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RESEARCH ARTICLE

A novel composite coating mesh film for oil-water separation

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Abstract Polytetrafluoroethylene-polyphenylene sulfide composite coating mesh film was successfully prepared by a simple layered transitional spray-plasticizing method on a stainless steel mesh. It shows super-hydrophobic and super-oleophilic properties. The contact angle of this mesh film is 156.3° for water, and close to 0° for diesel oil and kerosene. The contact angle hysteresis of water on the mesh film is 4.3°. The adhesive force between the film and substrate is grade 0, the flexibility is 1 mm and the pencil hardness is 4H. An oil-water separation test was carried out for oil-contaminated water in a six-stage super-hydrophobic film separator. The oil removal rate can reach about 99%.

Keywords super-hydrophobic, super-oleophilic, composite coating, mesh film, separation of oil and water

1 Introduction

Surface wettability is described by the contact angle (CA) of liquid droplets on solid surfaces. Generally, surfaces with water CA of greater than 150° are referred to as super-hydrophobic. These surfaces are often observed in nature on some plant leaves [1], insect legs [2] and wings [3]. It is reported that the micro- and nanostructure on these surfaces is the key to the super-hydrophobicity of these surfaces [4]. Several methods for the fabrication of super-hydrophobic surfaces were proposed, such as sol-gel [5,6], chemical or physical vapor deposition [7,8], etching and lithography [9–12], electrochemical deposition [13] and plasma technology [14–16]. In the present work, super-hydrophobic and super-oleophilic mesh film was fabricated with polytetrafluoroethylene (PTFE) and polyphenylene sulfide (PPS) for oil-water separation. PTFE is inherently hydrophobic and oleophilic. But the adhesive ability of PTFE on metal surfaces is unperfected, which should be improved for industry purposes. PPS shows excellent adhesive ability on metal surfaces [17]. We added PPS to the dispersed liquid of PTFE to fabricate a novel composite coating mesh film by a layered transitional spray-plasticizing method. This mesh film is super-hydrophobic and super-oleophilic and holds the excellent properties of both PTFE and PPS.

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2 Experimental

The experiments were carried out on the preparation and characterization of super-hydrophobic and super-oleophilic film. Materials were selected from the domestic market. The separation film was prepared through a suspension spraying and plasticizing procedure. Oil-water separation was done in a properly designed apparatus.

2.1 Materials

A 304 stainless steel wire mesh (elemental composition in wt-%: C-0.08, Cr-18.00, Ni-9.00, Mn-2.00, P-0.045, S-0.03, Si-1.00) with pore diameter from 0.026 to 0.440 mm, was selected as the substrate. A Spray gun (W-71), polytetrafluoroethylene (PTFE) suspension (solid content in wt-%: 60%) and polyphenylene sulfide (PPS) were used.

2.2 Pretreatment of stainless steel wire mesh

The stainless steel wire mesh substrates were immersed in the alkali solution (NaOH: 0.02 kg, Na_3PO_4: 0.05 kg, Na_2SiO_3: 0.03 kg, H_2O: 1.00 kg) for 10 min to remove grease at room temperature, in an acidic solution containing 10% H_2SO_4 for 3 min to remove rust, in the phosphating solution containing Manganese-Iron phosphate and $Zn(NO_3)_2$ for 60 min at 50°C-70°C to form a phosphating film to advance the adhesive force between coating and substrates and lastly, in a passivation solution containing 30% HNO_3 for 60 min at 50°C to avoid rusting. These pretreated meshes were washed with distilled water. They were dried in an oven before spraying.

2.3 Preparation of PTFE-PPS composite coating mesh films

PPS was mixed with PTFE in a variable ratio. The PTFE-PPS suspension was sprayed on the pretreated stainless steel wire mesh by a three-layer transitional method. Concrete operations are the following:

•Bottom layer: PTFE-PPS composite suspension is prepared by adding PPS, PTFE concentrated suspension, TiO_2 and Cr_2O_3 in 70/5/20/5 weight percentages into the proper promoter consisting of water, ethanol and n-butanol. And then, the suspension is sprayed on the pretreated stainless steel wire mesh with dry compressed air (0.2 – 0.3 MPa). At last, the stainless steel mesh was dried for 10 min at 80°C and plasticized for 10 min at 330°C–350°C in an oven.

•Interlayer: Here, the weight percentages of PPS, PTFE concentrated suspension, TiO_2 and Cr_2O_3 are 50/40/5/5. Drying temperature and time were 80°C and 10 min, respectively. Plasticizing temperature and time were 340°C–350°C and 15 min, respectively.

•Surface layer: Here, the PTFE concentrated suspension was sprayed on the interlayer directly. And then, the surface layer was dried for 10 min at 80°C and plasticized for 60 min at 350°C–360°C in an oven. The PTFE-PPS composite coating mesh film was cooled naturally in the oven with the power supply turned off.

2.4 7Characterization of coating mesh films

The hydrophobicity of the film is described by the water contact angle. The contact angle was measured with a 5 μL liquid droplet at room temperature with a video-optics contact angle tester (OCA20, Dataphysics Ltd., Germany). The values of CA are the averages of five measurements made on different points of the sample surface.

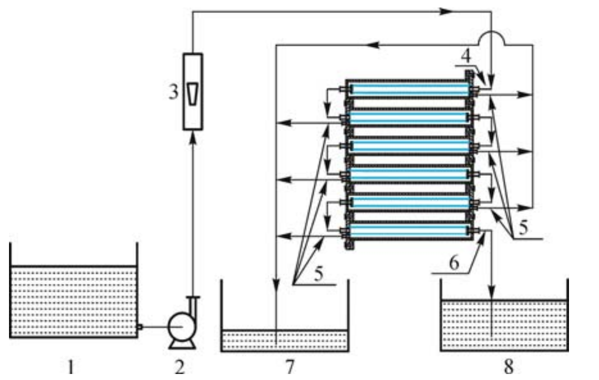
Surface morphology of this mesh films was observed by scanning electron microscopy (SEM) (KYKY-2800B, KYKY Technology Development Ltd.).

The adhesive force, flexibility, and the pencil hardness of this coating surface on the steel mesh were measured according to the national standard of China—GB/T 9286-1998(Paints and varnishes-Cross cut test for films), GB/T 1731-93(Determination of flexibility of films) and GB/T 6739-1996(Determination of film hardness by pencil test), respectively.

The corrosion resistance of the composite coating film was measured by immersing in different acid and alkaline solutions for 60 days.

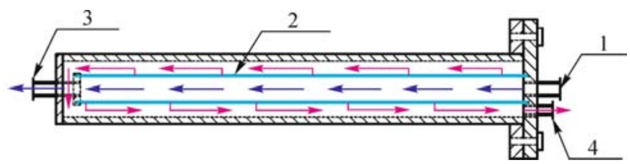
2.5 Separation of oil and water

In the present work, we used the prepared PTFE-PPS composite mesh film to design a flat-plate oil-water separator as seen in Figs. 1 and 2. In Fig. 1, oily feed water is pumped into the pipe and passes through the oil-water separator. The oil permeates the mesh film and is collected in the oil tank. The water discharges from water outlet and is collected in the water tank. Herein, the oil-water separator consists of six components, one of which is shown in Fig. 2. The oil content in each stream was analyzed according to petroleum and natural gas industry standard of China, SY/T 0530-93.



1 oily feed water tank; 2 pump; 3 flow meter; 4 oily feed water inlet; 5 oil outlet; 6 water outlet; 7 oil tank; 8 water tank

Fig. 1 Flow chart of oil-water separation



1 oily feed water inlet; 2 mesh film; 3 water outlet; 4 oil outlet

Fig. 2 Sketch of one-stage film separator

3 Results and discussion

Experiments were carried out on the preparation and characterization of super-hydrophobic and super-oleophilic film for oil-water separation. Experimental parameters were systematically changed to find feasible procedures in film fabrication, characterization and oil-water separation.

3.1 Hydrophobicity of PTFE-PPS composite coating mesh films

Stainless steel meshes with different pore diameters (0.026–0.440 mm) as substrates were sprayed with PTFE-PPS suspension. The hydrophobicity of the film was described by the measurement of its water contact angle. Figure 3 shows the relationship between pore diameter and the CA of water. The CA for water are about

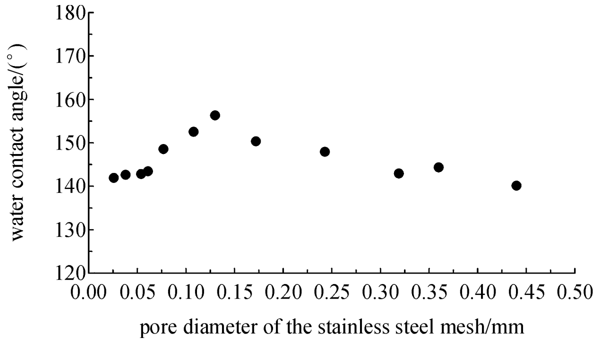


Fig. 3 Relationship between pore diameters and the CA of water on the corresponding mesh film

150° on the coating mesh film with pore diameters of about 0.077–0.243 mm, but become smaller when the pore diameters are less than 0.077 mm or greater than 0.243 mm. The hydrophobicity of coating films on the stainless steel mesh with 0.130 mm pore diameter is the best. This result indicates that the hydrophobicity of the coating mesh films is affected by the size of the pores. So, we selected the stainless steel mesh with 0.130 mm pore diameter as substrates to fabricate the mesh film and investigate its properties.

Figure 4 shows the shape of a small drop of water on this PTFE-PPS composite coating mesh film. The CA of water on this mesh film is 156.3° and the contact angle hysteresis is 4.3°, which shows that this coating mesh film is super-hydrophobic.

3.2 Oleophilicity of PTFE-PPS composite coating mesh films

PTFE on the surface layer of mesh films is not only hydrophobic, but also oleophilic. Herein, kerosene and diesel oil are selected as test oils to investigate the oleophilicity of PTFE-PPS composite coating mesh film. From Figs. 5 (a)–(f), it is seen that when some drops of kerosene are dripped on the mesh film, it can pass through easily. Eventually, kerosene goes through the mesh film in a stream with the increase of kerosene quantity. This reveals that this coating mesh film is super-oleophilic, with a CA of about 0° for oil.

In Fig. 6, a drop of water is dripped on the mesh film with a CA of 156.3°. Then, some drops of kerosene are dripped on the water drop on the mesh film. The kerosene glides along the surface of water drop and contacts with the mesh film. At last, kerosene passes through the mesh film, but the water drop is still on the mesh film and does not pass through the mesh film. The PTFE-PPS composite coating mesh film exhibits a desired oil-water separation effect.

3.3 Feasibility test of PTFE-PPS composite coating mesh films

For the approach to industrial applications, not only super-hydrophobic and super-oleophilic characteristics of the mesh films are considered, but also properties such as adhesive force, flexibility, pencil hardness and corrosion resistance should be studied.

At first, the pure PTFE concentrated suspension was directly sprayed on stainless steel mesh, which was used as contrast experiment under the same condition. From the Table 1, we can see that the adhesive force of PTFE-PPS composite coating mesh films is improved from grade 5 to grade 0, the flexibility is still favorable 1mm and the pencil hardness is increased from 4B to 4H. These results show that the shortcomings of PTFE are improved by introducing PPS.

Table 2 shows the corrosion resistance results of the prepared mesh films. The films were immersed in different solutions for 60 days, and the surface conditions were examined. It is shown that the mesh film inherits excellent corrosion resistance and can be used continuously for practical purposes.

3.4 Separation of oil and water

The separation effect of oil and water can be described by the oil removal rate. Herein, the oil removal rate is defined as the following equation:

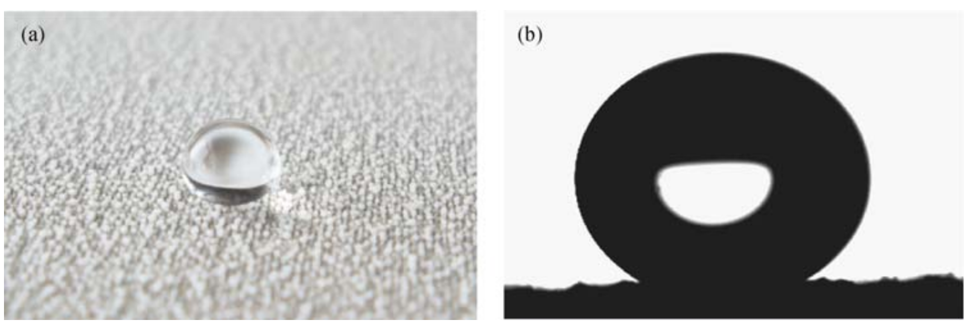


Fig. 4 (a) Digital photograph and (b) optical image of water droplet on the mesh film

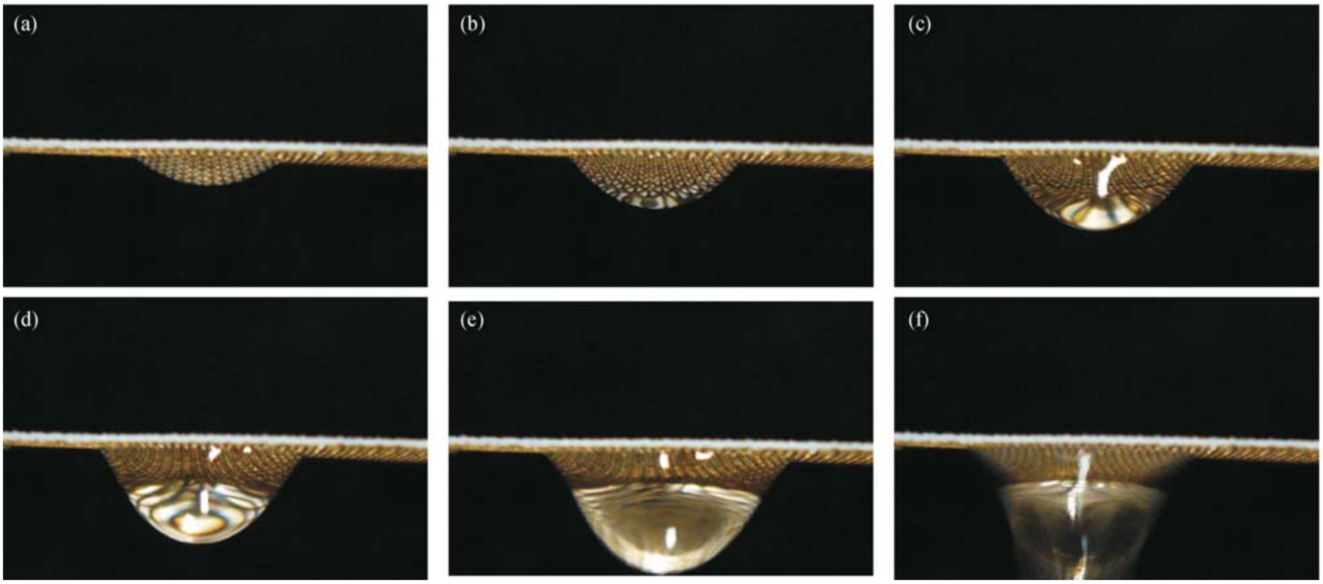


Fig. 5 Processes (a)–(f) of kerosene passing through the mesh film easily

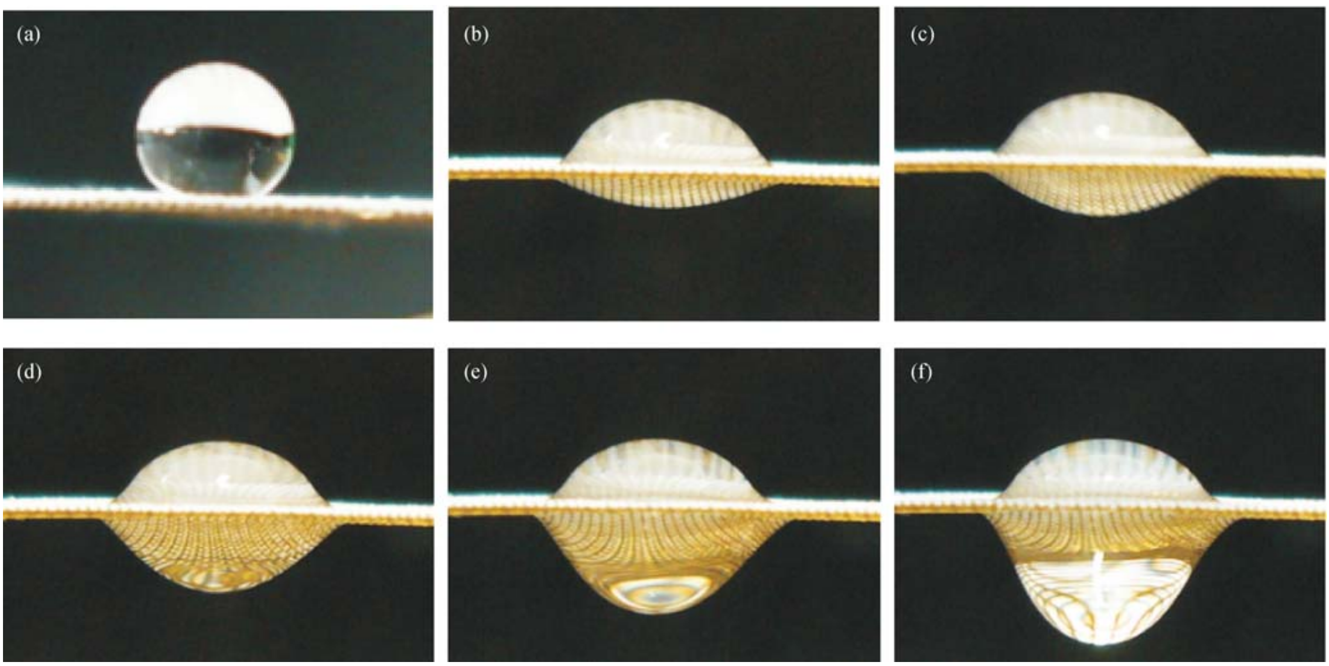


Fig. 6 (a) Firstly, a drop of water is dripped on the mesh film; (b)–(f) then some drops of kerosene are dripped on the water drop on the mesh film

Table 1 Feasibility test of PTFE-PPS composite coating mesh films

test items	PTFE	PTFE-PPS	test method
adhesive force	grade 5	grade 0	GB/T 9286-1998
flexility	1 mm	1 mm	GB/T 1731-93
pencil hardness	4B	4H	GB/T 6739-1996

$$\frac{C_0 - C_1}{C_0} \times 100, \quad (1)$$

where, C_0 is the content of oil in the initial feed and C_1 is the content of oil in the retentate. The oily feed water was

Table 2 Corrosion resistance test results of mesh films (being immersed in different solution for 60 days)[a)]

	concentration	performance	hydrophobicity	oleophilicity
H_2SO_4	98%	○	■	△
HCl	30%	○	■	△
HNO_3	65%	○	■	△
HF	40%	○	□	△
CH_3COOH	36%	○	□	△
$NH_3 \cdot H_2O$	25%	○	■	△
NaOH	50%	○	□	△
Acetone	—	○	□	△
Kerosene	—	○	□	△
Diesel oil	—	○	□	△
Atmosphere	—	○	□	△

a) performance: unchanged ○, damaged ●; hydrophobicity: unchanged □, lowered little but still hydrophobic ■; oleophilicity: unchanged △, changed ▲

prepared by mixing diesel oil in water. The feed water goes through the six-stage film separator. The oil-water separation effects were recorded as shown in Fig. 7. With the increasing of the number of separation stages, the content of diesel oil in the retentate decreases obviously and oil removal rate increases gradually up to about 99% for the initial feed containing 0.80 wt-% and 6.00 wt-% diesel oil, which shows that this mesh film can achieve a good oil-water separation.

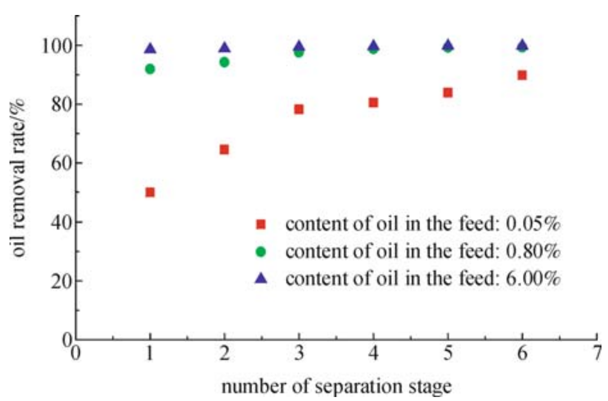


Fig. 7 Oil removal rate *vs.* the number of separation stage for different content of oil in feed

4 Mechanism analysis of super-hydrophobicity and super-oleophilicity

The prepared PTFE-PPS composite coating mesh film shows super-hydrophobic and super-oleophilic characteristics, which can be explained by the Wenzel model [18] described by Eq. (2).

$$\cos\theta_w = r\cos\theta_f, \tag{2}$$

where θ_f is the static CA on a smooth surface, θ_w is apparent CA on a rough surface, and r is the Wenzel roughness factor. r is defined as the ratio between the actual area of the rough surface and the geometric projected area, which is always larger than 1. From the Wenzel equation, we can draw a conclusion that the surface roughness enhances the hydrophilicity of hydrophilic surfaces ($\theta_f < 90°$) and the hydrophobicity of hydrophobic surfaces ($\theta_f > 90°$).

The roughness of PTFE-PPS composite coating mesh films was observed from SEM images as shown in Fig. 8. Figure 8 (a) shows the 80 times magnified image of the large-area coating film. The sprayed particles congregate on the grids. The average pore diameters of the mesh decreased to 0.062 mm. Figures 8 (b) and (c) are the further enlarged images of the coating film. The rough structure of the surface is described by the spherical particles. The sizes of the spherical particles are in a random distribution in microscale. In the 10000 times magnified image of the coating film, Fig. 8 (d), it is seen that on these spherical particles find reseaux of nanometer scale. These results indicate that the prepared coating mesh film has a rough surface with both micro- and nanostructures. The PTFE on the surface layer of mesh film is intrinsically hydrophobic and oleophilic. The surface layer of the mesh film becomes rougher through spraying. According to Eq. (2), the CA for water on this rough film will increase and that for oil will decrease. All of above shows that the PTFE-PPS composite coating mesh films hold super-hydrophobicity and super-oleophilicity and can be used to separate oil and water.

5 Conclusions

PTFE-PPS mesh films with a micro- and nanostructure rough surface was fabricated successfully. This mesh film

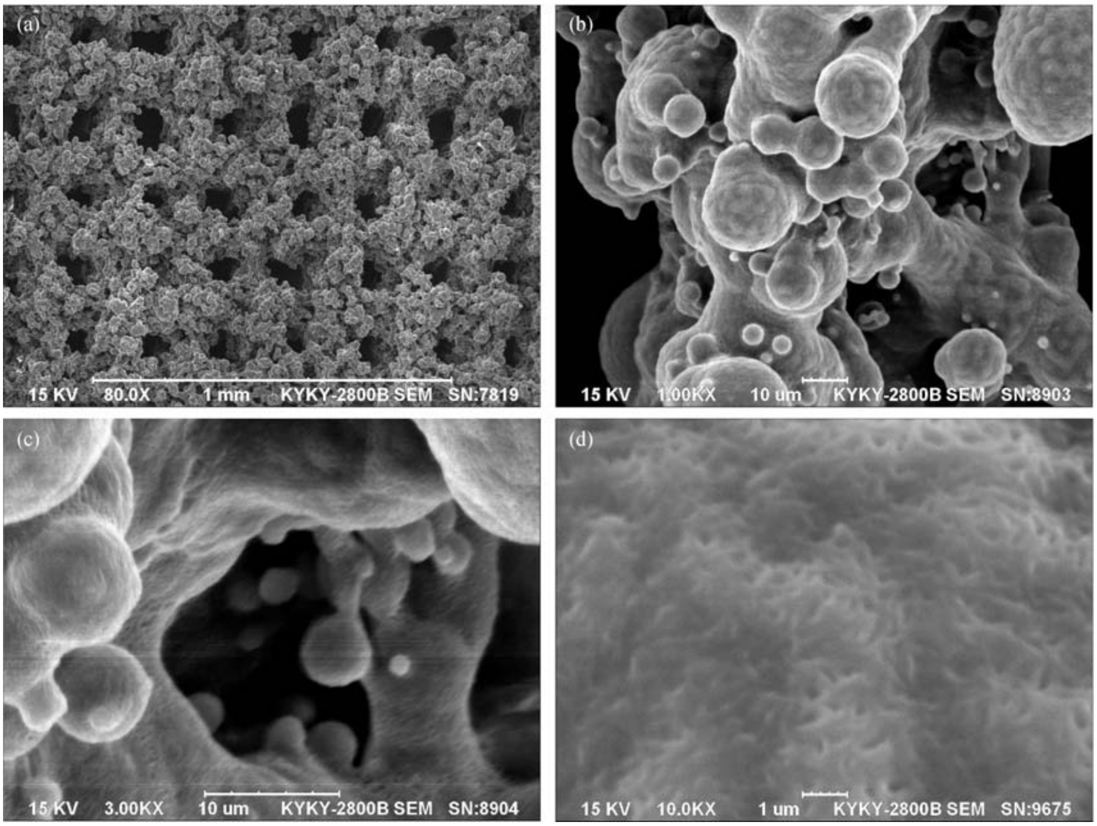


Fig. 8 SEM images of the prepared mesh film

shows both super-hydrophobic and super-oleophilic properties with a CA of 156.3° for water and close to 0° for diesel oil and kerosene. The super-hydrophobicity and super-oleophilicity can be well explained by the Wenzel theory. An oil-water separator with six stages was designed with the mesh film as the separation element. The oil removal rate of this oil-water separator reached about 99%. PPS improved the adhesive force and hardness of film effectively. The mesh film possesses good corrosion resistance.

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