Study on CO_2-based plasmas for surface modification of polytetrafluoroethylene and the wettability effects

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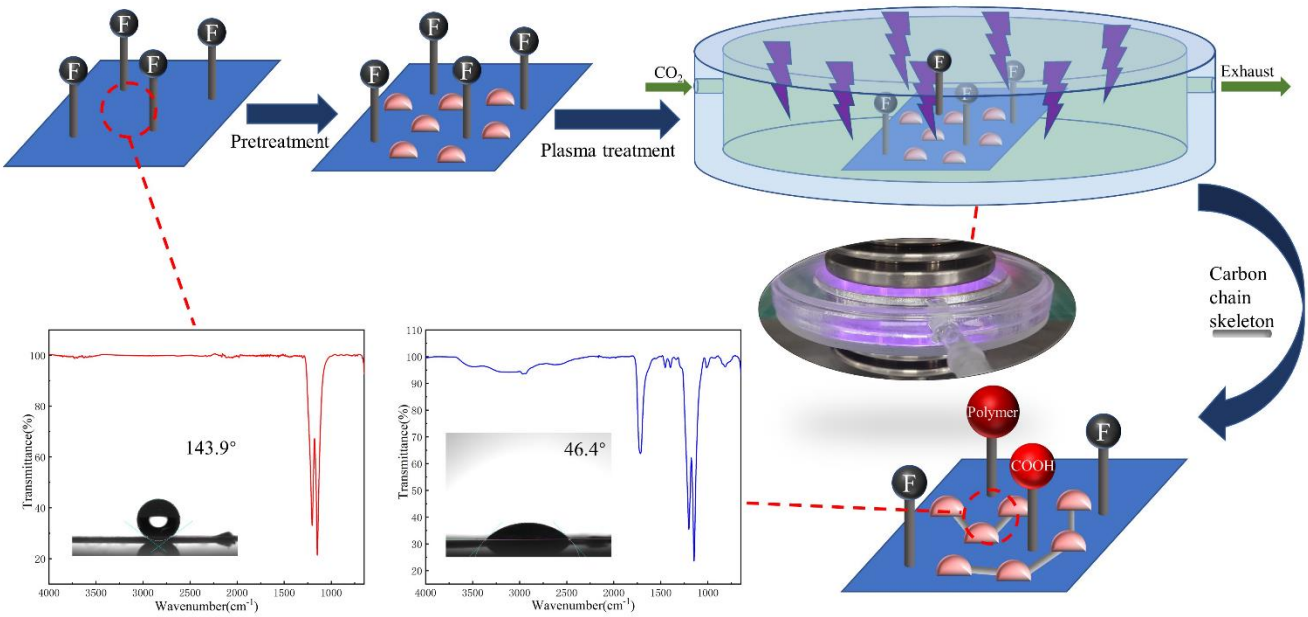

Abstract

Surface modification of polymers is an attractive way to endow them with new interfacial properties while maintaining desirable bulk properties, thus expanding their possible applications. In the present work, CO_2/N_2 DBD plasma was applied for the surface modification of polytetrafluoroethylene (PTFE) membranes by using acrylic acid as the precursor. Systematic experiments has been carried out to investigate the influence of the plasma gas composition and the plasma exposure time to the composition, morphology, and wettability performance of the PTFE membranes. It is shown that acrylic acid has been successfully grafted on the surface of PTFE to form carboxylic functional groups by the plasma technique, leading to improved hydrophilicity. The increase of the CO_2 content in CO_2/N_2 mixtures results in enhanced generation of C=O, C-O, and C-C species, suggesting CO_2 has been converted to functional groups on the surface of PTFE membranes. Moreover, at plasma exposure time of 0~60s, the hydrophilicity of the PTFE membranes can be improved, while longer plasma exposure time would lead to the degradation of the formed coating, leading to reduced hydrophilicity. This is also demonstrated by the quality of printed text on the corresponding PTFE membranes. The CO_2-based plasma method was further extend to the surface modification of substrates like polyethylene (PE), polyvinylidene fluoride (PVDF), and plexiglass, suggesting high versatility of the process to alter their wettability performance. This study provides useful insight for the utilization and conversion of CO_2 into value-added carboxylic groups on polymers via plasma technique.

Keywords: CO_2 conversion; DBD plasma; plasma surface modification; PTFE; wettability effects

1. Introduction

The greenhouse gas emission has brought a tremendous challenge to the ecosystem, such as global warming, sea-level rise and reduction in the glacier area [1,2]. CO_2 is considered to be the primary greenhouse gas, and its concentration in atmosphere has increased rapidly, from 280 ppm in 1813, to 411 ppm in 2018, 414.7 ppm in 2019, and reached a new record value of 417.2 ppm in 2020 [3–4]. The continuing rise of the CO_2 concentration in the atmosphere has exceeded the natural carbon cycle, leading to a wide range of environmental issues that threaten human development or even existence. Thus, policies and regulations have been made in countries across the world to reduce the emission of CO_2, among which the capture and conversion of CO_2 is regarded to be a promising approach to reach carbon neutral and facilitate the "carbon economy" [5–7]. In this manner, CO_2 can be effectively used in many fields such as the production of chemicals, fuel recovery and in food/beverage production industry.

Polytetrafluoroethylene (PTFE), being made of a carbon backbone chain with two fluorine atoms attached to each carbon, is probably the most extensively used chemically inert and thermally stable polymer. Both the C-F bonds and C-C bonds are typically considered to be nonreactive, endowing PTFE with superior mechanical and chemical resistance as well as wide operational temperature ranging from -195.6 °C to 370 °C [8]. Due to the unique properties, PTFE has been widely used in applications such as aerospace, machine, food packaging, filtration, and clinical fields. On the other hands, although the chemical-inert nature makes PTFE desirable for various purpose, the same attribute also limits PTFE for some practical applications. For example, the low surface energy and poor wettability of PTFE leads to poor adhesion with metals, thus limiting the options for the processing development. The extremely low tackiness makes the PTFE film skeleton difficult to combine with other materials, hindering its usage to form functional composite materials [9].

Surface modification is an attractive way to chemically alter a polymer. It can potentially maintain a polymer's bulk properties and meanwhile endow new different interfacial properties. Conventionally, it is achieved by increasing the surface energy through the incorporation of new chemical functionalities, branching, defluorination, oxidation, cross-linking, or formation of unsaturated sites that help to improve the adhesion property [10]. So far, many attempts have been

made to improve the wettability and adhesion of PTFE without changing their original excellent characteristics, like wet chemistry method, mechanical treatment, flame exposure, ions exposure, UV radiation, etc. However, the rather good chemical stability renders it difficult to modify and functionalize PTFE surface. As a consequence, conventional surface treatment processes suffer from major disadvantages like contamination, complexity, expensiveness, and large solvent consumption [9].

Plasmas are known to generate very high concentrations of reactive species like electrons, ions, excited atoms, etc., which help to accelerate chemical reactions or enable reactions that cannot be achieved by conventional methods [11–14]. Plasma polymerization, by using either the plasma state of monomers or reactive species created in the plasma state to form polymeric materials, has a series of advantages such as ultra-thin film formation, good adhesion to the substrate, independent deposition on the structure or type of the substrate, good chemical stability and physical durability of the coatings, flexible precursor choice with various surface functionalization [15–17]. During the plasma treatment process, gases such as Ar, O_2, N_2, CO_2, NH_3, H_2 are applied, leading to the formation of chemically active species [18]. These species further interact with the polymer surface by means of possible reactions such as etching, cross-linking, and chemical modification [19]. As a consequence, functional groups of desired surface properties are generated on the surface of polymers, such as -OH, -CO, -NH and -COOH groups [20]. A closer examination and analysis of the functional groups through complementary characterizations enables us to disclose the underlying mechanisms [21]. Up to date, many plasma polymerization processes have been developed, and a wide variety of organic and organometallic compounds have been polymerized to form thin films on the substrates placed in the plasma.

Generally in order to form uniform films with high molecular weight, plasma polymerizations are carried out at low pressures. Vacuum plasma is the most commonly adopted strategy for depositing thin films, but has limitations related to the expensive and large footprint of vacuum equipment as well as the unavoidable use of batch processing or complex transfer chambers. Atmospheric pressure plasma polymerization has the potential to address these limitations. Among them the dielectric barrier discharge (DBD) is one of the most popular and classical non-thermal plasmas. The average

temperature of electrons in DBD is very high (10^4~10^5 K), while the actual gas temperature is close to room temperature. Thus, it allows the treatment of temperature-sensitive substrates like polymers, bio-medical implants, fabrics, etc [22]. Furthermore, the formed coating has good stability, since the plasma-activated groups have strong bonds and are highly cross-linked.

Driven by their fascinating properties, in recent years, atmospheric DBD plasmas have been widely applied to introduce functional groups to polymers, such as hydroxyl, methyl, carbonyl, carboxyl, amino, phosphates, alkanoate, etc. Meanwhile, the generation of these functional groups can make the polymers more polar and less inert, leading to improvement of, e.g., wettability, adhesion property, and fouling resistant, therefore enhancing the performance of these materials in many applications [23]. For instance, polymer films consisting of carboxylic acid functional groups are attractive for bio-applications, since they are known for stimulating the adhesion and proliferation of fibroblasts and other kind of cells. Monomers bearing carboxylate functional groups have been widely utilized in plasma polymerization to improve the hydrophilicity of polymers. Among them, acrylic acid (AAc) featuring high volatility, good solubility in water, and a high ratio of carboxyl polar groups, is a commonly used precursor for the development of carboxylic group-containing coating [24].

In addition to the precursors, gases can also form functional groups on polymers when introduced in the plasma. For example, CO_2 plasmas are capable for adhesion promotion as they can form COOH groups on polymers surface, and are somewhat less destructive to polymer backbone chains than oxygen plasma [25]. N_2 plasmas allow the incorporation of N atoms into the surface of polymers to generate N-comprising functional groups, resulting in improved hardness and wear resistance [26]. On the other hand, CO_2 is considered to be the primary greenhouse gas contributing to the global warming, and N_2 is the main component of the Earth's atmosphere (78%). Since C and N are basic building blocks of all organisms and chemicals, the conversion of the CO_2 and N_2 molecules into high value-added products is of great importance for the fundamental research and industrial applications . However, both the CO_2 and the N_2 are highly thermodynamically stable gases and hardly dissociated by conventional strategies. Plasma-based technique exhibits high reactivity, and might open new paths for the conversion of the CO_2 and N_2 gases. Moreover, both the CO_2 and N_2 are cheap, non-flammable and non-explosive gases, making them practical choices from the economic and safety point of view.

Despite a tremendous effort has been made to develop plasma polymerization processes, most studies are focus on inert gas like argon, helium or reactive gas like O_2, air, or their mixtures. There is still quite limited research on surface modification of the PTFE using CO_2/N_2-based DBD plasma.

Motivated by the above discussions, in this study, an atmospheric pressure DBD plasma setup was used to graft acrylic acids onto the surface of the PTFE membranes, aiming to improve their wettability performance. Meanwhile, CO_2/N_2 mixtures were used as the working gas to explore the possibility of the plasma technique to convert CO_2 and N_2 into value-added functional groups. The influence of two key processing parameters, namely the plasma exposure time and the CO_2 content in the CO_2/N_2 mixtures, was investigated comprehensively in relation to the wettability performance of the PTFE membranes. Specifically, the plasma exposure time was adjusted in the range of 0-5 min (0s, 30s, 45s, 60s, 75s, 90s, 120s, 150s, 180s, 240s, and 300s), and the CO_2/N_2 molar ratio was set as 1:0, 3:1, 1:1, 1:3, and 0:1, respectively. Certain texts (*J CO_2 UTIL*) were printed on the surface of the bare/plasma-treated PTFE membranes to present a better overview of their wettability performance. At the same time, the evolution of the composition and morphology of the membranes was also researched through systematic experiments. Furthermore, the versatility of the CO_2-based plasma modification process was studied by extending the substrates to a series of materials, like polyethylene (PE), polyvinylidene fluoride (PVDF), and plexiglass.

2. Experimental section

2.1 Plasma-assisted surface modification of polytetrafluoroethylene

The surface modification of the PTFE membranes was carried out using a home designed & built dielectric barrier discharge (DBD) plasma reactor, as schematically shown in Figure 1(a). Briefly, two stainless steel (SS) disks (Diameter=5 cm) functioned as the high-voltage and ground electrodes, respectively, and were connected to an AC high voltage power supply (CTP-2000K, Nanjing Suman Electronics Co., Ltd., China). The charge (Q) and voltage (V) waveforms were recorded using a Tektronix-TBS1102 digital oscilloscope, and plotted to obtain V-Q diagrams (also known as Lissajous curves) for the characterization of the dissipated energy in the discharge. The average plasma power was calculated by multiplying the area with the frequency. The frequency of the DBD plasma used in

the present experiment is kept constant at 19.4 kHz. To get a better idea on the discharge characteristics of the DBD plasma, Figure S1(a) presents a typical V-Q diagram recorded during the plasma modification process, with an applied voltage of 18 kV from peak to peak. The corresponding Lissajous curve is shown in Figure S1(b), which exhibits a parallelogram shape. The energy dissipated in the plasma is calculated to be 6.2 W. A quartz reactor (Figure 1(b-c)) acting as a dielectric barrier was placed in the center of the SS electrodes, of which the bottom part is a dish (Diameter=10 cm, thickness=0.5 cm) containing a sample cell (Diameter=6 cm, depth=0.2 cm) for the plasma surface modification, while the upper part is a flat plate (Diameter=10 cm, thickness=0.1 cm).

In a typical procedure, PTFE membranes (20mm*0.15mm, Shanghai Shenfeng Co., Ltd., China) were immersed into a 20 wt% aqueous solution of acrylic acid (AAc, ≥99.0%, Sinopharm Chemical Reagent Co., Ltd) for 10 min, before being dried in air and placed into the sample cell for plasma treatment. The concentration of the AAc and the immersion time has been optimized based on its volatility and good solubility in water. All samples were prepared in the same manner to ensure the maximum possible consistency among samples. CO_2 (≥99.995%, Wuxi Taihu gas Co., Ltd) and N_2 (≥99.999%, Wuxi Taihu gas Co., Ltd) were used as the working gas and continuously feed into the quartz reactor via gas inlet at various volume ratios, and were released into a hood system through gas outlet after the plasma treatment. Mass flow controllers (MFCs, Bronkhorst) were used in each pipeline to adjust the corresponding gas flow rate. The total gas flow rate is maintained constant at 100 sccm in all experiments. Before each operation, the reactor was flushed using plasma working gas for 5 min to remove any possible impurities. The plasma was switched on to treat the PTFE samples for a certain time. After a desired processing time, the plasma was switched off, and the plasma-treated PTFE membranes were carefully taken out by tweezers for further characterization.

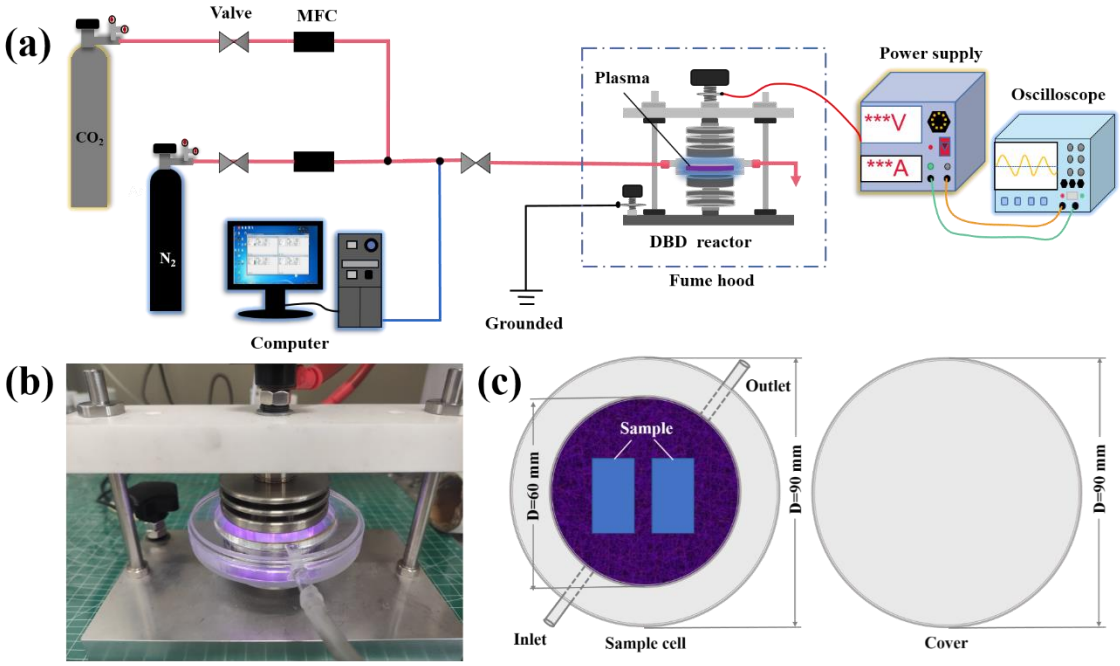

Figure 1. (a) Schematic diagram of the DBD plasma setup for the surface modification of the PTFE membranes; (b) photograph of the DBD quartz reactor; (c) the configuration details of the DBD reactor.

2.2 Characterization

The functional groups of the PTFE membranes were analyzed by Fourier-transform infrared spectrometer (FT-IR) (Nicolet 6700, Seymour Fisher Technology Co., LTD) using the transmittance mode. For the preparation of the FT-IR samples, the PTFE membranes were carefully placed on an infrared transparent silicon wafer, and then directly put into the FT-IR instrument for the collection of functional group information. The surface morphology of the membranes was firstly examined by an atomic force microscopy (AFM, MuLtimode 8, bruker). Afterwards, a VHX-1000 3D-super depth of field microscope (SDFM, Keyence, Osaka, Japan) was applied to analyze the surface roughness of the membranes. To obtain high-resolution images, the morphology was also characterized by scanning electron microscopy (SEM), which was performed on a S-4800 microscope (Hitachi Corporation of Japan) operated at 10 kV, with a silicon drift energy dispersive X-ray spectrometer (EDX) detector to examine the element composition and distribution. The surface chemical composition and binding information were further assessed by an X-ray photoelectron spectroscopy (XPS) using a Kratos Axis Supra DLD spectrometer equipped with an aluminum anode (Al Kα=1486.6 eV). The wettability of the samples was evaluated by water contact angle (WCA) measurement via a contact angle instrument (FTA 1000, USA) under static condition.

3. Results and discussion

Figure 2(a) shows the FT-IR spectra of the bare PTFE membrane as well as the membrane after the plasma treatment in CO_2 atmosphere for 60s. The detailed information of the IR bands is summarized in Table 1. For the bare PTFE membrane, two prominent bands are observed at 1213 cm^{-1} and 1155 cm^{-1}, which are assigned to anti-symmetrical and symmetrical stretching modes of the C-F bonds, respectively [27]. However, for the CO_2 plasma treated PTFE membrane, in addition to the above two strong bands, new absorption bands corresponding to the O-H stretching mode (3150 cm^{-1}), C=O stretching mode (1716 cm^{-1}), $-CH_2-$ bending mode (1457 cm^{-1}), C-O stretching mode (1396 cm^{-1}), and -OH bending mode (1010 cm^{-1}) have been detected, suggesting the formation of the carboxylate groups on its surface [28,29]. It is well-known C-F bonds are responsible for the hydrophobicity of the PTFE materials, while the incorporation of functional groups such as C=O, CO-, -OH, etc. into the polymer can considerably improve their hydrophilicity. This is also reflected by the inserted photograph, where water droplet exhibits slightly repellency on the surface of the bare PTFE membrane, but collapses on the CO_2-plasma modified PTFE membrane.

Table 1. The IR bands of the bare PTFE membrane as well as the PTFE membrane treated by the CO_2-plasma

Wavenumber range (cm^{-1})		Assignment
Bare PTFE membrane	CO_2 plasma-treated PTFE membrane	
	3150	O-H stretching
	1716	C=O stretching
	1457	$-CH_2-$ bending
	1396	C-O stretching
1213	1213	C-F in $-CF_3$ (anti-symmetrical)
1155	1155	C-F in $-CF_2-$ (symmetrical)
	1010	O-H bending

By adjusting the gas flow rate of CO_2 and N_2, the evolution of the functional groups on the PTFE surface with the CO_2 content in CO_2/N_2 mixtures is studied via the FT-IR spectra (Figure 2(b)). Absorption peaks related to the O-H, C=O, $-CH_2-$, C-O functional groups are observed in all spectra, even for the PTFE membranes treated by N_2 plasma. This is due to the dissociation of the acrylic acids

in plasma, since all PTFE membranes had been immersed in the 20 wt% AAc aqueous solution for 10 min before plasma treatment. However, no functional groups like N-H or C-N are formed, even in the pure N_2 atmosphere. A reasonable explanation is that N_2 molecules are more difficult to be dissociated than CO_2 molecules, since the bond-dissociation energy of N_2 and CO_2 are 9.79 eV and 5.51 eV, respectively [30,31]. In addition, the rise of the CO_2 content in the CO_2/N_2 mixtures also leads to a considerable increase of the peak intensities of the carboxylate groups, suggesting the successful conversion of CO_2 by the plasma technique. Therefore, it is inferred that both the CO_2 and AAc can contribute to the graft of carboxylate groups onto the PTFE surfaces.

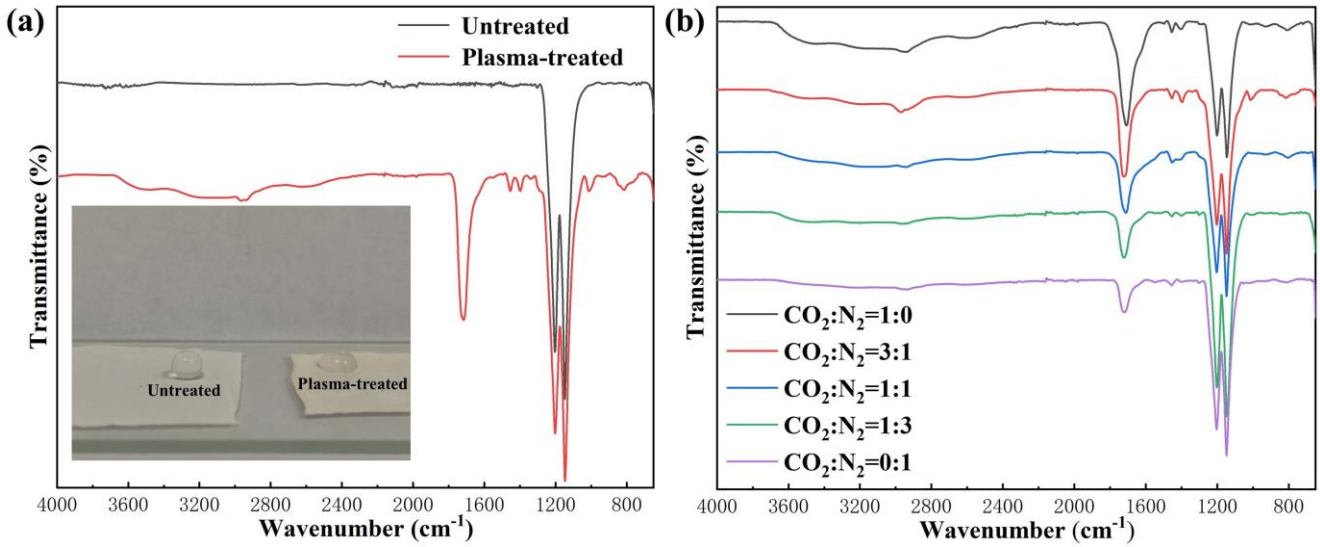

Figure 2. (a) FT-IR spectra of the bare PTFE membrane as well as the PTFE membrane treated by the CO_2 plasma. The insert shows a photograph of water droplets on both the PTFE membranes for comparison; (b) The FT-IR spectra of the PTFE membranes treated by the CO_2/N_2 plasmas with different gas compositions. The plasma exposure time is fixed at 60s.

Atomic force microscopy (AFM) characterization was firstly performed to examine the surface topography of the PTFE membranes before and after the pure CO_2-plasma treatment for 60s. The bright area in the images represents the higher point of the membrane surface, and the dark area indicates the lower regions of the membranes. Interweaved microfibers of ridge-valley configuration are clearly observed in the 3D AFM images of the bare PTFE membrane, revealing its network structure (Figure 3 a-b). However, the plasma-modified PTFE membrane shows a significantly different surface morphology, in which a smoother morphology of nodular structure is presented in Figure 3(d-e). The magnified AFM image further shows it is made up of a dense and continuous new

layer. Thus, the CO_2-plasma treatment not only reduces the roughness of the interknitting microfibers, but also narrows the large pores among fibers. In addition to the AFM characterization, the surface roughness of the PTFE membrane was also evaluated using a super depth of field microscope (SDFM). The bare PTFE membrane is shown to have higher surface roughness (24.31 μm, Figure 3c) compared to the CO_2-plasma treated one (19.67 μm, Figure 3f). Therefore, it is reckoned that AAc molecules underwent grafting polymerization in the plasma to form a new layer of material on the surface of the PTFE membrane, helping to alleviate the surface roughness and alter the morphology. Same phenomena were also observed in the PTFE membranes treated by plasmas for the same time but with different gas compositions, and the corresponding SDFM images are provided in Figure S2.

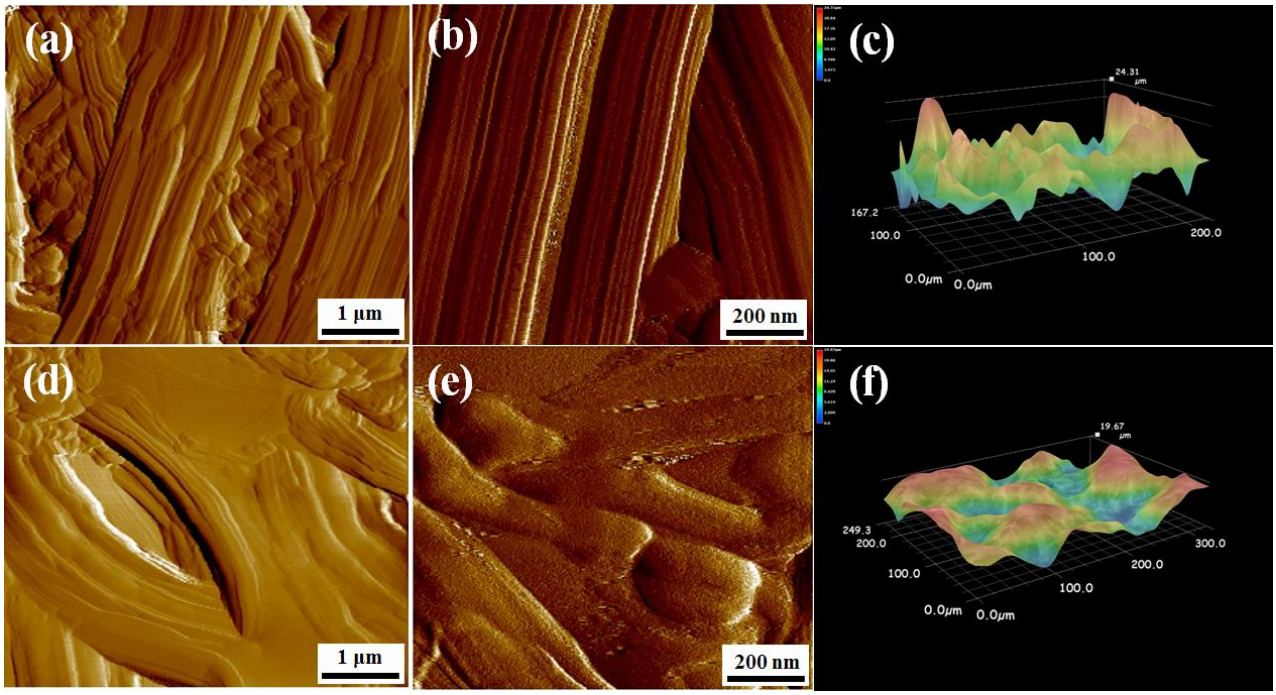

Figure 3. (a-b) AFM images and (c) SDFM image of the bare PTFE membranes; (d-e) AFM images and (f) SDFM image of the PTFE membranes treated by pure CO_2 plasma for 60s, and the CO_2 flow rate is 100 sccm.

SEM characterization was performed to further examine the surface morphology of PTFE membranes with respective to the plasma modification process. Microstructural observation via the cross-section SEM image of the PTFE membrane treated by CO_2 plasma for 60s clearly shows morphological differences between the coating and the substrate (Figure 4(a)). As can be seen in the bare PTFE membrane, there are microfibers interweaved randomly to present a fibrous morphology, with multi-scale pores dispersed on the membrane surface (Figure 4(d-e)). In contrast, plasma surface modification can significantly change the morphology, leading to the formation of a relatively smooth

and dense polymer layer above the PTFE membrane. Compared with the untreated PTFE membrane, the CO_2-plasma treated PTFE membrane has much reduced surface roughness and porosity, suggesting surface polymer crosslinking as well as thin film deposition (Figure 4(b-c)). The result is in agreement with the AFM and SDFM images.

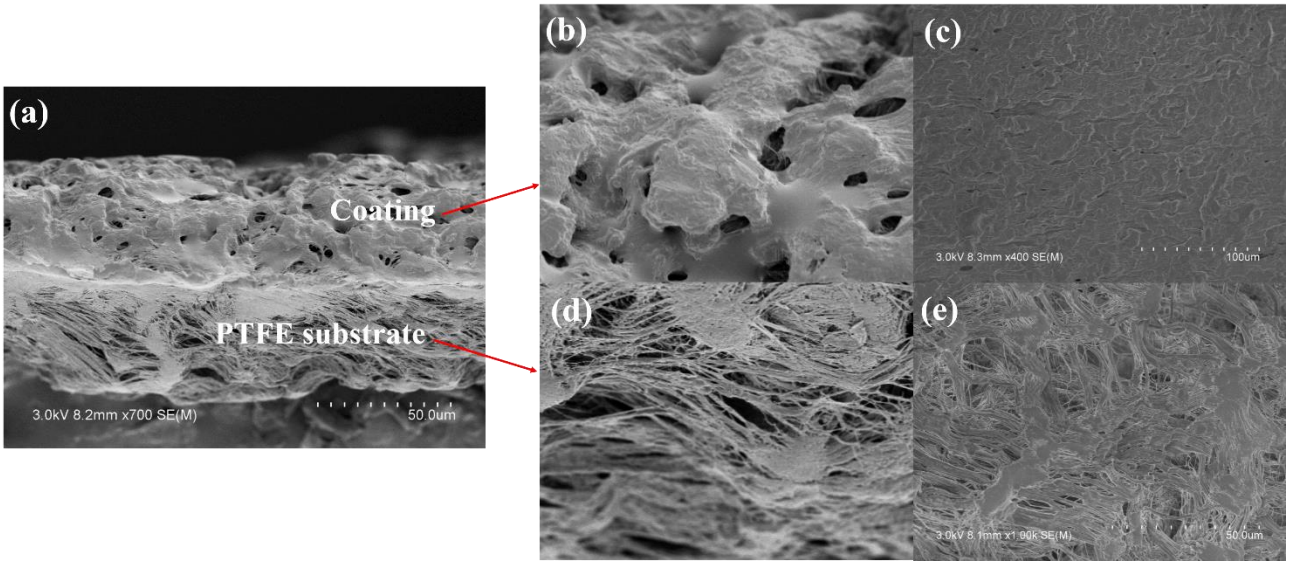

Figure 4. (a) Typical cross-section SEM image of the CO_2-plasma modified PTFE membrane; (b) Coating, cross-section view; (c) Coating, top view; (d) Substrate, cross-section view; (e) Substrate, top view. The plasma treatment time is 60s, and the total CO_2 flow rate was 100 sccm.

The evolution of surface morphology of the PTFE membranes with the plasma exposure time was also examined, as shown in Figure 5. One can see that a relatively smooth coating with randomly dispersed pores was formed on the PTFE membrane surface after plasma treatment for 30s. The coating becomes increasing dense and smooth with continuous plasma exposure, during which polymer crosslinking and film deposition can be easily noticed. After CO_2-plasma exposure for 60s, there are hardly any pores visible on the membrane surface. However, as the plasma treatment proceeds, increased porosity and surface roughness is observed on the coating, and completely changes to porous morphology at 240s. This is because the degradation of the polymer coating after long plasma exposure times.

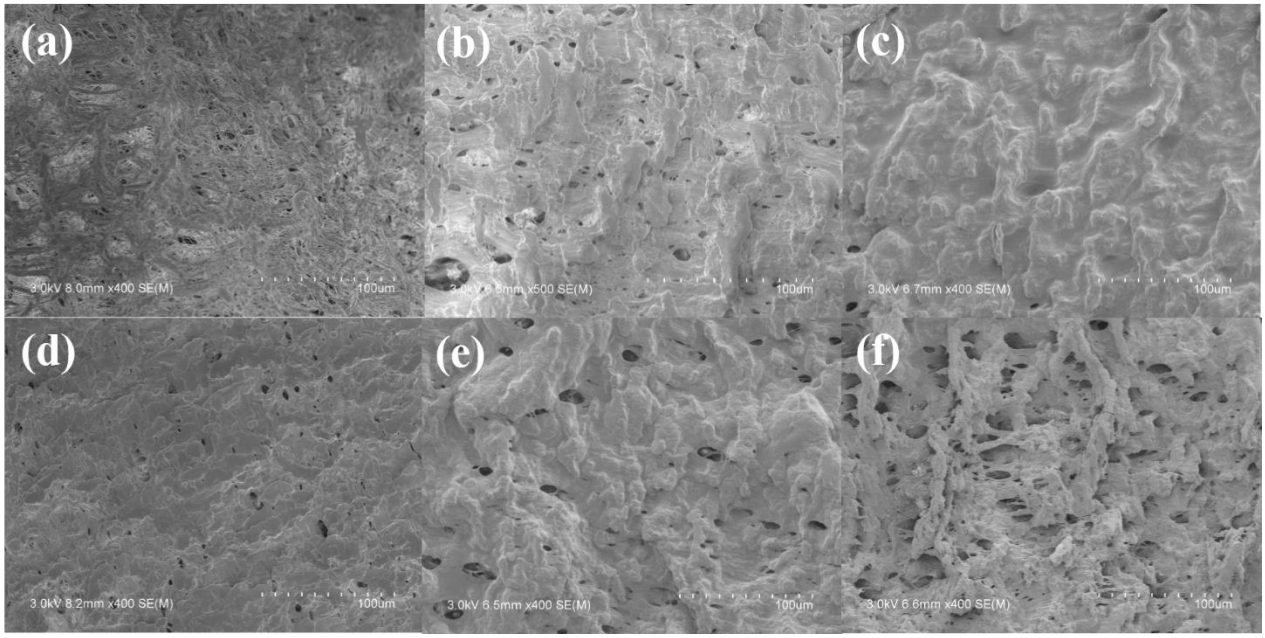

Figure 5. The surface morphology of the PTFE membranes treated by CO_2 plasma for different times: (a) 0s; (b) 30s; (c) 60s; (d) 90s; (e) 150s; (f) 240s. A coating was formed above the PTFE membrane after the plasma treatment, but at plasma exposure times more than 60s, the formed coating will be degraded.

The EDX spectra of the PTFE membranes obtained at different conditions are presented in Figure 6(a). For the bare PTFE membrane, it mainly consists of C (7%) and F (91%), whereas for the plasma-modified PTFE membranes, the content of C and O elements are found to increase with the rise of the CO_2 concentration in the CO_2/N_2 mixtures. Specifically, the content of C and O in the PTFE membrane treated by pure N_2 plasma are 14% and 6%, respectively, which changes to 18% (C) and 11% (O) when modified by the CO_2/N_2 plasma with the equal CO_2 and N_2 content (1:1), and further rises to 26% (C) and 19% (O) when modified by pure CO_2 plasma. Thus, it is inferred that CO_2 molecules have been dissociated in plasma to introduce a small amount of oxygen or carbon to the surface of the PTFE membrane. Besides, very low content of N element (0~1%) is observed in all cases, even with pure N_2 plasma, confirming that N_2 has not been dissociated and incorporated into the coating. It should be pointed out that the quantitative analysis of elements by the EDX technique is not be very accurate, especially for low atomic number elements. Further improvements (e.g. wavelength dispersive spectroscopy) are needed to get more accurate data. Element mapping analysis is also conducted to get a better understanding of the elemental distributions over the PTFE membranes (Figure 6(b-e)). It is indicated that C and O are homogenously dispersed within the F element, and

their signals increase with the CO_2 concentration, suggesting C-/O-functional groups are formed on the membrane surface.

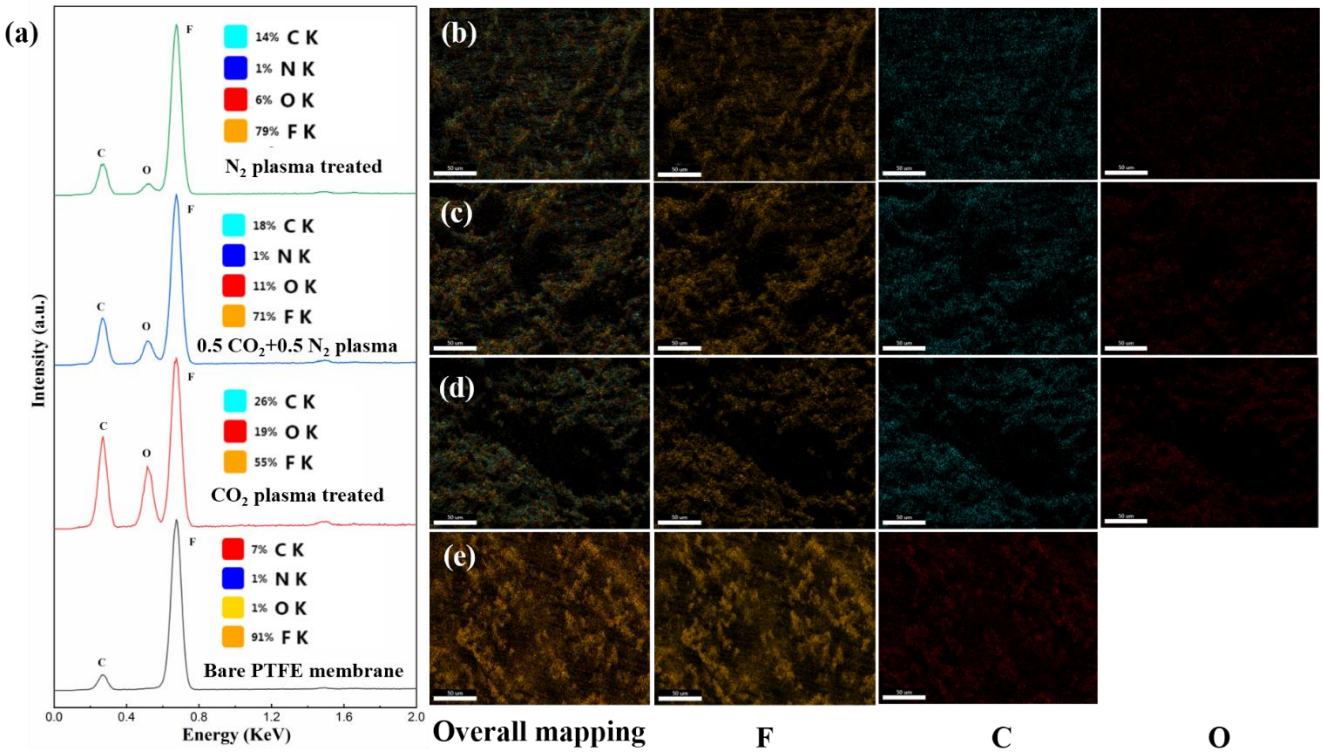

Figure 6. (a) The EDX spectra of the bare PTFE membrane as well as the membranes exposed to plasmas with different concentrations of CO_2/N_2; (b-e) the corresponding mapping distributions of elements (F, C, and O) in each membrane. The plasma treatment time is 60s, and the total gas flow rate is 100 sccm.

XPS analysis has been performed to evaluate the chemical composition of the untreated and plasma-treated PTFE membranes. It is worth mentioning that the plasma exposure time matters in tuning the wettability performance of the PTFE membranes. The wettability properties of the PTFE membranes are found to increase in the plasma exposure time of 0-60s, while decrease once the treatment time exceeds 60s, and become nearly constant at prolonged plasma exposure times more than 240s. Thus, detailed XPS studies were specifically performed for the PTFE membranes exposed to plasma for 60s and 240s. The overall XPS spectra of the bare PTFE as well as the PTFE exposed at plasma ($V_{N2:CO2}$=1:1) for 60s and 240s were plot in Figure 7(a). Only a very small amount of oxygen (0.3%) is detected on the bare PTFE surface. When the plasma exposure time is extended to 60s, O signals (8.47 %) were clearly observed, suggesting plasma can graft oxygen on the PTFE surfaces. The absence of N signals reconfirms that N_2 molecules have not been dissociated in plasma. At the same time, the F/C ratio decreases compared to the bare PTFE membrane, which is attributed the formation

of polymer layer on the membrane surface. With the further extension of the plasma exposure time, the O content (4.0 %) as well as the F/C ratio decrease again, suggesting that the coating was degraded.

To get further insight into the chemical bonds present on the surface of the PTFE membranes, curve fitting of the high-resolution C1s peaks are performed, as shown in Figure 7(b-d). Meanwhile, the concentrations of the different chemical bonds on the PTFE membranes are also presented based on the deconvoluted C1s peaks. The C1s spectrum of the bare PTFE membrane mainly consists of a prominent peak at binding energy of 292.3 eV, which is indexed to the CF_2 species. In addition, two smaller components at approximately 293.0 eV and 284.5 eV are observed. The previous one is assigned to the CF_3 species, and the latter one is due to adventitious hydrocarbon species presented on the membrane surface [34]. After a short plasma exposure in N_2+CO_2 (1:1) atmosphere for 60s, the intensities of the peaks at 289.0 eV and 284.4 eV rise considerably. Spectral decomposition of the C1s peaks suggests the co-existence of C-F (292.3 eV, 293.0 eV), C=O (288.8 eV), C-O (286.2 eV), and C-C (284.4 eV) species [35,36]. Therefore, it is concluded that CO_2 has been converted to form hydrophilic functional groups on the PEFT surfaces. However, at a prolonged treatment time of 240s, the peak intensity of C=O, C-O, and C-C components decreases, reflecting the coating are degraded.

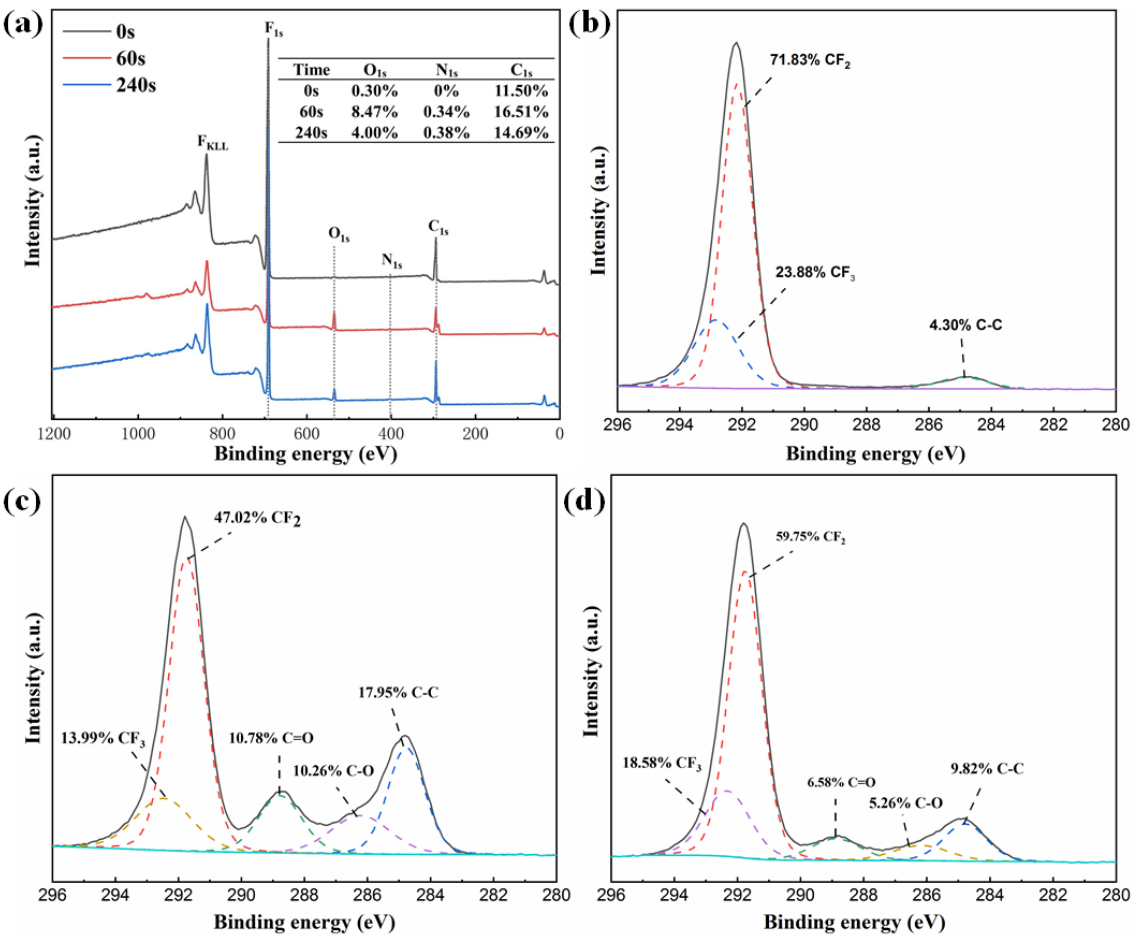

Figure 7. (a) Overall XPS spectra of the PTFE membranes exposed to the plasma ($V_{N2:CO2}$=1:1) for different times (0s, 60s, and 240s). The inserted table presents the atomic percentages of C1s, N1s, and O1s; (b-d) High resolution C1s peaks of (b) the bare PTFE membrane, (c) PTFE membrane treated by plasma for 60s; and (d) PTFE membrane treated by plasma for 240s.

The evolution of the water contact angle on the plasma-modified PTFE membrane as a function of the CO_2 content in the CO_2/N_2 plasma is shown in Figure 8(a). For the N_2 plasma treated PTFE membrane, the water contact angle is 110°, and gradually decreases with the rise of the CO_2 content in the plasma. For example, the water contact angle changes to 96.7° with the CO_2 volume ratio of 25%, and further decreases to 80.0°, 67.5°, and finally reaches 46.4° with the CO_2 volume ratio of 50%, 75%, and 100%, respectively. This is attributed to the formation of hydrophilic groups (e.g. C=O, CO-, -OH, etc.) on the surface of the PTFE membranes. The rise of the CO_2 content in plasma atmosphere will contribute to the formation of hydrophilic groups. This is in good agreement with the FT-IR (Figure 2) and the EDX spectra (Figure 6). Besides, the relationship between the water contact angle on the PTFE membranes and the plasma exposure time is also investigated. It is shown that the water contact angle of the bare PTFE membrane is 140.9°, and gradually decreases with increasing plasma exposure time. A minimum water contact angle (48.6°) is achieved at plasma exposure time of 60s. However, when the PTFE membranes are treated for more than 60s, the contact angle starts to increase, reaching a value of ~140° after an exposure time of 300s (Figure 8(b)). This also consists with the SEM and XPS characterization. Long plasma exposure times would lead to the degradation of the formed hydrophilic coating, which in turn, resulting in higher contact angle values.

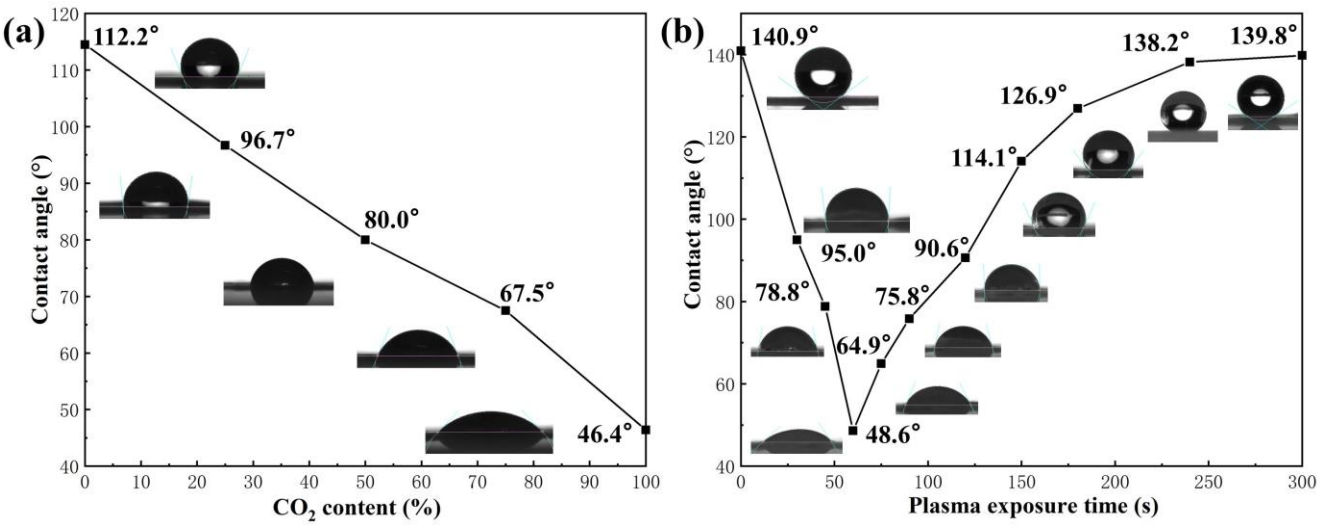

Figure 8. (a) Water contact angle on the plasma-treated PTFE membrane as a function of the CO_2 content in the plasma. All membranes were treated at a same plasma exposure time of 60s; (b) Water contact angle on the PTFE membrane treated by CO_2 plasma as a function of the plasma exposure time.

As demonstrated, the DBD plasma can tailor the wettability of the PTFE membranes by controlling the plasma exposure time and the plasma atmosphere, in a fast, inexpensive way without vacuum systems. At plasma exposure time within 60s, the hydrophilic property increases, which is due to the dissociation of AAc molecules to form a new coating on the PTFE surface. Meanwhile, at the same plasma exposure time, the increase content of CO_2 in plasma atmosphere results in enhanced generation of C=O, C-O, and C-C species, suggesting CO_2 has been converted to carboxylate groups. However, at prolonged plasma treatment time from 60s to 240s, the generated coatings would be degraded again, leading to a reduced hydrophilic property. In order to better demonstrate the ability to improve the wettability of the PTFE membranes using the DBD plasma technique, certain text (*J CO_2 UTIL*) has been printed on the bare PTFE membranes and the PTFE membranes treated by plasma at different conditions, as shown in Figure S3. The text printed on the bare membranes is unclear and very light. In contrast, when printed on the plasma-treated PTFE membranes, the text becomes very clear, suggesting improved hydrophilicity of polymers. No significant difference is observed for text printed on membranes treated by plasmas of different compositions (N_2, CO_2, or N_2/CO_2). However, text becomes blurry with increasing plasma exposure time, indicating reduced hydrophilic property. The result matches well with the water contact angle measurement. Figure 9 shows a schematic process for the plasma surface modification of PTFE membranes. Moreover, based on our experiment results as well as relevant literatures on surface modification using plasma-based technique [35,36], a hypothesized mechanism is presented in Figure S4 to illustrate how AAc molecules are grafted on the surface of the PTFE membranes in CO_2 plasma.

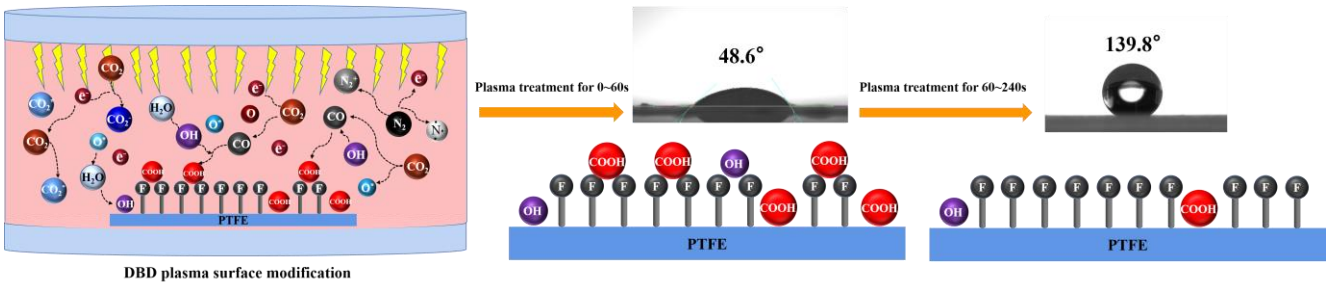

Figure 9. Schematic illustration of the DBD plasma for the surface modification of PTFE membranes.

To further explore the versatility of the demonstrated plasma modification technique, a series of substrates including polyethylene (PE) membrane, polyvinylidene fluoride (PVDF) membrane, and plexiglass plate are used. Similarly, all substrates were immersed into the 20 wt% AAc aqueous solution for 10 min, and then dried and treated by CO_2 plasma or N_2 plasma for 30s. Figure 10 shows the water contact angle on the surface of different materials before and after the CO_2/N_2 plasma treatment. It is apparently shown that all samples have improved hydrophilic property after plasma treatment, and CO_2 plasmas demonstrate better wettability effects compared to N_2 plasmas in all cases. For instance, the water contact angle on the PE surface changes from 91.7° before plasma treatment to 41.0° after treated by CO_2 plasma for 30s, in contrast to 50.7° when treated by N_2 plasma (Figure 10 a-c). For the PVDF membrane, the contact decreases from 127.6° to 59.4° and 78.9° after exposure to CO_2 plasma and N_2 plasma, respectively (Figure 10 d-f). Same phenomenon is also observed for the plexiglass plate, where the water contact angle reduces from 73.8° to 28.3° and 49.1° when treated by CO_2 plasma and N_2 plasma, respectively (Figure 10 g-i). Thus, it is shown the CO_2/N_2 plasma can considerably alter the wettability of materials, and the rise of the CO_2 content can improve the hydrophilicity of polymers to a large extent. Moreover, the FT-IR spectra of the PE and PVDF membranes with/without plasma treatment is presented in Figure S5, indicating the formation of carboxylic groups on the substrates after plasma treatment. Therefore, the DBD plasma has exhibited good versatility in improving the wettability performance of polymers.

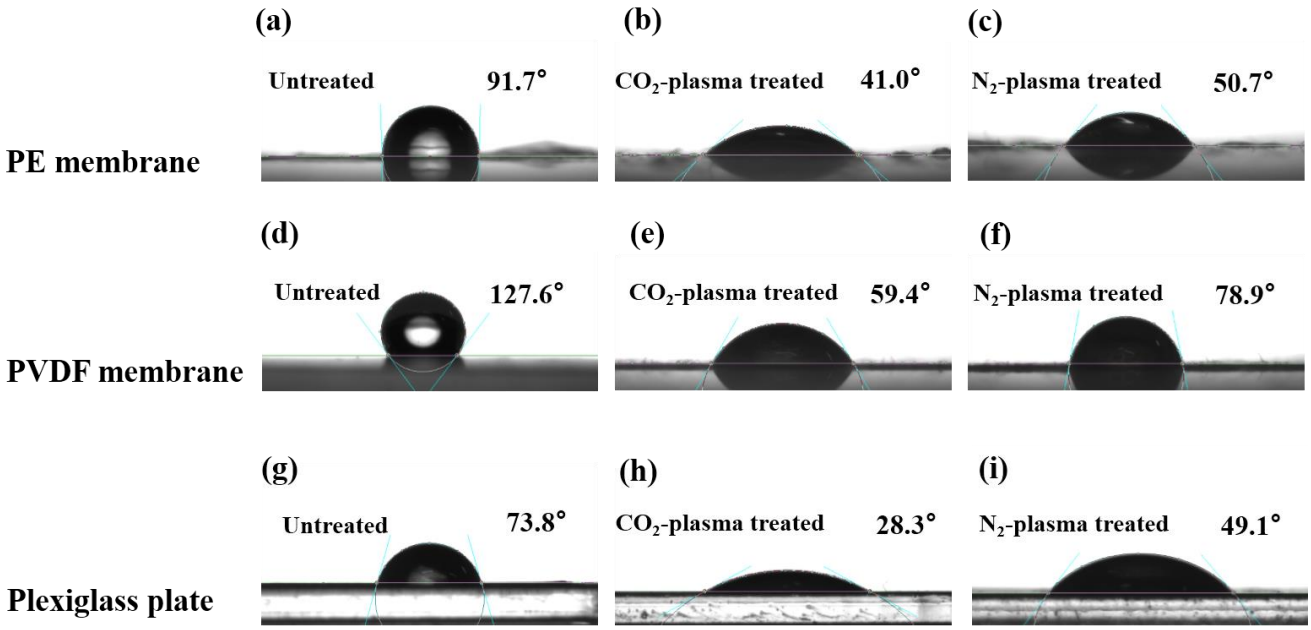

Figure 10. Water contact angle on the surface of different materials with/without plasma treatment: (a-c) PE membrane; (d-f) PVDF membrane; (g-i) Plexiglass plate. All experiment were performed at the same plasma exposure time (30s).

Table 2 gives a summary of state-of-art techniques of plasma process for the surface modification of PTFE. DBD plasma processes are mostly operated at atmospheric pressure, thus they don't require vacuum systems to maintain stable operation. Meanwhile, instead of using commonly adopted O_2 as the reactive gas, the demonstrated CO_2/N_2 DBD plasma in this study shows comparable ability to enhance the wettability performance of PTFE materials. This in conjunction with the utilization and conversion of the CO_2 into value-added carboxylic groups on the polymers surface makes the DBD plasma polymerization strategy meaningful and attractive.

Table 2. An overview of plasma-based processes for the surface modification of PTFE

Method	Precursor	Plasma power (W)	Plasma gas	Contact angle (°)	Pressure (Pa)	Comment	Ref.
DBD plasma	Acrylic acid	6.2	N_2/CO_2	48.6-140.9	Atmospheric	Rapid, flexible, controllable, no vacuum equipment; Small modification area, batch processing	This work
DC glow discharge	Orthophosphoric acid Tetraethoxysilane	24	Air	51-61	10-20	Rapid, strong controllability, stable products; Vacuum system required, complex process	[37]
DBD plasma	Acetone	600-2000	O_2	58-74	Atmospheric	Rapid, efficient, no vacuum equipment Large power consumption, has etching effect	[38]
RF magnetron plasma	Acetone	100-500	O_2	57-80	4.5×10^{-6}	Rapid, flexible, large-surface processing Vacuum system required, low electron density, PTFE surface could be severely etched and destroyed	[38]
Glow discharge	-	8.3	O_2/Ar	4-118	10	No precursors, fast, good wettability, commercial setup; The hydrophilic effect is not stable	[39]
DBD plasma jet	Acetone	3.16	Ar	30-128	Atmospheric	Rapid, low energy consumption, good hydrophilic effect; Small treatment area, unstable hydrophilic effects	[40]
Microwave plasma	-	400	Ar/H_2O	23.6-110	27-50	Rapid, high versatility, good hydrophilicity but not stable; Expensive equipment, vacuum system required	[41]
RF plasma jet	Anthraguinone Dimethylformamide	300	O_2	35.8-44.1	Atmospheric	High-efficient, good hydrophilicity, controllable; Complex pretreatment, rough surface	[42]
DBD plasma jet	Methanol Isooctane	2.31	Ar/CO_2	89-110	Atmospheric	Large power consumption, flexible, good hydrophilicity; Small treatment area, batch processing	[43]
RF plasma jet	Acrylic acid	125	Ar	72-110	Atmospheric	Large treatment area, flexible, durable hydrophilicity; Expensive setup, rough surface	[9]

4. Conclusions

In summary, we have demonstrated an atmospheric pressure CO_2-based DBD plasma method for the surface modification of PTFE membranes, in which acrylic acid was used as the precursor to form carboxylic functional groups on their surfaces. The plasma-treated PTFE membranes show considerably improved hydrophilicity, and CO_2 plasma exhibits better ability to enhance the wettability performance than N_2 plasma. This is due to the dissociation of CO_2 in plasma to form COOH groups on the PTFE surfaces, as evident by the enhanced generation of hydrophilic groups (C=O, C-O, C-C species, etc.) with the rise of the CO_2 content in the CO_2/N_2 mixtures. However, due to the rather high bond dissociation energy (9.79 eV), N_2 has not been converted to N-containing functional groups.

On the other hand, longer plasma exposure time (>60s) would induce the degradation of the formed polymer layers, leading to apparent porosity and surface roughness as well as decreased hydrophilicity. The evolution of the wettability properties of the PTFE membranes is also reflected by the quality of printed text on their surfaces. Based on the experiment results as well as relevant literatures on this field, a hypothesized mechanism of plasma-based PTFE surface modification is also proposed in this work.

In addition to the PTFE membranes, the DBD plasma method was also applied to a series of substrates like polyethylene, polyvinylidene fluoride, and plexiglass plate, demonstrating good versatility in improving the polymers' wettability performance. Therefore, the CO_2-based plasma method is capable to graft AAc and meanwhile to convert the greenhouse gas CO_2 into value-added carboxylic groups on the surfaces of polymers, leading to much improved hydrophilicity. This in combination with its non-flammable and non-explosive characteristics is expected to make the CO_2-based plasma technique being attractive for both the fundamental research and industrial applications.

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