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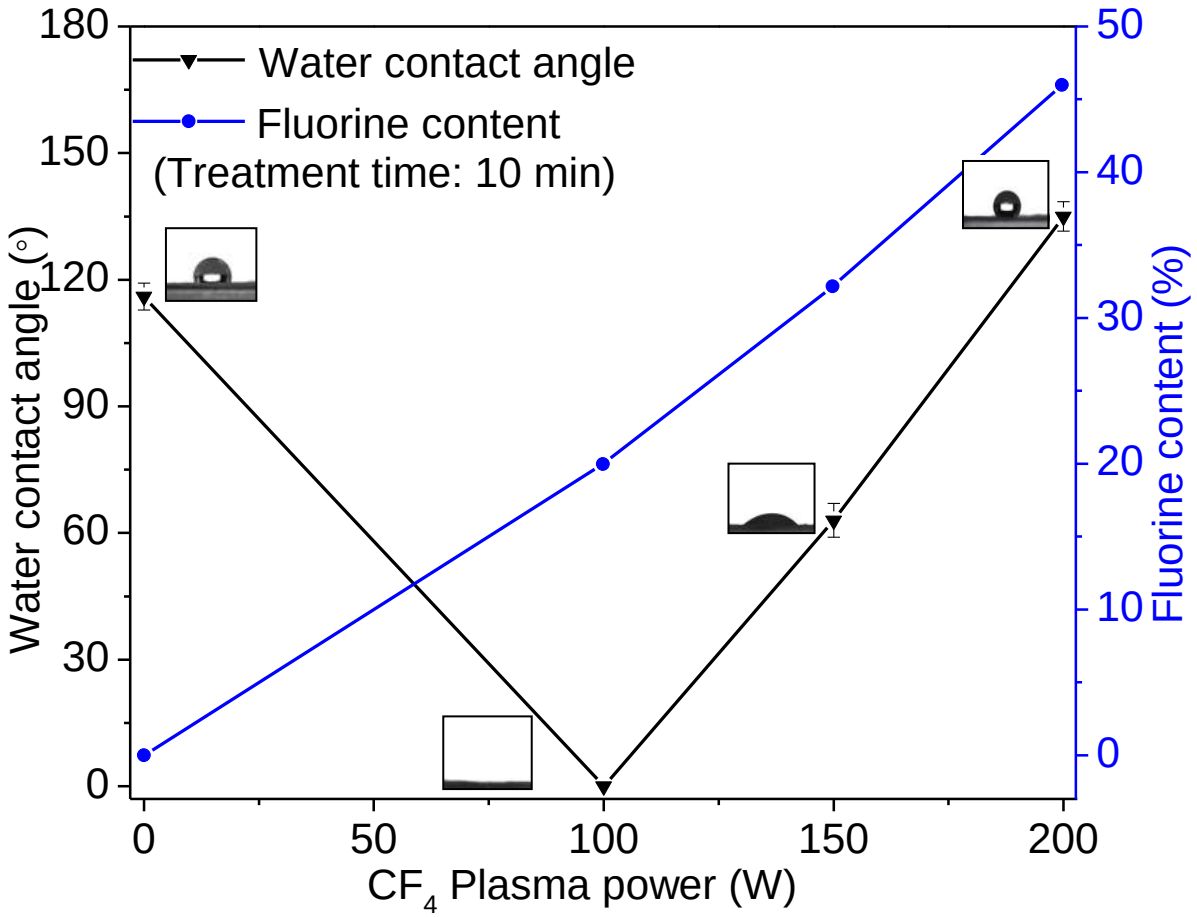
Graphical abstract



Abstract: A switchable surface that promotes either hydrophobic or hydrophilic wettability of poly (L-lactide) (PLLA) microfibrous membranes is obtained by CF_4 microwave plasma treatment in this paper. The results indicated that both etching and grafting process occurred during the CF_4 plasma treatment and these two factors synergistically affected the final surface wettability of PLLA membranes. When plasma treatment was taken under a relatively low power, the surface wettability of PLLA membranes turned from hydrophobic to hydrophilic. Especially when CF_4 plasma treatment was taken under 100 W for 10 min and 150 W for 5 min, the water contact angle sharply decreased from 116 ± 3.0 ° to ~0 °. According to Field-emission scanning electron microscopy (FESEM) results, the PLLA fibers were notably etched by CF_4 plasma treatment. Combined with the X-ray photoelectron spectroscopy (XPS) measurements, only a few fluorine-containing groups were grafted onto the surface, so the etching effect directly affected the surface wettability of PLLA membranes in low plasma power condition. However, with the plasma power increasing to 200 W, the PLLA membrane surface turned to hydrophobic again. In contrast, the morphology changes of PLLA fiber surfaces were not obvious while a large number of fluorine-containing groups grafted onto the surface. So the grafting effect gradually became the major factor for the final surface wettability.

Keywords: CF_4 plasma, hydrophobic-hydrophilic surface, poly (lactic acid), tunable wettability, electrospinning membrane

1 Introduction

Microfibrous structures fabricated by electrospinning are of particular interest due to their high specific surface area, high porosity and excellent mechanical properties that make them ideal candidates for polymer scaffolds [1-4]. However, since some polymer surfaces, such as poly (L-lactide) (PLLA), are hydrophobic and its insufficient reactive side-chain groups on surface usually lead to low performances[5], its further application is severely limited[2, 6-8]. Accordingly, various surface treatments such as surface coating process, ultraviolet irradiation or plasma treatment have been used to modify PLLA in order to improve wettability[3, 6, 9-18]. Among these methods, plasma treatment is one of the most widely used methods to modify surface properties for specific application needs. This method provides a wide range of surface functionalities[9, 12, 13, 19-21], which can change the surface wettability of the materials in the nanometer scale, without affecting the bulk properties, and it has been widely used in membrane surface modification. For instance, surface modification by reactive gas plasma treatment or plasma-assisted film deposition or polymer coating by using various extracellular matrixes and other active molecules via plasma treatment have been shown to improve the surface wettability of polymer materials [12, 16, 22-24].

In addition to studies devoted to the increase of the surface hydrophilicity of PLLA for promoting active molecular, the direct effect of plasma treatment on surface wettability has received significant attention. Depending on the conditions and the plasma species, surface properties of polymer, such as morphology and surface

wettability can be altered [25, 26]. Generally, plasma surface activation employs gases [27]. And the hydrophilic or hydrophobic surface properties can be obtained by plasma treatment with suitable gases.

On one hand, a great number of studies on plasma treatment for hydrophilicity improvement have been reported [9, 12, 28-30]. Hirotsu et al. [9] treated melt extruded poly (lactic acid) films with oxygen, helium, and nitrogen plasmas to improve the wettability. Yan et al. [29] used NH_3 plasma treatment to improve hydrophilicity of poly (lactic acid) scaffolds prepared using a particulate leaching technique. The NH_3 plasma created reactive amine groups on poly (lactic acid) scaffolds that anchored collagen through polar and hydrogen bonding interactions [26, 31]. These surface-modified scaffolds showed enhanced hydrophilicity. O_2 plasma treatment has been used to improve the surface wettability of poly (lactic acid) membranes [12, 31]. On the other hand, there is also many studies focus on the effect of plasma treatment of polymer membrane surface in enhancing the hydrophobicity properties [20, 26, 32-37]. Kwon [32] used saturated CF_4 plasma treatment to improve the resistance of polypropylene fabrics to water wetting. He [20] described a CF_4 plasma modification to turn a hydrophilic membrane into a hydrophobic one for membrane distillation. Kan [38] used CF_4 plasma to enhance hydrophobicity of polyester synthetic leather, and the static contact angle was greatly increased from values close to 0 °to 106 °after the plasma treatment.

Although the research works mentioned above have made considerable progress in changing the surface wettability, few studies on the regulatory function of single

type of plasma on hydrophobic and hydrophilic surface wettability properties have been mentioned. Most of studies focus on the application of plasma treatment for one-way regulation in enhancing the surface wettability. However, the interactions between the plasma and the surface molecules of polymers would lead to both physical etching [39-44] and chemical grafting effects [12, 22], so it's feasible to control the surface wettability of polymers by single plasma treatment.

In the present work, the surface wettability of electrospun PLLA microfibrous membranes was controlled by CF_4 microwave plasma treatment. Field-emission scanning electron microscopy (FESEM), water contact angle, Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) measurements were used to investigate the morphology changes and surface chemical contents of the PLLA microfibrous membranes before and after CF_4 plasma treatment. Therefore, the etching and grafting synergistic mechanisms of the CF_4 plasma treatment were proposed based on the analysis of all these results mentioned above.

2 Experimental

2.1 Materials

PLLA (biopla 6202F) was purchased from Ningbo Global Biological Material Co., Ltd. Its number-average molecular weights are 1.1×10^5g/mol. Chloroform and ethanol were purchased from Tianjin Weichen Chemical Reagent Co. Ltd. China.

2.2 Electrospinning

The electrospinning apparatus is schematically depicted in Figure 1, where the main components are shown. PLLA was dissolved in a mixture of chloroform and

ethanol (3:1 by volume) to prepare a 7 wt% solution, which was then loaded into a plastic syringe fitted with a stainless steel needle. The polymer solution was continuously supplied using a syringe pump at a rate of 3 mL/h. The voltage applied to the needle was 20 kV and the distance between the collector and the needle was 15 cm. The electrospinning process was carried out at room temperature of 25℃ and relative humidity of 30%. The obtained membranes were then vacuum-dried at 50 ℃ for 24 h and ready for further characterization.

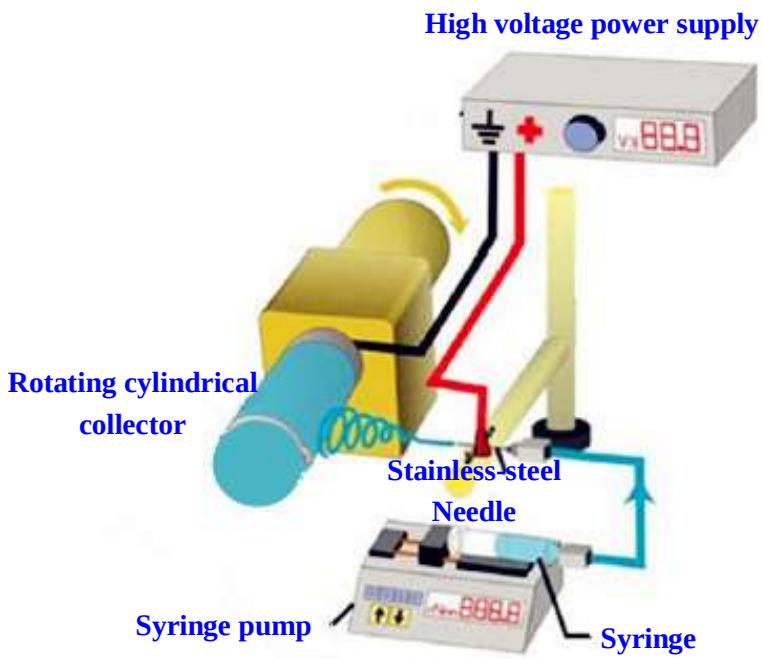


Figure 1 3-Dimentional drawing of the electrospinning apparatus

2.3 CF_4 microwave plasma treatment

CF_4 microwave plasma treatment was performed on a YZ-2 microwave plasma generator, and digital photo of the apparatus was shown in Figure 2. The electrospun PLLA membrane samples were placed on the plate of the plasma

chamber, and then the chamber was evacuated to 5 Pa at room temperature. Thereafter, the electrospun PLLA membrane samples were treated by CF_4 plasma at a gas flow rate of 1.5 L/h and a pressure of 30 Pa. The degree of the CF_4 microwave plasma treatment process is adjusted by controlling the plasma power and treatment time. The plasma power was 100 W, 150 W, 200 W and 250 W, and the treatment time was set for 5 min and 10 min, respectively (listed in Table 1). After the CF_4 plasma treatment, all PLLA membrane samples were taken out and preserved for further investigation.

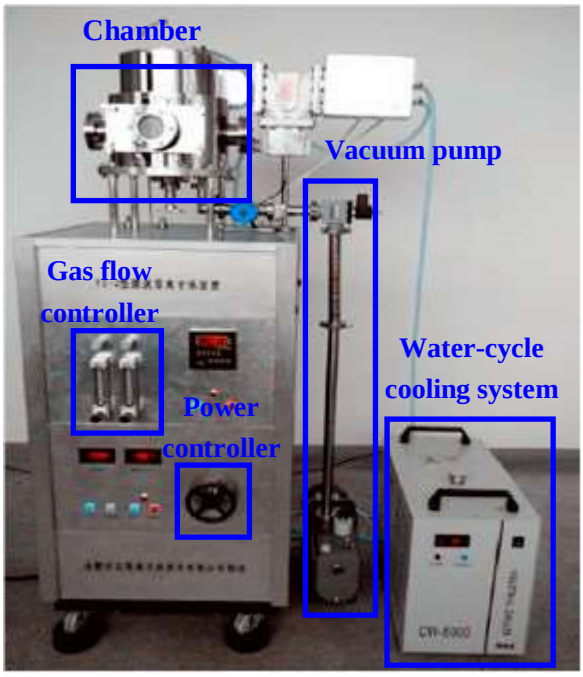


Figure 2 Digital photos of the microwave plasma apparatus

Table.1 Experimental conditions of CF_4 plasma treatment

Sample	Power (W)	Treatment time(min)
PLLA 100-5	100	5

PLLA 100-10	100	10
PLLA 150-5	150	5
PLLA 150-10	150	10
PLLA 200-5	200	5
PLLA 200-10	200	10
PLLA 250-5	250	5

2.4 Characterization

The surface morphologies of the electrospun PLLA microfibrous membranes were examined by FESEM (Quanta 200, Holland). All samples were coated with a thin layer for ~5nm of gold before being observed using FESEM. The water contact angle was measured with a contact-angle measurement apparatus (JYSP-180 Contact Angle Analyzer) according to the sessile-drop method. Briefly, a water droplet was deposited on a flat membrane surface and the contact angle of the droplet with the surface was measured. The instantaneous water contact angle obtained within 0.5 s (ensuring observable vibration of the liquid drop on the solid sample had already ceased) was recorded. Each final water contact angle value was obtained by averaging over more than five water contact angle values of different spots. FTIR was acquired using a Bruker Tensor 27 system in the 2400-800 cm^{-1} wave-number range to analyze the functional groups grafted onto the surface of electrospun PLLA microfibrous membranes before and after ozone modification. All the membranes were pressed into a pellet with potassium bromide (KBr) before measurement. The spectra were

collected by cumulating 32 scans at a resolution of 2 cm^{-1}. XPS investigations were carried out with a PHI 5700 ESCA System with Al Ka (1486.6 eV) radiation to characterize changes of the chemical components of electrospun PLLA microfibrous membranes and the pressure in the XPS analyzing vacuum chamber was less than 3×10^{-9} mbar.

3. Results and discussion

3.1 Surface morphology and water contact angle

Surface morphologies of the untreated and CF_4 plasma treated electrospun PLLA microfibrous membranes were observed by FESEM, which are illustrated in Figure 3 and Figure 4, and the water contact angle measurements of untreated and CF_4 plasma-treated electrospun PLLA micro-fibrous membranes are given in Figure 5. As can be seen in Fig. 3a, the as-spun PLLA micro-fibrous membrane is a highly porous nonwoven material with an average diameter of 847 $\pm$ 200 nm. More in detail, it was found that the untreated PLLA fiber had a comparatively smooth surface (Figure 3b). The as-spun PLLA microfibrous membrane showed a hydrophobic surface, and its water contact angle is 116 $\pm$ 3.0°. Compared with the two curves in Figure 5, the treatment time was not the decisive factor for the surface wettability properties of PLLA samples. The water contact angle of these samples did not change significantly with time prolong. With the plasma power increasing, the surface of PLLA membrane samples turned to hydrophilic first and then turned back to hydrophobic. Combined with the FESEM results shown in Figure 4a and 4b, when the plasma treatment power was 100 W, it can be found that the PLLA fibers were notably etched and roughened

by CF_4 plasma treatment, and some visible grooves and small notches were presented on these membrane sample surfaces. The water contact angle of PLLA 100-5, PLLA 100-10 is sharply decreased to 32 ± 3.6 ° and ~0 °, respectively. Then, with the plasma power enhancing to 150 W, the surface of PLLA membranes was still superhydrophilic in the first 5 min, and the water contact angle value of PLLA 150-5 was close to 0 °. However, when the treatment time was extended to 10 min, the water contact angle began to increase. In addition, many small holes and visible cross striations were generated on the membrane sample surfaces (Figure 4c and 4d). Furthermore, with the plasma treatment power increasing to 200 W, the water contact angle of PLLA 200-5 and PLLA 200-10 was increased to 123 ± 3.8 ° and 135 ± 3.5 °, respectively. In addition to the severe etching effect, some fibers of PLLA microfibrous membranes began to break (Figure 4e and 4f). And these changes may lead to the increase of the surface roughness of PLLA membrane samples [40, 44-46]. However, this phenomenon also cause the mechanical strength of the samples decreased a little bit. Moreover, when the plasma treatment power was further elevated to 250 W, most fibers of PLLA microfibrous membranes broke and the surface of PLLA fiber was etched drastically (Figure 4g). Since the PLLA 250-5 sample showed a poor mechanical performance, we didn’t discuss it in later part of this paper.

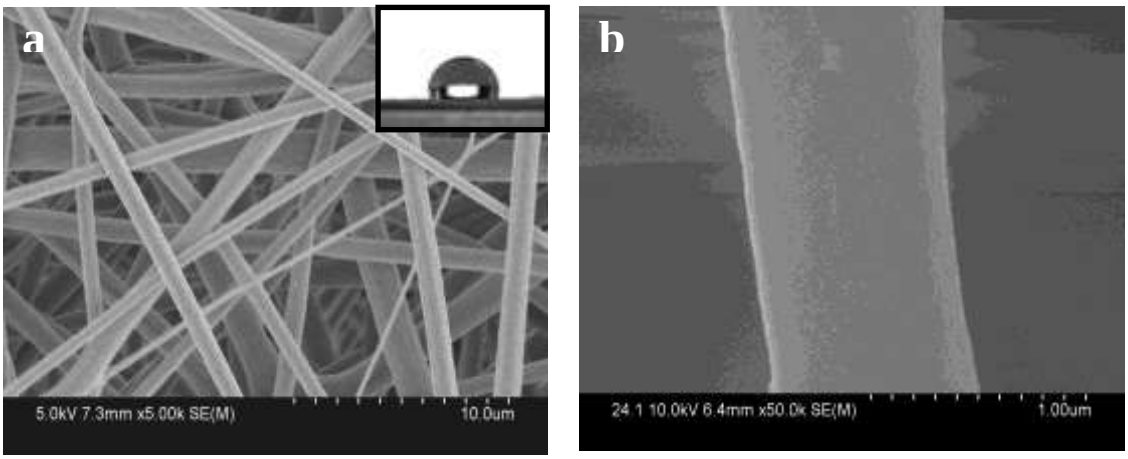
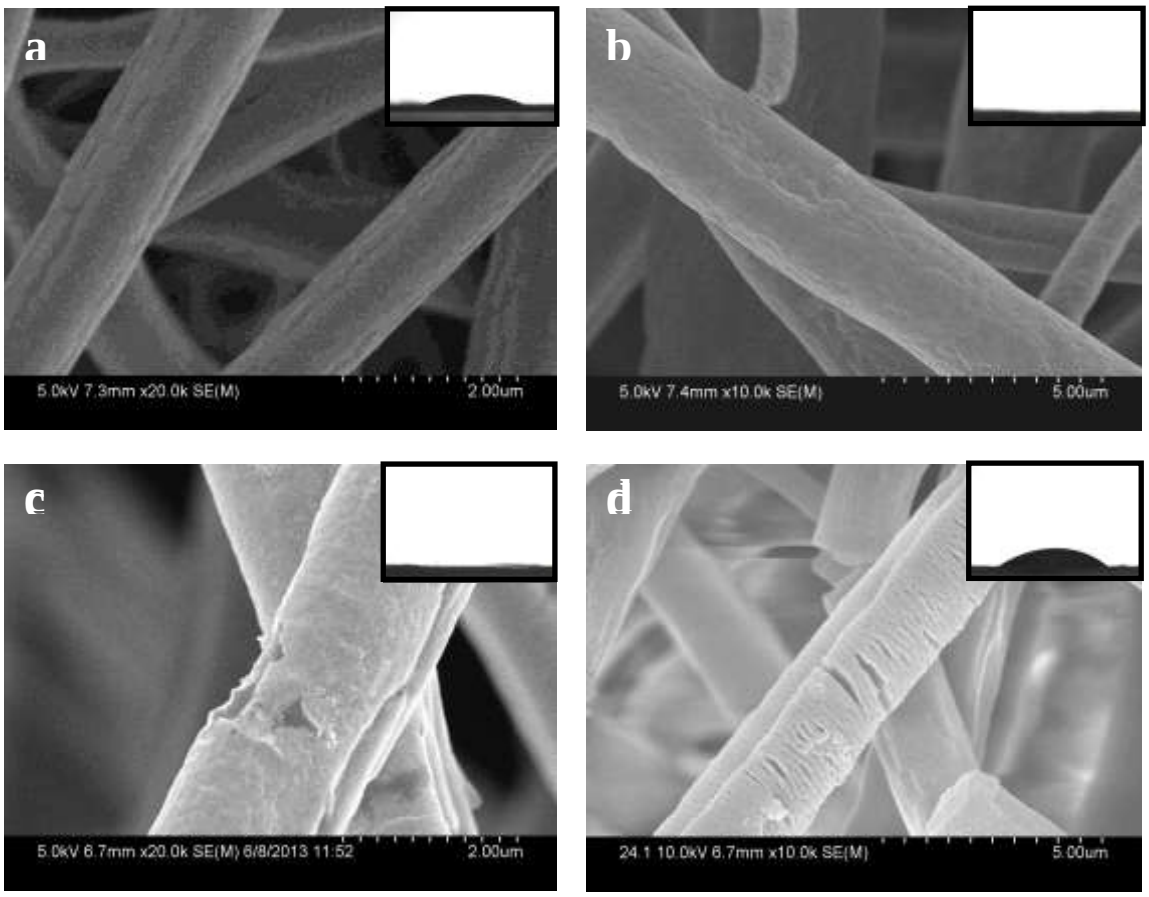


Figure 3 FESEM of the untreated PLLA sample: (a) ×5k (b) ×50k



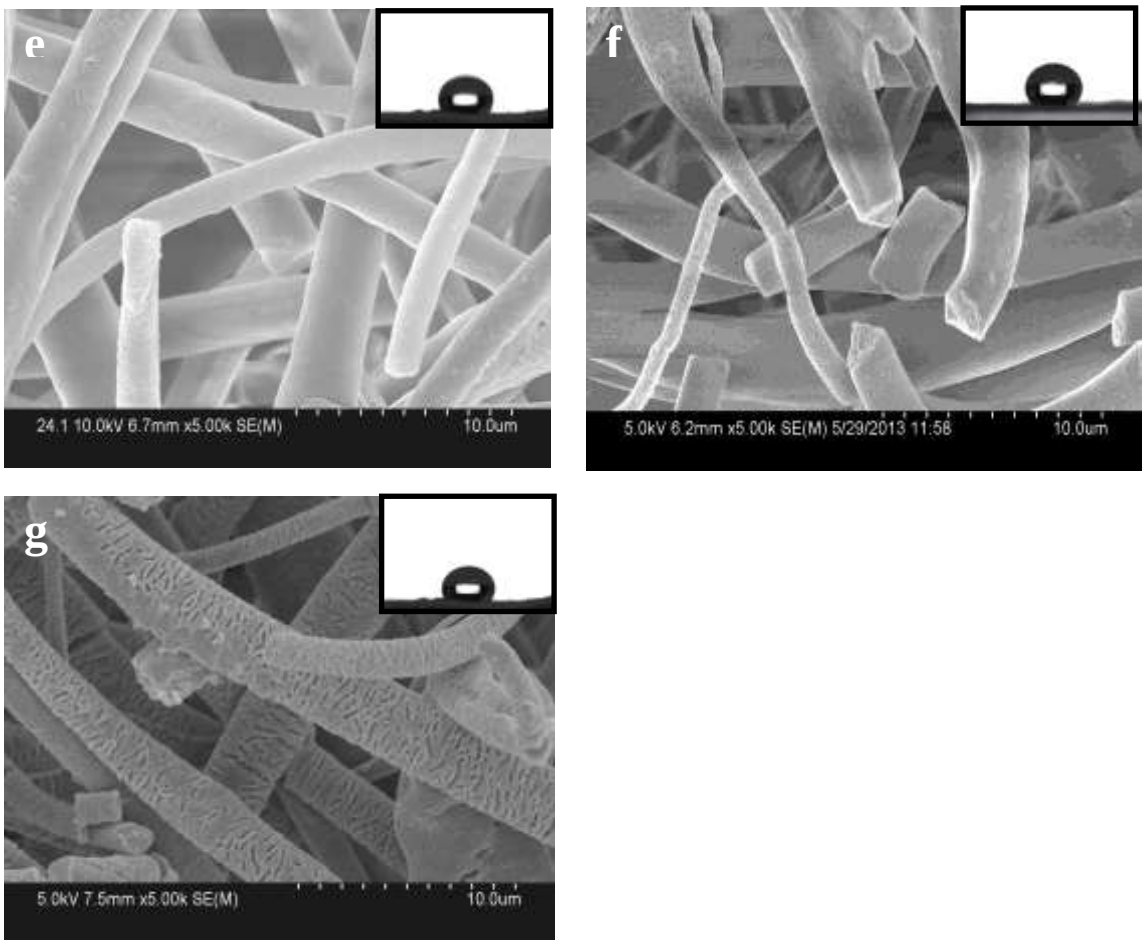


Figure 4 FESEM of CF_4 plasma treated electrospun PLLA microfibrous membranes. The insert shows a drop of water on the surface of PLLA microfibrous membranes, illustrating the wettability of the samples: (a) PLLA 100-5 (b) PLLA 100-10 (c) PLLA 150-5 (d) PLLA 150-10 (e) PLLA 200-5 (f) PLLA 200-10 (g) PLLA 250-5

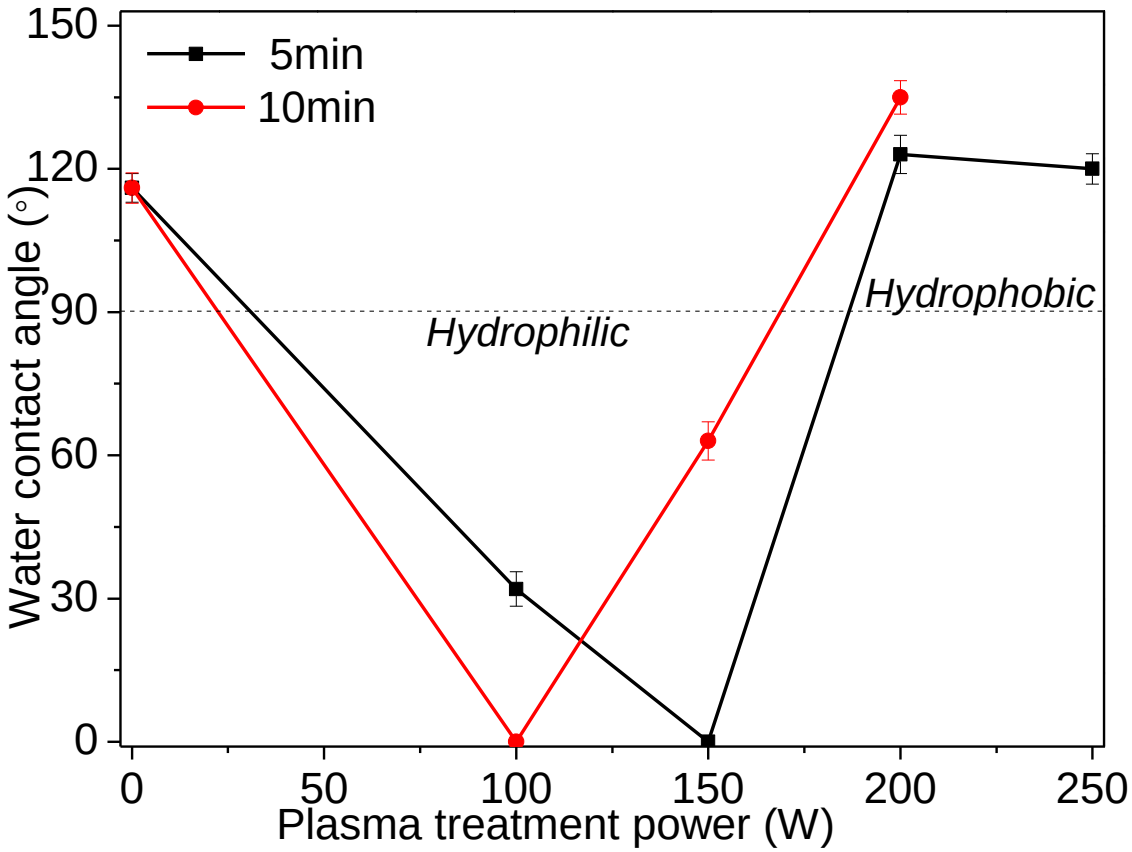


Figure 5 Water contact angle of untreated and plasma-treated electrospun PLLA microfibrous membranes

3.2 FTIR spectra

Figure 6 shows the FTIR spectra of PLLA samples before and after CF_4 plasma treatment. For untreated PLLA, the C=O stretch in the carbonyl group appeared at ~1760 cm^{-1}[12]. This band also appeared in the spectra of CF_4-treated PLLA samples, but the intensity of these samples was slightly weakened. After CF_4 microwave plasma treatment, new vibration peaks of C-F at 1340 and 1210 cm^{-1} appeared in the spectra of CF_4-treated electrospun PLLA microfibrous membranes [47, 48]. More in detail, the intensity of these two peaks became stronger with the plasma power and

treatment time increasing. These results indicate that a number of fluorine-containing groups were successfully grafted onto the surface of electrospun PLLA microfibrous membranes.

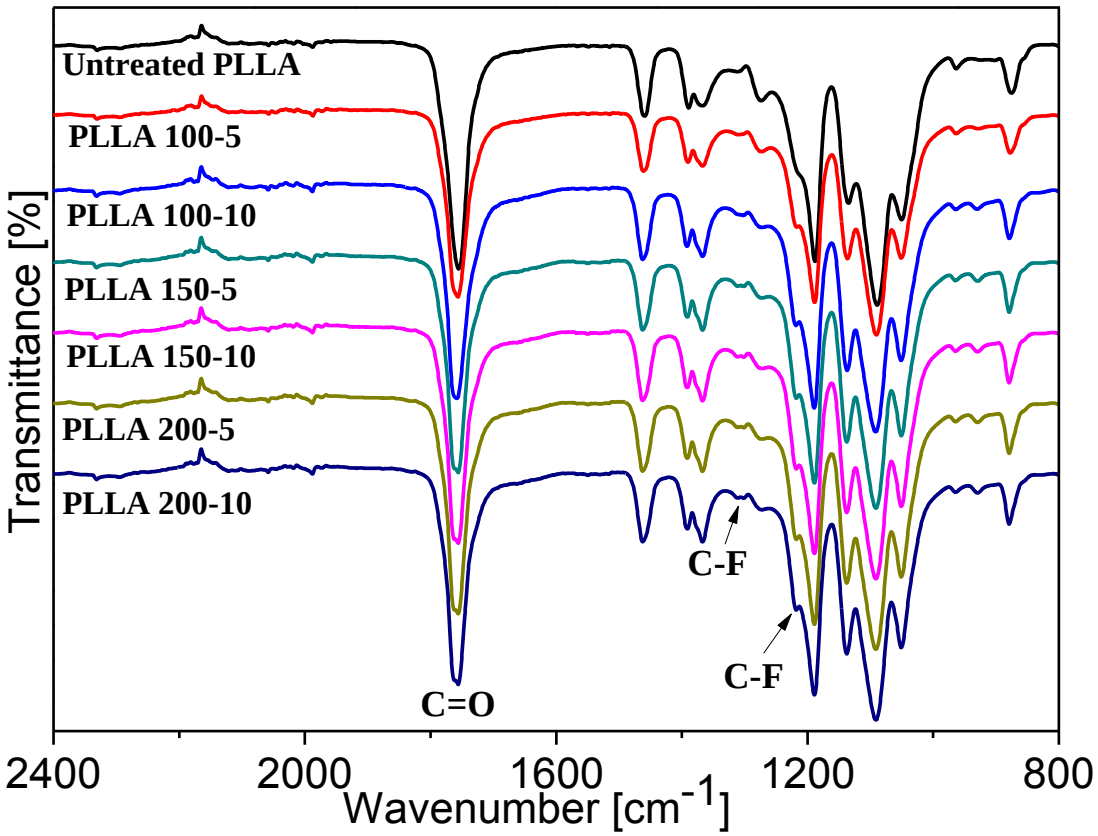


Figure 6 FTIR spectra of PLLA samples before and after CF_4 plasma treatment

3.3 XPS spectra

The surface chemical composition of the PLLA membrane samples was studied by XPS. The element contents of all electrospun PLLA microfibrous membrane samples were listed in Table 2. Compared the data in Table 2, it could be concluded that with the plasma treatment power increasing, the F content was gradually increased while the C and O content was reduced. More in detail, Table 2 also reveals that in the same plasma treatment power, the surface F content of PLLA samples

significantly increased with the treatment time extending.

For detailed studies of functional groups, peaks of C 1s were studied. We use XPSPEAK41 software to fit the peaks and analyze the C 1s spectra. And then we calculated the chemical composition of all the PLLA samples by calculating the relative ratios of each chemical group's peak area. Figure 7 and Table 3 show C 1s peaks of the PLLA samples before and after CF_4 plasma treatment. The spectrum from the untreated PLLA shows three components at 285, 287 and 289 eV, which may be assigned to the presence of C-C, C-O and O=C-O bonds in chain [9, 12, 22]. After CF_4 plasma treatment, the C1s spectra revealed new peaks at 292 and 294 eV, corresponding to the CF_2-CF_2 and CF_3 [49], which were not observed for the untreated PLLA. Due to the CF_4 plasma treatment, the percentage of oxygen-containing groups were lower whereas the percentage of fluorine-containing groups were higher than the untreated PLLA, which was also consistent with the element content data in Table 3.

Comparing the C1s spectra of all PLLA membrane samples, it can be concluded that when CF_4 plasma treatment was taken under a relatively low power (such as sample PLLA 100-5, PLLA 100-10 and PLLA 150-5), only a few fluorine-containing groups were grafted onto the surface of PLLA fibers, in contrast, oxygen-containing groups (C-O and O=C-O) didn't reduced obviously during the plasma treatment. As the water contact angle analysis shown in Figure 5, surfaces of sample PLLA 100-5, PLLA 100-10 and PLLA 150-5 were hydrophilic. Combined with the FESEM analysis (Figure 4), the interesting results may be due to the etching effect on PLLA

fibers during the plasma treatment. Then, with the plasma treatment power increasing to 200 W, the functional groups on the surface of PLLA membrane samples vary significantly. More in detail, a large number of fluorine-containing groups (CF_2-CF_2 and CF_3) were grafted onto the surface of PLLA fibers while the oxygen-containing groups sharply reduced during CF_4 plasma treatment. And the surfaces of these two PLLA membrane samples (PLLA 200-5 and PLLA 200-10) were turned to hydrophobic. The radical changes in the surface wettability of PLLA samples were mainly caused by the grafting effect in the CF_4 plasma treatment. Moreover, combined with the FESEM analysis in Figure 4e and 4f, we also found that a large number of PLLA fibers were broken when the treatment power was elevated to 200 W, and this may rapidly increase the surface roughness of PLLA membrane samples, which may be another reason for the hydrophilic membranes turning into hydrophobic.

Table 2 Element content of PLLA membrane samples

	C (%)	**O (%)**	**F (%)**
untreated PLLA	**64.55**	**35.45**	**0**
PLLA 100-5	**64.34**	**29.14**	**6.52**
PLLA 100-10	**55.82**	**24.20**	**19.98**
PLLA 150-5	**62.41**	**23.73**	**13.86**
PLLA 150-10	**48.40**	**19.43**	**32.17**
PLLA 200-5	**54.39**	**21.49**	**24.12**

PLLA 200-10	**42.28**	**11.74**	**45.98**

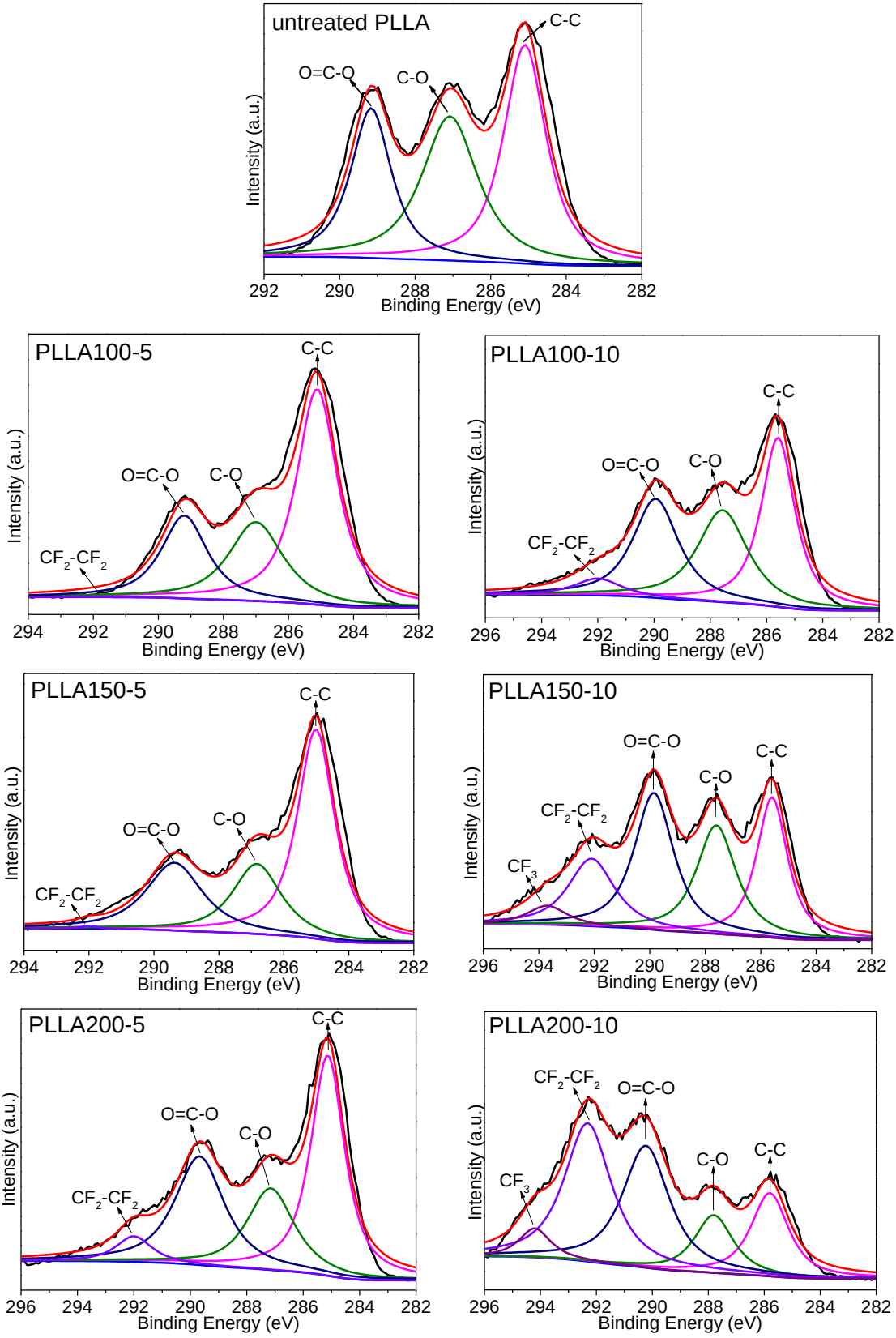


Figure 7 High-resolution of C1s spectra of PLLA membrane samples

Table 3 Chemical composition of PLLA membrane samples

	Functional group (%)				
Sample	**C-C**	**C-O**	**O=C-O**	**CF_2-CF_2**	**CF_3**
untreated PLLA	**40.08**	**34.43**	**25.79**	**0**	**0**
PLLA 100-5	**52.36**	**25.14**	**22.43**	**0.07**	**0**
PLLA 100-10	**36.66**	**29.53**	**28.83**	**4.98**	**0**
PLLA 150-5	**52.04**	**22.51**	**25.15**	**0.30**	**0**
PLLA 150-10	**24.39**	**23.98**	**30.06**	**17.39**	**4.18**
PLLA 200-5	**42.56**	**21.74**	**30.51**	**5.19**	**0**
PLLA 200-10	**17.01**	**12.03**	**30.88**	**35.10**	**4.98**

4 Conclusion

A facile method to control the surface wettability of electrospun PLLA microfibrous membrane via CF_4 microwave plasma treatment is investigated in this study. According to water contact angle analysis, both hydrophobic and hydrophilic surface could be obtained by adjusting the plasma power and treatment time during the CF_4 plasma treatment. Moreover, plasma power is crucial for the surface wettability of PLLA membranes. FESEM results demonstrated that CF_4 plasma treatment caused etching on PLLA fibers and made the membrane surface roughness greatly enhanced. The analysis results of FTIR and XPS indicated that a number of

fluorine-containing groups grafted onto the surface of PLLA microfibrous membranes after CF_4 plasma treatment. As a result, the mechanism of CF_4 plasma modification was explored by combining all these characterizations, which revealed that the etching and grafting process synergistically affected the final surface wettability of PLLA microfibrous membranes. When plasma treatment was taken under under 100 W or 150 W, the surface wettability of PLLA membranes mainly depended on the etching effect. However, with the plasma power further increasing to 200 W, the PLLA membranes were fluorinated severely, and the strong grafting effect gradually became the major factor for the surface wettability of PLLA membranes. Overall, this surface modification method shows its advantages in simple-operation, high-efficiency, and is expected to have wide application potential for preparing functional materials with switchable wettability.

Acknowledgments

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