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Doping and Superhydrophobic Modification for Improving Marine Antifouling Performance of Alkali-Based Geopolymer Coating

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Abstract: Although pure alkali-activated materials (AAMs) only depend on high alkalinity to resist biological pollution, the effects of which are inadequate, it is essential to add cuprous oxide to reinforce the antifouling effect. In this paper, triethoxycaprylsilane (TTOS) was used as a superhydrophobic modifier that was copolymerized with the exposed hydroxyl groups on the alkali-based geopolymers coating and then generated micro/nanostructures. Therefore, superhydrophobic geopolymer coating can achieve long-lasting controlled release of Cu²⁺ by controlling the inflow and outflow of water to achieve the aim of extending the antibiofouling life of coating when cuprous oxide is added to alkali-based geopolymer.

Keywords: alkali-activated geopolymers; superhydrophobic; stability; cuprous oxide; controlled release



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1. Introduction

Marine biofouling is considered one of the major culprits responsible for the excessive cost of marine industries and corresponding underwater equipment problems [1]. It is caused by the community of organisms that settle and grow on the external surfaces of submerged objects [1,2]. Marine biofouling occurs in four stages: (1) A slime layer, also called the base membrane, which is ascribed to the aggregation of organic molecules and inorganic compounds on the surface of the matrix [3]. (2) The microorganisms deposited on the base membrane react with extracellular macromolecules and form a biofilm on the surface of the base membranes [3]. (3) The algal spores and protozoa reattach to the biofilm. (4) Large fouling organisms, such as barnacles and bryozoans, attach to the surface of the biofilm, where they grow and reproduce quickly [3–5]. Marine antifouling technologies, mainly including physical methods (ionizing rays, ultrasonic, etc.) and chemical measures (coating method), have been proposed to solve the issue of marine antifouling [4]. Physical methods cannot be applied on a large scale due to complex equipment. Surface protection layer methods using antifouling agents can successfully reduce the attachment of fouling organisms [5,6]. Therefore, surface protection layers with antifouling agents have been widely applied in marine environments due to their broad antibacterial spectrum [7]. Currently, the main antifouling agents are iron oxide, lead tetroxide, mercury oxide, zinc oxide, organic amine antifouling agents, organic tin antifouling agents, and so on [3]. In recent years, Marine corrosion prevention has generally extended its service life using organic coatings to protect the substrate from seawater erosion and other corrosion phenomena [8,9]. However, they often have poor phenotypes in the face of harsh environments, which greatly reduces the corrosion resistance and service life of the coatings [10]. From the comprehensive consideration of the preparation process,

cost-effectiveness, toxicity, antifouling activity, and other aspects, cuprous oxide is usually used as an antifouling agent in the surface protection layer and is further applied in practical applications [7]. However, the traditional protective layer with cuprous oxide is prone to a sudden explosive release of Cu^{2+} in the initial stage [11]. The release rate of Cu^{2+} is generally unstable and uncontrollable, leading to local Cu^{2+} pollution as well as degradation of the antifouling effect, which threatens the long-term antibiofouling performance. Thus, a high content of antifouling agent must be added to a single antifouling surface protection layer to maintain the antifouling effect, which would pollute the surrounding marine environment and increase the cost [12]. Accordingly, under the premise of ensuring the antifouling effect in the antibiofouling layer, current efforts are mainly devoted to reducing the dosage and the release rate of antifouling agents [7]. The pore structure and the inflow and outflow of water are regarded as two crucial factors for controlling the release rate [13]. To the best of our knowledge, detailed studies on the effect of hydrophobic structures on the controlled release of cuprous oxide have not been reported thus far. Therefore, it is urgent to develop a superhydrophobic material with a controlled release of Cu^{2+} to fill the gap in related fields. Owing to their excellent chemical stability, corrosion resistance, mechanical properties, low cost and green low carbon, alkali-activated materials are widely used in structural materials [12–16]. In addition, alkali-activated materials with a high pH due to many unreacted alkali metal ions in the pores could render the material surfaces unsuitable for the growth of the community of organisms. Therefore, alkali-activated materials have powerful application potential in the surface protection of marine infrastructure (marine coatings, marine concrete, etc.).

Herein, we fabricated a superhydrophobic alkali-activated slag material doped with cuprous oxide as a surface antifouling protection material for marine structures. The present study successfully demonstrated the feasibility of lowering the release rate of Cu^{2+} due to superhydrophobic modification. This study is expected to introduce an effective way to prepare durable, environmentally friendly, and practical superhydrophobic antifouling protection materials.

2. Materials and Methods

2.1. Materials

Ground granulated blast furnace slag (GGBS) with irregular sheets and a mean size of approximately 10 μm was provided by Beihai Chengde Steel Company (Beihai, China). The chemical compositions of the slag were CaO , 43.40%; SiO_2 , 27.28%; Al_2O_3 , 3.22%; MgO , 9.95%; SO_3 , 1.75%; TiO_2 , 1.17%; K_2O , 0.60%; Na_2O , 0.54%; Fe_2O_3 , 0.29%; MnO , 0.13% and 0.01% LOI, which were determined by X-ray fluorescence (XRF). The SEM figure is shown in Figure 1a. Triethoxycaprylsilane (TTOS) ($\text{C}_{14}\text{H}_{32}\text{O}_3\text{Si}$ > 97%, AR) was supplied by Macklin Biochemical Technology Co., Ltd. (Shanghai, China). Commercial cuprous oxides with irregular shapes were delivered by Yexindun Alloy Co. LTD (Beijing, China). The SEM figure is shown in Figure 1b. Dry powder water glass (modulus $M = 2.8$ ($\text{SiO}_2/\text{K}_2\text{O}$ molar ratio)) was produced by the Zhongfa Water Glass Factory (Foshan, China). Q235 steel (Fe > 99%) and glass slides were acquired from Guantai Metallic Materials Co., Ltd. and Fangyuan Technology Co., LTD (Guangdong, China). Quartz sand (200 mesh) was provided by Ming Hai Environmental Protection Company (Shenzhen, China). *Phaeophyta tricornutum* was purchased from Xingxing Live Bait Company (Foshan, China). *Staphylococcus aureus* comes from Xinzhong Biological Engineering Co., LTD (Shanghai, China). Deionized water was prepared in the laboratory. All the raw materials were used directly without any further purification.

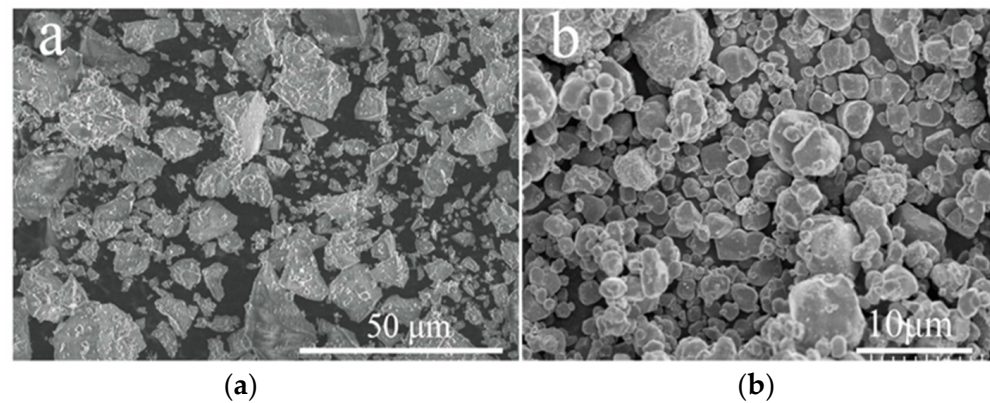


Figure 1. SEM of GGBS (a) and Cu_2O (b).

2.2. Fabrication of Superhydrophobic Alkali-Activated Materials Coating

The procedure for preparing the original geopolymers is shown in Figure 2. The preparation method of the original geopolymers referred to our previous works [17]. Quartz sands were added to improve the cracking resistance and roughness of the samples. The raw materials were slag, sodium silicate powder, quartz sand, and Cu_2O with a mass ratio of 10:3:20:1.3. First, the raw materials were placed in a plastic beaker, and then deionized water was added to adjust the liquid-to-solid ratio to 35 wt.%. After that, the composite slurry was stirred at 800 r/min for 5 minutes with a high-speed magnetic stirrer. Finally, the geopolymers were fabricated by brushing fresh paste on the substrate (Q235 steel or glasses) with a spatula and cured at a room temperature of 25 °C and 80% humidity without sealed conditions. The substrate was cleaned with acetone and polished with 400 sandpaper before use. The obtained geopolymers with Cu_2O were called GP- Cu_2O . For comparison, pure geopolymers without Cu_2O , which are referred to as GP, were prepared on the same substrate and cured under the same conditions.

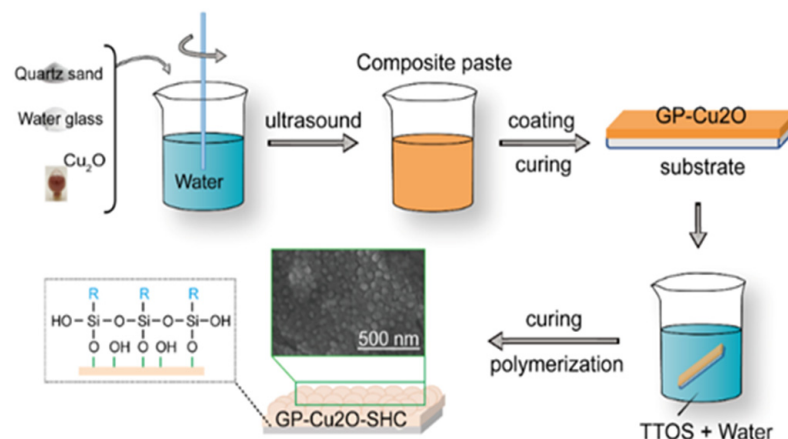


Figure 2. Schematic diagram of the preparation of GP- Cu_2O and GP- Cu_2O -SHC.

2.3. Preparation of Superhydrophobic Geopolymers

A schematic of the superhydrophobic modification is shown in Figure 2. First, the TTOS mixture composition (TTOS: deionized ratio water was 1.6 g:165 g) was ultrasonicated for 1 hour to prepare the modified fluid.

Then, the abovementioned GPs and GP- Cu_2O were immersed in modified composition fluid for 1 hour at room temperature of 25 °C and 80% humidity. Finally, the samples were dried at room temperature of 25 °C and 80% humidity without sealed conditions and then named GP-SHC and GP- Cu_2O -SHC, respectively.

2.4. Characterization

A contact angle meter (KRUSS, Germany, drop volume of approximately 3 μ L) was used to determine the hydrophobicity and superhydrophobicity of the resultant samples. The Hitachi SU822 (Hitachi, Tokyo, Japan) field emission scanning electron microscope (FE-SEM) system was equipped with an energy dispersive spectroscopy (EDS) system, and an FEI Quattro S (FEI, Hillsboro, OR, USA) FE-SEM was used to analyze the structure and composition of the samples at an accelerated voltage of 10.0 kV. The chemical structure of the samples was measured by Fourier transform infrared spectroscopy (FT-IR IRTracer-100, Shimadzu, Kyoto, Japan, and FT-IR Nicolet iS50, Thermo Fisher Scientific, Waltham, MA, USA). The crystal structure of the sample was characterized by X-ray diffraction analysis (XRD, Rigaku MinFlex 600, Rigaku, Tokyo, Japan). The microstructure of the surface area and the porosity were obtained from a nitrogen absorption method on a Gemini VII device (Micromeritics Instrument Corp., Norcross, GA, USA). The pH value of the sample and its leaching solution was determined with a pH meter (PHS-3E, Shanghai Yidian Scientific Instrument Co., Ltd., Shanghai, China). The mean pore size was calculated by the Barrett–Joyner–Halenda (BJH) method.

The samples were cured at room temperature for 7 days, and their water absorption rate was measured. For the accuracy of the experiment, the sample needs to be placed in a dryer at 60 °C for 1 day and then immersed in distilled water. The mass increase during soaking was recorded by weighing. The relationship in Equation (1) [7] was used to assess water absorption.

$$\text{Water absorption rate} = (M_2 - M_1) / M_1 \times 100\% \quad (1)$$

where M_1 is the sample mass after drying for 1 day, and M_2 is the sample mass after soaking. The antifouling materials with Cu_2O release Cu_2O particles into seawater in the initial state. Then, Cu^+ is oxidized to Cu^{2+} as Cu_2O reacts with hydrogen ions, chloride ions, and oxygen in the ocean, and Cu^{2+} can induce the denaturation of biological proteins to achieve antifouling properties [18]. The Cu^{2+} release rates of GP- Cu_2O and GP- Cu_2O -SHC samples in artificial seawater were determined by inductively coupled plasma absorption spectroscopy (ICP, Optima8000) from PerkinElmer Instrument Co., Ltd. (Waltham, MA, USA) and an ICP–AES (ICPS-7510) instrument from Shimadzu, Japan, under laboratory conditions. The prepared 5 cm $\times$ 5 cm samples were soaked in 200 mL artificial seawater, and then 10 mL artificial seawater was taken every 24 h. At the same time, 10 mL of fresh artificial seawater was added. In addition, 200 mL of fresh artificial seawater was replaced after an interval of 48 h.

2.5. Antifouling and Antibacterial Analysis

The antibacterial performance of the samples was tested by cocultivation and plate sample counting methods with *Staphylococcus aureus*. First, *Staphylococcus aureus* was cocultured with the samples for 48 h and then eluted. Then, the diluted eluate was spread on a solid medium and cultured at 37 °C for 18 h in a constant temperature incubator. Finally, the antibacterial activity was compared with the number of bacteria. Excessive alkaline substances dissolved from the surface of the original AAMs with rich active hydroxyl groups, which hindered the growth of *Staphylococcus aureus* [19,20].

Phaeophyta tricornutum, as a typical marine alga, is usually selected to evaluate the antibiofouling performance of samples. The samples were immersed in *Phaeophyta tricornutum* solution and incubated for 3 days and 7 days. Next, all samples were rinsed with artificial seawater 3 times to remove weakly adherent *Phaeophyta tricornutum*. Finally, a scanning electron microscope was used to observe the settlement of algae.

3. Results

3.1. Antibacterial and Antifouling Performance of GP and GP-SHC

The bacterial numbers of the GP and GP-SHC surfaces are shown in Figure 3a. As predicted, GP samples unveiled a strong antibacterial effect when they were not immersed, and the count of colonies was only 1.4×10^8 CFU/mL. The antibacterial properties of the GP-SHC materials were slightly lower than those of the GP materials without soaking, whose colony count was 3.0×10^8 CFU/mL when the samples were not soaked. Obviously, the most important reason for the high antibacterial property of GP samples before immersion in water is their high alkalinity, thus strongly hindering the growth of bacteria [19,20]. The GP-SHC samples have a worse antibacterial effect than GP in the initial stage due to the superhydrophobicity preventing water in air entry into GP-SHC materials to avoid leaching alkali metal ions. After the samples were immersed in artificial seawater for 3 days, the antibacterial effects of GP and GP-SHC all dropped vastly, with colony counts of 8.6×10^8 CFU/mL and 7.4×10^8 CFU/mL, respectively, because the GP and GP-SHC samples were merely dependent on surface alkalinity. As shown in Figure 3b, with increasing soaking time, a large number of alkali metal ions in the pores were dissolved, which led to a sharp reduction in the surface alkalinity over time for the first three days of immersion. Then, with the continuous increase in immersion time, the surface alkalinity of GP remained steady, resulting in the antibacterial properties of GPs not varying after 30 days. Overall, the GP showed a strong antibacterial effect in a short period of time. However, it cannot maintain a long-lasting high-efficiency antibacterial effect because water continues to enter the pores and brings out a large number of alkali-soluble ions, which leads to a sharp decrease in alkalinity in a short time. The GP-SHC prolonged its antibacterial life, but its antibacterial performance was still insufficient. Therefore, it is necessary to add cuprous oxide to strengthen the antibacterial properties of AAMs.

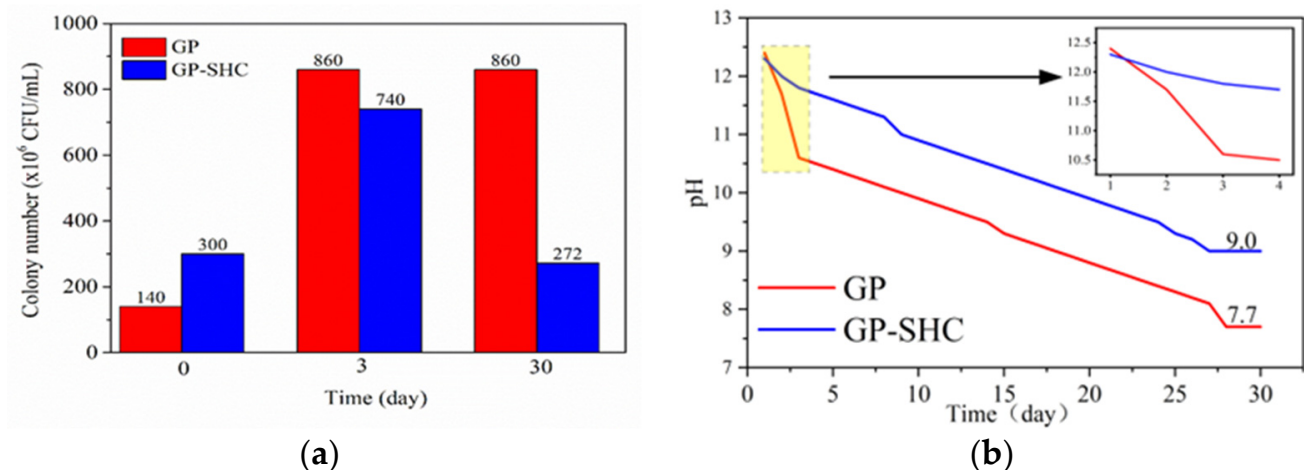


Figure 3. (a) Antibacterial (*Staphylococcus aureus*) performance and (b) pH of samples (GP, GP-SHC) under different soaking times (0 days, 3 days, 30 days).

SEM images of the prepared samples after immersion in *Phaeophyta tricornutum* culture medium for 3 days and 7 days under static conditions are shown in Figure 4. As shown in Figure 4(a-3,b-3), a few algae can be observed on the GP surface, and there were no algae on the GP-SHC surface. Figure 4(a-7,b-7) shows that obvious algal species were adsorbed on the GP sample surface, while no traces of algae were seen on the surface of GP-SHC after being immersed for 7 days, which indicates that superhydrophobic modification can also effectively suppress biofouling. The test confirmed that the GP-SHC samples had obvious anti-algae attachment performance compared with the GP samples.

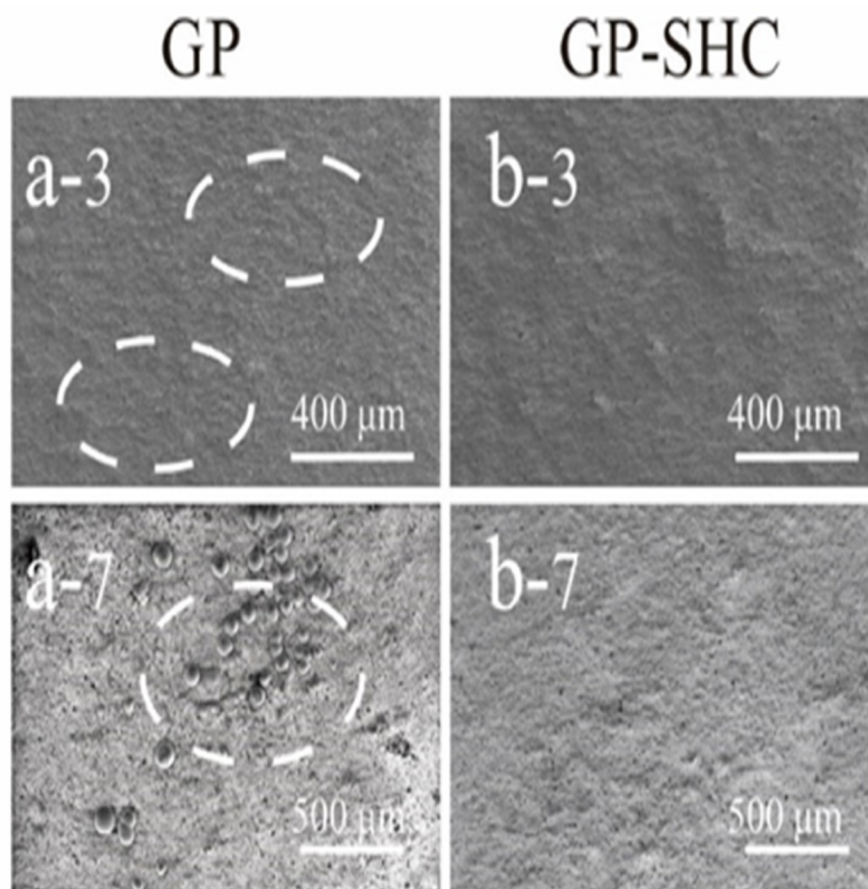


Figure 4. SEM images of samples (GP, GP-SHC) after immersion in a static culture medium inoculated with *Phaeophyta tricornutum* for 3 days and 7 days.

3.2. Wettability of GP-Cu₂O and GP-Cu₂O-SHC

The nonwettability characteristics of the samples were assessed by images of water droplets and the static contact angle (CA). Available studies have confirmed that the cured original AAMs are hydrophilic due to their surface containing many hydroxyl groups. Water droplets would quickly fall into the coating after touching the surface. The GP-Cu₂O surface CA was 81.3° (Figure 5a), which is close to a hydrophobic surface. We hold the opinion that the filler insertion of Cu₂O provided superhydrophobic particles that can improve the hydrophobicity of the samples. Images of water droplets on the GP-Cu₂O-SHC samples are shown in Figure 5b,c. As observed in Figure 5b,c, the water droplets of actual photographs on the surfaces and bottom of the GP-Cu₂O-SHC samples all exhibit regular spheres. The CA value of the GP-Cu₂O-SHC sample surfaces reached 153.4° (Figure 5b). Therefore, it confirms that the GP-Cu₂O-SHC samples display excellent superhydrophobicity after chemical modification.

Moreover, the prominent superhydrophobicity of the GP-Cu₂O-SHC samples was also demonstrated by testing its nonsticking property using a contact angle meter with an untreated injector needle. The process of approach, contact, squeezing, lifting, and departure of the water droplet is displayed in Figure 6a–e. The water droplet cannot adhere to the superhydrophobic surface even though the water droplet is squeezed to deform, demonstrating the excellent nonsticking property of the GP-Cu₂O-SHC. Figure 6f shows that water droplets retain their spherical shape on the newly exposed surface of GP-Cu₂O-SHC, which proved that GP-Cu₂O-SHC surfaces still maintain a superhydrophobic surface after the block was broken into two pieces by a hammer. It also confirmed that the superhydrophobicity of the prepared superhydrophobic samples can withstand shock and peel, which is beneficial to practical applications.

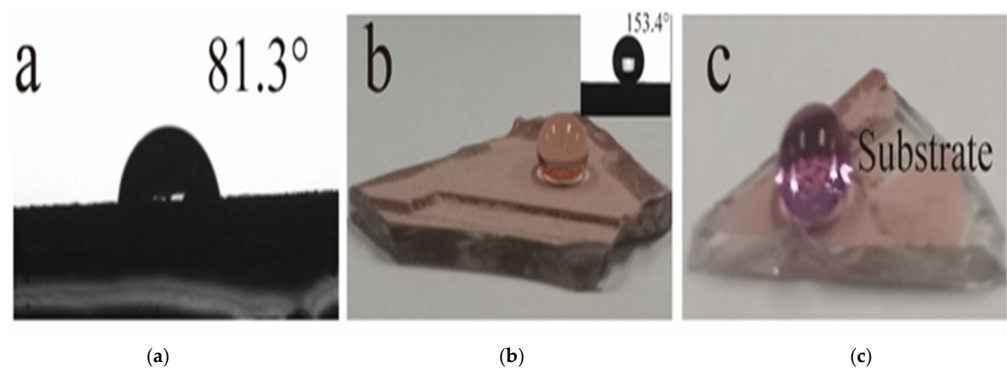


Figure 5. Optical image of a static 3 µL water droplet of GP-Cu₂O (a); a photograph of the water droplets on GP-Cu₂O-SHC samples: surface (b), bottom (c).

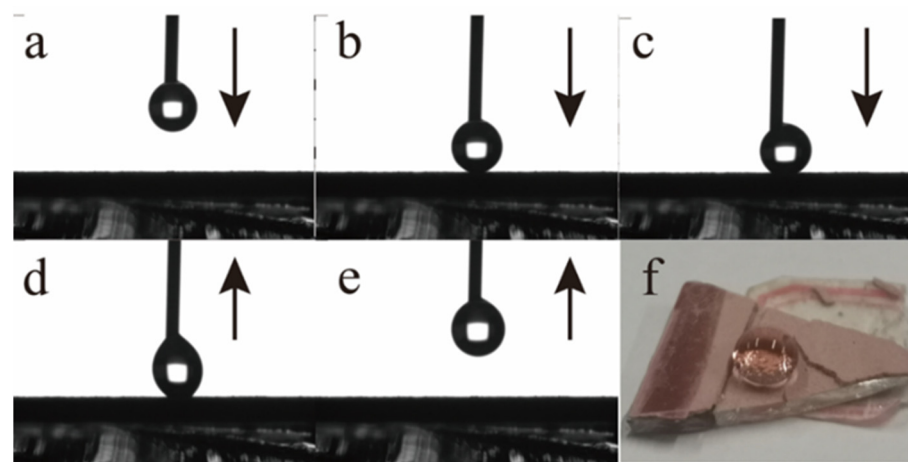


Figure 6. Process of 3 µL water droplet nonstick property evaluation of GP-Cu₂O-SHC coating droplet approach (a), contact (b), squeezing (c), lift (d), and departure (e); a photograph of the water droplets on the damaged GP-Cu₂O-SHC coating (f).

3.3. Surface Structure Characterization of GP-Cu₂O and GP-Cu₂O-SHC

The surface microstructures of the samples were investigated by FE-SEM, as shown in Figure 7. After Cu₂O fillers were added (Figure 7a,b) to the AAMs, the fracture surfaces formed irregular swelling structures with sizes ranging from 500 to 1000 nm, and all Cu₂O particles were covered with AAM gel layers with some cracks. This obviously indicates that Cu₂O may be encapsulated within films as fillers rather than directly reacting with the AAMs. It is well known that surface morphology and chemical composition are the two key factors of fabricated superhydrophobic surfaces. Thus, it may be beneficial to further prepare superhydrophobic surfaces because Cu₂O provides a more pronounced rough structure. In contrast, the GP-Cu₂O-SHC grew nanostructures and arranged into regular spherical shape structures that led to closely oriented nanostructures, and the gap between the nanostructures was tens of nanometers (Figure 7c,d). Additionally, the width and depth of surface cracks were significantly reduced, and gel structures were closely arranged after hydrophobic modification, which may reduce the porosity. For some small pores, the structure of flower petals, such as lotus stretches, can be grown in the pores to thin the structure of pores after modification.

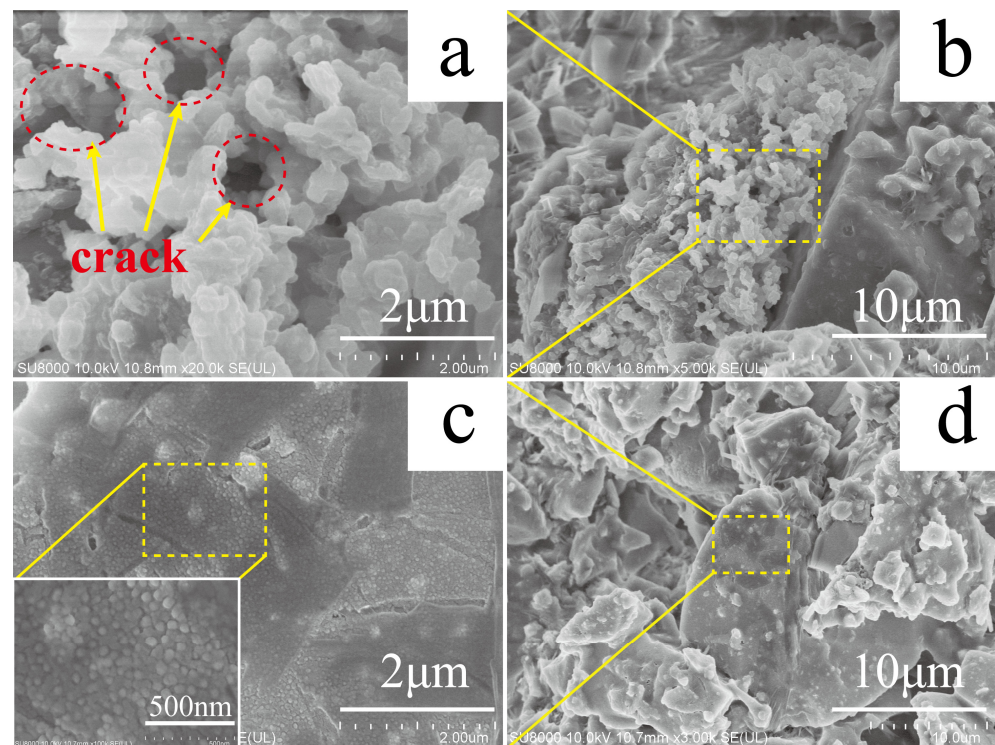


Figure 7. SEM images of different samples: GP-Cu₂O (a,b), GP-Cu₂O-SHC surface (c,d).

3.4. Physical and Chemical Characteristic Analysis

The crystal structure of the sample was analyzed by XRD, as displayed in Figure 8a. XRD investigations demonstrate that Cu₂O did not change the crystal structure of GP-SHC because the addition of Cu₂O was minimal (only 4 wt.%), and Cu₂O was wrapped well by the AAMs gel, so they were not observed in the XRD spectra. FT-IR was used to analyze the chemical composition, as shown in Figure 8b. When cuprous oxide was added, a new peak at 632 cm^{−1} was observed, which is the standard peak of Cu-O bonds [21]. In addition, compared with the GP-Cu₂O samples, GP-Cu₂O-SHC exhibited new peaks at 2926 cm^{−1} and 2856 cm^{−1}, which are attributed to C-H tensile vibration peaks and are provided by TTOS [22]. The results demonstrated that methyl groups successfully adhered to the surface of GP-Cu₂O-SHC after siloxane modification, which reduced the surface energy. In addition, a new peak at 1425 cm^{−1} emerged, which was attributed to the stretching vibration of Si-CH₂ methylene [12]. This further confirms that TTOS is related to superhydrophobic forming.

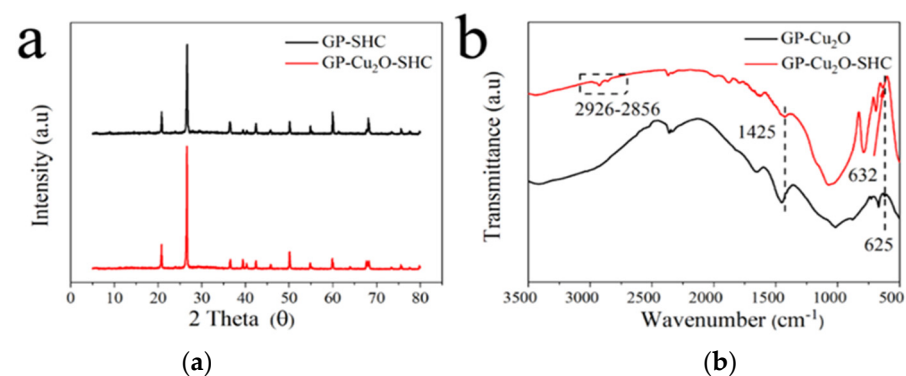


Figure 8. XRD analysis (a), FT-IR analysis (b).

The pore structure of the AAMs plays a key role in the influent process. When water molecules invade, harmful pores provide transport channels for the antifouling material,

causing some ions to migrate from within the AAMs to the surface. AAMs are typically composed of two types of pores: pores formed by the interspaces of the aluminosilicate gel phase (<10 nm) and capillary pores, which are formed by the evaporation of water from the original water-filled space (10–100 nm) [11,22]. The pore size structure of the GP-Cu₂O and GP-Cu₂O-SHC samples is shown in Figure 9. The GP-Cu₂O sample has a wide pore size distribution, ranging from 2 to 100 nm. After modification, the pore size distribution decreased to 2–50 nm, and the number of holes was significantly reduced (Figure 9a). The minimum average pore size of the GP-Cu₂O samples was 15.54 nm, while the minimum average pore size of the GP-Cu₂O-SHC samples was reduced to 5.57 nm. The BET-specific surface area decreased from 10.02 m²/g to 8.30 m²/g⁸. These results indicate that TTOS effectively reduces the porosity of the AAM samples and thus controls the entry of water to a certain extent. The reduced porosity may be due to the lotus structure in the modified pores blocking the pores.

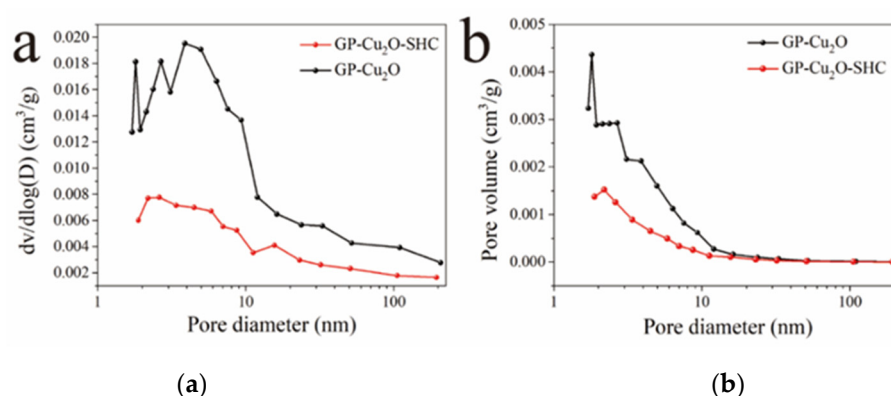


Figure 9. Distribution of pore structure (a) Distribution of pore volume (b).

Water absorption is a useful tool for assessing the potential of capillary transport through alkali-activated material pore networks [20]. As shown in Figure 10, the seven-day water absorption rate of prepared GP-Cu₂O approached 2.5%. Even with the addition of cuprous oxide as a filler, the GP-Cu₂O samples cannot effectively prevent the rapid entry of water. The water absorption of GP-Cu₂O essentially reached saturation on the sixth day. However, after hydrophobic modification, the water absorption rate of the GP-Cu₂O-SHC samples was still less than 0.5% in seven days, and it only reached the water absorption saturation point on the fourteenth day. The superhydrophobic surface and the lotus structure inside the pores act as a physical barrier for water transport, which reduces the absorption of water by capillary action and effectively prevents the entry of water.

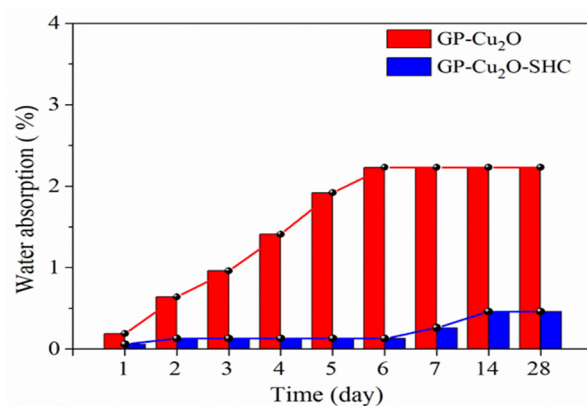


Figure 10. Water absorption of GP-Cu₂O and GP-Cu₂O-SHC.

The pH measurement results for the leaching behavior of alkalis in the samples are shown in Figure 11. The pH values of all samples gradually decreased over time. The

GP-Cu₂O samples exhibited high pH values in the initial stage, with values of 10.28 and 9.41, respectively, after 1 day and 2 days of leaching, which were higher than the standards of high alkaline (pH > 9) antifouling samples [23]. The GP-Cu₂O-SHC samples expressed a low pH value of 7.84 after 2 days of leaching, which was far lower than 9. Notably, it was a transition point of 3d leaching for GP-Cu₂O samples whose pH value dropped to 8.93. These results revealed that the GP-Cu₂O-SHC samples can slow the ion rate.

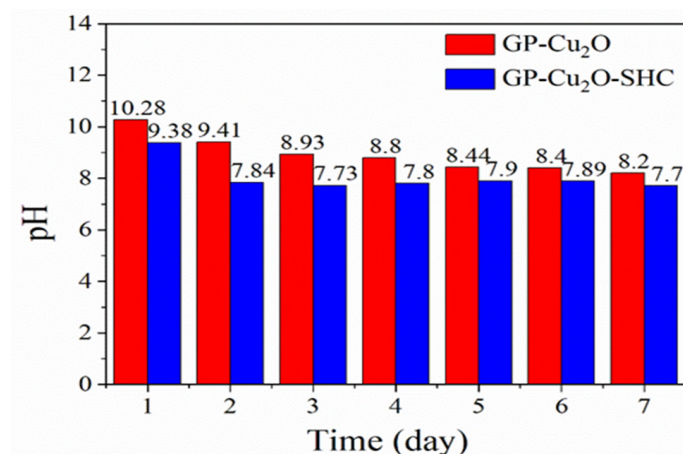


Figure 11. Leachate pH results.

In marine antifouling samples, the release rate of Cu²⁺ can be controlled to realize effective antifouling and minimize adverse effects on the environment [24]. Figure 12 shows the Cu²⁺ release rate of the samples before and after modification. The Cu²⁺ release rate of the GP-Cu₂O samples decreases in two stages. On the fourth day, the release rate peaked at 960 µg/cm² d. In the initial stage, the release rate of Cu²⁺ was the fastest due to the large amount of Cu₂O in the samples. Then, the release rate decreased with the decline in Cu²⁺ on the surface. With the passage of immersion time, the internal structure was incompact, and the cuprous oxide release rate reached a new peak. Then, the release rate gradually decreased. However, for the GP-Cu₂O-SHC samples, the release rate was initially close to zero in the first two days, which was due to the superhydrophobic surface preventing water intrusion. Then, the Cu²⁺ began to be released due to the superhydrophobicity gradually being reduced, resulting in water entering and exiting the samples on the third day. Then, the release rate gradually increased with increasing soaking time because the content of Cu²⁺ in the samples was high, and the superhydrophobicity of the surfaces was lost layer by layer. Compared with the unmodified samples, the overall release rate of the modified sample was lower and more stable, which was attributable to hydrophobic lotus petal-like structures growing in the pores and further preventing water entry.

The count of colonies on the GP-Cu₂O-SHC is shown in Figure 13. The GP-Cu₂O-SHC and GP-SHC samples had a similar effect of controlling the release of soluble ions to decrease the leaching of alkali at the beginning. The count of colonies on GP-Cu₂O-SHC was 2.2×10^8 CFU/mL when it was not soaked. Nevertheless, GP-Cu₂O-SHC played a more effective role in antibacterial performance than GP-SHC at all times, which was ascribed to the intensified antibacterial effect of Cu₂O [25]. The antibacterial effect of GP-Cu₂O-SHC was strengthened, and the colony count was 1.58×10^8 CFU/mL after the samples were immersed in artificial seawater for 3 days. Here and now, the antibacterial effect of GP-Cu₂O-SHC closely relied on Cu²⁺ rather than alkalinity because Cu₂O was gradually leached. The antibacterial effect of GP-Cu₂O-SHC was nearly variable, with a colony count of 1.50×10^8 CFU/mL after the samples were immersed in artificial seawater for 30 days. This also proved that the release rates of GP-Cu₂O-SHC, copper ions, and alkali metal ions were controllable and steady. In general, the antibacterial activity of GP-Cu₂O-SHC samples showed a strong effect and a small fluctuation range. Logically, the

GP-Cu₂O-SHC samples have long-term antibacterial application potential because Cu²⁺ can be controllably released.

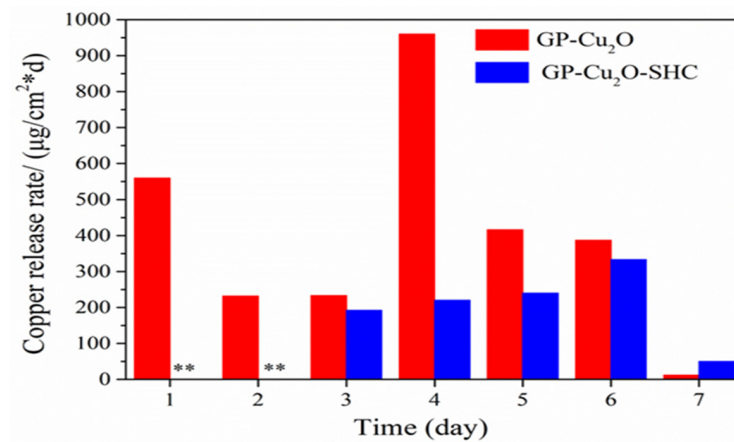


Figure 12. Copper release rate of GP-Cu₂O and GP-Cu₂O-SHC (** is a concentration of copper ions less than 0.0003 mg/L).

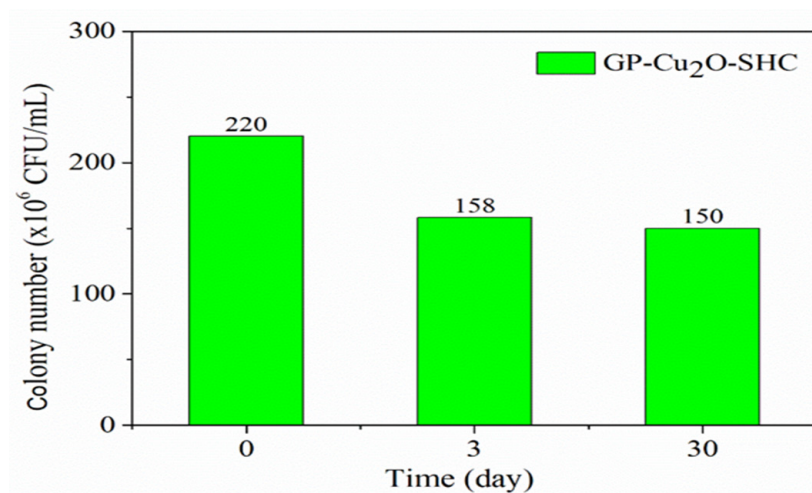


Figure 13. Antibacterial (*Staphylococcus aureus*) performance of GP-Cu₂O-SHC on the colony count under different soaking times (0 days, 3 days, 30 days).

After the anti-algae adhesion test, there was no algae on the surface of GP-Cu₂O-SHC, indicating that superhydrophobic modification can also effectively suppress biofouling. This confirmed that the GP-Cu₂O-SHC samples had obvious anti-algae attachment performance.

3.5. Mechanism Analysis

Accordingly, the water inhibition mechanism of the modified structure related to the release of Cu²⁺ is presented in Figure 14. The release rate of both modified and nonmodified samples decreased to the lowest on the seventh day. Compared with the relevant literature [7,24,26], the release rate of cuprous oxide can be reduced by the alkali-activated material samples themselves and can be further reduced after hydrophobic modification. Therefore, adverse effects on the natural environment can be significantly reduced, and more acceptable release rates that ecosystems can tolerate can be obtained [24].

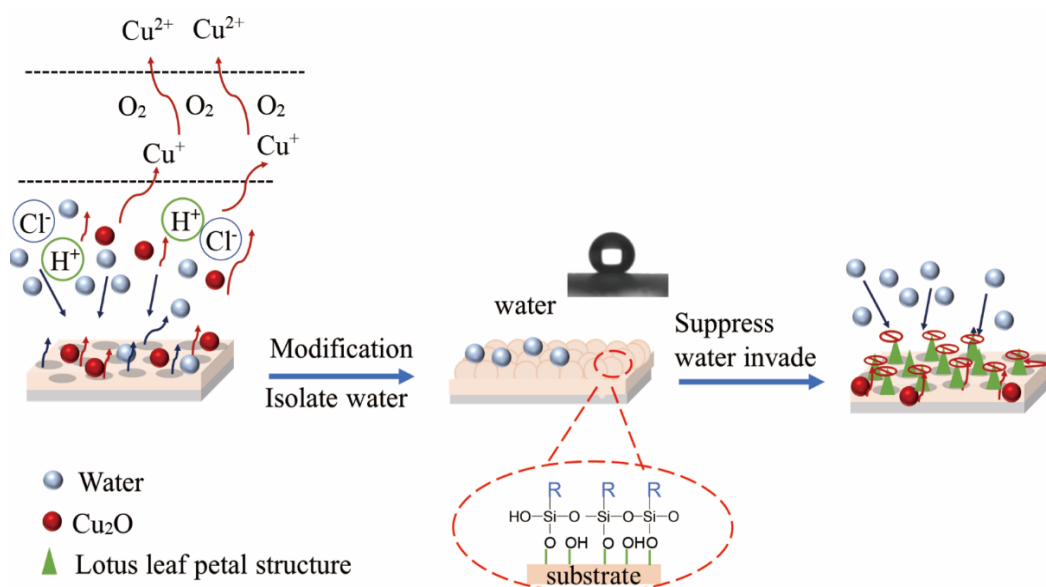


Figure 14. Sustained release mechanism of cuprous oxide.

4. Conclusions

In this study, the superhydrophobic composition materials of geopolymers with Cu_2O used for marine antifouling protection were prepared and preliminarily characterized.

TTOS, as a modification agent, was hydrolyzed and then self-polymerized and copolymerized with the geopolymers to grow nanoparticles. The superhydrophobic samples provided high stability against external force damage, maintaining viscoelastic properties due to the overall hydrophobic modification.

In addition, the controlled release of Cu^{2+} was realized by superhydrophobic modification, and the controlled release mechanism of Cu^{2+} was due to the pores growing into the lotus structures and superhydrophobic structures, which effectively hindered the entry of water and blocking the channels of cuprous oxide. The biocidal Cu^{2+} controlled release rate was successfully realized by preparing superhydrophobic geopolymers.

In addition, the superhydrophobic modified coating showed excellent anti-biological and anti-algal adhesion properties. It not only achieved the goal of lasting antifouling but also provided a new idea for the application of marine biological antifouling samples.

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