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A robust copper oxide-based superhydrophobic microfiltration membrane for moisture-proof treatment of trace water in transformer oil

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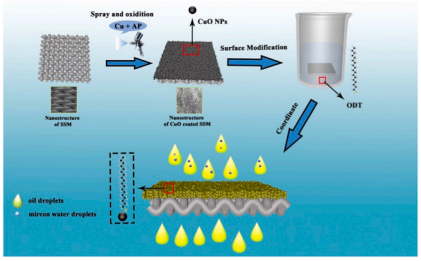
HIGHLIGHTS

- The prepared membranes expand the method for the efficient separation of water-in-transformer oil emulsions.
- The inorganic binder aluminum phosphate was used to enhance the mechanical properties.
- Rapidly self-assemble surface modification octadecanethiol (ODT) is the basis for reversible repair of the membrane.
- The separation of all water-in-transformer oil emulsions was driven solely by a micro pump.

GRAPHICAL ABSTRACT



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ABSTRACT

The excellent properties of superwetting materials make it possible to deal with complex interfacial problems such as water-in-oil emulsions separation. However, it remains a challenge to develop an efficient and facile method to eliminate the adverse effects of trace water in transformer oil. In this work, a robust copper oxide-based superhydrophobic microfiltration membrane was prepared by a simple spray-coating method for moisture-proof treatment of trace water in transformer oil. For the first time, the emulsion separation was carried out by the combine of inorganic aluminum phosphate and metal oxide. After oxidation and rapid surface modification by octadecanethiol, the fabricated membrane become extremely repel water and can separate various of transformer oils with the efficiency higher than 99.995%, and the efficiency can remain stable even after 20 separation cycles. TGA test reveal that the collected transformer oils possess same thermal stability as original transformer oil. Moreover, after 50 abrasion cycles, only a simple re-modification process is required to restore the separation efficiency of the membrane. Besides, the membrane also displayed prominent chemical resistant to acid, alkali, and salt solutions. This work provides a new method for purifying water-in-transformer oils emulsions with high efficiency and low energy consumption, which advances the moisture-proof treatment for transformer oil.

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1. Introduction

In human industrial production and daily life, oil-immersed transformers are of great importance in maintaining the stable running of the power supply network [1–3]. The major material of insulation in such transformers is oil-paper insulation composed of insulating paper and transform oil [4–6], and the oil-paper insulation plays an irreplaceable role in transformer system [7,8]. However, the performance degradation of transformer oil due to water pollution has attracted widespread attention all over the world [9–16]. Water can unexpectedly infiltrate into transformer oil via the initial manufacturing to the final commissioning stage. Besides, although the transformer cabinet is an airtight structure, the covers and bushings are not tightly sealed, and moisture may invade during transportation, operation and overhauled [12,17,18]. Particularly, free water in transformer oil will seriously affect the insulation performance, accelerate aging, and greatly shorten insulation life of the oil-paper insulation system. According to relevant research, the oil-paper insulation system will become aged under the influence of multiple factors such as temperature, electric field, and vibration. Furthermore, the insulating cardboard fibers will gradually degrade and produce moisture, and the oxidative cracking of transformer oil will also produce moisture, which will cause the damp of the transformer core, and reduce its insulation ability [19–22], more seriously, the oil may be emulsified by the presence of slight water [23,24].

In order to minimize the moisture content in the transformer oil, water removal processes such as vacuum drying, vacuum oil injection and hot oil circulation are required. Nevertheless, the moisture content of the transformer oil still cannot be reduced to a minimal value [2,25]. Therefore, a method that can efficiently separate slight water in transformer oil emulsion is urgently needed. In recent years, membrane separation has been widely used to remove small amounts of water from emulsions [26–32]. Bai et al. treated the modified ZnO NPs coated meshes with stearic acid (SA) and NaOH solutions for 15 min. The fabricated products can achieve on-demand separation of various types of emulsified oil and water mixtures [33]. Yin et al. fabricated superhydrophobic copper hydroxide coated meshes (SCMs) via a facile spraying and modifying approach. The separation efficiency of the as-prepared SCMs for a wide range of highly stable water-in-oil emulsions was more than 99.0%. The separation can proceed only driven by gravity [34]. From the perspective of operation safety of the oil-immersed transformers and the recovery and utilization of transformer oil, the application of membrane separation instead of traditional technology to separate slight water from transformer oil emulsion is a facile, energy-saving, and low-cost approach. However, there is no relevant research to purify emulsified transformer oil.

In this study, the copper oxide-based superhydrophobic microfiltration membranes with superoleophilic property were fabricated through innocuous and secure spraying and rapid surface modification. Aluminum phosphate (AP) was selected as inorganic binder and sprayed on the surface of stainless steel meshes (SSMs) with Cu NPs. After being oxidized at high temperature and coordinated with octadecanethiol (ODT), the obtained superhydrophobic microfiltration membranes can efficiently separate transformer oil emulsion. This work provides a facile and low energy consumption method to efficiently remove trace water from transformer oil, which also expands the emulsion separation system based on metal oxide. The current work can be regarded as a guide to replace the traditional moisture-proof work of transformer oil.

2. Experimental work

2.1. Materials

Sodium hydroxide (96%) was purchased from Li Anlong Bohua (Tianjin) Medicine Chemistry Co., Ltd., concentrated phosphoric acid (85%) was purchased from Chengdu kelong chemistry Co., Ltd., concentrated sulfuric acid (65%) was purchased from beijing chemical works. Copper nanoparticles (Cu NPs, 99.9%) were obtained from Nangong Xindun Alloy Welding Material Spray Co., Ltd. SSMs (AISI 316L, 2300 mesh size) were purchased from the local market. GaoQiao10#, ZhongHai10#, HengLi10# and QingYuan10# transformer oils were obtained from Shanghai Qixi International Trade Co., Ltd. Solid octadecanethiol (ODT, 96%) was purchased from Alfa Aesar (China) Chemical Co., Ltd. All the chemical reagents were used without further purification.

2.2. Fabrication of the superhydrophobic microfiltration membrane

The original SSMs (3 cm × 3 cm) were cleaned with ethanol and deionized water in an ultrasonic cleaner. To prepare AP, phosphoric acid (H_3PO_4, diluted to 60%) was mixed with aluminum hydroxide, and the molar ratio was 1:3. Then the mixture was stirred at 100 °C for 3 h. 4 g of AP was dissolved in 10 mL of deionized water and vibrated to transparent in the ultrasonic cleaner. After that, 30 mL anhydrous ethanol was dispersed in the AP solution and was stirred to uniform. At last, 1.6 g Cu nanoparticles (NPs) were added to the above mixture under intense stirring. The prepared suspension was uniformly sprayed on 4 pieces of SSMs in a distance of 30 cm. The homogeneous suspension with Cu NPs and AP was uniformly sprayed on the surface of SSMs, then SSMs covered by coating were treated with high temperature so that the AP can be cured and the curing temperature should be held at 120 °C for 2 h and 240 °C for 1 h. Then the temperature was increased to 300 ℃ for 2 extra hours to make Cu NPs oxidized to build the CuO-AP coated SSMs. Depending on the coordination reaction between ODT and CuO at room temperature [35], the CuO-AP coated SSMs were soaked in 50 mL of ethanol solution containing 2 mM ODT for 20 min. Then the samples were cleaned with ethanol and dried with a blower to get the superhydrophobic CuO-AP-ODT coated SSMs.

2.3. Water-in-oil emulsion separation test

Four kinds of transformer oil (GaoQiao10#, ZhongHai10#, HengLi10# and QingYuan10#) were chosen to be mixed with water at a volume ratio of 100:1 and the mixtures were sonicated to stable. The emulsion separation process was driven by different pressure difference in a glass microanalysis filter holder (Millipore). A vacuum pump (Millipore, WP6122050) was used to provide the pressure difference. The filtrates were collected for oil purity analysis. 3 pieces of CuO-AP-ODT coated SSMs were selected to carry out the test to get the standard deviation of flux and efficiency. The SSMs were washed with ethanol and dried with a drying cabinet every 5 cycles. The experiment was carried out in a dry environment at room temperature.

2.4. Robustness and re-modification test

The robustness of the superhydrophobic microfiltration membrane was studied via the sandpaper abrasion test. The obtained CuO-AP-ODT coated SSM was placed face down on the rough surface of sandpaper (grit no. 800) in mechanical robustness test. A 50 g standard weight was placed on the sample, then the sample was pull back and forth in a distance of 10 cm. The mass of superhydrophobic microfiltration membranes and the water contact angles of the sample were measured after each 5 cycles, when the values of the water contact angles were lower than 150°, the sample would be immersed into the ODT in ethanol solution for 10 mins to regain superhydrophobic property. 3 pieces of prepared CuO-AP-ODT coated SSMs were selected for the test.

2.5. Characterization

The water contact angles (WCA) and slide angles (SA) of the CuO-AP-ODT coated SSMs measurements were performed using a JC20001 contact angle system (Shanghai Zhongchen Digital Equipment Co., Ltd.). The elemental composition was investigated via X-ray photoelectron

spectroscope (XPS, Thermo Fisher Scientific ESCALAB 250Xi). A scanning electron microscope (SEM, FEI Quanta 650 FEG) was used to observe the surface morphology. The element distribution was measured by an energy-dispersive X-ray spectroscopy (EDS, EDAX). X-ray diffractometer (XRD, PANalytical X′Pert PRO) was used to analyze the crystal structure of the sample. Fourier Transform Infrared Spectrometer (FT-IR, Nexus 870) was used for functional group analysis. TGA measurements (NETZSCH STA 449C) were used to characterize the thermal stability of transformer oil before and after separation. The microscope photos of all kinds of water-in-transformer oil emulsions before and after separation were obtained by an optical microscope (OLYMPUS BX53). The water contents of the collected emulsion were measured by a Karl Fischer titrator (Metrohm 831 KF). All optical photos were taken by a camera.

3. Results and discussion

3.1. Characterization of the prepare membrane

A robust CuO-based superhydrophobic microfiltration membrane was developed for the separation of transformer oil emulsions. Inorganic aluminum phosphate (AP) was selected as adhesives for its stable performance and resistance to oil corrosion [36–38]. Fig. 1(a-c) shows the process of the fabrication of the CuO-AP-ODT SSMs. In the high temperature curing process, the hydroxy groups contained in the AP binders will produce condensation–polymerization reaction through the dehydration of intermolecular and intramolecular hydroxyl groups. On the other hand, the molecular attractive forces between the binding phase and the surfaces of the substrates or fillers are decided by the adhesive property of the binding phase. Rationally, the hydrogen (or coordination) bonds between the functional groups of the AP binder and oxygen (or metal) atoms on the surfaces of the substrates or fillers may also have ability to increase adhesion [39]. After the coating was cured, the temperature was raised to 300 ℃ again so that all Cu NPs can be completely oxidized. Then the CuO-AP coated SSMs can be fabricated. The contact angle of the original SSM and CuO-AP coated SSM are shown in Fig. S5. After that, the formed coating was further modified by the coordination method with ODT to get superhydrophobic CuO-AP-ODT coated SSMs. Self-assembly reaction will occur between ODT and CuO-AP coating through the chemical bonding interaction of strong bonds between CuO and S atoms, following the cleavage of an SAH bond [35,40,41], which can significantly reduce surface energy.

To get better surface roughness, 3 groups of suspensions with different Cu NPs content were prepared to spray on the original SSMs, the masses of Cu NPs in group 1 to group 3 are 0.8 g, 1.6 g and 2.4 g, respectively. The slide angles and contact angles of fabricated CuO-AP-ODT coatings with different contents of Cu NPs are shown in Fig. 1h, from which we can conclude that when the content is 1.6 g, the contact angle reaches the maximum (155.5°) and the slide angle is the minimum value (1.5°, Movie S1). The scanning electronic microscopy (SEM) images of original SSMs, CuO-AP coated SSMs, and CuO-AP-ODT coated SSMs with different content of Cu NPs are shown in Fig. 1d-g and Fig. S1. From the SEM images, the uniformly covered CuO-AP and CuO-AP-ODT coating can be seen and small pores with a diameter about 0.4 μm can be clearly observed, which can do contribute to the passage of water-in-oil droplets. As Fig. S1 presented, when the content of Cu NPs is 0.8 g, it can be seen that the substrate is exposed and the sample surface is relatively smooth. When the content of Cu NPs is 2.4 g, there is no difference in surface morphology compared with the content is 1.6 g. And from Fig. S2 the micro-/nanohierarchical structure can be clearly observed. According to the Cassie model, the hydrophobicity was emphasized by such rough surface architectures. [42] The element distribution of

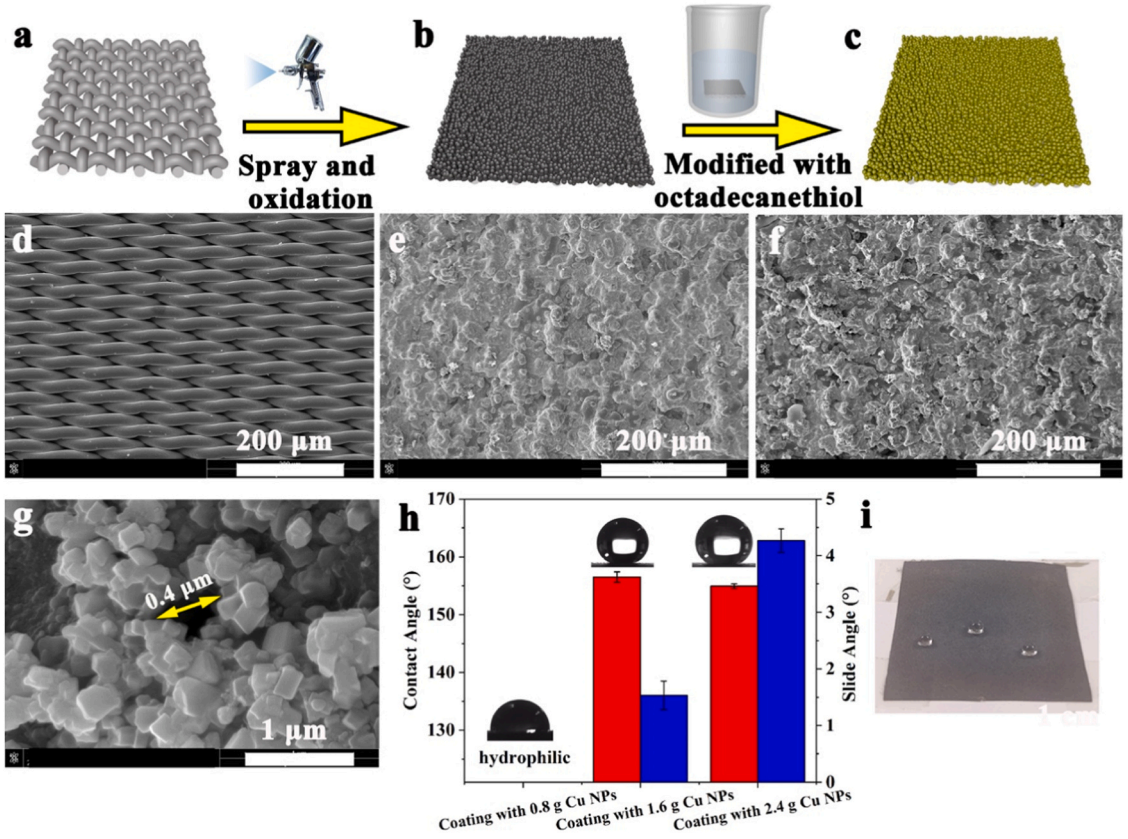

Fig. 1. (a-c) Illustration of the fabrication of the CuO-AP-ODT coated SSM. (d) SEM images of original SSM, (e) SEM images of CuO-AP coated SSM, and (f and g) CuO-AP-ODT coated SSM with 1.6 g Cu NPs. (h) Relationship between Cu NPs content and contact angle and Slide angle. (i) The photograph of a water droplet on the surface of CuO-AP-ODT coated SSM and photographs of CuO-AP-ODT coated SSM.

original SSM and CuO-AP-ODT coated SSM from EDS analysis were shown in Fig. S3 and Fig. S4.

Supplementary material related to this article can be found online at doi:10.1016/j.colsurfa.2021.126843.

As shown in Fig. 2a, the appearance of Cu 2p3 peak in the XPS spectrum of CuO-AP coated SSM and the disappearance of the Fe 2p and Cr 2p peaks in the XPS spectrum of original SSM peaks demonstrated that CuO were densely sprayed on the original SSM. The appearance of S 2p peak demonstrated the ODT was successfully coordinated with CuO. The fine spectrum of S 2p peak was shown in Fig. S6. As the fine spectrum of copper element shown in Fig. 2b, the peaks at the value of Binding Energy near 933, 945, 955 and 970 prove the presence of copper oxide [43], which proves that Cu NPs were sufficiently oxidized.

Fig. 2c is the FTIR spectra of the ODT and CuO-AP-ODT coated SSM. The absorption peaks of S-C groups can be observed both in the ODT spectra and CuO-AP-ODT coated SSM spectra when the wavenumber is 1466.73 cm^{-1}. However, the characteristic peak of –SH group at 2557 cm^{-1} can only be observed in the ODT spectra, which confirms that the ODT is attached to the CuO-AP-ODT coated SSM via CuO-S coordinate bonds [44].

The X-ray diffraction pattern of original SSM, CuO-AP coated SSM and CuO-AP-ODT coated SSM was shown in Fig. 2d. Compared with the original SSM, the corresponding diffraction peaks at $2\theta = 36.4°$and $2\theta = 61.4°$ can be recognized as the CuO with the Miller indices of (1 1 1) and (2 2 0) respectively. The corresponding diffraction peaks at $2\theta = 43.3°$ can be recognized as the Cu with the Miller indices of (2 0 0), from unoxidized Cu NPs [43]. Combined with the XPS analysis results, it can be concluded that a small amount of unoxidized Cu NPs were existed in the fabricated superhydrophobic microfiltration membranes, but it did not affect the overall surface modification effect.

3.2. Water removal

As Fig. 3b present, take water-in-Gaoqiao10# emulsion as an example, many tiny water-in-oil droplets were observed in the fabricated emulsion under a 20x objective lens. However, there were no droplets detected in the collected filtrate, which indicated that the water droplets could be efficiently separated from water-in-transformer oil emulsions by the superhydrophobic microfiltration membrane. The droplet distribution images of other emulsions are shown in Fig. S7, it can be found that all the emulsions become transparent after separation.

The droplet size distributions of water droplets in various water-in-transformer oil emulsions were measured by DLS. As displayed in Fig. 3a, the water droplets of water-in-transformer oil emulsions ranged from 0.1 to 10 μm, most of which were between 2 and 10 μm. It can be obviously observed from Fig. 5c that after separation, the droplet diameters were less than 10 nm.

Driven by the vacuum pump, the transformer emulsion can be separated. In order to ensure oil purity of filtrate while maintaining high flux, the relationship between flux and oil purity of filtrate was studied in the experiment. The value of oil purity of filtrate and flux were obtained from formula (1) and (2) respectively [45,46]:

$$E = \left(1 - \frac{C_S}{C_O}\right) \times 100\% \quad (1)$$

Where, E is the oil purity of filtrate. C_S and C_O are the water content of the collected filtrate and the original water-in-transformer oil emulsions.

$$F = \frac{V}{ST} \quad (2)$$

Where, V (L) is the volume of the emulsions after filtration, S (m^2) is the effective contact area between the emulsions and the SSM, and T (h)

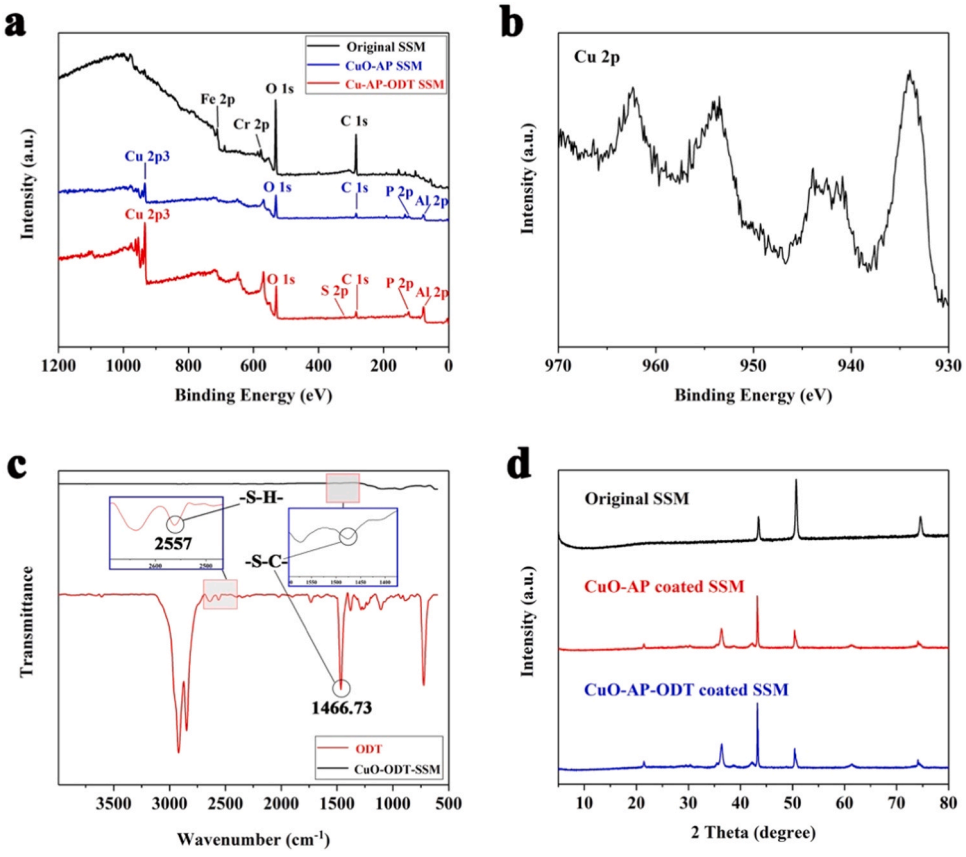

Fig. 2. (a) XPS spectrum of the original SSM, CuO-AP coated SSM and CuO-AP-ODT coated SSM. (b) Fine spectrum of copper element. (c) FTIR spectra of the ODT and CuO-AP-ODT coated SSM. (d) XRD spectrum of the original SSM, CuO-AP coated SSM and CuO-AP-ODT coated SSM.

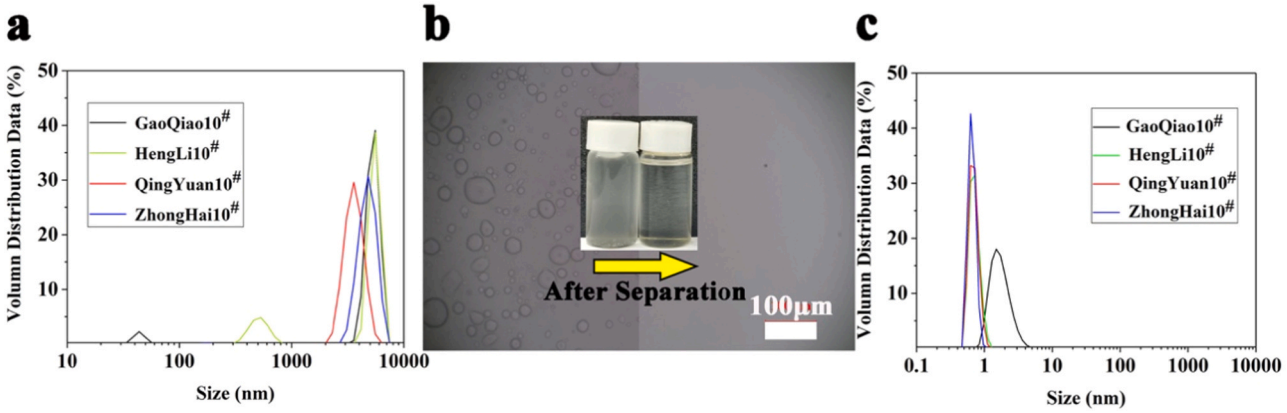

Fig. 3. (a) The droplet size analysis of water-in-Gaoqiao10# emulsion before separation, (b) droplet distribution images of water-in-Gaoqiao10# emulsion before and after separation. Insert image shows 100/1 water-containing Gaoqiao10# before and after emulsion separation. (c) the droplet size analysis of water-in-Gaoqiao10# emulsion after separation.

represents the time required to pass a certain volume of emulsions. The oil purity of filtrate and flux of each emulsion were measured three times, and the same sample was used for the separation of each emulsion.

As shown in Fig. 4a, take water-in-Gaoqiao10# emulsion as an example, the value of the emulsion flux increases as the pressure was enlarged, at the same time, the oil purity of the filtrate exhibited a downward trend. When the pressure was increased to 12.5 kPa, the separation efficiency was still higher than 99.995%, but the flux can be greatly increased to about 433.3 L/m^2·h. When the pressure further increased to 15 kPa, the oil purity steeply declined to 99.99%, therefore, under the premise of ensuring the high efficiency and high flux of separation, 12.5 kPa was chosen as the most suitable separation pressure. The oil purity of the filtrate and flux of other emulsions varies with pressure is shown in Fig. S8, From the perspective of energy saving and ensuring high flux, the optimum pressure is still 12.5 kPa. When the pressure is 12.5 kPa, the relationship between oil purity of filtrate and flux of all the water-in-transformer oil emulsions was shown in Fig. 4b.

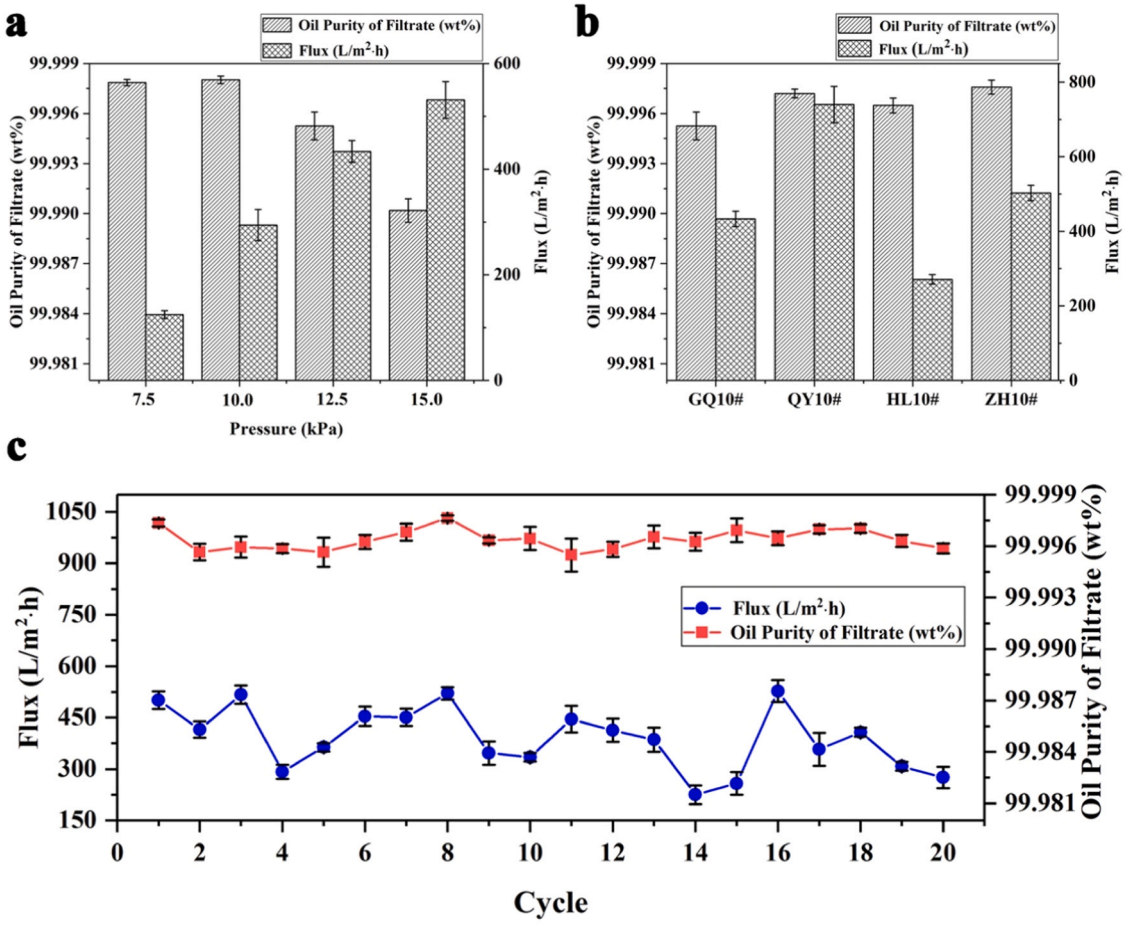

Fig. 4. (a) The oil purity of filtrate and flux of Gaoqiao10# emulsion under different pressure. (b) The oil purity of filtrate and flux of different transformer oil emulsions under a pressure of 12.5 kPa. (c) Oil purity of filtrate and flux change of water-in-Gaoqiao10# emulsion separation cycle under a pressure of 12.5 kPa.

The four emulsions are defined in the figure as follows: Gaoqiao10# - GQ10#, Qingyuan10# - QY10#, Hengli10# - HL10# and ZhongHai10# - ZH10#. The water-in-Hengli10# has the lowest value of flux, which is still higher than 271.2 L/m^2·h, and the separation efficiency of all emulsions is higher than 99.995%. Therefore, only a relatively low pressure was required to ensure high separation efficiency and relatively high flux separation.

In order to ensure that the superhydrophobic microfiltration membrane can be reused, the recyclability property was tested. By taking water-in-Gaoqiao10# emulsions as instance, the separation efficiency and flux versus cycle numbers was further investigated. For 20 cycles, the change of flux and oil purity of filtrate was shown in Fig. 4c, it can be seen from the variable curve of flux, there is an overall downward trend in every five cycles before cleaned by ethanol. The flux value of each SSM showed a decreasing trend, this is due to the retention of transformer oil on SSMs, which affected the flow of emulsion, but after simple cleaning, the separation performance of SSMs will be basically restored, and as presented in the oil purity of filtrate curve, the separation efficiency won't be unduly affected by the emulsion residue, which is sufficient to prove that the microfiltration membrane has good recycling ability.

In order to better explain whether the properties of transformer oil were affected before and after separation, the thermal stability of original Gaoqiao10# transformer oil, water-in-Gaoqaio10# emulsion and the purified Gaoqiao10# transformer oil were compared by TGA test. The thermogravimetric curves of original Gaoqiao10# transformer oil, water-in-Gaoqaio10# emulsion and the purified Gaoqiao10# transformer oil are shown in Fig. 5, it can be obvious observed that the mass of all samples dropped sharply when the temperature rose to 160–285 °C, however, compared with the water-in-Gaoqaio10# emulsion, the thermogravimetric curve of the purified Gaoqiao10# transformer oil has a closer trend and inflection point to original Gaoqiao10# transformer oil. It can be proved that the thermal stability of transformer oil after emulsion separation is guaranteed. The changes of kinematic viscosity of the transformer oil, water-in-transformer oil emulsion before and after separation were also tested by pinnacle capillary viscometer, as shown in Fig. S10.

3.3. Checking the reusability of the used membrane

The CuO-AP-ODT coated SSMs were placed face down on the rough surface of sandpaper (grit no. 800) with a standard weight on it, then the sample was pull in a distance of 10 cm, which was recognized as a cycle. After 50 abrasion cycles, the micro-/nanohierarchical rough structure was observed by a closer inspection through SEM images (Fig. 6a-b). It is indicated that the abrasion test has significant impact on the surface structures, which damaged the morphology to a certain extent.

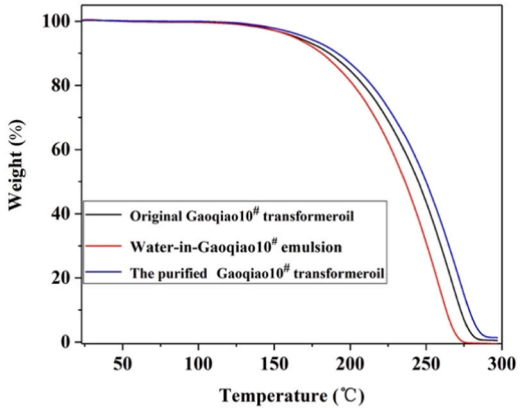

Fig. 5. Thermogravimetric curves of original Gaoqiao10# transformer oil, water-in-Gaoqaio10# emulsion and the purified Gaoqiao10# transformer oil.

As Fig. 6c presented, the water contact angles and the mass loss were used to show the mechanical robustness property of the CuO-AP-ODT coated SSMs. After 50 abrasion cycles, the mass loss of the membrane was less than 1.7%, which proved the robustness of the superhydrophobic microfiltration membrane. This is mainly due to the existence of inorganic binder AP, which makes CuO nanoparticles not easy to fall off and cause quality loss. In the 30th cycle, the WCA was lower than 150°, this is because only the ODT can only modify the CuO particles on the surface of the coating. As the number of cycles increases, unmodified CuO NPs exposed. After a 10 mins re-modification process in 50 mL of ethanol solution containing 2 mM ODT, the membranes could regain superhydrophobic property and can be used for emulsion separation. As the change curve of WCAs shown, after re-modification process, the water contact angles are all above 150°, which can be recognized as the process of repairing the damaged morphology.

To evaluate the effect of separation, the CuO-AP-ODT coated SSMs which had gone through the abrasion cycles were used to separate above water-in-transformer oil emulsions. As shown in Fig. 6d, the purities of the collected transformer oils are all higher than 99.993%, and the flux of various oils are all higher than 450 L/m^2·h, which proved that the separation ability of the superhydrophobic microfiltration membranes were not affected after 10 min of rapid modification. Even after 50 sandpaper abrasion cycles the superhydrophobic property of the membrane still can be restored, and the membrane still maintained the high purification efficiency of water-in-transformer oil emulsions. The element distribution of CuO-AP-ODT coated SSM after abrasion cycles from EDS analysis was shown in Fig. S11.

NaOH and H_2SO_4 were used to prepare aqueous solutions with pH values varied from 1 to 13. As shown in Fig. 7a, the acidic/alkaline-resistant ability of the obtained superhydrophobic microfiltration membranes was studied by measuring the WCAs of water droplets with different pH values. The CuO-AP-ODT coated SSMs shows superhydrophobic property to the acidic and alkaline solutions with CAs larger than 150°. The WCAs are significant increase as the pH value is increased to 14, which demonstrates the better resistance of the membrane to alkaline aqueous solutions, it can indicate that the membranes have outstanding local resistance to both acid and alkali.

In order to better demonstrate the overall environmental tolerance of the superhydrophobic microfiltration membrane, the change curve of WCA for the CuO-AP-ODT coated SSM is shown in Fig. 7b plotted against immersion time in deionized water, 3.5 wt% NaCl solution and pH 10 NaOH solution. The change curves all have a trend of slowly descending. However, the WCA value in pH 10 NaOH solution was relatively stable with no large fluctuations, which can more concretely explain the CuO-AP-ODT coated SSMs have better tolerance to alkaline solutions. As the soaking time increased to 3 h, the WCAs of membranes in 3.5 wt% NaCl solution is reduced slightly below 150°, which would be ascribed to the corrosion of unmodified CuO NPs. These experimental data illustrate the superhydrophobic microfiltration membranes also have excellent local resistance to acid and alkali and overall environmental tolerance property. Even if the microfiltration membrane is exposed to the air for 30 days, it can still maintain superhydrophobic property (Fig. S9).

4. Conclusions

In summary, the CuO-based superhydrophobic microfiltration membrane with superoleophilic property were prepared with a facile and low-cost method, which was used for separating various of water-in-transformer oil emulsion with an efficiency of exceeding 99.995%. The membrane has perfect recycling performance, which can maintain high efficiency and the flux can be easily restored after simple cleaning with anhydrous ethanol, moreover, the separated transformer oil still maintained its original thermal stability. In addition, the incorporation of AP considerably improves the mechanical resistance of membrane, even after 50 abrasion cycles on sandpaper, efficient separation can still be carried out after the rapid re-modification process. Besides, the exist of

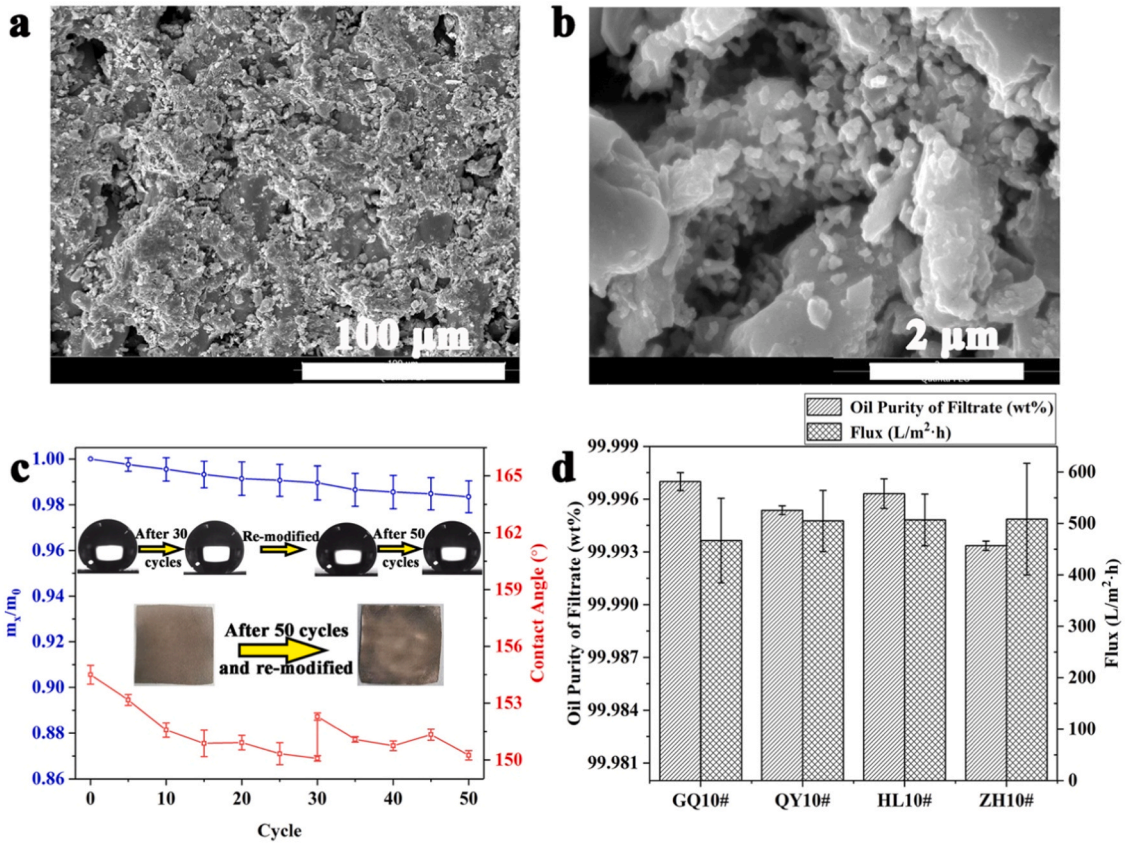

Fig. 6. (a-b) SEM images of the CuO-AP-ODT coated SSM after the abrasion and re-modification cycles. (c) The change curve of abrasion and re-modification cycles with water contact angles and mass loss. m0 and mx are the mass of the CuO-AP-ODT coated SSMs before and after abrasion cycles, respectively. Insets show images of water droplets before and after abrasion and re-modification cycles and photographs of CuO-AP-ODT coated SSM before and after 50 abrasion cycles with sandpaper. The red curve belongs to contact angle and the blue curve belongs to weight loss. (d) The separation efficiency and flux of various of transformer oils after abrasion and re-modification cycles.

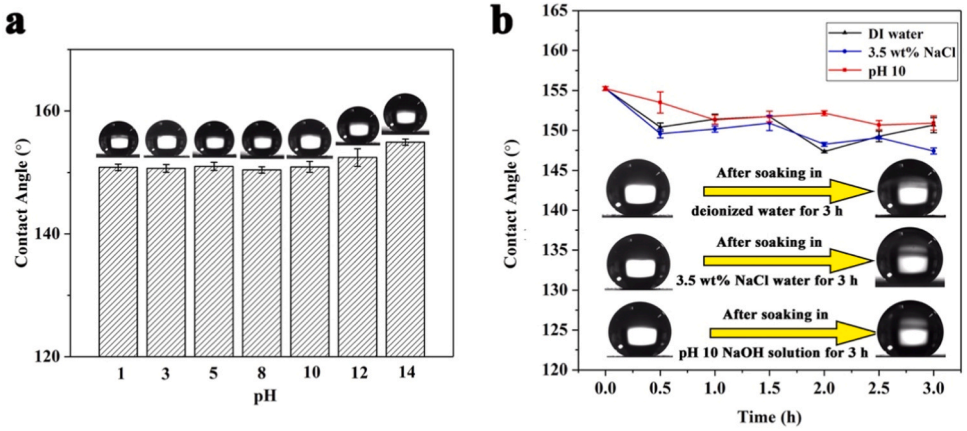

Fig. 7. (a) The contact angles of water droplets with different pH on the CuO-AP-ODT coated SSMs. Insets show images of droplets with corresponding pH. (b) The change curve of WCA for the CuO-AP-ODT coated SSMs plotted against immersion time in deionized water, 3.5 wt% NaCl solution and pH 10 NaOH solution.

ODT can reasonably make the membrane has better chemical resistance, even the water droplets with strongly acidic or strongly alkalinity can reach a superhydrophobic state on the membrane, and the CuO-AP-ODT coated SSM remained superhydrophobic after being soaked in alkali and salt solutions for 3 h. This work provides a feasible solution for the efficient moisture-proof treatment of transformer oil.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.colsurfa.2021.126843.

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