1. Introduction

Water shortage is a growing global problem that affects billions of people around the world [1]. The reuse of treated wastewater is the most economical and efficient way to address this problem [2]. Wastewater treatment methods include both physical methods such as adsorption and filtration and chemical methods such as coagulation and pH adjustments [3-7]. Among all the wastewater treatment methods, microfiltration is widely used for removal of suspended particles, cells and bacteria due to its low cost, ease of use and superior reliability [8, 9]. In microfiltration, suspended particles and bacteria can be stopped and rejected by a porous membrane with micro to nano-size pores. The electrospun nanofibrous mat (ENM), which exhibits high porosity, high rejection rate, and flexibility in material selection, has been widely used in microfiltration [10-14]. Owing to its high porosity, the ENM typically has a high filtrate flux, for example, up to 5,541 L m\(^{-2}\) h\(^{-1}\) at 20 kPa driving pressure, superior to many other membranes whose filtrate flux is below 1,000 L m\(^{-2}\) h\(^{-1}\) [15-17]. Moreover, the ENM does not have straight-through pores. As a result, particles have to pass through tortuous pathways to penetrate the membrane, which is extremely conducive to the rejection of particles and bacteria [18].

Despite the superior structure and filtration features, the ENM should also be mechanically strong enough to efficiently separate suspended particles and bacteria from liquid streams [1, 19, 20]. Indeed, the membrane often exposes to a broad range of mechanical stresses applied by transmembrane pressure, hydraulic pressure, mechanical vibration and abrasive particles during microfiltration [21]. Such stresses may lead to shape deformation and structure disintegration, further resulting in internal fouling [22, 23]. A transmembrane pressure, for example, drives dead-end filtration while causing the membrane to bend. Moreover, a large bending deflection

Combinatory electrospray and electrospinning to produce multi-layered membrane with enhanced mechanical property

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Received January 11, 2022 Revised March 29, 2022 Accepted April 02, 2022

ABSTRACT

Electrospun nanofibrous mats (ENM) have been extensively used for removal of suspended particles, cells and bacteria in membrane filtration because of its high porosity and permeability. However, microfiltration process is driven by a certain transmembrane pressure, and the filtration performance of traditional ENM are thereby hindered by its limited mechanical property. In this study, we propose a new strategy that sandwich the ENM between two layers of electrospray-deposited microparticles to enhance the mechanical properties of ENM membrane. Through a suitable thermal treatment, the microparticles stick with each other forming firm networks, while the ENM is rarely influenced. The mechanical tests show that the tensile strength and elastic modulus of the sandwich-structure composite membrane are 5 times and 7 times higher than those of the fibrous membrane, respectively. Meanwhile, the filtration tests show that the rejection rate of the composite membrane is also higher than the fibrous membrane. Our study implies the composite membrane fabricated by layer-by-layer deposition via electrospray and electrospinning has a great potential in microfiltration applications.

Keywords: Electrospinning, Electrospray, Filtration, Mechanical property
leads to a large bending stress, which may further break the membrane [24, 25]. Unfortunately, a plain ENM generally has low mechanical properties due to its intrinsic features, including high porosity, nano-size fibers and weak binding at junctions. Hence, various methods have been used to enhance the mechanical property of the ENM, such as hot-press process [18], thermal treatment [26], polymer blending [27, 28], solvent induced inter-nanofiber bonding [29], addition of nanoparticles [30]. However, most of these methods either change the non-woven and highly porous nature of ENM or complicate the fabrication process, while the enhancement of mechanical property is limited [31, 32]. Moreover, the mechanical property is coupled with the filtrate property, which makes it difficult to vary the mechanical property or the filtrate property individually. Therefore, a trade-off occurs between the mechanical property and the filtration performance.

As stated above, the membrane exposed to a transmembrane pressure will exhibit a bending behavior during the microfiltration process as shown in Fig. 1(a). Further, this bending behavior could be simplified as a circular plate applied with a continuously distributed load \( p \). The continuously distributed load is determined by the transmembrane pressure. Timoshenko [33] has calculated the bending deflection of such a circular plate with clamped edges:

\[
w = \frac{p}{64D} (a^4 - r^4)
\]

(1)

where \( w \) is the deflection of a point in the circular plate, \( r \) is the radial distance between the point and the center, \( a \) is the radius of the circular plate, \( D = \frac{8hE}{12(1-v^2)} \) is the flexural rigidity of the plate, \( E, v \) and \( h \) are the elastic modulus, Poisson’s ratio and thickness of the plate, respectively. The maximum deflection occurs at the center of the plate, which is equal to

\[
w_{\text{max}} = \frac{pa^4}{64D}
\]

(2)

According to these equations, the deflection of the plate is dominated by the flexural rigidity, radius of the circular plate and the transmembrane pressure.

By reducing the transmembrane pressure and radius of the membrane, or increasing the flexural rigidity, the deflection could be effectively reduced. However, the reduction of transmembrane pressure and membrane radius will lead to the decrease of the filtrate flux. Hence, the most proper way is to increase the flexural rigidity \( D \). According to structural mechanics, flexural rigidity mainly depends on the stiffness of the surface layers [25, 33]. Fig. 1(b) shows the schematic of a bending beam. For pure bending, there is a layer called neutral plane in which the stress and strain equal zero and the length remains constant during deformation. Moreover, the strain on the layers parallel to the neutral plane increases linearly with the distance between the layer and the neutral plane. Hence, the top and bottom surfaces have the largest strain. According to Hooke’s law, for elastic deformation the strain is equal to

\[
\varepsilon = \frac{\sigma}{E}
\]

(3)

where \( \varepsilon \) and \( \sigma \) are the strain and stress respectively. Thus, increasing the elastic modulus of the top and bottom surfaces could effectively decrease strains as well as deformations, which further contributes to a decrease in bending deflections.

Accordingly, we propose a new strategy in which two layers of poly (lactic-co-glycolic acid) (PLGA) microparticles sandwich the polyacrylonitrile (PAN) ENM to form a composite membrane with enhanced mechanical properties (Fig. 2). The composite membrane is fabricated by layer-by-layer deposition using electrospray and electrospinning (Fig. 2(b)). Particulate and nanofibrous layers can effectively be combined due to the residual organic solvent in the fabrication process, preventing layer-to-layer disintegration. Moreover, the PLGA microparticles could form a firm network after thermal treatment at an optimized temperature. Since the glass transition temperature (\( T_g \)) of PLGA is much lower than \( T_g \) of PAN, the thermal treatment process hardly changes the fibrous structure of ENM. The stiffness of the particulate layer is much higher than that of the fibrous layer. Hence, the particulate layer provides effective mechanical support to the sandwich-structure composite membrane, while the fibrous layer can prevent suspended particles and bacteria from passing through the membrane. As a result, the elastic modulus and tensile strength of the composite membrane are much higher than the fibrous membrane. This leads to an increase in the rejection rate of suspended particles and bacteria. Accordingly, the proposed sandwich-structure composite membrane will promote the industrial applications of ENM for removal of suspended particles and bacteria in wastewater microfiltration.
2. Materials and Methods

2.1. Materials

Poly (lactic-co-glycolic acid) (PLGA, 50:50, Mw = 10,000) was purchased from Shandong Institute of Medical Instrument (Shandong, China). Polyacrylonitrile (PAN, Mw=150,000), rubbing alcohol, acetone, ethyl acetate, dichloromethane (DCM), N, N-dimethylformamide (DMF) and SiO2 nanoparticles with 200 nm diameter were purchased from Shanghai Aladdin Biochemical Technology Co., LTD (Shanghai, China). P. aeruginosa ATCC 15692 (PAO1) was purchased from American Type Culture Collection (ATCC). Luria-Bertani broth (LB broth) and LB agar plates were obtained by Yasong Biotechnology Co., Ltd. (Nanjing, China). The deionized water (DI water) was produced by a pure infinity water purification system (Barnstead International, Dubuque, USA).

2.2. Fabrication of Particles and Fibers

The particle and fiber fabrication system consists of two syringe pumps (WK101P, Nanjing Anerke Electronics Technology Co., Ltd, China), two high voltage DC power supplies (Gamma High Voltage Research, Inc., USA), two 18G stainless steel needles, a CCD camera (Allied Vision Technologies, Inc., USA) and a computer. The solution was pumped through the needle by the syringe pump at a constant feeding rate. The DC power supplies applied a positive potential to the solution and a negative potential to the collector. The collector was an aluminum plate with a diameter of 10 cm. The distance from needle tip to the collector was fixed at around 22 cm.

PLGA was dissolved in acetone, ethyl acetate or DCM at a concentration of 5% (w/v) for the fabrication of microparticles using electrospray. The feeding rate of the solution was 1 mL h⁻¹. The positive voltage was 8.5 kV and the negative voltage was -7.0 kV. The deposition time of the particulate membrane was 3 h. For the fabrication of nanofibers, PAN was dissolved in DMF at the concentration of 16% (w/v). The feeding rate of the solution was 0.8 mL h⁻¹. The positive voltage was 12.5 kV and the negative voltage was -2.5 kV. The deposition time of the fibrous membrane was 6 h. For the fabrication of fiber/particle composite membrane, the PLGA particles were deposited for 1.5 h followed by the 4-h deposition of the PAN fibers. Finally, another layer of the PLGA particles was deposited on the fibers for 1.5 h.

2.3. Thermal Treatment

All microparticles and nanofibers were placed in a fuming cupboard for 12 h after fabrication to evaporate the residual organic solvent. After that, the microparticles were baked for 30 min at 50°C in the constant-temperature shaker to form particulate membranes. The optimization of the thermal treatment parameters is discussed in Supplementary materials. The fibrous membrane and fiber/particle composite membrane were also baked at the same parameters.

2.4. Mechanical Test

The fabricated membranes were cut into 15 cm × 20 cm pieces for further mechanical tests. The thickness was measured with a coating pachymeter (AR932, ARCO Science & Technology Ltd., China). The mechanical test was performed with an Instron 3369 Testing Machine (Instron Corporation, MA, USA) with a head travel...
speed of 5 mm min⁻¹. The stress-strain curves were obtained based on the mechanical test and the sizes of the samples. All the mechanical tests were repeated 3 times.

### 2.5. Filtration Performance Measurement

The evaluation of the microfiltration performance including the pure water flux test, nanoparticle rejection test and bacterial rejection evaluation was performed using a dead-end filtration system (Fig. S2) driven by a vacuum pump (SCJ10, Xi’an Shuangchijie Co., LTD, China). The membranes were cut into disc shape with a diameter of 20 mm to conduct these tests. For the pure water flux test, the membrane was first wetted with pure water to eliminate the air bubbles inside, and then tested at the driving pressure of 5 kPa. For the nanoparticle rejection test, 500 ppm SiO₂ suspension was prepared by dispersing the 200 nm SiO₂ nanoparticles in pure water and via ultrasonic treatment for 30 min. After pre-wetting the membrane, SiO₂ nanoparticle suspension was fed into the dead-end filtration system at the driving pressure of 60 kPa. The concentrations of the feeding and permeating suspensions were measured using a UV2150 UV/VIS spectrophotometer and the standard calibration curve of SiO₂ nanoparticle suspension is given in Fig. S3. The flux was calculated by the following equation:

\[
J_F = \frac{V_F}{S \cdot t}
\]  

where \(J_F\) is the flux, \(V_F\) is the permeated volume (\(V_F = mL\) for the pure water flux and filtrate flux tests), \(S\) is the area of the membrane and \(t\) is the time. To determine the variation of the filtrate flux with the increase of permeated volume, \(t\) was recorded every 50 mL. The rejection rate was calculated by the following equation:

\[
R_j = 1 - \frac{C_F}{C_P}
\]

where \(R_j\) is the rejection rate, \(C_F\) and \(C_P\) are the concentration of the feeding and permeating suspensions, respectively.

The non-supported filtration was conducted to verify the mechanical enhancement. A syringe pump with two channels (Longer Pump, LSP02-2A, China) was used to feed the 500 ppm SiO₂ suspensions at a constant feeding rate. Firstly, the fibrous and composite membranes were cut into round pieces (2 mm in diameter). Then, the round membranes were mounted into the membrane holders. After pre-wetting the membrane, the suspensions were fed into the membrane holders at the feeding rates of 0.1, 0.3, 0.5, 0.7 and 0.9 mL h⁻¹. After the filtration, 1 mL of permeated suspensions were collected for concentration measurements using the spectrophotometer. Finally, the rejection rates were calculated using Eq. (5). All the filtrate tests were repeated 3 times.

The 10⁶ CFU mL⁻¹ PAO1 suspension was used for the bacterial rejection evaluation. The suspension was shaken for 3 h with the constant-temperature shaker at 37°C. The membrane was sterilized with rubbing alcohol and fixed in a sterilized membrane holder. Then, the filtration was performed with a 5 mL sterilized syringe in gnotobasis. After the filtration, the permeated suspension was cultured in the LB culture medium for 12 h at 37°C.

### 2.6. Characterization

The material property and sample morphology were characterized as follows [34]. The X-ray powder diffractometry (XRD) of PLGA and PAN microparticles was performed on a XPert MPD (Phillips) equipped with a Cu X-ray source operating at 40 kV and 40 mA and a secondary monochromator allowing to select the Cu Kα line (0.15418 nm). Calibration of the goniometer was done with the special insert provided by the manufacturer for the 0° position and then verified with a quartz sample reference. Measurement was done from 5° to 60° with speed of 0.02° min⁻¹ and a step time of 2 s.

The Fourier transform infrared (FT-IR) spectra were investigated to detect the functional groups of the compounds. Spectra were recorded using a Nicolet 8700 FT-IR spectrometer (Thermo Scientific, USA) with a resolution of 4 cm⁻¹ and cooled mercury cadmium telluride A (MCT A) photo detector. Dried PLGA or PAN microparticles were mixed with spectroscopic grade KBr (Sigma-Aldrich) in an agate mortar. The KBr-sample mixture was pressed into a pellet under a 10-ton load for 2-4 min and the spectrum was recorded immediately.

The thermogravimetric analysis (TGA) were carried out using TGA Q5000IR (TA Instruments) to obtain thermal stability information of PLGA and PAN. The polymers were heated at a rate of 10°C per min from 30 to 400°C under nitrogen atmosphere.

The specific surface areas of PAN nanofibrous mat and PLGA particulate membrane were measured by the BET (Brunauer, Emmett and Teller) adsorption method using a surface area analyzer (Tristar II 3020M).

The morphologies of the microparticles and nanofibers before and after the thermal treatment were characterized using a scanning electron microscope (SEM, Zeiss Gemini SEM-500, Germany). The porosity and pore size distribution for particulate membranes and fibrous membranes were measured based on more than 1,000 individual pores in three SEM images at the same magnification using the ImageJ software.

### 3. Results and Discussion

#### 3.1. Characterization of the Particulate and Fibrous Membranes

Fig. 3(a) presents the XRD patterns of PLGA and PAN. Both XRD patterns exhibit one single crystalline peak at 2θ = 17°, which corresponds to orthorhombic (110) reflection [34, 35]. Fig. 3(b) presents the FT-IR spectra of PLGA and PAN. The characteristic peak of PLGA was observed at 1,760 cm⁻¹ (C=O stretching). The spectrum of PAN shows the -CH₂- absorption band at 2,943 cm⁻¹, the C≡N absorption band at 2,344 cm⁻¹ as well as CH₂ and CH₃ absorption bands at 1,454 cm⁻¹, which is in accordance with formula of PAN ((C₃H₇N₉)₂) [36, 37]. Fig. 3(c) presents the TGA curves of PLGA and PAN. The main decomposition of PLGA is observed at the range of 212.6 to 336.7°C with a mass loss of 98.27%. The main decomposition of PAN occurs at 307.4°C. The mass loss is 31.21% when the temperature increased to 400.0°C. These results imply that the polymers are thermally stable during the thermal treatment process. The specific surface areas of the nanofibrous and particulate membranes were evaluated using BET adsorption method. The BET surface areas of the nanofibrous and particulate membrane are 5.33 ±
0.12 and 1.52 ± 0.08 m²g⁻¹, respectively. The nanofibrous membrane has larger BET surface area, which means more open pores, higher permeability while weaker mechanical property.

The morphologies of microparticles were observed using SEM, as shown in Fig. S4. As the mechanical properties of the particulate layer depend on its topology, 3 kinds of microparticles with different morphologies are generated. The microparticles show spheroid, rod and red cell-like shapes. As previous researchers’ demonstration, the chain entanglement density, which is influenced by the concentration, the chain length and the type of solvent, is a critical parameter altering the morphology of microparticles in electrospray [38, 39]. During electrospray, the droplets emitted from the Taylor cone are highly charged and the charges accumulate along the surface, which induces an electrostatic repulsion called Coulomb repulsion. The droplets stretched by Coulomb repulsion may break into smaller microdroplets if the entangled network of polymer chains is too weak. Such a phenomenon is called Coulomb fission. In contrast, if the entangled network is strong, the stretched nonspherical shapes of microdroplets are retained after solvent evaporation forming microparticles with various shapes, as shown in Fig. S4. Moreover, if the entangled network is strong enough, the microjet emitted from the Taylor cone does not break into droplets. Actually, it is stretched and may experience any of several instabilities forming micro and nanofibers after solvent evaporation, which is a typical electrospinning process [40].

The microparticles and nanofibers after thermal treatment are shown in Fig. 4(a)-(d). As the SEM images show, the microparticles partially melt and stick with each other firmly because of the thermal

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Fig. 3. (a) XRD patterns of PAN and PLGA. (b) FT-IR spectra of PAN and PLGA. (c) TGA curves of PAN and PLGA.

Fig. 4. (a)-(c) The microparticles fabricated using 5% PLGA acetone, DCM and ethyl acetate solutions after thermal treatment, respectively. The insets show the porosities and the pore size distributions. Scale bar: 10 μm. (d) The nanofibers fabricated using 16% PAN DMF solution after thermal treatment. The inset shows its porosity and pore size distribution. Scale bar: 5 μm.
treatment, while the nanofibers are not influenced. This is because the temperature used in thermal treatment is higher than $T_g$ of PLGA ($T_g \approx 50^\circ C$) while far below that of PAN ($T_g \approx 95^\circ C$) [41, 42]. According to previous studies [43-45], when the temperature is below $T_g$ of a polymer, the polymer chains are frozen and the volume barely changes. Nevertheless, the mobility of the molecular chains is enhanced when the temperature is close to or higher than $T_g$, which induces partially melting of microparticles and forming a firm network with well mechanical properties. Moreover, the polymer solution is subjected to a high electric field during electrospray, which induces inner stress and a high degree of alignment and orientation of polymer chains [46, 47]. Hence, the polymer chains rapidly relax to random coil state due to the enhancement of chain mobility leading to a shrinking behavior of the volume. The shrinkage also contributes to the enhancement of the internal interactions of microparticles and the mechanical properties of the particulate structure, which has been demonstrated before [45]. As the temperature used for thermal treatment is below $T_g$ of PAN, the nanofibrous mat is barely influenced. In the sandwich-structure composite membrane, the particulate layers are served as the mechanical-support layers and the nanofibrous layer is served as the retention layer. Accordingly, the mechanical property and the filtration property of the composite membrane are decoupled.

3.2. Mechanical Performance

The mechanical properties of the particulate, fibrous and composite membranes were probed via the tensile test. The stress-strain curves of the particulate membranes generated from 5% PLGA acetone, ethyl acetate and DCM solution (marked as A5-P, E5-P and D5-P, respectively) are shown in Fig. 5(a). The A5-P membrane has the lowest tensile stress and total strain. The D5-P membrane has the largest total strain while the E5-P membrane has the largest tensile strength. This is due to the different shapes of the microparticles and different contact areas. The A5-P is composed of small porous microparticles, which may result in the weakest mechanical property. The D5-P has a high porosity and large particle-particle contact area, which may lead to the highest total strain. The contact area of E5-P is larger than others, which leads to the strongest network. Hence, the E5-P has the largest tensile strength. Furtherly, E5-P is used as the particulate layer of the composite membrane.

The stress-strain curve of the PAN fibrous membrane was also measured and shown in Fig. 5(b). Compared with the curves of particulate membranes, the total strain of the fibrous membrane is more than 5 times that of the particulate membranes. In addition, the tensile strength is much lower. The stress-strain curve of the fiber/particle composite membrane is shown in Fig. 5(c). Comparing the stress-strain curves, the total strain of the fibrous membrane is larger than that of the composite membrane, while the tensile strength of the fibrous membrane is much lower than that of the composite membrane. What’s more, the strain of the composite membrane is lower than that of the fibrous membrane at the same stress. It means less deformation occurs on the composite membrane.

Fig. 5. (a) The stress-strain curves of particulate membranes composed of different microparticles. (b) The stress-strain curve of the fibrous membrane. (c) The stress-strain curve of the fiber/particle composite membrane. (d) The tensile strength and the elastic modulus of different membranes. (e) The relative displacement of different composite membranes under shear force.
at the same tensile force. For example, when the stress is 12 MPa, the strain of the fibrous membrane is around 35%, while it is less than 5% for the composite membrane. The tensile strength and elastic modulus of the particulate, fibrous and composite membranes were also calculated and shown in Fig. 5(d). According to these data, the tensile strength and elastic modulus of the particulate and composite membranes are higher than that of the fibrous membrane. A large elastic modulus leads to a high flexural rigidity and a low bending deflection during microfiltration according to Eq. (1). Hence, the mechanical property of the filter membrane is successfully enhanced.

The composite membrane is fabricated by layer-by-layer deposition of microparticles and nanofibers using electrospray and electrospinning. The two processes share the same setup and can be changed quickly. Moreover, the residual organic solvent helps to bond the particulate layers and the fibrous layer. To validate this, the slippery displacement under shear force was also measured and shown in Fig. 5(e). As a control group, the fibers were directly deposited on filter paper. According to these curves, the relative displacement of the fiber/particle composite membrane is much lower than that of the fiber/paper membrane under the same shear force. This means that the layer-by-layer deposited fiber/particle composite membrane has less deformation when it suffers shear force. Moreover, strong inter-layer adhesion also contributes to avoiding the sliding between particulate and fibrous layers, which is conducive to reduce the shape deformation of fibrous layer.

3.3. Filtrating Performance

The filtration behavior was measured using a dead-end filtration setup. The 500 ppm SiO$_2$ aqueous suspension was used for the rejection test. The pure water flux, filtrate flux and rejection rate are shown in Table 1. It could be found that the pure water flux of the composite membrane is much lower than that of the fibrous membrane. This is because the particulate layer of the composite membrane has larger resistance than that of the fibrous membrane. Therefore, the particulate layer dominates the pure water flux of the composite membrane. However, the filtrate flux of the composite membrane is only a little lower than that of the fibrous membrane. Based on Darcy’s law, the filtrate flux is equal to:

$$J = \frac{\Delta p}{\mu R_{tot}} = \frac{\Delta p}{\mu (R_h + R_c)}$$

### Table 1. The Filtration Performance of the Fibrous and Composite Membranes

| Membrane          | Pure water flux (L. m$^{-2}$ h$^{-1}$) | Filtrate flux (L. m$^{-2}$ h$^{-1}$) | Rejection rate (%) |
|-------------------|----------------------------------------|-------------------------------------|--------------------|
| Fibrous membrane  | 15,854.74 ± 1,526.50                   | 2,261.18 ± 86.76                    | 92.25 ± 1.36       |
| Composite membrane | 5,155.51 ± 123.01                     | 1,817.58 ± 57.46                    | 97.09 ± 1.14       |

Fig. 6. (a) The filtrate flux variation with the increase of feeding volume of the SiO$_2$ suspension. (b) The SiO$_2$ suspensions before and after filtration. Here are SiO$_2$ suspensions before filtration, after filtration with fibrous membrane and after filtration with fiber/particle composite membrane, respectively. (c) The non-supported filtration setup. (d) The rejection rate of the fibrous and fiber/particle composite membranes at different suspension feeding rates in the non-supported filtration tests.
where $J$ is the filtrate flux, $\Delta p$ is the transmembrane pressure, $\mu$ is the dynamic viscosity, $R_{\text{tot}}$ is the total resistance, $R_m$ is the resistance of the membrane and $R_c$ is the resistance of the filter cake. The filter cake is formed by the rejected SiO$_2$ nanoparticles, which grows thicker with the increase of feeding suspension. So, the resistance of the filter cake plays a critical role in filtrate flux. To validate this, the filtrate flux varying with the increase of feeding suspension volume was measured and shown in Fig. 6(a). The cumulative filtrate flux of both membranes dramatically decreases when the feeding suspension volume increases from 50 to 300 mL. Hence, although the particulate layer dramatically reduces the pure water flux of the composite membrane, it has limited influence on the filtrate flux. The rejection rate of the composite membrane is higher than that of the fibrous membrane. It is due to the superior mechanical property preventing the deformation of the membrane during microfiltration. The suspensions before and after filtering are shown in Fig. 6(b).

Additionally, non-supported filtration tests were conducted to validate the enhancement of mechanical properties. The setups are shown in Fig. 6(c). The SiO$_2$ suspensions were fed into the membrane holders containing the fibrous or fiber/particle composite membrane at different flow rates using the syringe pump. The calculated rejection rates are shown in Fig. 6(d). The results indicate that the rejection rate of the fiber/particle composite membrane is higher than that of the fibrous membrane at any feeding rate ranging from 0.1 mL h$^{-1}$ to 0.9 mL h$^{-1}$. This is due to the higher elastic modulus of the composite membrane, which leads to lower bending deformation during the filtration tests.

The surface area of the filter membrane is also a critical parameter influencing the mechanical property and flow rate of the filtrate. In Eq. (1) and (2), the increase in membrane radius $a$ causes a dramatic increase in the membrane bending deflection $w$ since $w$ is in direct proportion to $a^4$. Besides, the membrane diameter affects the filtrate flux by influencing the resistance of the filter cake. The thickness of filter cake $h_c$ is equal to

$$h_c = \frac{\left(\frac{f_1-5}{1+5}\right)\rho \frac{1}{\pi a^2}}{\delta (1-\varepsilon)}$$

where $V_p$ is the permeated suspension, $\rho$ is the density of the suspended nanoparticles, $\varepsilon$ is the porosity of filter cake. According to Carman–Kozeny equation [48], the resistance of the filter cake

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**Fig. 7.** The filtration performance of PAO1 bacteria suspensions. (a)-(c) The cultured bacteria of PAO1 suspensions before and after filtration with fibrous and fiber/particle composite membranes. (d) The measured colony forming units before and after filtration.
\( R_c \) is equal to

\[
R_c = \frac{180(1-\varepsilon)^2}{d^2 \varepsilon^2} h_c = \frac{180(1-\varepsilon)^2 (G_r - G_p) \gamma_p - \frac{1}{\alpha^2}}{\pi p}
\]  

(8)

where \( d \) is the diameter of the suspended nanoparticles. Accordingly, \( R_c \) is in direct proportion to \( \frac{1}{\alpha^2} \). As the filtrate flux \( J \) increases with the decrease of the filter-cake resistance \( R_c \), the increase of membrane diameter induces the increase of filtrate flux. However, it also leads to the increase in bending deflection, which may further break the membrane. In other words, enhancing the mechanical property of the filter membrane indirectly increases the critical filtrate flux by increasing the critical membrane diameter.

Furthermore, the filtration of bacteria is also critical in the treatment of water waste. Here, the PAO1 suspension was used as an example to illustrate the filtrate property of the composite membrane. After the filtration, the initial and permeated suspensions were cultured and shown in Fig. 7(a)-(c). In the bacteria rejection test, the composite membrane also performed better than the fiber membrane based on the calculated colony forming units shown in Fig. 7(d). In summary, the particulate layer can promote the filtrate performance of the composite membrane by enhancing the mechanical property while having limited influence on the filtrate flux.

Actually, as various polymers have been used for the fabrication of microparticles and nanofibers via electrospray and electrospinning, such as polymethylmethacrylate [49], polystyrene [50], wheat gluten [51] and polyethersulfone [52], the mechanical properties and filtration behaviors can be tuned severally according to specific applications.

4. Conclusions

In this paper, we proposed a new strategy to fabricate the composite filter membrane with enhanced mechanical property by electrospaying microparticles on the double-side of electrospun nanofibrous membrane. With the thermal treatment at a temperature of 50°C, the microparticles stick with each other forming a firm network with high tensile strength and elastic modulus, while the electrospun nanofibers are not deformed. Mechanical tests indicate that the tensile strength of the composite membrane is 56.60 ± 5.20 MPa, which is more than 5 times that of the fibrous membrane. The elastic modulus is also increased from 111.02 ± 17.10 MPa to 1468.18 ± 307.38 MPa in the comparation of the fibrous membrane with the composite membrane. The resultant increase in flexural rigidity of membrane further decreases its bending deflection. The increased rejection rate of SiO\(_2\) nanoparticle and bacteria suspension on fibrous membrane (92.25%) and composite membrane (97.09%) verifies the role of enhanced mechanical property in improving microfiltration performance. Moreover, we have also theoretically discussed the influence of mechanical property on the filtrate flux, suggesting that a higher mechanical strength leads to a higher critical filtrate flux. Hence, the proposed strategy may further promote the potential applications of electrospray and electrospinning in microfiltration.

**Acknowledgments**

This work is supported by the Strategic Priority Research Program of the Chinese Academy of Sciences (No. XDA16021303), the National Natural Science Foundation of China (No. 120040731), the National Key R&D Program of China (No. 2021YFC2401402) and the Key Program of Natural Science Project of Educational Commission of Anhui Province (No. KJ2021A0248).

**Conflict-of-Interests**

The authors declare no conflict of interest.

**Author Contributions**

Y.X. (Ph.D. student) conducted all the experiments and wrote the manuscript. Z.Z. (Master student) helped with the fabrication of microparticles and particulate membranes. G.L. (Ph.D.) helped with the mechanical tests. S.S. (Ph.D.) and R.X.X. (Professor) revised the manuscript.

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