Cellulose Nanospheres Coated Polylactic Acid Nonwoven Membranes for Recyclable Use in Oil/Water Separation

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Abstract

Oily wastewater has always been an environmental issue that we are concerned about and committed to managing. Although the superwetting membranes have been extensively studied and widely used in oil/water separation, the abundant discarded membranes are still headaches due to their non-degradable nature. In this work, all-around green, as well as superhydrophilic polylactic acid (PLA) nonwoven membrane, is designed by coating cellulose nanospheres (CNCs) with the aid of polydopamine (PDA). Abundant hydroxyl groups and hierarchical rough structure synergistically contribute to the superhydrophilicity and excellent oil/water separation performance of the resultant CNCs/PDA/PLA nonwoven membrane. Interestingly, the oil/water separation efficiency can be maintained above 98% after 100 times of repeated use. With outstanding durability, and easy controllability, the CNCs/PDA/PLA nonwoven membrane may provide effective solutions to simultaneously manage the oily wastewater and secondary pollution of the used membrane itself.

Introduction

The industrial production processes, such as petrochemical, textile, leather, steel processing and metal surface processing, and frequent oil spills have produced abundant oily wastewater, which has a long-term and fatal impact on the ecological environment and human health (Cardona et al. 2019; Bhardwaj et al. 2018; Kizil et al. 2020). The superwetting filter membrane is considered to be one of the effective means to manage oily wastewater due to its large-scale production, high filtration efficiency, and excellent mechanical properties (Li et al. 2020). However, the commonly used superwetting membranes, for instance, polytetrafluoroethylene (PTFE) (Zhu et al. 2020), poly (vinylidene fluoride) (PVDF) (Zhang et al 2013), and polypropylene (PP) (Wang et al. 2020) membrane, are petroleum-based polymer materials, which are difficult to degrade in nature. In particular, the lipophilic oil/water separation material is easy to be polluted in the treating of oily wastewater that leads to poor reusability (Padaki et al. 2015). Biodegradable oil/water separation membrane with high flux, anti-pollution, and durability is a promising way to efficiently purify oily wastewater without causing secondary pollution to the environment.

In recent decades, biodegradable polylactic acid (PLA) has been widely studied in various fields including filter membranes as a result of its excellent comprehensive performance (Mehboob et al. 2020; Kurzina et al. 2020; Hamad et al. 2018). The mechanical strength of electrospun PLLA/PDLA membrane by was improved by welding at low temperatures and the resultant membrane with enhanced inter-fiber adhesion can be used to separate chloroform/water effectively utilizing the solvent resistance of stereocomplex (sc) crystallites (Jing et al. 2017). Multifunctional and self-cleaning superhydrophilic electrospun sc PLA membrane was fabricated via gallic acid (GA)-modified TiO_2 coating (Zhang et al. 2020). The GT-sc membrane shows the versatility that can efficiently separate multiplicate oil/water mixtures and oil-in-water emulsions. Electrospun membranes are conveniently modified and used for oil/water separation due to their super-high porosity. However, owing to its low strength and poor flexibility, the electrospun membrane is difficult to be practically manufactured and used in the purification of abundant oily wastewater. PLA nonwoven membrane has reasonable porosity, relatively good mechanical properties,

and has been widely used in air filtration, medical protection, and other fields by industrial production (Fang et al. 2020; Phuong et al. 2019). It can also be seen as a promising candidate for eco-friendly oil/water separation materials with high permeate flux.

The two key factors determining the wettability of membrane surface are the surface energy influenced by surface composition and the roughness affected by surface microstructure (Baig et al. 2019; Ismail et al. 2020). As the most abundant macromolecular polysaccharide in nature, cellulose has a large number of hydroxyl hydrophilic groups (Song et al. 2020; Shi et al. 2020), which is beneficial to realize all-around green PLA oil/water separation material. Based on the above concepts, polydopamine (PDA) (Li et al. 2019; Delparastan et al. 2019) was used as a kind of adhesive bonding firmly to the surface of PLA nonwoven membrane and inducing the deposition of cellulose nanospheres (CNCs). The surface wettability and separation efficiency for oil/water mixtures of the resultant CNCs/PDA/PLA nonwoven membrane will be systematically studied, as well as the recyclability will be carefully evaluated. This work provides a new pathway to fabricate eco-friendly oil/water separation material with high separation efficiency and outstanding durability.

Experimental Section

Materials

All the materials used in this study are commercially available. The raw PLA nonwoven materials (diameter 20-25μm) were kindly supplied by Zhejiang Hisun Biomaterials Co., Ltd., which were rinsed off with anhydrous ethanol and dried thoroughly before using. Commercial lyocell fibers with a diameter of about 10 μm were purchased from Suzhou Baosida Chemical Fiber Co., Ltd. HCl, H_2SO_4 , and NaOH were purchased from Zhejiang Sanying Chemical Reagent Co., Ltd. Dopamine (≥99%) were received from Aladdin (Shanghai) Co., Ltd., China.

Preparation of cellulose nanospheres

2g of swelled lyocell fibers were added to 100ml NaOH solution for pretreatment. After being treated for 3h at 70℃ and thoroughly washed with deionized water, the obtained MCC were freeze-dried and further used in the preparation of CNCs by the method of H_2SO_4/HCl mixed acid hydrolysis. Specifically, 2g of MCC were added to 100ml mixed acid aqueous solution (3 mol/L) with H2SO4/HCl/deionized water weight ratio of 3:1:6. The reaction was carried out under ultrasonic conditions for 10 hours, and the resulted suspension was filtered and thoroughly washed. The sulfonate ion in the suspension was removed with a dialysis bag. Finally, CNCs were obtained by freeze-drying.

Preparation of Superhydrophilic CNCs/PDA/PLA Nonwoven Membranes

Superhydrophilic CNCs/PDA/PLA nonwoven membrane was fabricated by constructing a hierarchical rough structure on PLA nonwoven membrane. Specifically, the pristine PLA nonwoven membrane was thoroughly rinsed by using ethanol and sonication for 10 min. After drying in a vacuum oven at 80℃ for

24h, the dried PLA nonwoven membrane was immersed in the mixed dopamine aqueous solution with a certain concentration as 0.1g/300ml, 0.2g/300ml, 0.3g/300ml, 0.4g/300ml, 0.5g/300ml, 0.6g/300ml, 0.8g/300ml, 1.0g/300ml. The Tris-buffer solution was used to fix the pH at around 8.5. After reacting at 25 °C for 6 h, CNCs were further added into the dopamine solution with stirring for another 6 h. Finally, the resultant CNCs/PDA/PLA nonwoven membrane was ultrasonically rinsed with ethanol to remove undecorated CNCs and further vacuum dried at 80 °C.

Characterization

Fourier Transform Infrared spectra were recorded using a Thermo Nicolet FTIR spectrometer with a resolution of 4 cm^{-1} and 32 scans. The absorption spectra of the samples were acquired by using the KBr disk technique in the range of 4000–400 cm^{-1}. Microscopic morphology of MCC and CNCs were performed on field emission scanning electron microscopy (FE-SEM, Verios G4) at the voltage of 3.0 kV. The prepared powder was dispersed in deionized water, and the dispersion was dropped on a silicon wafer. After being dried by using an infrared lamp, the powder was sputter-coated with a thin gold layer for imaging. The morphology of PLA nonwoven membranes before and after coating was also investigated by using FE-SEM. The microstructures of prepared CNCs were characterized as well by transmission electronic microscopy (TEM, JEM-2100 microscope). The diameter of CNCs was investigated with a laser dynamic light scattering instrument (LB-500v) from Horiba, UK. Each sample was tested three times, and the average was taken as the particle size. The pore size of the membrane before and after modification was tested by the instrument PMI Capillary Flow Porometer (CFP-1500AE). The surface wettability of the membrane was studied by visualized results of static water contact angles (WCA) using JY-82B.

Fluxes of Superhydrophilic CNCs/PDA/PLA Nonwoven Membranes

The filtration efficiency of CNCs/PDA/PLA nonwoven membrane was calculated using the following equation

$$flux = \frac{V}{St} \tag{1}$$

where V (L) represents the permeated water volume, S (m^2) represents the surface area of the nonwoven membrane, and t (h) is the operation time. Each sample was tested 5 times and taken the average.

Oil/Water Separation

An oil/water mixture consisting of 50 mL organic solvent and 50 mL water was separated by the prepared CNCs/PDA/PLA nonwoven membrane driven by gravity. By the way, the water and organic solvent (n-hexane) were dyed by $CuSO_4$ and oil red O, respectively. The separation efficiency of CNCs/PDA/PLA nonwoven membrane was calculated using equation (2):

$$\text{Separation efficiency (SE)} = 1 - \frac{O_2}{O_1} \times 100\% \qquad (2)$$

where O_1 (ppm) is the oil content in the pristine oil/water mixtures, O_2 (ppm) is the oil content in the filtered water.

Water-Absorption Performance

The superhydrophilicity of CNCs/PDA/PLA nonwoven membranes can also be well reflected by water absorption properties. The prepared sample was completely immersed in water for 1min and then placed on the screen to dropping freely for 60 s. The absorption capacity, G, was calculated according to equation (3):

$$G = \frac{m_1 - m_0}{m_0} \qquad (3)$$

where m_0 (g) and m_1 (g) are the weights of the dry and wet superhydrophilic CNCs/PDA/PLA nonwoven membrane, respectively.

Results And Discussion

Microstructure of CNCs

The SEM image (Figure 1(a)) of the prepared MCC shows that the diameter is about 10μm, and the length ranges from tens to hundreds of microns. During the hydrolysis process, acid can penetrate the cellulose network quickly and hydrolyze the amorphous region (Johar et al. 2012). At the same time, the crystalline region of cellulose is more resistant to weak acid hydrolysis, which is due to the stronger hydrogen bond interaction between adjacent cellulose molecules in the crystal region compared with the non-compact amorphous region. As shown in Figure 1(b), uniform spherical CNCs with a diameter of about 37 nm are observed under SEM. However, due to their small size, strong interaction, and large specific surface area, the agglomeration of nanoparticles is also obvious. TEM was further used to confirm the morphology and diameter of CNCs. Figure 1(b') clearly shows that the prepared CNCs are spherical with a smooth surface and uniform diameter distribution.

Furthermore, the effects of reaction temperature and time on the diameter of CNCs were carefully studied. As shown in the distribution diagram in Figure1(c), the influence of temperature and time on the size of CNCs has a similar trend, that is, with the increase of time and temperature, the diameter decreases. The

diameter decreases from 98 nm to 37 nm when the reaction time increases from 6 h to 12 h while the temperature is kept at 80 °C. When the reaction is processed at 60 °C for 12 h, the particle size of CNCs is larger than 200 nm. Besides, the particle diameter gradually decreases to 32 nm while the temperature further increases to 90 °C. However, due to the existence of high concentration sulfuric acid in the mixed acid, it is easy to cause CNCs to yellow under high reaction temperature and long reaction time. Therefore, the optimal condition of using 80 °C for 12h was selected as the befitting parameter to prepare CNCs in the following section.

Surface Morphology and Wetting Behaviors

The commercial PLA nonwoven membrane was modified via coating CNCs onto the surface of the PLA fibers by using PDA as an adhesive. The coating ratio of CNCs is closely related to the attaching weight of PDA which is due chiefly to the concentration of dopamine in the reaction solution. As shown in Figure 2, when the concentration of dopamine increases from 0.1 g/300 ml to 1 g/300 ml, the weight fraction of CNCs increases from 1% to 2.5%. With the lower concentration, the consumption of dopamine monomer can be timely replenished, so the weight fraction of CNCs increases. However, when the concentration of dopamine reaches a certain value of 0.5 g/300 ml, the change of weight fraction of CNCs tends to balance. The maximum weight fraction of CNCs is obtained as about 2.5%.

The microstructures of pristine and modified PLA nonwoven membranes were characterized by SEM. As shown in Figure 3, the pristine PLA nonwoven membrane has a 3D porous network structure building up of microfibers with a smooth surface and a diameter of about 20 μm. After treated with dopamine, a PDA layer appears obviously on the fiber. This layer of PDA may be broken and cracked due to bending and folding in the sample preparation. However, it can be seen from figure 3(b’) that the PDA layer is smooth and even in thickness in the relatively intact area. Further being attached by CNCs (~37nm), these nanoparticles are distributed on the surface of PLA fibers in the form of polydisperse aggregates. Besides, CNCs are not limited to the surface but infiltrated and fixed in the fiber network due to the large pore size of nonwovens. This will also reduce the pore size from 223 μm to 128 μm as shown in Figure 4. What’s more, the enlarged micrograph of figure 3(c’) clearly shows the rough surface of PLA fibers, which is in obvious contrast to the smooth fiber of pure PLA nonwoven membrane (figure 3(a’)). The protruding morphology will endow the CNCs/PDA/PLA nonwoven membrane a hierarchical rough structure, which is the key to constructing a superhydrophilic membrane.

Figure 5 shows the WCA of the original PLA nonwoven which is about 121 ± 1.9 °. The chemical structure of PLA consisting of hydrophobic ester groups determines that the nonwoven membrane presents a hydrophobic surface. After coating with PDA, the WCA of the PDA/PLA membrane decreases significantly to 58.5 ± 1.6 °. This is because the PDA film wrapped on the surface of PLA fiber contains a large number of hydrophilic groups such as hydroxyl groups and amino groups. However, the WCA of 58.5 ± 1.6 ° results in the PDA/PLA nonwoven membrane having hydrophilic and lipophilic properties at the same time, so it still cannot be used for oil/water separation. Upon being further attached CNCs, the roughness of the surface can amplify the original wetting characteristics to a certain extent, the WCA of

CNCs/PDA/PLA nonwoven membrane reduces to 0 °, and water can quickly spread and penetrate the membrane. The transformation of PLA nonwovens from hydrophobic to superhydrophilic is realized. To the specific, the multi-level rough structure formed by CNCs on the surface of the PLA fiber and the hydrophilic groups (hydroxyl groups) rich in CNCs plays a synergistic role in the acquirement of superhydrophilic CNCs/PDA/PLA membranes.

Separation Performance and Water Adsorption

The superhydrophilic surface wettability and porous internal structure of CNCs/PDA/PLA nonwoven membrane make it a superior choice for oil/water separation and water adsorption. As shown in Figure 6(a) and (a'), the separation performance of CNCs/PDA/PLA nonwoven membrane was investigated by using n-hexane/water mixtures. In the separation process, water can quickly wet the CNCs/PDA/PLA nonwoven membrane and penetrate through the membrane, while oil is trapped on the upper surface of the membrane. The separation efficiency can be as high as 99% indicating outstanding oil/water separation performance. Reusability is an important aspect to evaluate the durability and environmental protection of oil/water separation materials especially for these coated with particles, which are easy to wear and tear in repeated use. 100 cycles of separation tests were carried out and it is found that after 100 cycles of repeated use, the separation efficiency is still above 98% stating exceptionally well in durability (Figure 6(b)). This makes modified PLA nonwoven membrane become a very practical environmental protection material for oil/water separation.

Water adsorption is also discussed since it is important for some absorbent and water retaining materials. As shown in Figure 6(c), the water absorption ratio of the original PLA nonwoven is only about 270%. After being modified by PDA, the water absorption ratio of PDA/PLA membranes reaches 778%. It further enhances up to 1000% by attaching CNCs nanoparticles for CNCs/PDA/PLA membranes. The water absorption ratio is closely related to the wetting behavior of the membrane. For the pristine PLA nonwoven membrane, water is difficult to withholding in the material. Whether it is modified by PDA or further coated by CNCs, the modified PLA nonwovens have a good water retention effect. Also, the flux maintains as high as 3710 $Lm^{-2}h^{-1}$ for the CNCs/PDA/PLA membrane.

Mechanical Properties

The excellent mechanical properties are the basis of improving the practicability of PLA nonwoven membrane as oil/water separation materials. In particular, the flexibility of nonwovens tends to deteriorate after post-treatment, which has adverse effects on the storage, handling, and use of membranes. The mechanical strength of pure PLA nonwoven membrane is only 114 N due to the disorderly arrangement of fibers (Figure 7(a)). For nonwovens, the bond fastness of interlaced fibers is the key factor affecting mechanical strength. Since PDA can not only wrap on the surface of the fiber but also adhere to the intersection of the fibers, which plays the role of chemical crosslinking, the mechanical strength of the PDA/PLA nonwoven membrane is increased to 150N. It is further increased to 168N for the CNCs/PDA/PLA membrane, which is 47% higher than that of the original PLA sample. Also, the

modified PLA nonwoven membrane maintains good flexibility, and the elongation at break is about 60%. This should be ascribed to the uniform loading of PDA and CNCs on the fiber surface, which is conducive to the stability and uniform deformation of the nonwoven membrane.

The mechanical strength of oil/water separation materials will be damaged after repeated use, which will affect its service life. The mechanical strength of CNCs/PDA/PLA nonwoven membrane after a certain number of uses was carefully studied. After observation of the trend of mechanical strength with the using times, there is a sudden decrease when used more than 40 times. The microstructure of fiber cross-section of CNCs/PDA/PLA nonwoven membrane after 1 and 40 applications is compared in Figure 8. The surface of PLA fiber in the membrane used for 1 time is relatively smooth without observed defects. However, after 40 times of use, it can be found that there are irregular cavities with diameters ranging from several nanometers to hundreds of nanometers in the enlarged SEM image (Figure 8(b')). This corresponds well to the decrease in mechanical properties. Nevertheless, the decrease of mechanical strength is as low as 15% after 50 cycles. Even after 90 times of repeated use, the mechanical strength of CNCs/PDA/PLA nonwoven membrane is still higher than that of pure PLA membrane, showing excellent durability.

Conclusions

Briefly, we have developed an easy-controlled approach to fabricate all-around green and superhydrophilic CNCs/PDA/PLA nonwoven membrane utilizing dopamine-modified CNCs coating. CNCs provide hydrophilic groups as well as hierarchical rough structures which directly leading to superhydrophilicity. The resultant CNCs/PDA/PLA nonwoven membrane exhibits high selectivity when they are employed as oil/water separation materials. Besides, the strong adhesion of PDA endows the modified CNCs/PDA/PLA membrane excellent durability, which is manifested in stable filtration efficiency and mechanical strength in the process of reuse. With full green sources, exceptional durability, and high selectivity, cost-effective superhydrophilic CNCs/PDA/PLA nonwoven membrane may provide a good example as environmentally friendly oil/water separation material that can be used in practice.

Declarations

Acknowledgments

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Conflicts of interest

The authors have no conflicts of interest to declare that are relevant to the content of this article.

Ethical approval

This article does not contain any studies with human participants or animals performed by any of the authors. In this experiment, we did not collect any samples of human and animals.

Informed consent

Informed consent was obtained from all individual participants included in the study

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Figures

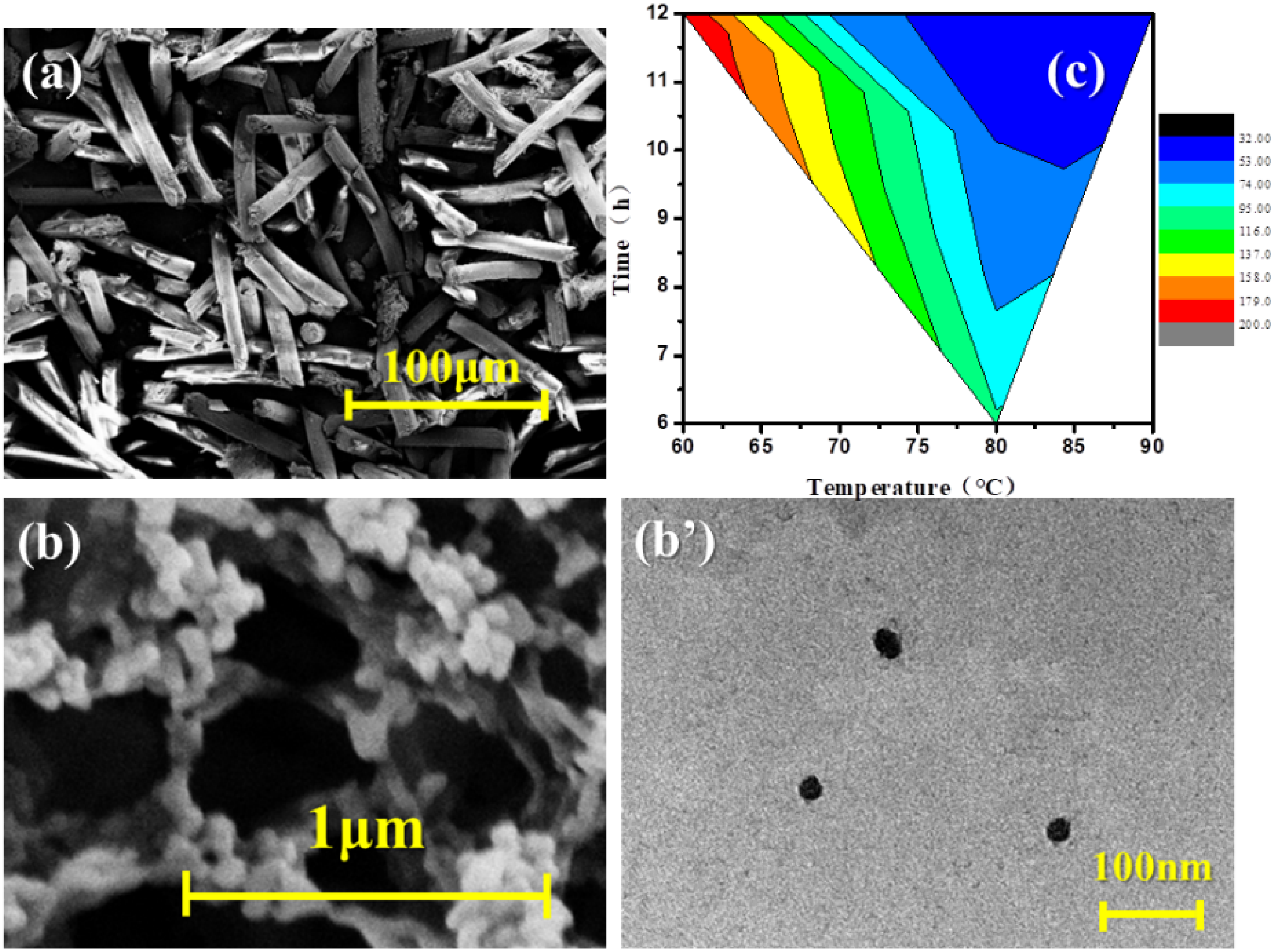

Figure 1

SEM micrographs of (a) MCC, (b) CNCs, (b') TEM image of CNCs, (c) Diameter of CNCs changed with reaction temperature and reaction time.

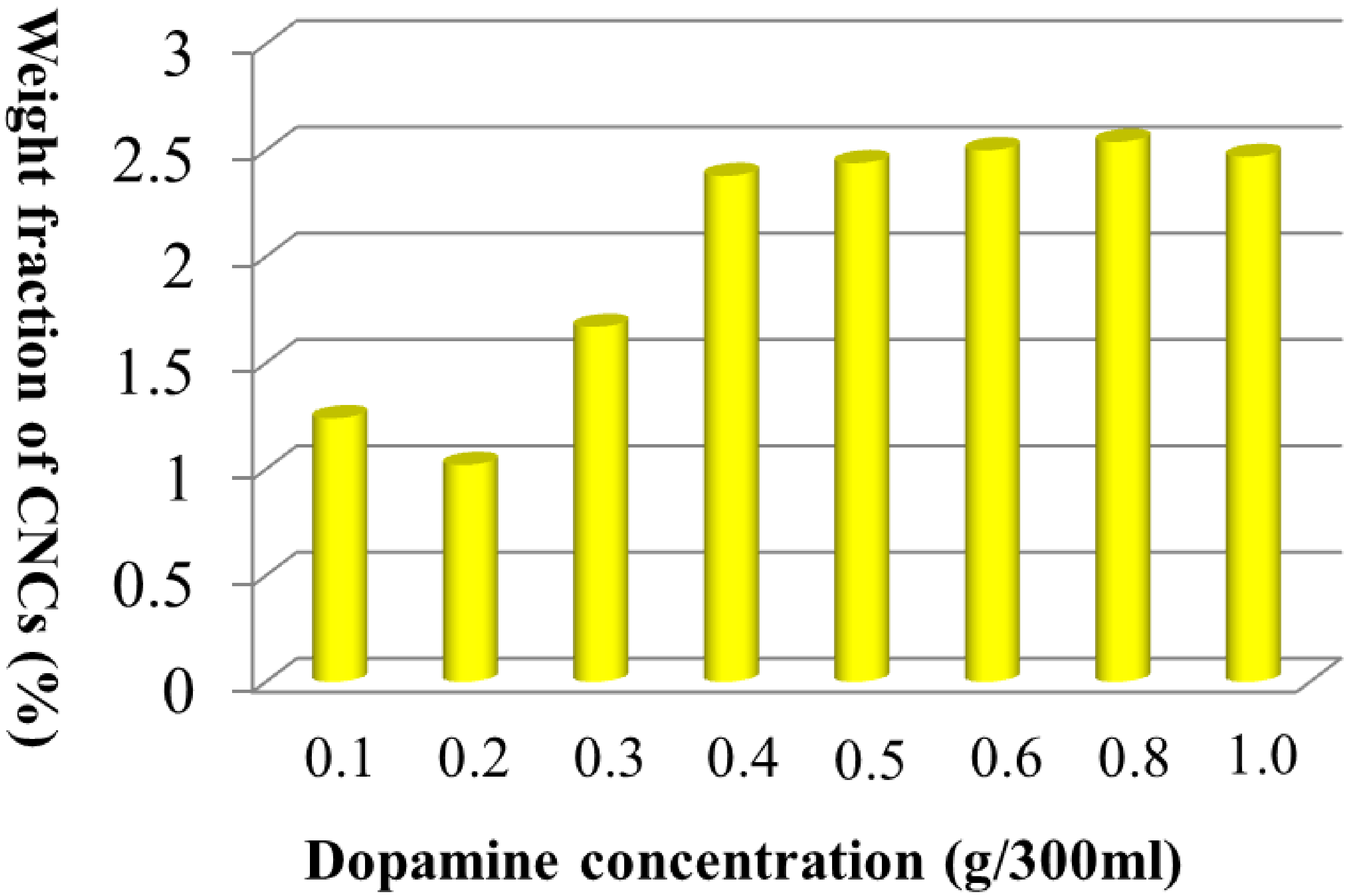

Figure 2

The weight fraction of CNCs affected by dopamine concentration.

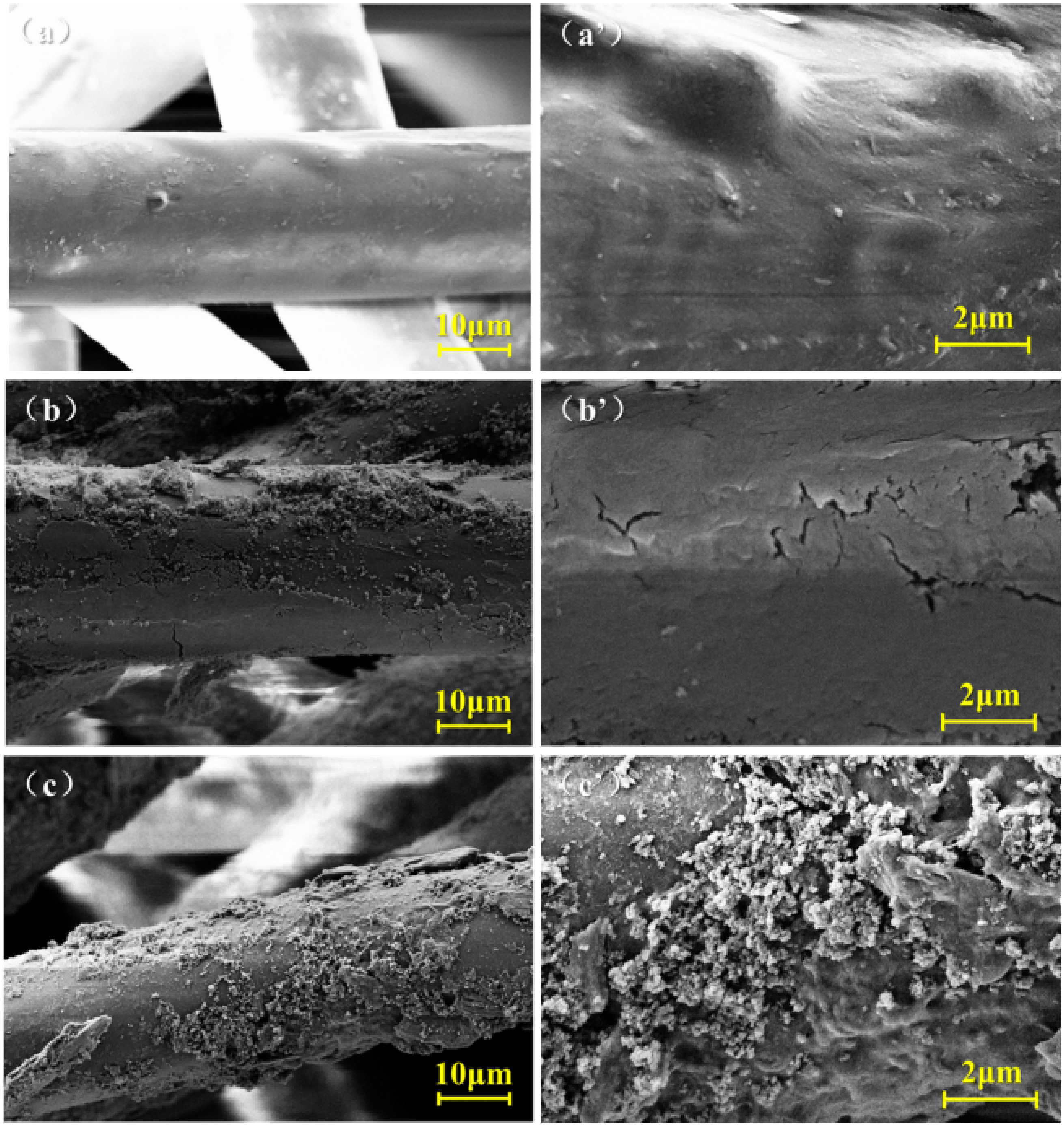

Figure 3

SEM micrographs of (a)(a') Pure PLA, (b)(b') PDA/PLA, (c)(c') CNCs/PDA/PLA nonwoven membranes.

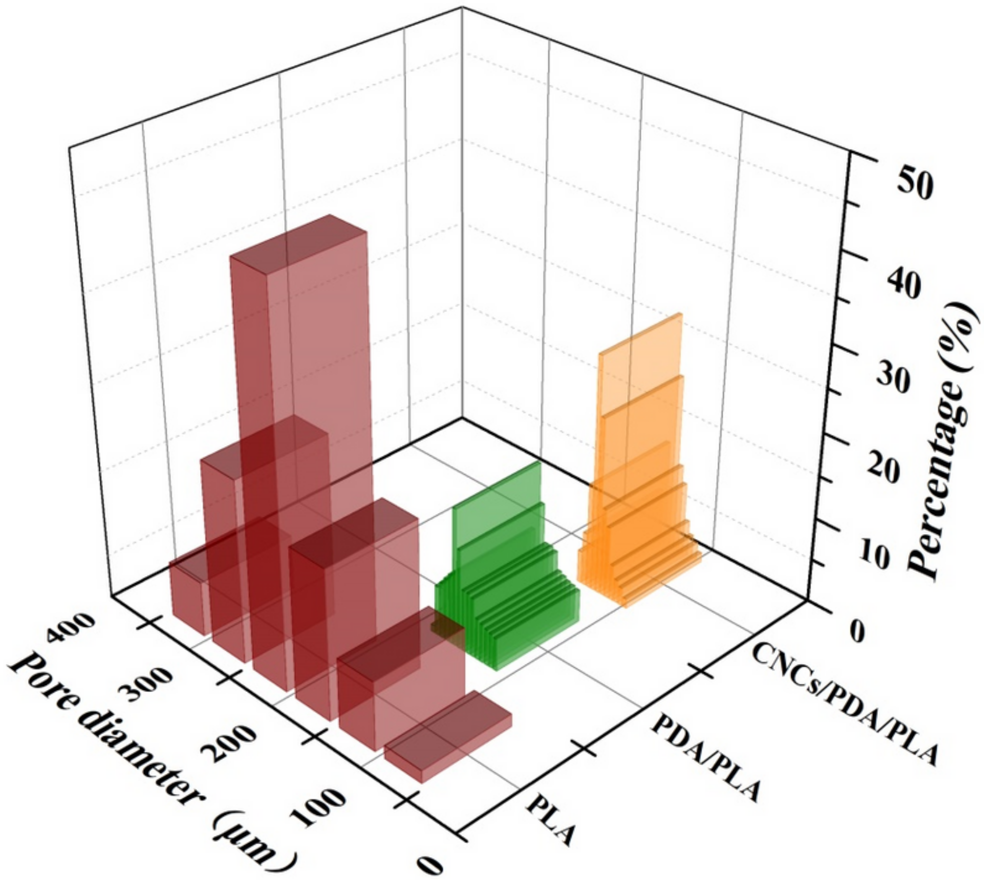

Figure 4

The pore diameter of pure PLA and CNCs/PDA/PLA nonwoven membranes.

Figure 5

The water contact angles of pure PLA, PDA/PLA, and CNCs/PDA/PLA nonwoven membranes.

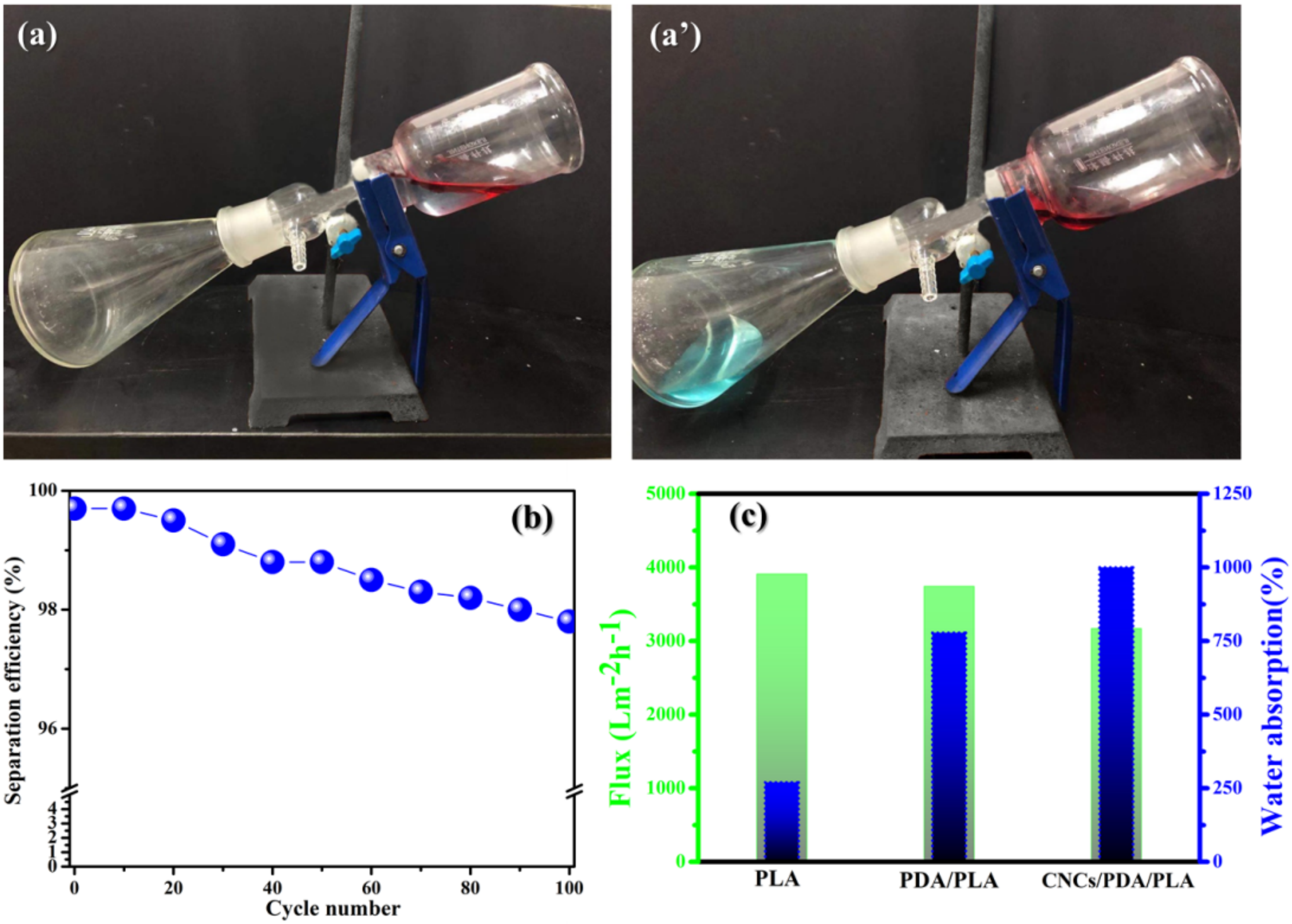

Figure 6

(a)(a') Photographs showing the separating process of n-hexane/water mixture by CNCs/PDA/PLA membrane; (b) Separation efficiency changed with cycle numbers of CNCs/PDA/PLA membrane; (c) Flux and water adsorption of pure PLA, PDA/PLA and CNCs/PDA/PLA nonwoven membranes.

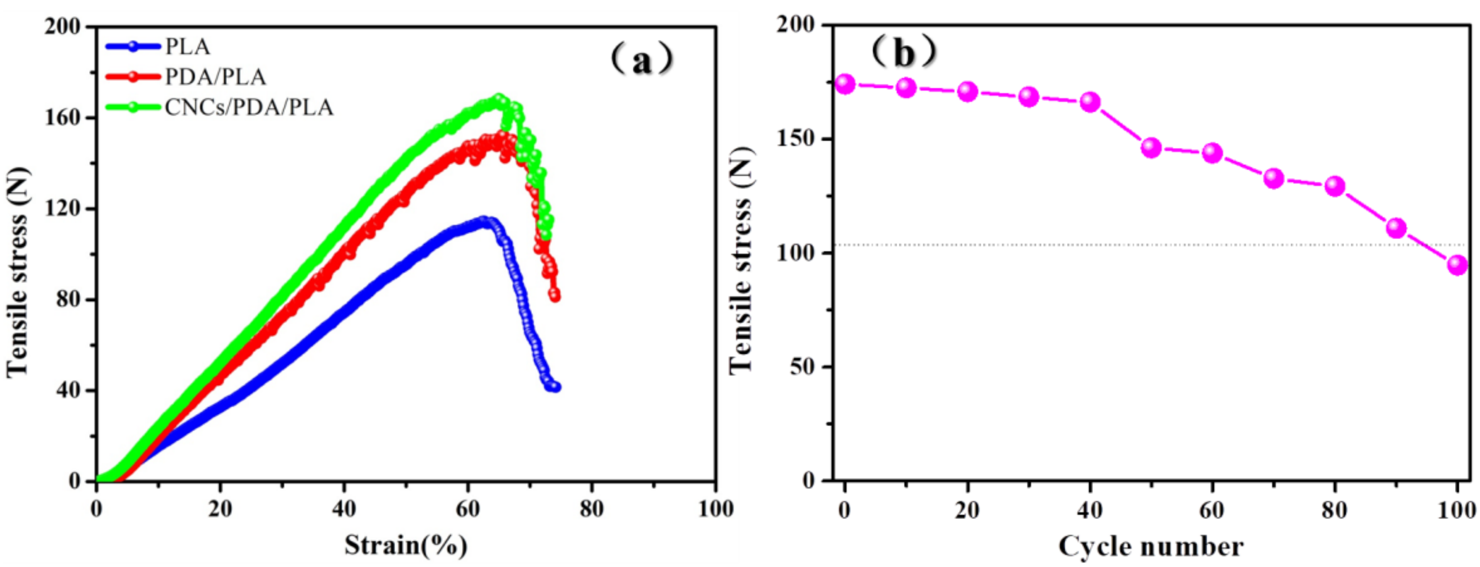

Figure 7

(A) Tensile stress-strain curves of pure PLA, PDA/PLA, and CNCs/PDA/PLA nonwoven membranes; (B) Tensile strength of CNCs/PDA/PLA nonwoven membrane changed with reuse cycle numbers.

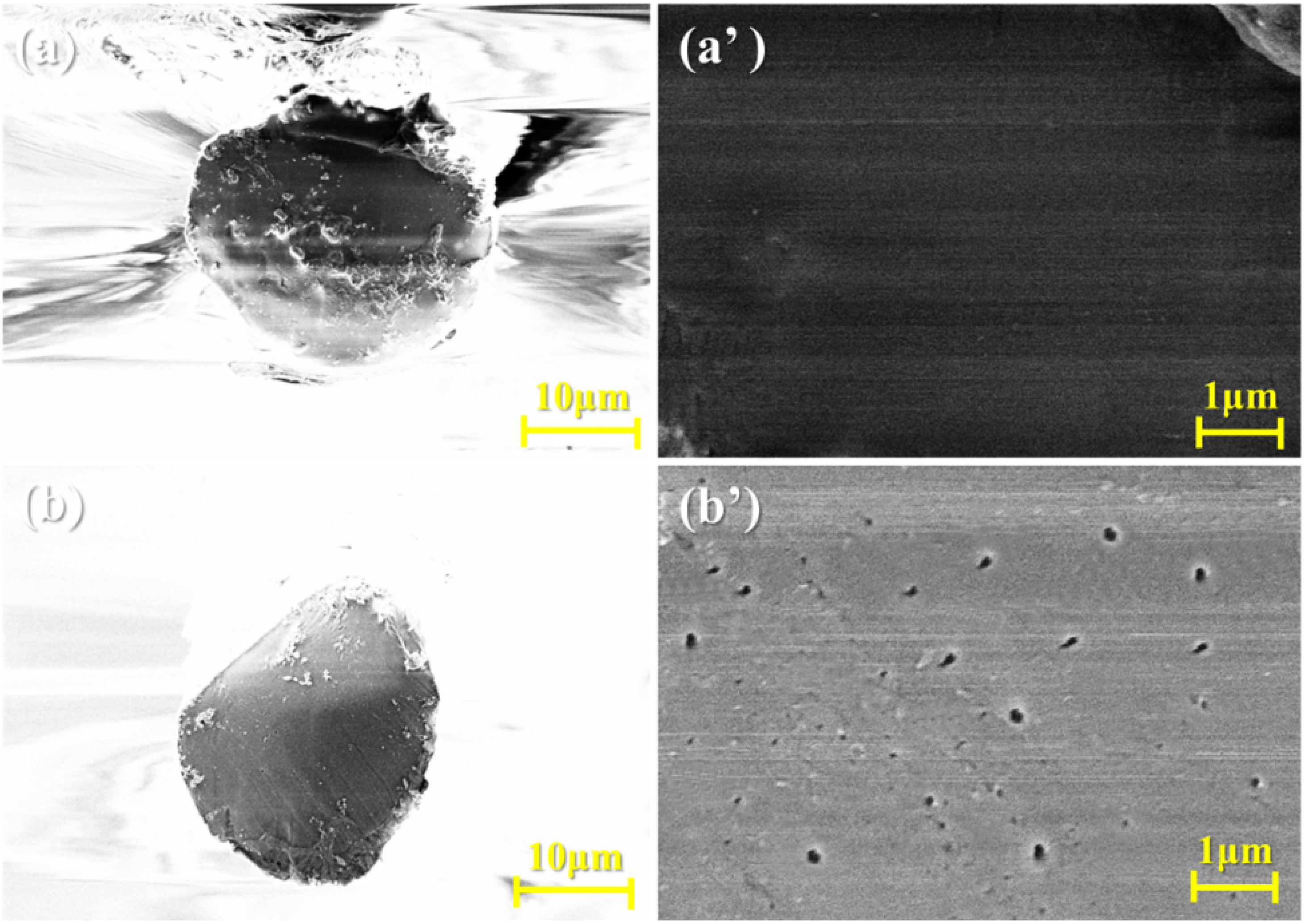

Figure 8

SEM images of reused membranes: (a)(a') used for 1 time, (b)(b') used for 40 times.

Supplementary Files

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- fig7.png