

Fabrication of Self-Cleaning Poly(vinylidene fluoride) Membrane with Micro/Nanoscaled Two-Tier Roughness

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ABSTRACT: Based on the “lotus effect” principle, smooth microreliefs of polyvinylidene fluoride (PVDF) membrane were prepared via thermally induced phase separation process. Hydroxyl groups were introduced into PVDF membrane by pretreatment with KOH/alcohol solution. Subsequently, these hydroxyl groups grafted with $(\text{CH}_3)_2\text{SiCl}_2/\text{CH}_3\text{SiCl}_3$ to form nano-clusters, which were decorated on the microreliefs of PVDF membrane. Scanning Electronic Microscopy (SEM) and Atomic Force Microscope (AFM) analysis showed the micro- and nano-scale structures, similar to lotus leaf,

were successfully fabricated on the PVDF membrane surface. The water contact angle and sliding angle on the fabricated lotus-leaf-like PVDF membrane surface were 154° and 4° , respectively. Self-cleaning test indicated that the lotus-leaf-like surface of PVDF membrane has excellent superhydrophobic and self-cleaning properties. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1268–1274, 2011

Key words: polyvinylidene fluoride; lotus effect; superhydrophobic; self-cleaning

INTRODUCTION

Polyvinylidene fluoride (PVDF) membrane has the chemical stability and flexibility.¹ It is widely used as topcoat of membrane structures, such as tension membrane structures, architectural umbrellas, car shelters and tent fabrics.^{2,3} Further modified PVDF membrane with self-cleaning property may be even superior as the coating layer. The dust on these surfaces would be washed away easily by rain, which saves a great deal of manpower and cost for cleaning services.

In nature, many plant leaves have superhydrophobic properties.⁴ The water contact angle of lotus leaf is larger than 150° , and the water droplets roll off the surface at a small sliding angle. It has been observed that the surface of lotus leaf is created by papillose epidermal cells and an additional layer of epicuticular waxes. The roughness of lotus leaf leads to a reduced contact area between lotus leaf and a liquid drop (or a particle).⁵ As a result, contaminating particles can be picked up by the liquid and carried away as the droplet rolls off the leaf. The self-cleaning property of lotus leaf was called the “lotus effect” by Barthlott and Neinhuis.⁴

By mimicking the lotus effect, lots of superhydrophobic surfaces have been fabricated in many different ways such as sol-gel technique,⁶ electrospinning,^{7,8} plasma treatment of the surfaces,^{9,10} electrochemical deposition,¹¹ and layer-by-layer assembling technique.¹² Due to the chemical stability, PVDF membrane is distinguished by its outstanding properties: excellent resistance to chemicals, heat, fungal attack and radiation.^{13–15} Therefore, it is difficult to give PVDF membrane superhydrophobic property. The superhydrophobic PVDF membrane has been prepared by the method of NaOH enhancing chemical bath deposition in our previous work.¹⁶ But to introduce the active groups on the PVDF surface, the PVDF membrane was treated with 30% NaOH solution for 3 h at 60°C . In this work, the KOH/alcohol solution was used to replace the NaOH solution. This method has prominent advantages of both cost and time saving. The mixture of $(\text{CH}_3)_2\text{SiCl}_2$ and CH_3SiCl_3 was also used to generate the nano-scale materials, which was decorated on the microreliefs of PVDF membrane.

EXPERIMENTAL

PVDF powder was purchased from ShangHai 3F New Material Co. Ltd, China. $(\text{CH}_3)_2\text{SiCl}_2$ and CH_3SiCl_3 were purchased from Tianjin Guangfu Chemical Research Institute, China. KOH, KMnO_4 , alcohol, toluene, and *N,N*-dimethyl-formamide were all analytical grade and supplied by Tianjin Kermel Chemical Reagent Co., Ltd, China. The PVDF powder (2.5 g) was dissolved in *N,N*-dimethyl-formamide

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(DMF, 50 mL) at 60°C. After stirring for 1 h and standing for 0.5 h, the PVDF solution was cast on a clean glass plate. After drying at 120°C for 0.5 h, the PVDF membrane was formed and removed from the glass plate. This preparation process was usually called thermally induced phase separation.

PVDF membranes were immersed in 4–15% KOH/alcohol solution at 25–80°C and stirred for 2–8 min, then the samples were rinsed in distilled water to quench the reaction. After treatment with KOH/alcohol solution, the PVDF membranes were immersed in (4%) KMnO₄/KOH solution (30%) for 10 min at 25°C. Subsequently, the modified PVDF membranes were rinsed with water and dried.

(CH₃)₂SiCl₂ (DDS, 2.3 mL) and CH₃SiCl₃ (MTS, 1.7 mL) was diluted with 16 mL toluene. After treatment with KMnO₄/KOH, the PVDF membranes were grafted for 20 min in DDS/MTS solution under 80% relative humidity at 25°C. Subsequently, PVDF membranes were rinsed with toluene, alcohol, alcohol/water (volume ratio 1 : 1), then water, progressively, and finally oven-dried at 120°C.

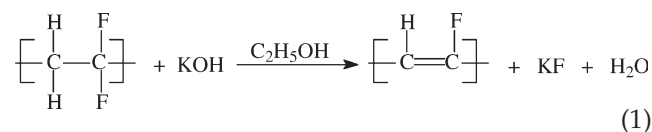
The water contact angle and sliding angle were tested with a 0.05 and 0.1 mL droplets, respectively, at room temperature by a contact angle goniometer (JY-82, China). The structures of the PVDF membranes were investigated by infrared spectroscopy (Tensor37, Germany). Screw micrometer (Links, China) was used to measure the thickness of PVDF membrane. The tensile strength of PVDF membrane was tested using electronic fabric strength machine (YG065, China) according to China national standard GB/T1040.3-2006. Morphology of PVDF membranes surface was investigated by scanning electron microscope (SEM, Quanta2000, Czech) and atomic force microscope (AFM, Agilent 5500, USA). Elemental composition of the nanostructures formed on PVDF membrane was measured by X-ray photoelectron spectroscopy (XPS, K-Alpha, Britain). To illustrate the self-cleaning property of PVDF membrane surface, carbon dusts (powdered activated carbon, analytical reagent, accorded with China national standard HG/T 3491-1999) were sprayed onto the surface of PVDF membrane. Subsequently, 0.1 mL water drops were sprayed onto the PVDF membrane surface, and the PVDF membranes were tilted some angle to the horizontal to test the self-cleaning property of the surface.

RESULTS AND DISCUSSION

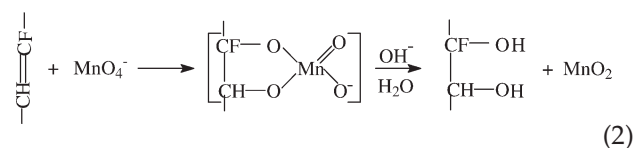
Surface modification of PVDF membrane by alkaline treatment

Previous investigations of the modification of PVDF involved treatment with chemicals,^{17,18} irradiation,

heat and microwave.¹³ It was found that pretreatment of PVDF membrane in alkaline solutions could promote the grafting reaction due to the change of its functional groups. This attracts us to investigate the effect of alkaline treatment of PVDF membrane on its functional groups. The elimination of HF from PVDF membrane by KOH/alcohol solution¹⁹ was shown below:



KF was formed on the membrane surface by the reaction of HF and KOH. As KF can not be dissolved in KOH/alcohol solution, so it left the membrane surface during the stirring process. The C=C double bonds formed on the polyene chain can be oxidized by dilute KMnO₄/KOH solution at room temperature.¹⁹ Then the hydroxyl groups can be introduced into the surface of PVDF membrane as follows:



The effects of some major factors such as concentration of KOH, the treating temperature and time on the water contact angle of PVDF membrane surface were investigated as follows.

Figure 1a showed the water contact angle of the surface of PVDF membrane untreated by KOH/alcohol solution was 88°. After the chemical treatment, the contact angle greatly decreased in Figure 1(a). When the concentration of KOH was 4%, the surface of PVDF membrane obtained the lowest contact angle 59°. Figure 1(b,c) showed the contact angles gradually decreased with prolonging the treating time or increasing the treating temperature. However, if the treating time was longer than 4 min [Fig. 1(b)] or the treating temperature was higher than 40°C, the PVDF membrane surface would become yellow gradually. Therefore, the optimum color and contact angle [59°, Fig. 1(a or c)] were obtained when the PVDF membrane was treated in 4%KOH/alcohol solution for 3 min at 40°C. The concentration of alkali solution, treating time and treating temperature were all greatly decreased compared with PVDF membrane modified by NaOH solution.¹³

The modified PVDF membrane possesses hydrophilic property due to the changes of its functional

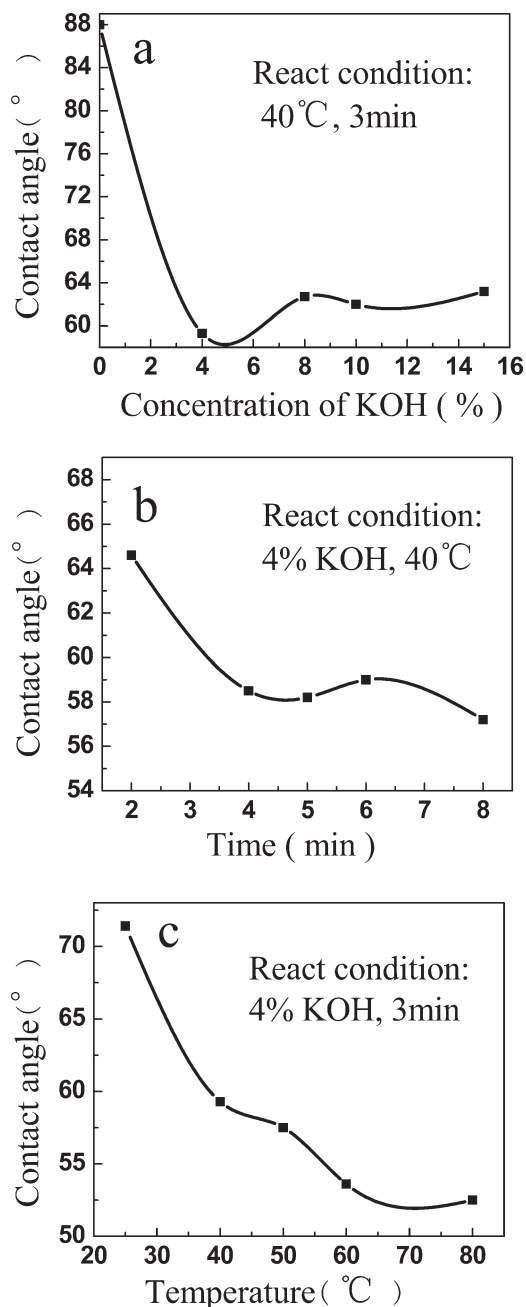


Figure 1 Influential factors of surface modification of PVDF membrane by KOH/alcohol solution.

groups or structure of the chain.¹³ To investigate the functional groups and structures of the modified PVDF membrane, infrared spectroscopy of PVDF samples was shown below.

Figure 2a showed the FT-IR spectrum of the original PVDF membrane. Figure 2(b,c) showed the FT-IR spectra of the PVDF membranes after treatment with KOH/alcohol and KMnO_4/KOH , respectively. Compared with the spectrum of Figure 2(a), the intensities of C-F ($1399, 1068\text{--}1300\text{ cm}^{-1}$) were all decreased and peaks at 2923 cm^{-1} from unsaturated bond (C—H) appeared in Figure 2(b,c). In Figure

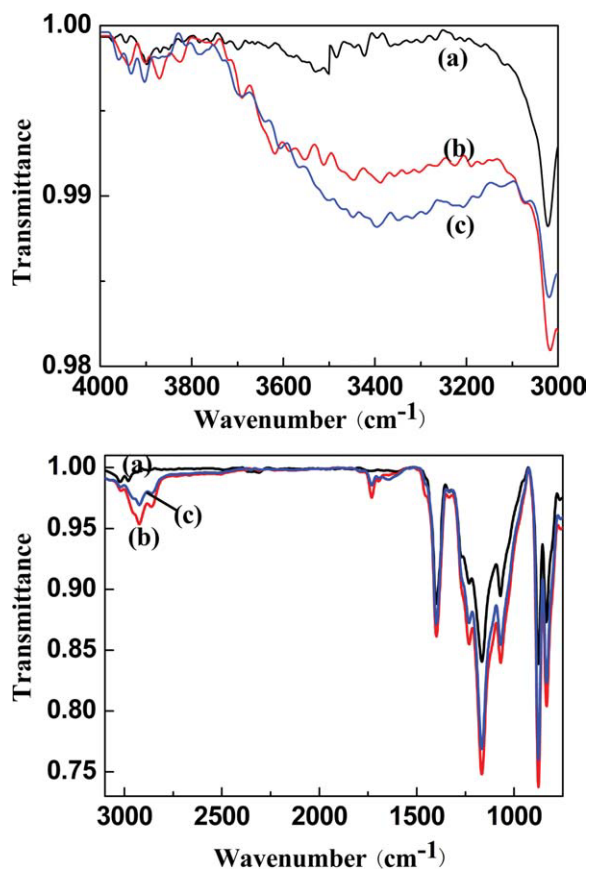


Figure 2 Infrared spectra of PVDF membranes: (a) unmodified (b) after treatment with KOH/alcohol (c) after treatment with KMnO_4/KOH solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

2(b), a vibration from $1675\text{ to }1500\text{ cm}^{-1}$ could be a result of the C=C bond formed by elimination of HF. In Figure 2(c), the $3400\text{--}3200\text{ cm}^{-1}$ broad band of medium intensity was assigned to the formation of hydroxyl group, which formed by the oxidation of dilute KMnO_4/KOH solution. The weak intensities of C=C band and hydroxyl groups indicated the reactions were not so bitter as to destroy the skeleton structure of PVDF membrane.

To know the reaction degree of PVDF membrane in alkali solution, the thickness and tensile strength of the PVDF membrane before and after modified were tested in Table I. After modified with KOH

TABLE I
 Physical Properties of PVDF Membranes Before and After Modified with Alkaline Solution

PVDF membrane samples	Unmodified	Modified with alkaline solution
Thickness (μm)	24	24
Tensile strength (N)	12.3	12.25
Strength retention (%)	100	99.6

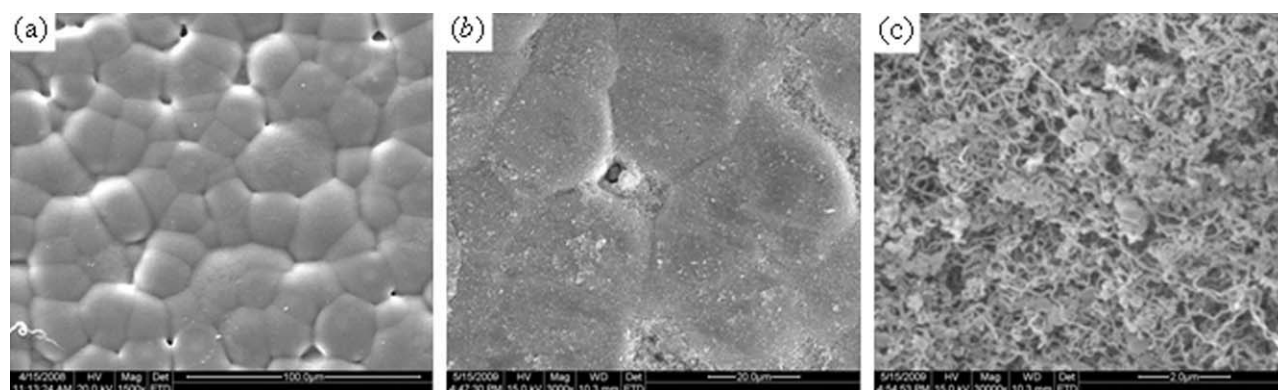


Figure 3 SEM images of surfaces (a) original PVDF membrane, (b) PVDF membrane deposited with DDS/MTS (3000 \times), and (c) magnified image of (b) (30,000 \times).

solution, the thickness of PVDF membrane was also 24 μm , the tensile strength of PVDF membrane had little decreased, and the strength retention also attained 99.6% (Table I). This improved that alkaline reaction only occurred on the surface of PVDF membranes under the treatment conditions used in this work, and the backbone of PVDF membrane was not destroyed.

Surface morphology of PVDF membrane deposited with DDS/MTS

The surface morphology and roughness of the PVDF membrane deposited with DDS/MTS solution were investigated by SEM and AFM. Elemental compositions of the nanostructures formed on the deposited PVDF membrane surface were explored by XPS as follows.

Figure 3a showed that PVDF membrane was constructed by smooth microreliefs on the coated surface. The microreliefs were formed from the aggregation of PVDF molecules during the evaporation of solvent, and the number and size of the microreliefs depended on the volatile conditions of the solvent. Figure 3(b) showed the PVDF membrane deposited

with DDS/MTS solution, and it looks like frost covered on the surface of PVDF microreliefs. Its enlarged view [Fig. 3(c)] displayed clearly that such frost was constructed by fibrous materials and interconnected branches. Both DDS and MTS can react with water contained in the air to form silanol groups, which can react with hydroxyl groups on PVDF membrane surface to form filaments, and also can react with each other to generate molecular structures as interconnected branches.²⁰ MTS hydrolyzed with water and grew in three dimensions; however, the silanol groups of DDS grew in two dimensions, and the dimethylsilanol groups inhibited further reaction near them.²¹

It can be seen from Figure 4a that the surface of undeposited PVDF membrane was constructed by many smooth, regular microreliefs. The data estimated by AFM machine showed that the average diameter of microreliefs was about 7.5 μm , the height was about 5 μm and the distance between microreliefs was 4 μm . Figure 4(b) showed the material deposition on PVDF membrane was constructed by nano-clusters in the 2D image. In its 3D image [Fig. 4(c)], the microreliefs of PVDF membrane surface were covered by many small peaks. The

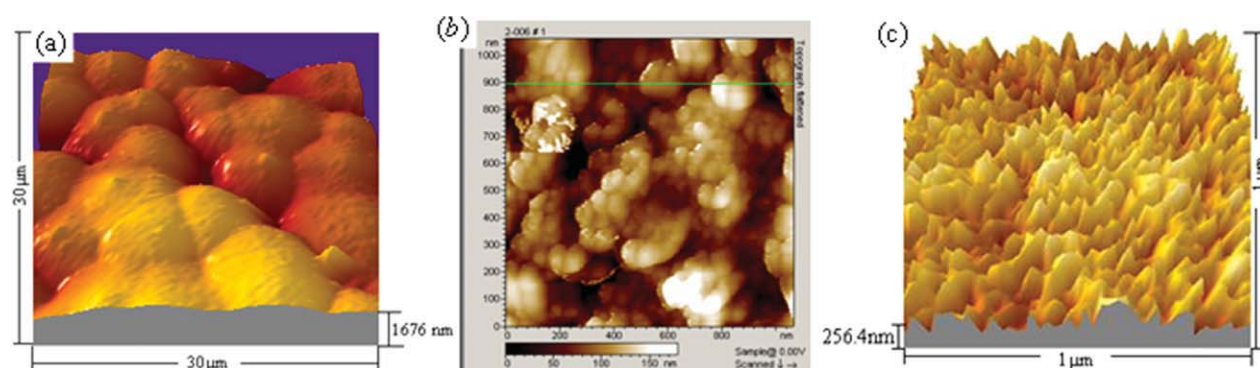


Figure 4 AFM images of PVDF membrane surface (a) undeposited, (b) deposited for 2D image, and (c) deposited for 3D image. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

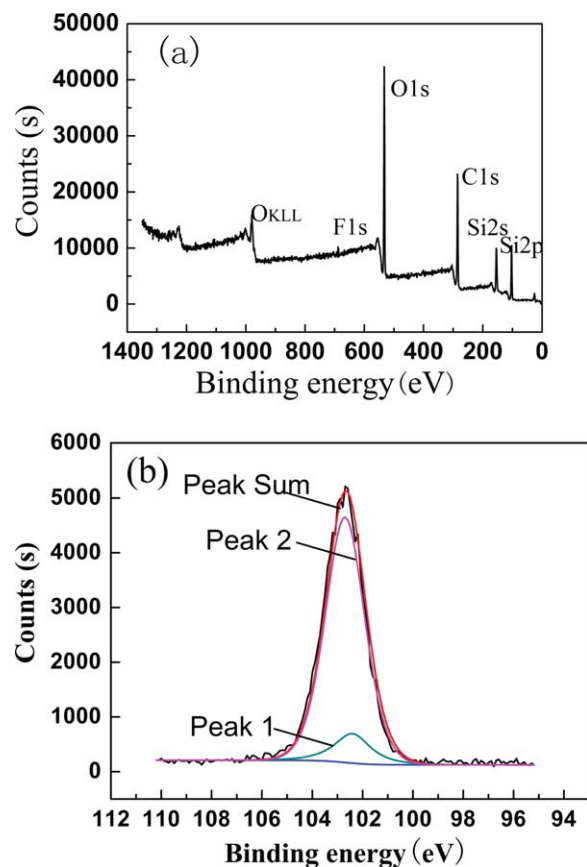


Figure 5 XPS spectra obtained from the PVDF membrane deposited with DDS/MTS (a) the wide spectra and (b) the narrow spectra of Si2p element. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

average diameter of the peaks was about 200 nm and the height was 120 nm. The distance between peaks was about 80 nm. The nanoscale peaks distributed uniformly on the microstructure surface of PVDF membrane. After deposited with DDS/MTS, the micro- and nanoscale structures, similar to the

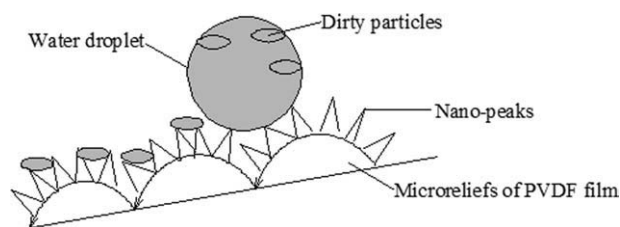


Figure 7 Illustration of the water droplet (or particles) residing on the deposited PVDF membrane.

lotus leaf, were obtained on the PVDF membrane surface.

Figure 5 showed that XPS spectra were obtained from the PVDF membrane surface deposited with DDS/MTS solution. Three elemental compositions (Si2s at 153eV, Si2p at 102.4–102.7eV, C1s at 284.8eV and O1s at 530.4 eV) were clearly observed. The Si2p, Si2s, C1s, and O1s components originated from the Si–CH₃, Si–O, CH₃–Si, and O–Si groups, respectively. The spectrum of Si2p at 102.4–102.7 eV was combined by the (CH₃)₂–Si stretching vibrations at 102.4 eV [peak 1 in Fig. 5(b)] and the CH₃–Si stretching vibrations at 102.7 eV (peak 2 in Fiber 5b). On the basis of these XPS data, the chemical composition of the superhydrophobic surface was represented as polydimethylsiloxane and polymethylsiloxane. Main peak was the polymethylsiloxane stretching vibration at 102.7 eV.

Hydrophobic and self-cleaning properties of deposited PVDF membrane

The hydrophobic and self-cleaning properties of the deposited PVDF membrane surface were examined as follows.

Figure 6 illustrated the images of 0.05 mL water droplets residing on the surfaces of PVDF membrane. The water contact angle of the

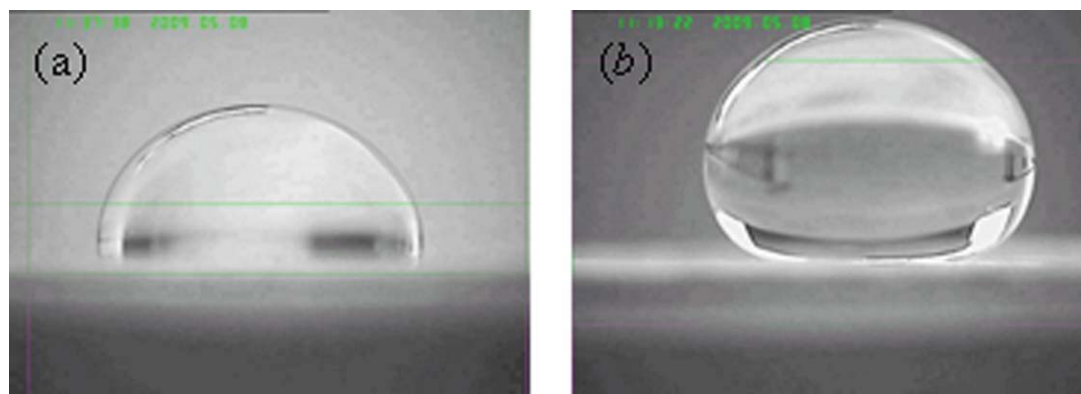


Figure 6 Water droplets residing on (a) original PVDF membrane and (b) PVDF membrane deposited with DDS/MTS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

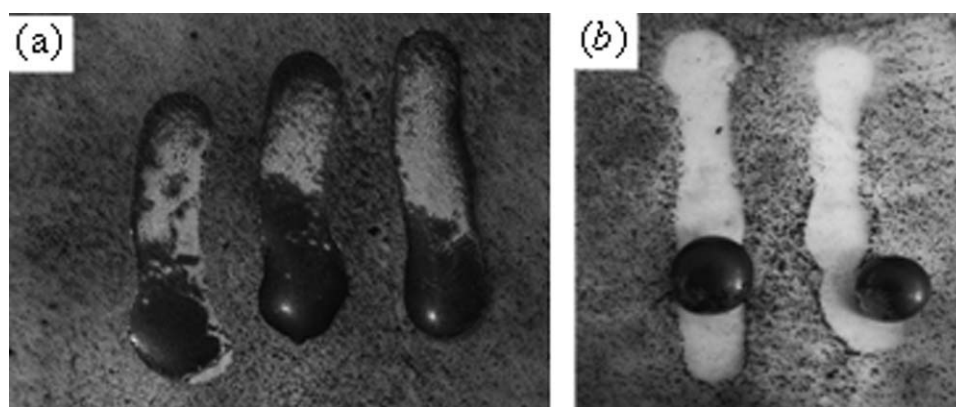


Figure 8 Self-cleaning test of the PVDF membrane surfaces (a) undeposited and (b) deposited with DDS/MTS.

original PVDF membrane surface was 88° in Figure 6(a) and the water droplet had a little spreading. When the water droplet was dripped on the PVDF membrane surface deposited with DDS/MTS solution, the contact angle was as high as 154° [Fig. 6(b)]. Compared with Figure 6(a), the water droplet in Figure 6(b) showed less contact area with the solid surface.

The influence of surface roughness on the wettability has been explained by Wenzel model and Cassie-Baxter model.²² The Wenzel model was described as the complete penetration of the liquid drop within the structured surface. The Cassie-Baxter model on superhydrophobic surfaces indicates that only the hills of the rough surfaces are wetted, while the water drop does not penetrate into the valleys. The superhydrophobicity of the deposited PVDF membrane with the two-tier micro/nanoscaled roughness prefers to obey the Cassie state, demonstrated by Figure 6(b).

According to the Cassie-Baxter model, when the water droplet (or particles) dripped on the PVDF membrane surface deposited with DDS/MTS, it sat on the micro- and nanometer scale roughness (Fig. 7), and the "air pockets" were formed between the water droplet (or particles) and the PVDF membrane surface. For a part of water droplet (or particles) sitting on air, the contact area of water droplet (or particles) to the PVDF membrane decreased, and the adherence strength between water droplet (or particles) and PVDF membrane surface decreased, too, so the dirt particles on roughness surface was easily taken away by water droplet. This was further confirmed by the self-cleaning test in Figure 8.

The self-cleaning test of the PVDF membrane was shown in Figure 8(a) that the water droplets on the undeposited PVDF membrane surface failed to carry away the carbon dust when tilting 12° . However, when the PVDF membrane surface de-

posited with DDS/MTS titling 4° , the water droplets formed spheres and can easily roll off with the dirty particles, leaving an extreme clean surface as shown in Figure 8(b). This validates that the developed method was successfully mimicked the self-cleaning mechanism of lotus leaf.

CONCLUSION

Based on the lotus effect principle, the self-cleaning PVDF membrane was successfully fabricated. Pretreatment of PVDF membrane in KOH solutions could promote the grafting reaction due to the introduction of hydroxyl groups. This hydrophilic modification has prominent advantages of both cost and time saving compared with PVDF membrane modified by NaOH solution. After deposited with DDS/MTS solution, nano-clusters were formed on the surface of PVDF membrane. In the 3D image, the nano-clusters like many small peaks were decorated on the PVDF microreliefs. XPS data shows the chemical composition of the nano-clusters were polydimethylsiloxane and polymethylsiloxane. On the surface of lotus-leaf-like PVDF membrane, the water contact angle and sliding angle were 154 and 4° , respectively. Self-cleaning test exhibited that the deposited PVDF membrane has excellent superhydrophobic and self-cleaning properties.

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