to either air or oil. *Science 2015*, 347, 1132–1135. [CrossRef] [PubMed]

24. Gao, L.; McCarty, C.W. How Wenzel and Cassie Were Wrong. *Langmuir* 2007, 23, 3762–3765. [CrossRef]

25. Sebastian, D.; Yao, T.J.; Nipa, L.; Lian, I.; Twu, G. Corrosion Behavior and Mechanical Properties of a Nanocomposite Superhydrophobic Coating. *Coatings* 2021, 11, 652. [CrossRef]

26. Ke, C.; Li, Z.; Zhang, C.; Wu, X.; Zhuo, Z.; Jiang, Y. Investigation of the Effects of Component Ratios on the Properties of Superhydrophobic Polyurethane/Fluorinated Acrylic Co-Polymer/SiO2 Nanocomposite Coatings. *Coatings* 2021, 11, 174. [CrossRef]

27. Chatzigrigoriou, A.; Karapanagiotis, I.; Poulios, I. Superhydrophobic Coatings Based on Siloxane Resin and Calcium Hydroxide Nanoparticles for Marble Protection. *Coatings* 2020, 10, 334. [CrossRef]

28. Manoudis, P.N.; Karapanagiotis, I.; Tsakalof, A.; Zouburtikidis, I.; Panayiotou, C. Superhydrophobic Composite Films Produced on Various Substrates. *Langmuir* 2008, 24, 11225–11232. [CrossRef] [PubMed]

29. Niskanen, I.; Forsberg, V.; Zakrisson, D.; Reza, S.; Hummelgård, M.; Andrés, B.; Fedorov, I.; Suopajärvi, T.; Liimatainen, H.; Thungström, G. Determination of nanoparticle size using Rayleigh approximation and Mie theory. *Chem. Eng. Sci.* 2019, 201, 222–229. [CrossRef]

30. Hříbalová, S.; Pabst, W. Light scattering in monodisperse systems—from suspensions to transparent ceramics. *J. Eur. Ceram. Soc.* 2020, 40, 1522–1531. [CrossRef]

31. León, J.M.; Pura, J.L.; Bernardo, V.; Reza, S.; Rodríguez-Pérez, M.A. Transparent nanocellular PMMA: Characterization and modeling of the optical properties. *Polymer* 2019, 170, 16–23. [CrossRef]

32. Liu, Y.; Chen, X.; Xin, J. Can superhydrophobic surfaces repel hot water? *J. Mater. Chem.* 2009, 31, 5457–5668. [CrossRef]
33. Lyu, J.; Wu, B.; Wu, N.; Peng, C.; Yang, J.; Meng, Y.; Xing, S. Green preparation of transparent superhydrophobic coatings with persistent dynamic impact resistance for outdoor applications. *Chem. Eng. J.* 2021, 15, 126456. [CrossRef]

34. Shi, C.; Wu, Z.; Xu, J.; Wu, Q.; Li, D.; Chen, G.; He, M.; Tian, J. Fabrication of transparent and superhydrophobic nanopaper via coating hybrid SiO2/MWCNTs composite. *Carbohydr. Polym.* 2019, 1, 115229. [CrossRef] [PubMed]

35. Han, Z.; Wang, Z.; Li, B.; Feng, X.; Jiao, Z.; Zhang, J.; Zhao, J.; Niu, S.; Ren, L. Flexible Self-Cleaning Broadband Antireflective Film Inspired by the Transparent Cicada Wings. *ACS Appl. Mater. Interfaces* 2019, 11, 17019–17027. [CrossRef]

36. Tsai, Y.C.; Shieh, J. Growing invisible silica nanowires on fused silica plates provides highly transparent and superwetting substrates. *Appl. Surf. Sci.* 2019, 15, 619–625. [CrossRef]

37. Yokoi, N.; Manabe, K.; Tenjimbayashi, M.; Shiratori, S. Optically Transparent Superhydrophobic Surfaces with Enhanced Mechanical Abrasion Resistance Enabled by Mesh Structure. *ACS Appl. Mater. Interfaces* 2015, 8, 4809–4816. [CrossRef]

38. Gurav, A.B.; Shi, H.; Duan, M.; Pang, X.; Li, X. Highly transparent, hot water and scratch resistant, lubricant-infused slippery surfaces developed from a mechanically-weak superhydrophobic coating. *Chem. Eng. J.* 2021, 15, 127809. [CrossRef]

39. Lin, Y.; Han, J.; Cai, M.; Liu, W.; Luo, X.; Zhang, H.; Zhong, M. Durable and robust transparent superhydrophobic glass surfaces fabricated by a femtosecond laser with exceptional water repellency and thermostability. *J. Mater. Chem. A* 2018, 6, 9049–9056. [CrossRef]

40. Liu, Y.; Xu, Q.; Lyongs, A.M. Durable, optically transparent, superhydrophobic polymer films. *Appl. Surf. Sci.* 2019, 15, 187–195. [CrossRef]