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FABRICATION OF SUPERHYDROPHOBIC COATING WITH SELF-CLEANING AND OIL-WATER SEPARATION PROPERTIES

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A facile route to prepare superhydrophobic coating was proposed based on liquid phase deposition of $(NH_4)_2SiF_6$ *followed by modification of n-dodecanethiol. The prepared sponge exhibited excellent superhydrophobicity with water contact angle (WCA) of 157.2º. Owing to its water repellency and self-cleaning property, the prepared sponge was successfully applied in oil-water separation, with high separation efficiency of up to 97% for various mixtures. The separation efficiency retained above 92% after 15 separation cycles, indicating excellent sustainability. Moreover, the coating showed outstanding performance against corrosive solutions, long-time storage in environment and high temperature. The proposed facile technique provides a new route for durable superhydrophobic materials fabrication.*

Keywords: superhydrophobic; sponge; SiO_2; separation; oil-water mixture

1. Introduction

Biomimetic surfaces found in nature have garnered significant interest due to their distinctive surface wettability [1]. Superhydrophobic surfaces, characterised by their ability to reject water, possess a water contact angle (WCA) over 150º and a slide angle (SA) below 10º [2]. Superhydrophobic materials have the potential to be utilized in several applications, such as self-cleaning [3], anti-fouling [4], anti-corrosion [5], anti-fogging [6] and oil-water separation [7]. In these applications, oil-water separation has garnered significant public interest as a result of the escalating discharge of wastewater containing oil. The prevailing belief is that the chemistry industry and oil leak catastrophes are the primary factors responsible for this occurrence. Coalescer, centrifugation, flotation, and other similar techniques are commonly employed in classic separation processes. Nevertheless, it has been argued that these methods have disadvantages of inefficiency, high energy consumption, lengthy processing times, and complexity [8,9]. Consequently, there exists a significant need for the development of manufacturing techniques for

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superhydrophobic materials, as they hold the potential to effectively address the challenges associated with oil-water separation.

Superhydrophobic materials have been synthesized through various methods, including the sol-gel method [10,11], dip-coating [12,13], hydrothermal [14,15], etching [16], electrospinning [17], electrodeposition [18]. The creation of superhydrophobic surfaces involves shaping rough structures and establishing low-energy surface characteristics. Notably, fluoroalkylsilane compounds have garnered significant attention in the development of superhydrophobic materials due to their low surface energy properties. However, a critical drawback associated with fluoroalkylsilanes is their adverse environmental and health impacts [19]. Thus, finding eco-friendly superhydrophobic materials applied in oil-water separation is an urgent problem. Inorganic nanoparticles have emerged as a viable option for achieving surface roughness and superhydrophobicity [20]. SiO_2 nanoparticles, renowned for their chemical stability and resistance to aging, have garnered considerable interest in superhydrophobic surface preparation [21]. Dong et al. [22] employed SiO_2 nanoparticles embedded poly(vinylidene fluoride) using an electrospinning method, subsequently modified with fluoroalkylsilane, for superhydrophobic material synthesis Wang et al. [23] successfully fabricated superhydrophobic cotton fabric based on oxidized cellulose-SiO_2 hybrids, yielding a WCA of 158.6º. Zhang et al. [24] created a superhydrophobic sponge by modifying SiO_2 microspheres with vinyltriethoxysilane and hexadecyltrimethoxysilane, demonstrating its utility for oil-water separation.

In this study, SiO_2 nanoparticles were deposited onto the sponge surface using an in-situ liquid phase deposition technique involving $(NH_4)_2SiF_6$, resulting in the formation of a rugged surface structure. The introduction of n-dodecanethiol, with its inherently low surface energy, interacted with SiO_2 nanoparticles by hydrogen bond, ultimately yielding a superhydrophobic coating on the sponge surface. The prepared sponge demonstrated remarkable performance in separating oil-water mixtures, with an efficiency exceeding 97%, coupled with exceptional reusability. Stability evaluations of the prepared coating proved outstanding chemical and thermal resistance, further substantiating its suitability for practical applications. Notably, the coating remained stable even after prolonged exposure to air for a period of 2 months. Consequently, this study presented a straightforward and efficient method for the preparation of superhydrophobic sponges, showcasing their promise in oil-water separation applications.

2. Experimental

2.1. Materials

Ammonium fluosilicate ($(NH_4)_2SiF_6$), boric acid (H_3BO_3, ≥99.5%), tetrachloromethane (CCl_4, 98%), dichloromethane (CH_2Cl_2,99%), ethyl acetate

($C_4H_8O_2$,99%), absolute ethyl alcohol (C_2H_5OH), n-dodecanethiol ($C_{12}H_{26}S$, 98%) were supplied by Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Sponge was bought from local market.

2.2. Fabrication of the coating

As shown in Fig. 1, the superhydrophobic coating was prepared by in-situ deposition method. The sponges (0.5×0.5×2cm) were pretreated by rinsing in ethanol and deionized water to remove any impurities. 0.1 mol/L $(NH_4)_2SiF_6$ and 0.45 mol/L H_3BO_3 were stirred at 60 ºC for 1 h. After standing for 1 h at 50 ºC, the sponge was moved to oven drying to obtain SiO_2 coated sponge. Then, the superhydrophobic sponge was obtained after immersion in 2.5% n-dodecanethiol aqueous solution for 5 h and subsequent heating.

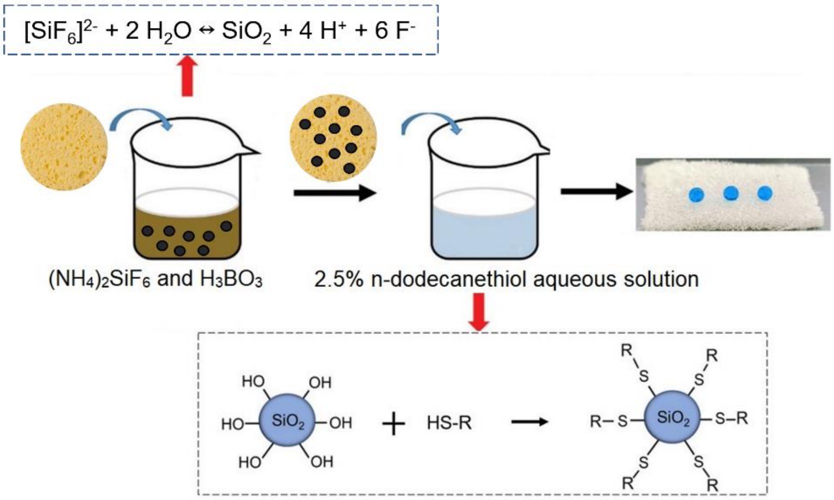

Fig. 1 Schematic illustration for the fabrication process.

2.3. Oil/water separation

Oils (tetrachloromethane, dichloromethane, ethyl acetate) and water with equal volume were mixed together to acquire immiscible oil-water mixtures. The separation process was designed using the funnel under the force of gravity. Water was dyed blue using methylene blue, while oils were dyed red using Sudan III. The separation efficiency was calculated based on the following equation:

$$\eta = M_2/M_1 \tag{1}$$

where M_1 was the oil mass in mixture before separation, M_2 was the oil mass collected after separation.

2.4. Characterization

The chemical compositions of samples were characterized by a Magna-IR 560 Fourier transform infrared spectroscopy (FTIR, Thermo Nicolet, USA) collected in the 500-4000 cm^{-1} region. The micro structure and surface morphology was observed by a Quanta 200 scanning electron microscope (SEM, FEI, USA). The water contact angle (WCA) and sliding angle (SA) were carried out on a TST-200H contact angle measurement instrument (Shenzhen testing equipment Co., Ltd., China) with 5 μL of probe liquid. Average values of WCA from three different locations were calculated.

3. Results and discussion

3.1. Surface wettability behavior

The wettability of the coated sponge was comprehensively characterized through measurement of CA and SA. The untreated sponge showed inherent hydrophobic property, with a WCA of 118.3º. In stark contrast, the WCA of the modified sponge dramatically increased to 157.2º, affirming its outstanding superhydrophobic nature. This superhydrophobicity was visually evident as water droplets retained a nearly spherical shape on the modified sponge surface, as illustrated in Fig. 2.

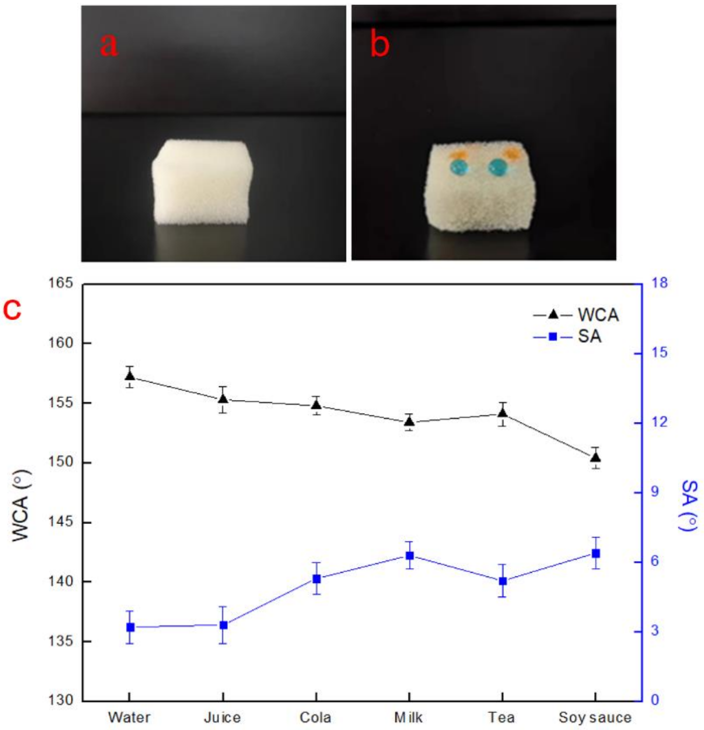

Fig. 2 Photos of untreated (a) and modified sponge (b); c, static contact angles of various liquid droplets on modified sponge.

Conversely, oil droplets (tetrachloromethane) promptly wetted the surface, displaying a contact angle of 0º. Furthermore, a variety of common beverages encountered in daily life, including juice, cola, milk, tea, and soy sauce, were utilized to assess the static contact angles on the modified sponge (Fig. 2c). Impressively, all tested liquids exhibited static contact angles exceeding 150º, accompanied by SA of less than 10º. This exceptional wettability transformation can be chiefly attributed to the surface roughness and chemical composition of modified sponge, which played a pivotal role in achieving superhydrophobicity. The retention of abundant air entrapped within the modified surfaces further contributed to the observed superhydrophobic behavior.

3.2. Structure characterization

Fig 3 illustrated the surface morphology of both untreated and modified sponges, offering insight into their structural differences. The pristine sponge surface exhibited a smooth and relatively uniform texture. However, following the coating process with SiO_2/dodecanethiol, the modified surface underwent a dramatic transformation with a highly rugged topography. The SEM images revealed clear evidence of SiO_2 nanoparticle deposition on the sponge during the liquid-phase deposition process. These SiO_2 nanoparticles contributed to the formation of a hierarchical structure on the sponge surface. Upon closer examination at higher magnification, it was evident that the irregular microscale pits formed by the SiO_2 nanoparticles clustered together, effectively covering the entire surface of the sponge.

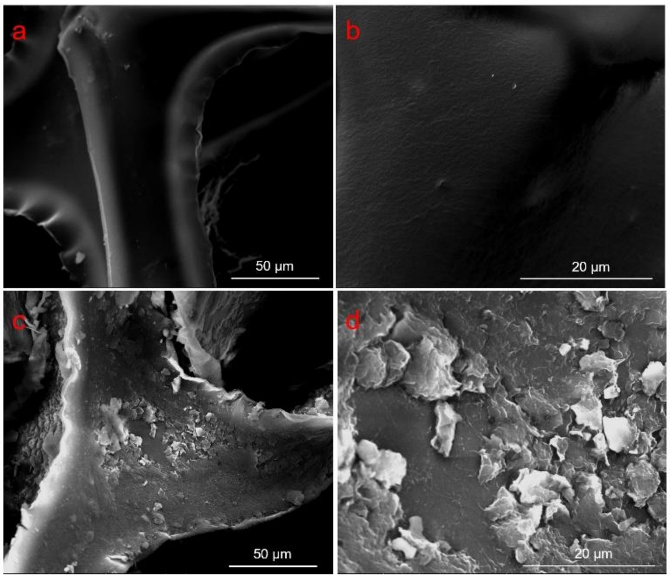

Fig. 3 SEM images of pristine (a,b) and modified sponge (c,d)

FTIR spectra were employed to analyze the chemical composition of the superhydrophobic sponge. In Fig. 4, both the pristine and superhydrophobic sponges exhibited the characteristic peak associated with N-H bonds in the sponge at 3425 cm^{-1}. In the spectra of the superhydrophobic sponge, a distinct C-S stretching vibration attributable to n-dodecanethiol emerged within the range of 705-570 cm^{-1}. The appearance of peaks at 2917 and 2862 cm^{-1} corresponded to the symmetric vibrations and asymmetric stretching vibrations of $–CH_3$ and $–CH_2$ groups within the long alkyl chain, serving as clear indicators of the successful modification of the long-chain alkyl substance, n-dodecanethiol. As depicted in Fig. 1, it could be observed that n-dodecanethiol interacted with SiO_2 nanoparticles through a dehydration condensation reaction. The SiO_2 nanoparticles not only contributed to the creation of hierarchical micro/nanostructures but also served as a binding agent with n-dodecanethiol, facilitating the formation of a superhydrophobic surface.

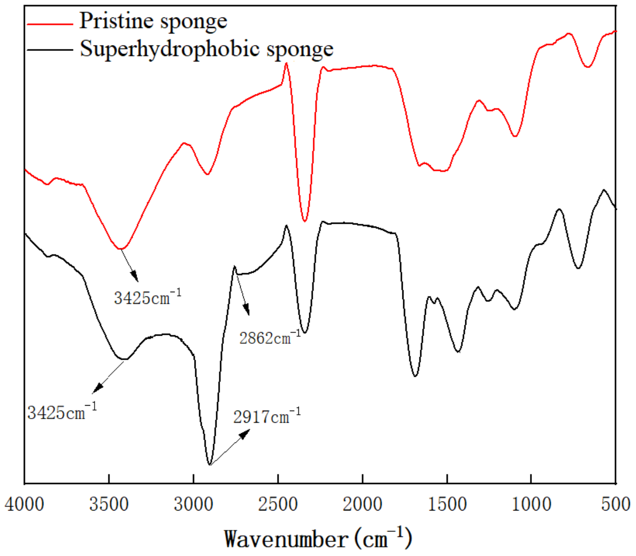

Fig. 4 The FTIR patterns of pristine and superhydrophobic sponge.

3.3. Oil-water mixtures separation

Based on its remarkable superhydrophobic and superoleophilic properties, the prepared sponge demonstrated significant potential for separation of oil-water mixtures. Various oils, including tetrachloromethane, dichloromethane, and ethyl acetate, were employed to assess the versatility of the superhydrophobic sponge for this purpose. To perform the separation, the superhydrophobic sponge was placed within a funnel, as illustrated in Fig. 5. The tetrachloromethane-water mixture was introduced into the funnel from above. The tetrachloromethane contacted with the coated sponge, permeated through and was collected in the beaker positioned below. In stark contrast, water, hindered by non-wettable characteristics of the sponge, remained in the funnel, resulting in a high degree of separation efficiency.

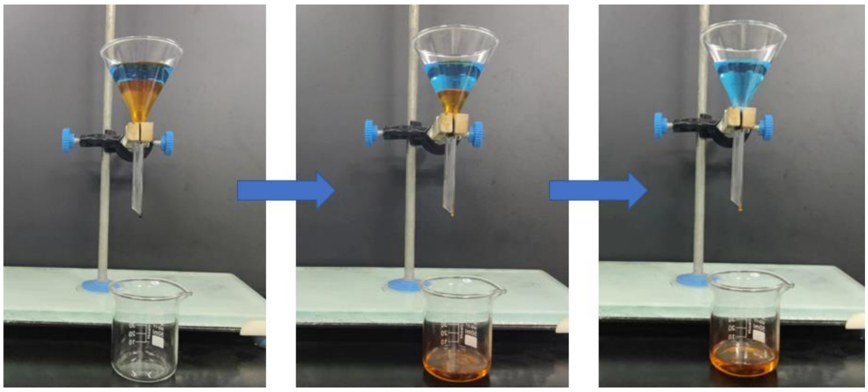

Fig. 5 oil-water separation process

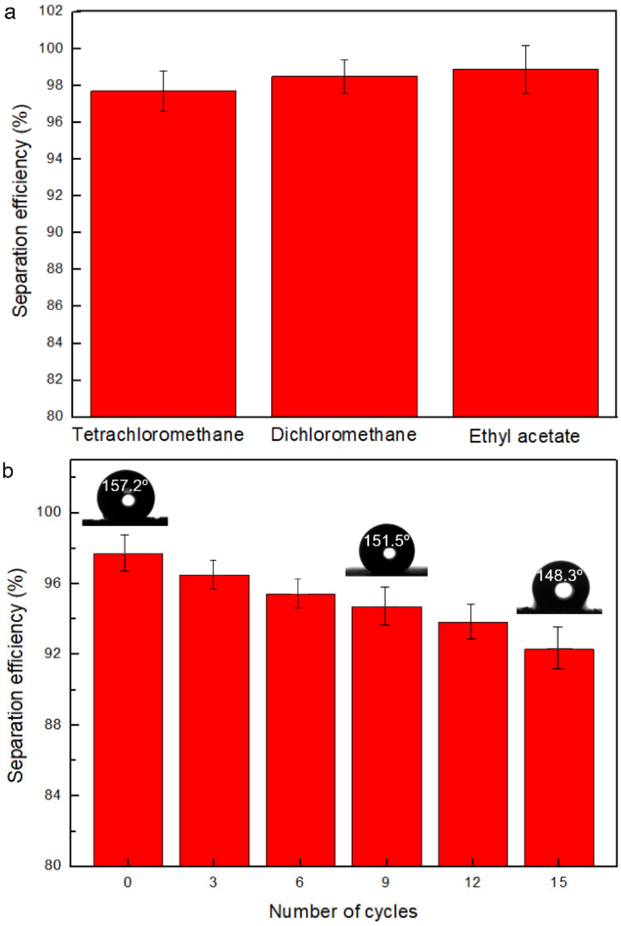

Fig. 6. Separation efficiency for different oils (a) and its variation with separation cycles.

As depicted in Fig. 6a, diverse oil-water mixtures were effectively separated with efficiency of up to 97%. Additionally, an investigation into the reusability of the prepared sponge, a critical aspect for practical applications, was conducted using tetrachloromethane. The separation process was repeated 15 times to evaluate the reusability of the superhydrophobic sponge. As demonstrated in Fig. 6b, even after 15 cycles, the separation efficiency exhibited only a slight decrease from 97% to 92%, demonstrating its outstanding reusability. Furthermore, the superhydrophobic sponge retained its wettability with a water contact angle (WCA) of 148.3º after 15 cycles. In summary, the prepared coating demonstrated remarkable durability and stability for oil-water separation applications.

3.4 Self-cleaning properties

The prepared sponge also exhibited remarkable self-cleaning capabilities, rendering it highly practical for various applications. To assess this property, both pristine and superhydrophobic sponges were immersed in water dyed with methylene blue. As depicted in Fig. 7a, the pristine sponge was swiftly saturated by the methylene blue solution, leaving its surface heavily stained.

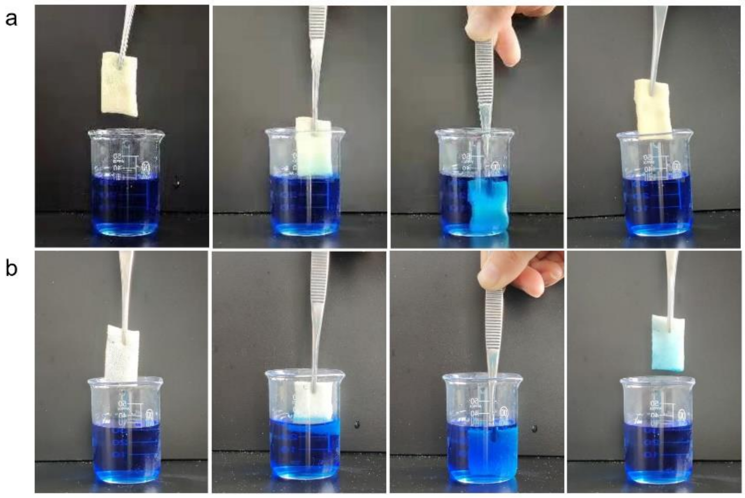

Fig. 7. The self-cleaning performance of pristine (a) and superhydrophobic sponge (b).

In stark contrast, the superhydrophobic sponge remained virtually untouched by the solution, as illustrated in Fig. 7b, presenting an immaculate surface devoid of any pollution. This outstanding self-cleaning performance could be attributed to the presence of trapped air between the coating and the water, which facilitated the formation of a protective layer on the sponge surface, thereby preventing the adhesion of contaminants.

3.5 Stability tests

Ensuring the stability of the superhydrophobic coating is important for its practical utility. In real-world applications, such as oil-water separation, exposure to corrosive solutions or elevated temperatures can be common. Consequently, the separation performance under demanding conditions was examined. As depicted in

Fig. 8a, the WCAs of different pH aqueous solutions on the superhydrophobic sponge consistently remained above 155º.

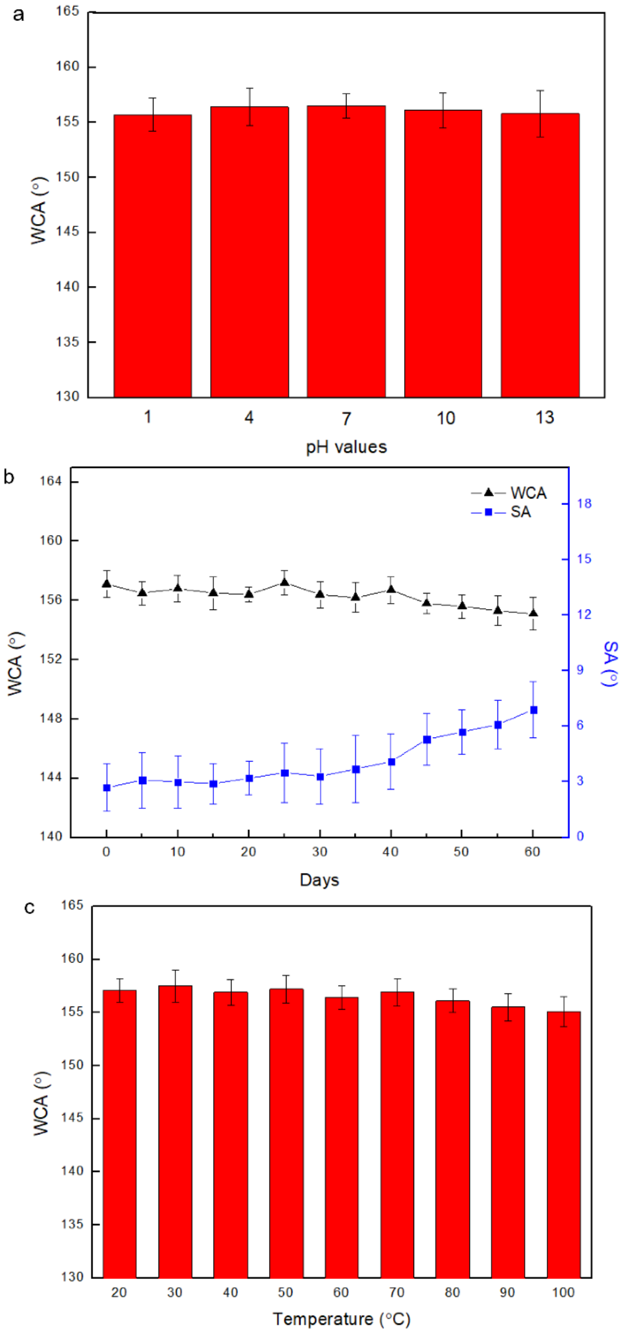

Fig. 8. a, WCAs of different pH aqueous solutions on the superhydrophobic sponge; b, long-term stability; c, heating resistance.

This excellent performance against corrosive solution was attributed to the protective layer of air trapped within the hierarchical structure, providing corrosion inhibition capabilities. Furthermore, the coated sponge was subjected to a 2-month exposure to ambient air to assess its long-term stability. Remarkably, the prepared sponge retained its superhydrophobic properties, with WCA of 155.4° and SA of 6.9° after 60 days (Fig. 8b), thus affirming its superior performance across various applications. Additionally, the superhydrophobic sponge was subjected to a 1-hour heating process to evaluate its resistance to elevated temperatures. As evidenced in Fig. 8c, the WCAs consistently exceeded 150° under these elevated temperature conditions. These findings demonstrated excellent stability of the prepared coating under a series of challenging conditions, confirming its practical applicability.

4. Conclusions

In summary, a stable superhydrophobic coating was prepared through liquid-phase deposition of $(NH_4)_2SiF_6$ combined with modification of n-dodecanethiol. This coating exhibited exceptional repellency towards various liquids, with water contact angles (WCA) consistently exceeding 150°. The superhydrophobic sponge demonstrated its efficacy in efficiently separating oil-water mixtures, with consistent performance over 15 cycles. Furthermore, the prepared sponge exhibited impressive self-cleaning properties, and maintained its wettability even under harsh conditions such as exposure to acidic or alkaline solutions, long time storage in ambient and high temperature heating. Importantly, a cost-effective, straightforward preparation for superhydrophobic coating was proposed without the need for fluorine-based reagents. With its demonstrated capabilities and versatility, this coating holds significant promise for practical applications.

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