

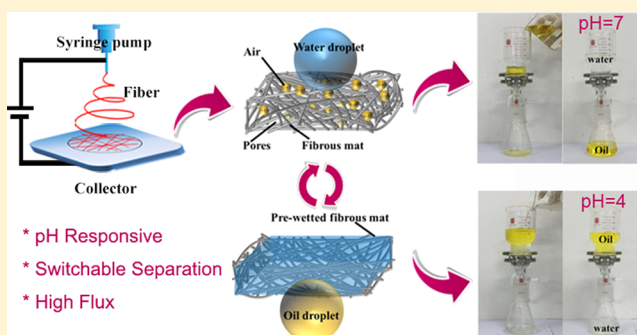
Electrospun Fibrous Mat with pH-Switchable Superwettability That Can Separate Layered Oil/Water Mixtures

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Supporting Information

ABSTRACT: Oil/water separation has inspired much research interest because of the damages caused to our natural environment due to oily wastewater. As a leader of advanced separation materials, electrospun polymeric fibrous mats having the properties of special surface wettability, high specific surface area, and high porosity will be a good membrane material for the separation of oily wastewater. Herein, we first prepared pH-responsive polymer poly-(dimethylsiloxane)-*block*-poly(4-vinylpyridine) (PDMS-*b*-P4VP) mat using electrospinning technology. The PDMS-*b*-P4VP fibrous mat with a thickness of around 250 μm exhibits good pH-switchable oil/water wettability and is able to effectively separate oil or water from layered oil/water mixtures by gravity driven through adjusting the pH value. Stemming from its porous structure and pH-switchable superwettability, the electrospun PDMS-*b*-P4VP fibrous mat achieved controllable separations with high fluxes of approximately 9000 $\text{L h}^{-1} \text{m}^{-2}$ for oil (hexane) and 27 000 $\text{L h}^{-1} \text{m}^{-2}$ for water. In addition, extended studies on the polymer/silica nanoparticle (silica NP) composite fibrous mats show that the addition of an inorganic component improves the thermal stability, pH-switchable wettability, and separation performance of the fibrous mats (approximately 9000 $\text{L h}^{-1} \text{m}^{-2}$ for hexane and 32 000 $\text{L h}^{-1} \text{m}^{-2}$ for water). It can be concluded from the results that both polymer fibrous mats and silica-filled composite fibrous mats are good candidates for on-demand layered oil/water mixture separation.



1. INTRODUCTION

Oil pollution resulting from various industries has caused a long-term damaging effect on the ecological environment.^{1–3} Therefore, novel, economical, and efficient technologies and materials for oil/water separation are urgently desired. The advanced interface science and bionics inaugurate materials with special wettability as brand-new separation materials. Because of the advantages in recuperability, separating feed, and efficiency, the special wettability-controlled separation has a promising application in the field of wastewater treatment.^{4–7} Generally, special wettable separation materials fall into three categories: “oil-removing” materials,^{8–10} “water-removing” materials,^{11,12} and smart switchable materials.^{13–25} Oil-removing materials are superhydrophobic and superoleophilic and can selectively separate oil from oil/water mixtures. Conversely, superhydrophilic and superoleophobic materials are usually called “water-removing” materials. Smart materials with switchable wettability can realize controllable separation processes by adjusting the external stimuli such as pH,^{13–15} light,^{16–18} temperature,^{19–21} electric fields,^{22,23} and gas.^{24–26} As the most potential candidate for the development of a smart and convenient separation method, stimuli-responsive special wettable materials attract increasing interest whether in the fundamental or practical application studies.^{4,5}

Currently, a variety of routes are available for fabricating superwettability surfaces used in separating water and oil mixtures, including solution casting,^{15,19–22} surface grafting,^{13,14,18} solution dip coating,^{16,26} and so on. In comparison, the electrospinning technique can easily fabricate fibrous membrane materials with superwettability.^{27,28} Their high surface-to-volume ratio and porous structure make electrospun fibrous materials a promising candidate for separation applications; thus, there has been a rapid expansion of research on oil/water separation using fibrous membranes.^{29–33} More recently, studies on controllable separation using smart polymer fibrous membranes with switchable oil/water wettability have been reported.^{20,25,34} On the other hand, composite fibrous membranes, especially silica-filled composite fibrous membranes, which have advantage in the surface micro–nano structure, thermal stability, mechanical strength, and permeability, have gained increasing attention in the separation process recently.^{35–41} However, as far as we know, there is no open report that has dealt with stimuli-controllable oil/water separation using electrospun composite fibrous membranes.

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Block copolymers, containing two chemically different blocks that can exhibit their own properties independently and also affect each other, are good candidates for constructing smart interfaces. In this work, we prepared block polymer poly-(dimethylsiloxane)-*block*-poly(4-vinylpyridine) (PDMS-*b*-P4VP) fibrous mats through electrospinning for the first time. PDMS-*b*-P4VP was chosen as the precursor polymer, in which the weak polybase P4VP with pK_a of 4.5 is an extensively studied pH-responsive polymer. The wettable property of P4VP-containing copolymer films can exhibit a pH-triggered transition because of the protonation and deprotonation of pyridyl groups.^{42,43} The other block (PDMS) as an intrinsic hydrophobic and underwater oleophilic polymer is preferred in fabricating special wettable surfaces for oil/water separation owing to its excellent properties such as thermal stability, nontoxicity, and high flexibility.^{13,44,45} On the basis of the synergistic effect of pH-responsive P4VP and hydrophobic/underwater oleophilic PDMS as well as the porous structure of the surface, the as-prepared fibrous mat is expected to exhibit a special pH-switchable wettability and further to realize a pH-controllable separation of layered oil/water mixtures. Finally, PDMS-*b*-P4VP/silica nanoparticulate (NP) composite fibrous mats were fabricated, and preliminarily investigations about the effects of silica NP loading on the fibrous surface morphology, the pH-switchable water/oil wettability, and the separation performance of the composite fibrous mats were carried out.

2. EXPERIMENTAL SECTION

2.1. Materials. pH-Responsive block copolymer PDMS-*b*-P4VP was prepared through copper(0)-mediated reversible-deactivation radical polymerization.^{46,47} The molecular weight (M_n) of the as-prepared PDMS-*b*-P4VP was 15 100 g/mol. The details of the experiment are presented in the [Supporting Information](#). Chloroform (CHCl₃, 99%) and dimethyl formamide (DMF, 99%) were dried before use. The fumed silica particles with silanol on the surface were purchased from Sigma Aldrich. The known average particle size and surface area were 14 nm and $200 \pm 2 \text{ m}^2 \text{ g}^{-1}$, respectively.

2.2. Preparation of a Pure Polymer Solution. The polymer solution was prepared by dissolving PDMS-*b*-P4VP in a mixture solvent of DMF/CHCl₃ (v/v = 1/2) under stirring for 12 h. The concentration of the polymer in the solution was 25 wt %.

2.3. Preparation of Silica NPs/Polymer Solution. A predispersed silica NP/DMF solution mixture was prepared using ultrasonic dispersion. Subsequently, a certain amount of silica NP solution mixture was added to the polymer solution with a mixture solvent of DMF/CHCl₃. The solution was stirred for 12 h. The concentration of the polymer/silica NP solution mixture was fixed at 25 wt % PDMS-*b*-P4VP and 0.25, 0.5, or 1.0 wt % silica NPs.

2.4. Preparation of Polymer or Polymer/Silica Composite Fibrous Mats. Fibrous mats were prepared using the electrospinning technique. The as-prepared precursor solution (silica-free or silica-filled polymer solution) was charged into a syringe with a metal needle. The needle was fixed at a distance of 15 cm from the collector. The applied voltage was approximately 14.5 kV, and the solution feeding rate was 0.5 mL/h. All fibrous mats were obtained after 16 h of electrospinning. The obtained fibrous mats were dried at 50 °C for 12 h before use.

2.5. Oil/Water Separation Experiments. A simple separation device was first assembled as follows: the as-prepared (polymer or silica-filled composite) fibrous mat was mounted between a 300 mL graduated funnel and a support base with a stainless steel mesh (350 mesh size) using an aluminum clamp, and a conical flask was placed below as the container. All oil (including hexane, gasoline, heptane, diethyl ether, and petroleum ether)/water mixtures used in the gravity-driven separation experiments were layered and made immiscible. Separations were carried out by straightly pouring 200 mL of the layered mixture of water and oil with 1/1 volume ratio into the

graduated funnel. Hexane was dyed yellow by using ferrocene. The separation efficiency was obtained by comparing the liquid weight before and after separation, and the flux of liquid was estimated from the separation video. The valid area is $0.96 \times 10^{-3} \text{ m}^2$.

2.6. Characterization. The morphology and thickness of the as-fabricated mats were analyzed using field emission scanning electron microscopy (FESEM, Zeiss Ultra Plus). Elemental analyses were performed using energy-dispersive X-ray spectroscopy (EDX, Zeiss Ultra Plus FESEM). Contact angles at different pH values were recorded on a contact angle measuring instrument (Kruss, DSA30). Thermogravimetric (TG) analysis was conducted on a Q5000 thermal gravimetric analyzer at a heating rate of 20 °C/min from room temperature to 800 °C under a nitrogen gas atmosphere.

3. RESULTS AND DISCUSSION

3.1. Fabrication and Morphology of the Polymer Fibrous Mat. Polymer fibrous mat was prepared using electrospinning, as illustrated in [Figure 1a](#). As shown in [Figure](#)

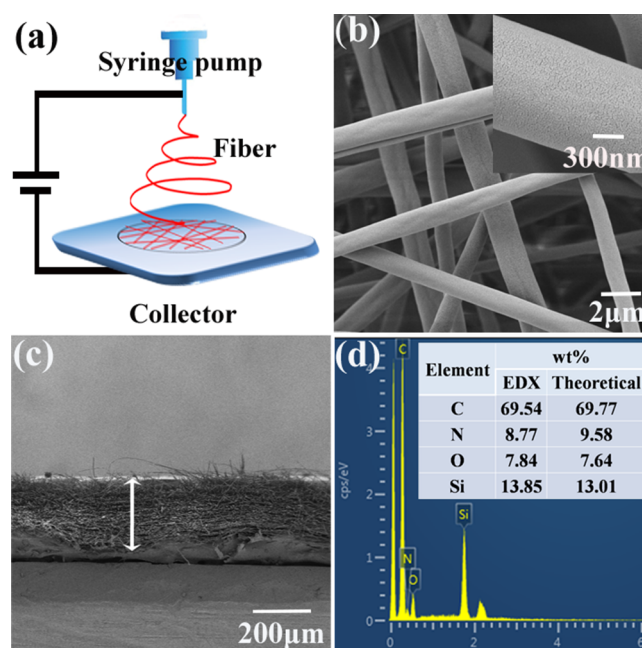


Figure 1. (a) Schematic illustrating the electrospinning process. (b) Representative SEM image of polymer fibers; inset is the zoomed-in image of the surface of a single fiber. (c) Cross-sectional morphology and (d) EDX spectrum of the polymer fibrous mat (inset table shows the element content obtained using EDX and theoretical calculations).

[1b](#), taut bead-free fibers with an average diameter of approximately 800 nm were obtained. The zoomed-in image shows that the fibrous surface is smooth. [Figure 1c](#) shows the representative cross-sectional view of the fibrous mat, which has a thickness of approximately 250 μm after 16 h of electrospinning. The membrane is thick enough to be peeled off easily from the collector, which greatly enhances its applicability. In addition, the composition of the as-prepared mat characterized using EDX is shown in [Figure 1d](#). The strong peaks in the EDX spectrum confirm that the fibers are mainly composed of C, N, O, and Si. The results of the EDX spectrum analysis indicate that the element weight of the contents is consistent with the theoretical value.

3.2. pH-Switchable Wettability of the Polymer Fibrous Mat. To evaluate the pH-responsive wettability of the as-prepared fibrous mat, static water contact angle (WCA) measurements in air were carried out. As shown in [Figure 2a](#), a

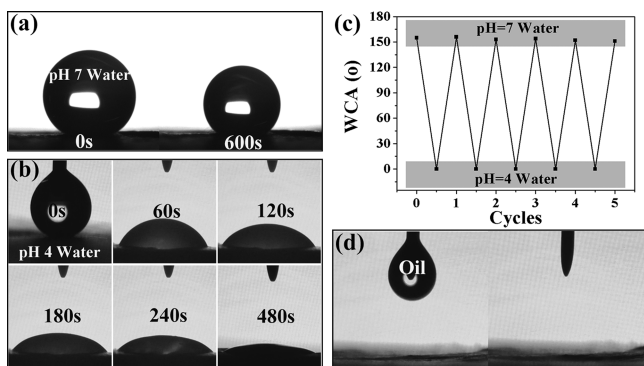


Figure 2. Contact angle measurements of the as-prepared polymer fibrous mat in air. (a) Images of a neutral water droplet on the mat surface at 0 s (left) and 600 s (right). (b) Dynamic images of a pH 4 water droplet spreading over the mat gradually within 480 s. (c) pH-Switchable water wettability of the as-prepared mat between superhydrophobicity and superhydrophilicity. (d) Absorption of the hexane droplet as soon as it contacts the surface.

pH 7 water droplet on the surface of the mat has a WCA of approximately 155° ; the water droplet stably remains spheroidal even after 10 min, except shrinkage to some extent, indicating a stable superhydrophobicity⁴⁸ to the neutral water of the mat. It is believed that the superhydrophobicity of the polymer fibrous mat arises from both the low surface energy of the PDMS block and the 3D porous network structure of the fibers. When it is in contact with pH 7 water, pyridyl groups of the weak polybase P4VP are deprotonated, and the deprotonated P4VP chains thus exhibit a collapsed conformation. Meanwhile, the highly flexible PDMS block with a lower surface energy may prefer to stretch out and stay at the exterior of the fiber, which ensures that the surface remains hydrophobic.^{13,44,45,49} In addition to the chemical composition, topography is another important influencing factor on the surface wettability.⁵⁰ Here, air can be trapped in high-density pores of the hydrophobic mat, which substantially reduces the contact area between water and the mat surface and further amplifies the hydrophobicity, resulting in the superhydrophobicity of the mat. This can be explained by the Cassie–Baxter model, which indicates that the trapped air in the rough area can facilitate the construction of the super antiwetting surface.⁵¹

On the contrary, when a pH 4 water droplet is applied to the mat, it gradually wets the mat and spreads over the surface thoroughly after 480 s (Figure 2b). The mat exhibits superhydrophilicity to acidic water.⁴⁸ Triggered by the acidic water droplet, pyridyl groups of P4VP become protonated, and the electrostatic repulsion among the protonated pyridyl groups makes P4VP chains extend and stretch out to the exterior of the fiber. With the protonated P4VP exposing to the surface, the mat is endowed with the hydrophilic property. It should be noted that the affinity of the mat to acid water can be further enhanced because of the increased surface roughness, resulting in the superhydrophilicity of the mat. This is consistent with the Wenzel model, which indicates that the roughness can enhance both the wetting and antiwetting behaviors of liquid on the surface.⁵² Importantly, the switchable water wettability is stable and remains the same after five switch cycles, as shown in Figure 2c. Figure 2d shows the oil wettability in air. A hexane droplet is absorbed by the mat as soon as it contacts the mat surface. Because the surface energies in air of the component blocks PDMS and P4VP are 21.3^{53} and 50.0 mJ/m^2^{54}

respectively, both of which are higher than the surface tension of hexane (18.4 mN/m),⁵⁵ the mat exhibits a high affinity to oil. Additionally, the wetting behavior is improved by the porous structure of the fibrous mat, leading to superoleophilicity.

Having demonstrated the pH-switchable water wettability and superoleophilicity of the mat in air, further measurements of the oil wettability under an aqueous medium with different pH values, using an *n*-hexane droplet as probe oil, were carried out. As shown in Figure 3a, the mat is wetted by hexane under

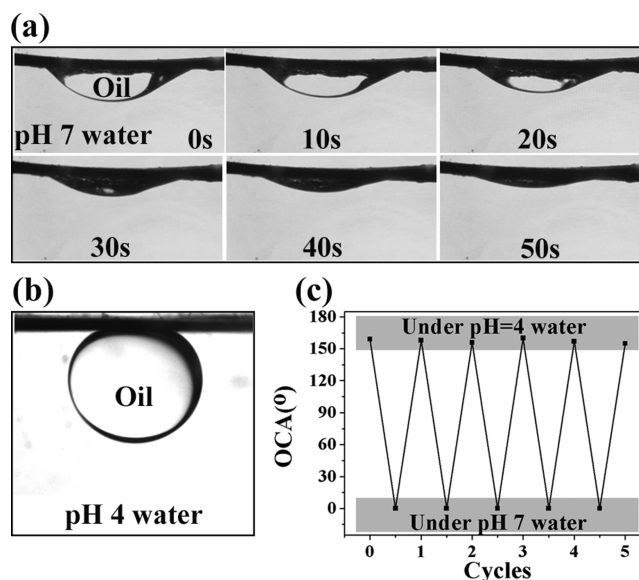


Figure 3. Oil wettability of the as-prepared polymer mat under an aqueous medium with different pH values. (a) Dynamic images of an oil droplet (hexane) spreading over the mat within 50 s under pH 7 water. (b) An oil droplet on the mat under pH 4 water with an OCA of approximately 158° . (c) Reversible oil wettability of the as-prepared mat in different aqueous media.

pH 7 water, and the hexane droplet gradually spreads out on the mat surface within 50 s. As discussed earlier, when the polymer fibrous mat is immersed in pH 7 water, the deprotonated P4VP chains exhibit a collapsed conformation and the exposed PDMS chains prevent the mat from being wetted by water. Furthermore, when the mat transfers from air to water, the air can be trapped in the porous structure, thereby suppressing the water wetting behavior. Upon contact of the mat with hexane, the oleophilic PDMS chains tend to stretch out and dissolve into the oil phase, and then the air trapped in the porous structure of the surface is gradually replaced by the oil, leading to superoleophilicity in pH 7 water.

By contrast, as the aqueous medium changes to pH 4 water, the oil wettability of the mat experiences a transition from superoleophilicity to superoleophobicity. As shown in Figure 3b, the hexane droplet stably attaches to the mat with an oil contact angle (OCA) of approximately 158° . In this situation, P4VP chains become protonated and extend to the exterior of the fiber; the mat becomes hydrophilic and traps a layer of water on its surface. The high repellency between the water and oil molecules effectively avoids the imbibition of the oil droplet and thus makes the mat exhibit superoleophobicity in pH 4 water. Similarly, the switchable wettability can be maintained after 5 cycles with slight fluctuation in responsivity (Figure 3c).

3.3. Controllable Oil/Water Separation of the Polymer Fibrous Mat. Because of the pH-switchable wettability, the as-

prepared polymer fibrous mat is expected to be applied in the controllable water/oil separation. To verify this idea, a series of separation experiments were performed. When 200 mL of the layered mixture of water and *n*-hexane at 1/1 (v/v) ratio is poured straightly into the separation device (Figure 4a), the

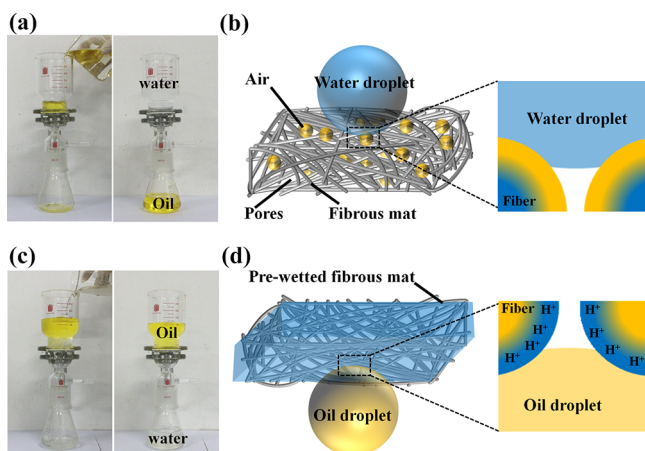


Figure 4. pH controllable oil/water separation processes. (a) Oil (*n*-hexane colored with ferrocene) passes through the filter and is collected in a conical flask, whereas water remains in the graduated funnel. (b) Schematic mechanism of the superhydrophobic mat under neutral conditions. (c) Water selectively permeates through the mat pretreated by pH 4 water, while oil remains. (d) Schematic mechanism of the underwater superoleophobic mat that is pretreated by acid water.

mat is permeable to oil but not to pH 7 water, resulting from its superhydrophobic and superoleophilic properties under neutral conditions. As demonstrated in Figure 4b, the PDMS block with a low surface energy at the exterior of the fiber and the air trapped in the high-density pores of the mat act synergistically on the superhydrophobicity of the fibrous mat surface. The separation process is recorded in Movie S1. In comparison, if the as-prepared mat is first saturated by pH 4 water, the separation is reversed, namely, water selectively passes through and oil is repelled as shown in Figure 4c and Movie S2. This result is illustrated in Figure 4d. The fibrous mat is pretreated to make the protonated P4VP block move to the exterior of the fiber. Then a layer of water can be locked in the fibrous mat, which effectively blocks the oil access. Subsequently, the mat is rinsed with copious amounts of neutral water and dried under a nitrogen flow, so it can recover to the initial separation state easily (oil permeates through, and water is repelled).

In addition to hexane, the mat exhibits a similar gravity-driven separation behavior for other types of oil, including gasoline, heptane, diethyl ether, and petroleum ether. The performance of the fibrous mat during separations was evaluated using separation efficiency and liquid flux as indicators. As shown in Figure 5a, the mat achieves an excellent efficiency of higher than 98.5% for all separations. Results summarized in Figure 5b show that the mat obtains an oil flux of 8500–9500 L h^{−1} m^{−2} and a water flux of 26 000–28 000 L h^{−1} m^{−2}. The good liquid flux can be ascribed to the porous network structure of the fibrous mat.

Despite the good switchable wettability and the separation performance of the as-prepared polymeric mat, introducing silica NPs into the polymer fibrous mat is expected to improve some properties of the polymer fibrous mat.

3.4. Morphology of Polymer/Silica Composite Mats.

Silica NPs were incorporated into the polymer fibrous mat through electrospinning 25 wt % PDMS-*b*-P4VP solutions blended with varying amounts of silica NPs. The thickness of all as-prepared polymer/silica composite fibrous mats is approximately 250 μm. Compared with those of the polymer fibrous mat shown in Figure 1b, SEM images of the composite fibrous mats in Figure 6a–c do not display much difference in the

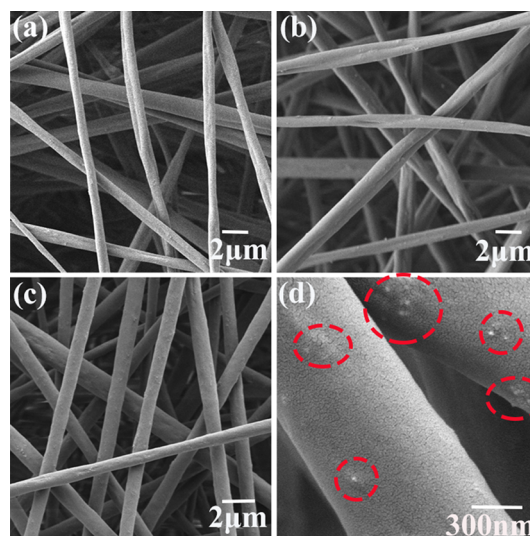


Figure 6. SEM images of polymer/silica composite fibrous mats with varying amounts of silica NPs: (a) 0.25, (b) 0.5, (c) 1.0 wt %, and (d) the magnified image of the sample with 1.0 wt % silica NPs.

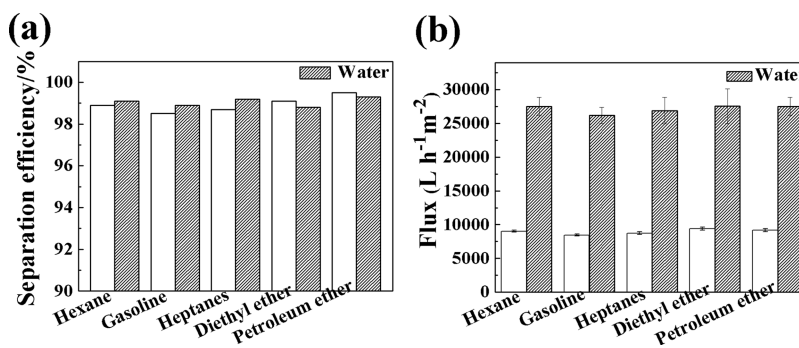


Figure 5. Separation performances of the as-prepared polymer fibrous mat: (a) separation efficiency and (b) oil and water fluxes for the different layered oil and water mixture separations.

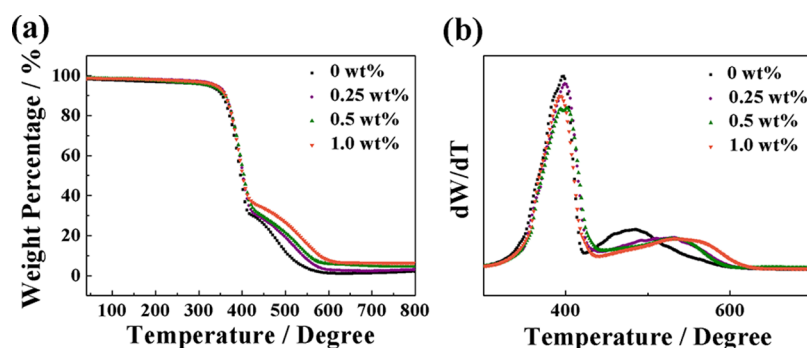


Figure 7. (a) TG curves of pure polymer and polymer/silica composite fibrous mats. (b) First derivative of the TG curves in (a).

average diameter of the fiber; all their diameters range from 600 to 800 nm. However, the surface roughness of the obtained composite fibers becomes rougher and rougher with the increase in the silica NP content. Some silica NP aggregates on the fibrous surface were observed in the sample containing 1.0 wt % SiO₂, as shown in Figure 6d.

3.5. Thermal Property of Polymer/Silica Composite Mats. Degradation behaviors of the composite mats (Figure 7a) show that the first thermal degradation of all curves begins at approximately 325 °C and completes at approximately 425 °C, which belongs to the P4VP segment; the temperature range of the second degradation from 425 to 600 °C is attributed to the PDMS segment. On further heating, the residual mass of fibrous mats at 800 °C increases gradually from 3.0 to 6.3 wt % as the percentage of silica NP component increases from 0.25 to 1.0 wt %. Compared with the polymer fibers, the composite fibers exhibit a less steep weight loss and stabilize at a higher temperature. As seen, the thermal stability of the fibrous mat is enhanced by adding silica NPs.

To more intuitively observe the silica NP loading-introduced improvement in the thermal stability of the fibrous membrane, the weight loss rate derived by taking the first derivative of the TG curve is shown in Figure 7b. The fastest weight loss rate for the PDMS segment (the second highest peak in the differential curves) is delayed with increasing silica NP content. It appears at approximately 535 °C for the composite fibrous mat containing 1.0 wt % silica NPs, which is 50 °C higher than that for the polymer sample. The reason for the enhancement in the thermal stability can be the thermal insulation effect of silica at high temperatures and the interaction between organic and inorganic silicon.³⁹

3.6. pH-Switchable Wettability of Polymer/Silica Composite Mats. To examine the effect of silica NP loading on the wetting behavior of the fibrous mats, we measured the WCA and OCA of silica-filled composite mats and compared the results to those of polymer fibrous mats. As shown in Figure 8, pH 7 water droplets sitting on the surfaces of the composite mats with 0.25, 0.5, and 1.0% silica NPs have a WCA of approximately 156°, 158°, and 159°, respectively. All water droplets retain their spherical shape after 10 min. There is no significant difference in the WCA between the silica-filled composite mats and the polymer mats. The composite fibrous mats remain superhydrophobic to neutral water, despite the fact that the silica NPs containing hydroxyl surface groups were added to the fibers. This is attributed to the hierarchical roughness of the composite fibers. According to the rough solid surface wetting theory, a rough structure is a key factor for the construction of a super antiwetting surface and air cushion

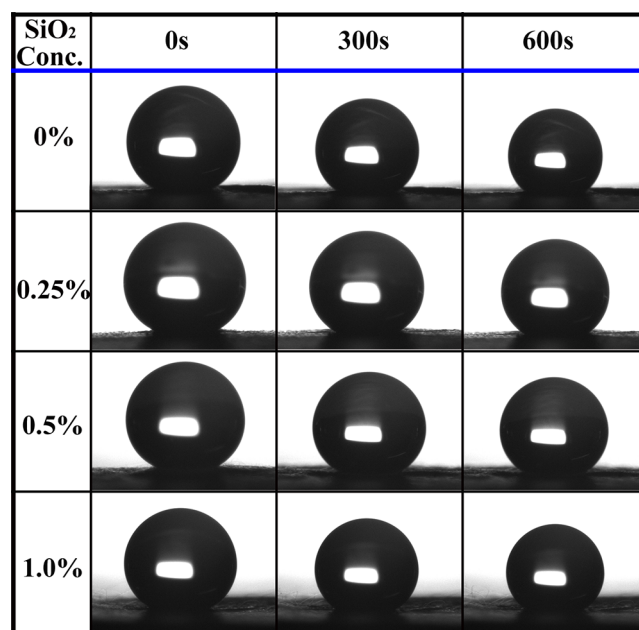


Figure 8. Images of a pH 7 water droplet on the polymer and polymer/silica composite fibrous mats over time.

formed on the surfaces with a hierarchical structure further leads to superhydrophobic surfaces.^{50,51}

When pH 4 water droplets are applied to the composite mats, they gradually spread over the surface and eventually are absorbed into the mats. Compared with the wetting behavior of polymer fibrous mats under the same condition, the addition of silica NPs accelerates the permeation rate of the composite fibrous mats toward pH 4 water. From the water droplet profiles illustrated in Figure 9, the absorption of pH 4 water becomes faster with the increase in silica NP content in the composite fibrous mat. In this situation, the protonated P4VP chains extend and stretch to the exterior of the fiber, which endow the fibrous mat with a high affinity to acidic water. Hydroxyl groups on the surface of silica NPs effectively strengthen the interactions between the mat and the water, resulting in a faster permeation of pH 4 water on the composite fibrous mats.

As shown in Figure 10, oil droplets are shape-unstable under pH 7 water: they spread out on the mat surface within 20 s. By contrast, the oil wettability changes from superoleophilicity to superoleophobicity when these composite fibrous mats are immersed in pH 4 water. Oil droplets stably attach to the fibrous mats with OCAs of approximately 159°. Overall, the

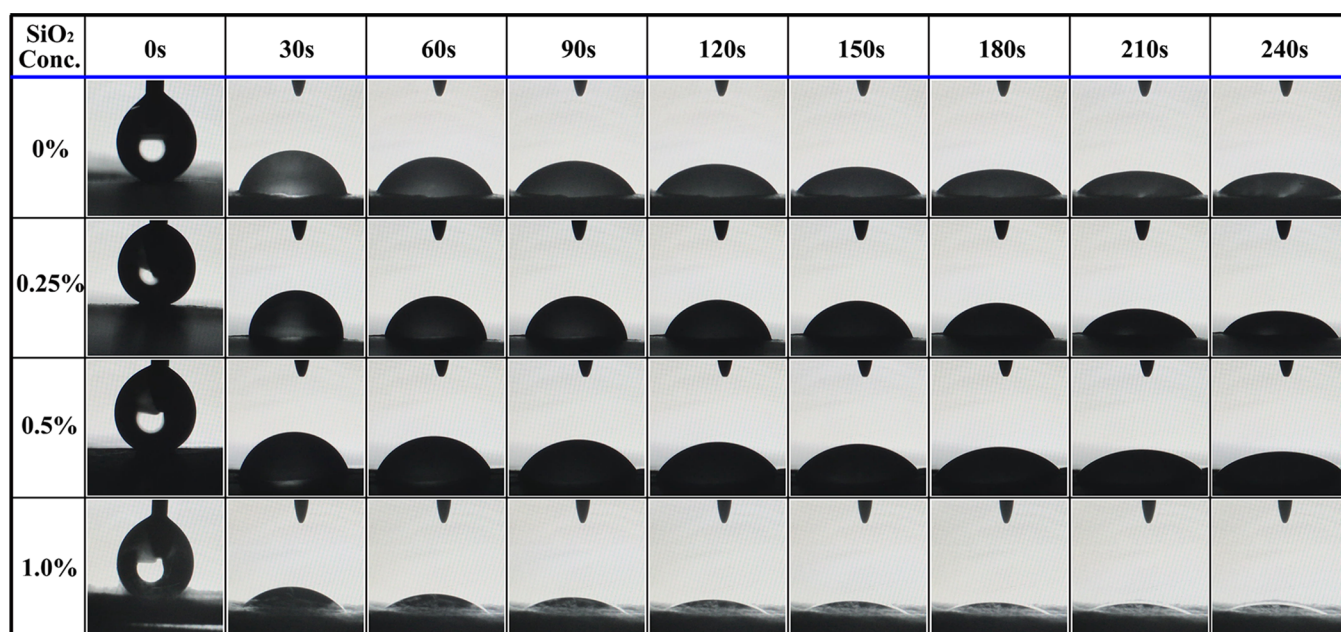


Figure 9. pH 4 water droplets spread out on the polymer and polymer/silica composite fibrous mats over time.

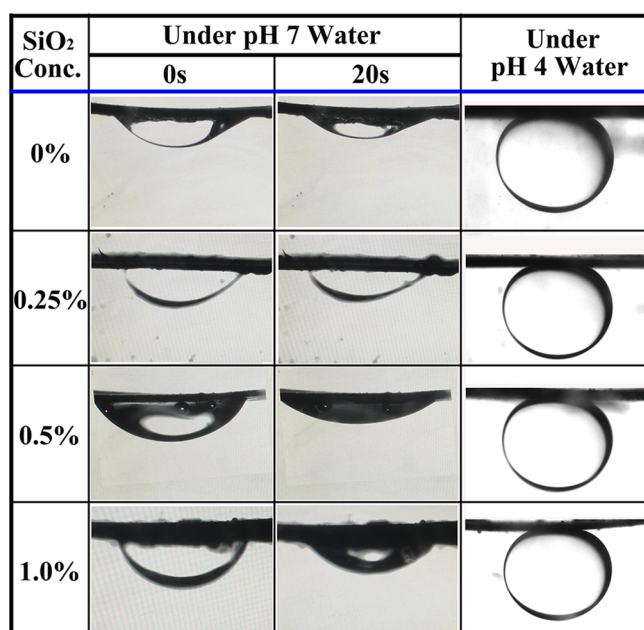


Figure 10. Oil wettability of pure polymer and polymer/silica composite fibrous mats under an aqueous medium with different pH values.

pH-switchable underwater oil-wetting behavior of fibrous mats is not affected by the silica NP loading.

3.7. Controllable Oil/Water Separation of Polymer/Silica Composite Mats. The comparison of wetting behaviors between polymer and silica-filled composite fibrous mats reveals that the pH-switchable wettability of composite fibrous mats can be sustained and even improved when silica NPs are added to the fibrous mats. Therefore, the application of polymer/silica composite fibrous mats for oil/water separation was investigated. Taking the layered mixture of hexane and water as an example, all silica-filled composite mats realize gravity-driven pH-switchable oil/water separation. Oil permeates through the mats, and water is repelled in the initial state;

the reverse separation occurs if the mats are presaturated by pH 4 water. Separation performances in Figure 11a show that all composite mats containing various amounts of silica NPs separate the layered oil and water mixture effectively and the efficiency is as high as 98%. By comparing the liquid fluxes in Figures 5b and 11b, it can be seen that the composite fibrous mats display a higher water flux ($30\,000\text{--}32\,000\text{ L h}^{-1}\text{ m}^{-2}$) than pure polymer mats ($\sim 27\,000\text{ L h}^{-1}\text{ m}^{-2}$). As a proof of concept, the separation using the composite fibrous mat containing 1.0 wt % SiO_2 for oil-removal and water-removal is shown in Movies S3 and S4. In addition, given the improved thermal stability, the composite fibrous mat containing 1.0 wt % SiO_2 maintained good repellent characteristics of 80°C to hot water, as shown in Figure S3, implying the good stability of the as-prepared mats under high-temperature conditions.

It is worth noting that the separation performances of both the polymer and composite fibrous mats are comparable to or even better than other fibrous membranes for layered oil/water separation. For example, Barakat et al. reported that the water flux for the polyamide-modified polysulfone electrospun nanofiber mat is approximately $230\text{ L h}^{-1}\text{ m}^{-2}$, and the electrospun nanofiber mat obtained using polysulfone/amorphous silica NPs has an oil flux of 4170, 4800, and $7800\text{ L h}^{-1}\text{ m}^{-2}$ for gasoline, kerosene, and hexane, respectively.^{31,32} Recently, Yuan et al. have fabricated a CO_2 -responsive nanofibrous membrane for controllable separation with a water flux of $9500\text{ L h}^{-1}\text{ m}^{-2}$ and a hexane flux of $17\,000\text{ L h}^{-1}\text{ m}^{-2}$.²⁵ Moreover, a thermal-responsive fibrous membrane having fluxes of $9400\text{ L h}^{-1}\text{ m}^{-2}$ for water and $4200\text{ L h}^{-1}\text{ m}^{-2}$ for hexane was prepared by Luo et al.²⁰ Ding et al. reported a fluorinated composite fibrous membrane toward oil/water separation with an oil (dichloromethane) flux of approximately $3310\text{ L h}^{-1}\text{ m}^{-2}$.³⁸ Last but not the least, Sun and co-workers introduced an electrospun carbon/silica composite nanofibrous membrane for separating petroleum spirit, iso-octane, and hexane from oil/water mixtures with an oil flux of 3030, 1720, and $2650\text{ L h}^{-1}\text{ m}^{-2}$, respectively.³⁹ According to the results mentioned above, the electrospun fibrous mats used in the present work will have a bright future in oily water disposal.

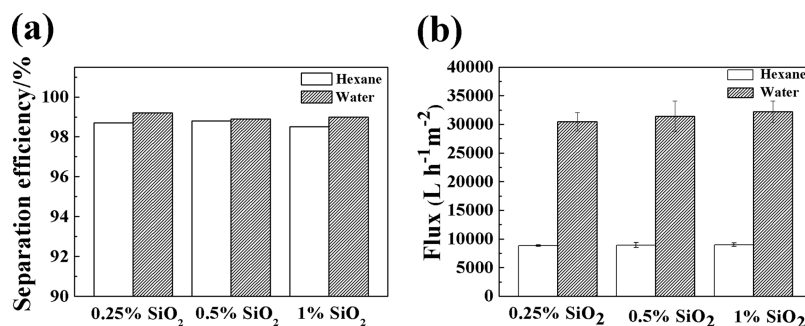


Figure 11. Separation performances of polymer/silica composite fibrous mats: (a) separation efficiency and (b) hexane and water fluxes of the as-fabricated mats.

4. CONCLUSIONS

To sum up, pH-responsive PDMS-*b*-P4VP and PDMS-*b*-P4VP/SiO₂ NPs fibrous mats were fabricated using electrospinning technology. As investigated using SEM, the obtained fibers with an average diameter of approximately 800 nm are taut bead-free and the fibrous mats possess a thickness of around 250 μ m. Ascribing to the pH-responsive PDMS-*b*-P4VP and the porous structure, the as-fabricated polymer mat exhibits good pH-induced oil/water wettability and stable switch ability. Under neutral conditions, the wettability of the surface is superhydrophobicity and underwater superoleophilicity. On the contrary, the wetting properties of the mat become superhydrophilic to acid water and superoleophobic under pH 4 water. On the basis of the understanding of the mechanism, the mat is able to separate oil or water from layered oil/water mixtures by gravity driven through adjusting the pH value. High porosity makes the PDMS-*b*-P4VP fibrous mat achieve separations with high fluxes of approximately 9000 L h⁻¹ m⁻² for oil (hexane) and 27 000 L h⁻¹ m⁻² for water as well as a high efficiency of over 98%.

Compared with the polymeric fibers with a smooth surface, the composite fibers have a rougher surface, and silica NPs were observed on the sample containing 1.0 wt % SiO₂. Further studies show that the addition of silica NPs into the polymer fibrous mat improves the thermal stability and pH-switchable wettability. Benefiting from the improved surface wetting properties, the composite fibrous mats show a better separation performance with a higher water flux of approximately 32 000 L h⁻¹ m⁻².

These promising results show that electrospinning is a powerful and economical technique for fabricating smart oil/water separation materials. Definitely, we also got some positive results on the separation of surfactant-free water-in-oil emulsions. However, further investigations on promoting the stability and durability of the composite fibrous mats under extreme environmental conditions and the separation of emulsified oil/water mixtures should be undertaken.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.langmuir.6b03627](https://doi.org/10.1021/acs.langmuir.6b03627).

Synthetic outline of the block copolymer, ¹H NMR spectra, switchable separation processes under high-temperature conditions, and videos of switchable separation processes (PDF)

Separating oil from the layered mixture of water and *n*-hexane at 1/1 (v/v) ratio using polymer fibrous mat (AVI)

Separating water from the layered mixture of water and *n*-hexane at 1/1 (v/v) ratio using polymer fibrous mat (AVI)

Separating oil from the layered mixture of water and *n*-hexane at 1/1 (v/v) ratio using the composite fibrous mat containing 1.0 wt % SiO₂ (AVI)

Separating water from the layered mixture of water and *n*-hexane at 1/1 (v/v) ratio using the composite fibrous mat containing 1.0 wt % SiO₂ (AVI)

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