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Electrospun Porous Structure Fibrous Film with High Oil Adsorption Capacity

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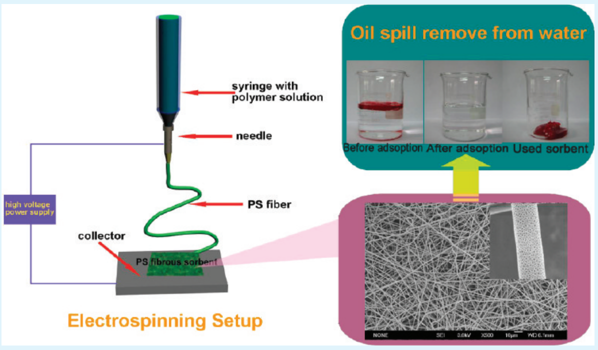
ABSTRACT: A low-cost, high-oil-adsorption film consisting of polystyrene (PS) fibers is fabricated by a facile electrospinning method. Different fiber diameter and porous fiber's surface morphology play roles in oil adsorption capacity and oil/water selectivity. The results showed that oil adsorption capacity of PS oil sorbent film with small diameter and porous surface structure for diesel oil, silicon oil, peanut oil and motor oil were approximate to 7.13, 81.40, 112.30, and 131.63 g/g, respectively. It was higher than normal fibrous sorbent without any porous structure. The thinner porous PS oil sorbent also had excellent oil/water selectivity in the cleanup of oil from water.



KEYWORDS: *oil sorbent, nanofibers, electrospinning, superhydrophobic, oleophilic*

INTRODUCTION

Oil spill is a risk during the processes of oil being explored, transported, stored, and used, and causes significant and serious environmental damage. With the increasing level of attention focused on the preservation of the environment, researchers have developed a great deal of materials as the adsorbents to concentrate, transfer, and adsorb spilled oils. Properties of an ideal sorbent material for oil spill cleanup include hydrophobicity and oleophilicity, high oil sorption capacity, low water pickup, inexpensive cost, and ready availability.[1,2] Recently, superhydrophobic and superoleophilic sorbents have attracted much attention because of their wide application.[3−12] There are mainly three classes of oil sorbent materials: inorganic mineral products, organic natural products, and synthetic organic products.[13] Among them, organic synthetic fibers play an important role in oil spill cleanup for their tunable hydrophobic and oleophilic property, relatively low cost, and available usage in large scale. However, the oil sorption capacity of the majority of these samples are only tens gram of oil per gram of sorbent, which needs to be improved for practical application.[14−18]

To date, numerous routes have come into being for fabrication oil spill cleanup, such as template-based techniques,[19] self-assembly of block copolymers,[20] layer-by-layer assembly,[21] dry-state spinning of nanotube yans,[22] et al. Many existing methods face the challenge for practice use because of their multistep procedures of fabrication and limitation in substrate sides. Electrospinning is widely recognized as a simple top-down method of fabricating fibrous materials with diameters from tens of nanometers to submicrometers process by stretching a viscous conductive fluid into a thin jet via electrostatic force.[23−25] Herein, the commercial polystyrene (PS) fibrous sorbents were fabricated by electrospinning. Four kinds of oils (diesel oil, motor oil, peanut oil, and silicon oil) that can represent the main oil pollutions in industry and daily life are taken up as the oil solvents to investigate the adsorption characteristics of as-prepared sorbents. Interestingly, by controlling the diameter and creating porous morphology on the superhydrophobic-oleophilic PS fibers, high oil sorption capacity, oil/water selective adsorption can be obtained. The adsorption capacity of porous PS sorbent for certain oil spill can reach to about 100 g of oil per gram of sorbent, which can be employed for efficient adsorption of oil/water system as well as be efficiently and widely used in technological areas.

EXPERIMENTAL SECTION

Preparation of Polystyrene (PS) Fibers. PS (M_w = 350 000, Sigma-Aldrich) was dissolved in DMF (Beijing Yili Fine Chemical Co.) by stirring for 4 h to form 20 wt % precursor solution. Nearly 2 mL of precursor solution was placed in a 5 mL syringe. To form PS fibers with different diameters, different metal needles of 0.5, 0.6, 0.7, 0.9, 1.2, and 1.6 mm inner diameter were equipped. A stainless steel plate covered with a sheet of aluminum foil was employed as the collector. The distance between the needle tip and collector was 25 cm, and the voltage was set as 12 kV. The samples were named F5, F6, F7, F9, F12 ,and F16. The PS fibrous films with porous structure on fibers were prepared by electrospinning PS/THF solution. PS (M_w =

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350 000, Sigma-Aldrich) was dissolved in THF (Beijing Yili Fine Chemical Co.) by stirring for 4 h to form 20 wt % precursor solution. Then spinneret needles with 0.5, 0.7, and 1.2 mm inner diameter were equipped on the syringes. The electrospinning distance and the voltage were the same as mentioned above. The samples were named PF5, PF7, and PF12, respectively.

Oil Adsorption Tests. To analyze the maximum oil sorption capacity of PS sorbents, we placed 1.0 g of oil sorbent in a glass beaker filled with 100 mL of oil. After 40 min of sorption, the wet sorbent was drained for 5 min until no residual oil droplet was left on the surface. Oil sorption capacity of all sorbents was determined by the following equation[26]

$$q = \frac{[m_f - (m_0 + m_w)]}{m_0}$$

Where q is the sorption capacity (g/g), m_f is the weight of the wet sorbent after 5 min of drainage (g), m_0 if the initial weight of the sorbent (g), and m_w is the weight of adsorbed water (g). In the pure oil medium without any water, m_w is equal to zero. To determine the selectivity absorptive capacity of PS fibrous film sorbents, we placed 0.1 g of PS sorbents in oil/water mixture. The weight ration between oil and water was 1: 10. After 20 min of absorption, wet sorbents were removed, drained for 5 min, and weighed.

Instruments and Characterization. SEM images were taken by scanning electron microscope. (JSM-6700F, Japan). The diameter of the fibers was measured on the basis of SEM images. Contact angles were measured on an OCA 20 contact-angle system (Dataphysics, Germany) at 25 °C. Two microliters of deionized water and motor oil droplets were dropped onto the surface, respectively. The average contact angle value of both water and oil were obtained by measuring at five different positions of the same sample.

■ RESULTS AND DISCUSSION

Images in Figure 1 show the scanning electron microscopy (SEM) images of the electrospun polystyrene (PS) fibrous sorbents. Different metal needles of 0.5, 0.6, 0.7 0.9, 1.2, and 1.6 mm inner diameter were equipped to achieve PS fibers with different diameters. Accordingly, the samples were named F5, F6, F7, F9, F12, and F16. Figure 1a–f are the typical images of as-prepared sorbents. The fibers are randomly oriented on the scaffold, and the average external diameters are 0.565, 0.667, 0.918, 1.473, 2.454, and 3.716 μm, respectively. Meanwhile, there are large amounts of interconnected voids among fibers, and microstructures such as linear grooves existed on the fiber surfaces, which cause that the fiber surfaces are not very smooth (Figure 1a, inset). Figure 1g–j are the SEM images of porous structured PS fibrous film named PF5, PF7, and PF12, respectively. The fibers diameters are approximate to 0.540 μm, 1.020, and 2.135 μm, which are similar to sample F5, F7, and F12. For the above samples produced from PS-THF solution, nanopores were observed on the fibers' surface. The pore sizes are ranging from 100 to 200 nm (Figure 1h). This may attribute to the vapor-induced phase separation mechanism. During vapor-induced phase separation, the polymer solution undergoes phase separation by penetration of nonsolvent from the vapor phase. Since THF is a low boiling point solution and easy to volatile. THF vaporizes at much higher rate therefore the process of phase separation is unable to take place sufficiently before THF fully vaporized. In the meantime, due to rapidly solvent evaporation, the fibrous surface temperature decreases significantly during electrospinning process. When the surface cools down, moisture in the air may be condensed and grow in the form of droplets. Small imprints will be left on the surface of fibers.[27] Theses nanoscale pores increase the specific surface, which is helpful for the adhesion and adsorption of oil on the fiber surface.

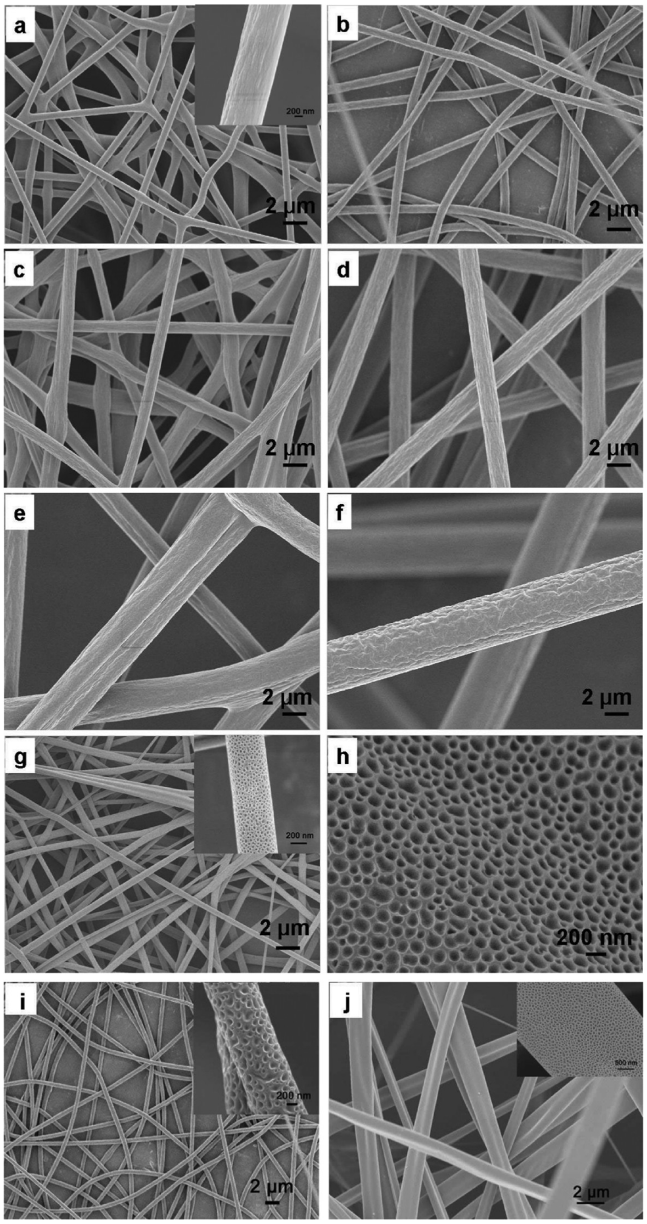

Figure 1. SEM images of PS fibrous films. (a–f) SEM images of as-prepared samples without porous structure. To form PS fibers with different diameters, different metal needles of 0.5, 0.6, 0.7, 0.9, 1.2, and 1.6 mm inner diameter were equipped (the samples were named F5, F6, F7, F9, F12, and F16). The average diameters of these above fibers are 0.565, 0.667, 0.918, 1.473, 2.454, and 3.716 μm, respectively. Inset of a shows the magnified morphology of F5. (g–j) Image of porous PS fibrous film (named PF5, PF7, and PF12). The fiber diameters are approximate to 0.540, 1.020, and 2.135 μm. Insets to g, i, and j show the magnified morphology of the samples. (h) Amplification of PF5 sample's fiber. There are nanopores on the surface of PF5, and pore sizes range from 100 to 200 nm.

The wettability of as-prepared sorbent films was carried out as shown in Figure 2. A water droplet about 2 μL allowed to contact the surface of the PF5 sample, and the water contact angle (WCA) was 151.3 ± 1.6°, indicating that the PF5 fibrous sorbent film is superhydrophobic (Figure 2a). In contrast, when 2 μL motor oil droplet was dropped on its surface, the motor oil droplet immediately spread on the film with oil contact

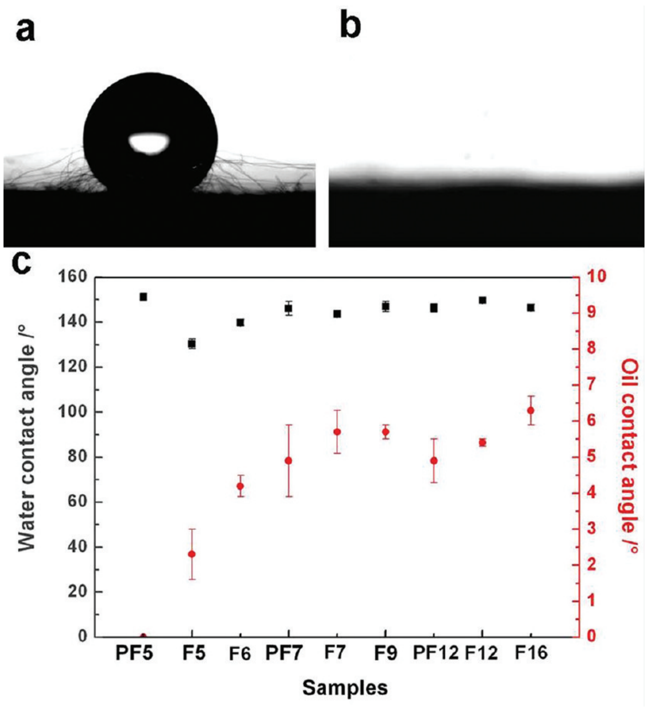

Figure 2. Wettability of as-prepared samples. (a) Water droplet (2 μL) on the PF5 sample with a water contact angle (WCA) of 151.3 ± 1.6°. (b) Oil droplet (motor oil, 2 μL) on the PF5 with oil contact angle (OCA)of 0°. (c) Hydrophobic and oleophilic properties of as-prepared samples with different morphology. With increasing of fibrous diameter, both the WCA and OCA of fibrous film without porous morphology increased, and the porous fibrous film exhibited higher WCA and lower oil OCA.

angle (OCA, motor oil) of 0°, which indicates that the sample is superoleophilic (Figure 2b). The different diameter and porous morphology also show tiny influence to the wettability of as-prepared samples. Figure 2c shows the WCA and OCA of each as-prepared sorbents. With the increasing of fibrous diameter, both the WCA and OCA of fibrous film without porous morphology increased slightly, and the porous fibrous film exhibited higher WCA and lower OCA. That is, the polystyrene natural property and the presence of PS fibrous film with high surface roughness could have been the main reason for its superhydrophobicity and superoleophilicity.

To investigate the maximum oil sorption capacity of fibrous sorbents, the adsorption test was performed on pure oil system without any water. Figure 3a shows the oil adsorption capacities of nonporous fibrous sorbents with different diameters for four different kinds of oils. The adsorption capacity of F5 is higher than any other samples, and adsorption capacity of peanut oil, silicon oil, motor oil and diesel oil is 98.71, 67.11, 113.0, and 6.28 g/g, respectively. Among four kinds of oils, the adsorption capacity decreases as shown in the following order: motor oil > peanut oil > silicon oil > diesel oil. Meanwhile, the adsorption capacities of other sorbents show the same trend for above four kinds of oils. Figure 3b exhibits the oil adsorption capacity of porous structured samples (PF5, PF7, and PF12). The sample PF5 with thinner diameter and porous structure shows the highest oil adsorption capacity among all samples, and the adsorption capacity of peanut oil, silicon oil, motor oil and diesel oil is 112.3, 81.4, 131.6, and 7.13 g/g, respectively. Furthermore, the comparison of oil adsorption capacity between the nonporous samples and porous structured samples with similar diameters are shown in Figure 3c. All as-prepared porous structured samples possess relatively higher oil adsorption capacity.

The different absorption capability for these four different kinds of oils can be attributed to the viscosity and surface tension of the oil solvents. High viscosity can lead to two effects which are the relation of a mutual competition. For one thing, it can increase sorption capacity by improving the adherence of oil onto the fiber surface. For another thing, sorption capacity can be decreased for heavier oil inhibiting the oil penetration into the interior of film sorbents.[28−31] Surface tension is the resultant intermolecular force when one fluid exerts on anther surface or liquid. Low value of surface tension suggests that oil could penetrate the sorbents and remain trapped with the solid sorbent.[32] Oil properties are listed in Table 1. The oil adsorption capacity mentioned above is agreed with the decreasing tendency of oil viscosity. In our study, the four kinds of oils that we choose normally used in daily life and production show inconspicuous difference between their surface tension but obvious different in viscosity. It can be seen that although low surface energy of as-mentioned oil solvents give rise to superoleophilicity and adsorption capacity, the oil solvent viscosity plays a important role in difference of adsorption capacity among these oil sorbent.

Figure 3d exhibits the diameter and pore volume of as-prepared samples. The pore volume V_p of the dry sorbents was estimated though uptake of methanol. Since methanol is a nonsolvent for polystyrene polymer, it can only enter into the pores of the polymer networks.[33] The total volume of pores V_p of the sorbents was found to be 1.861 ± 0.069, 1.792 ± 0.081, 1.693 ± 0.10, 1.302 ± 0.098, 0.806 ± 0.136, and 0.561 ± 0.125 mL/g for F5, F6, F7, F9, F12, and F16, respectively. Compared with as-mentioned nonporous samples, the V_p of PF 5, PF7, and PF12 are 2.145 ± 0.032, 1.737 ± 0.045, and 1.132 ± 0.12 mL/g, respectively, which are larger than those of nonporous samples. That is, V_p decreases with increasing the fibers' diameters, which is means that by increasing of the fibers' diameter, the specific surface area decreased. Meanwhile, it also can be seen that with increasing fiber diameter, the large volume of voids increases, which leads oil to be relatively expelled from the large interwoves rather than be retained among them.

The high sorption capacity of PS porous fibrous film is the combined results of oleophilicity which caused by lower surface tension, voids between interconnected fibers and porous structure which cause the action of the capillary force and increase the specific surface area. At the initial stage of oil sorption onto the films surfaces, the oleophilic interaction and van der Waals forces could play an important role between the experimental oils and film's surfaces. Chemical compatibility between oils and PS films leads to minimum surface tension and OCA, which provided minimum energy barrier for oil to penetrate to the fiber voids or fibrous porous structures. When minimum energy barrier is overcome, the presence of specific surface area of the PS films caused by void fractions as well as porous structure would predominantly affect the sorption capacity. Higher amount of effective specific surface area increases the oil sorption capacity, i.e., such effective specific surface area provide larger oil contacting areas on PS film and mount of capillary force for oil absorption. In addition, oil viscosity also plays an important role in the difference of oil adsorption capacity. The adsorption capacity increased with the increasing of oil viscosity due to the improving adherence of oil

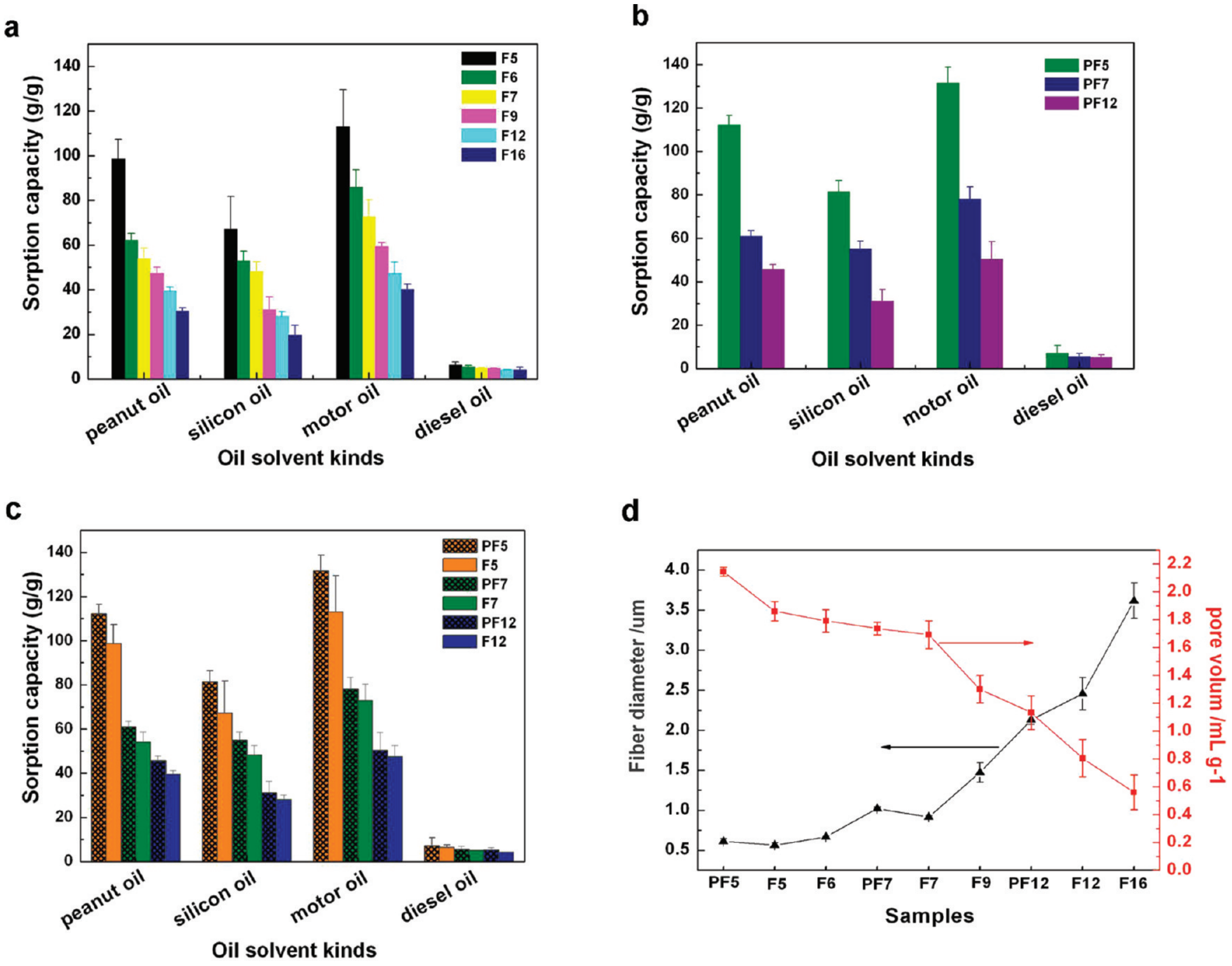

Figure 3. (a) Maximum oil adsorption capacities of nonporous fibrous sorbents with different diameters for different kinds of oils. Compared with other samples, F5 shows higher adsorption capacity. Among four kinds of oils, the adsorption capacity of all samples decreased as show in the following order: motor oil > peanut oil > silicon oil > diesel oil. (b) The oil adsorption capacity of porous structured samples. (c) The comparison of oil adsorption capacity between the nonporous samples and porous structure samples with similar diameters PF5 shows highest oil absorption capacity among all samples. The adsorption capacity of peanut oil, silicon oil, motor oil and diesel oil is 112.3, 81.4, 131.6, and 7.13 g/g, respectively. (d) Fiber diameters and pore volume of as-prepared samples. The total volume of pores V_p of the sorbents was decreased with increasing fiber diameter. PF5 owns a relatively larger V_p than any other sample, as a result of its thinner diameter and porous fibrous surface structure.

Table 1. Characteristics of Studied Oils at Room Temperature (25°C)

oil	viscosity (Pa S^{1-})	density (g cm^{-1})	surface tension (μN m^{-1})
peanut oil	0.20	0.91	23.17
silicon oil	0.13	0.93	19.61
motor oil	0.29	0.89	23.53
diesel oil	0.05	0.72	24.39

onto the fiber surface.[34,35] Although, the rate of oil penetration into a capillary is inversely proportional to the oil viscosity,[36] yet the reduced fiber diameter, voids between fibers, and porous structure on fiber surfaces have the advantage to heavy oil adhesion.

In addition, sorption selectivity in oil/water medium is an important parameter for oil sorbent used in spill cleanup. To qualitatively demonstrate the adsorption of oil from oil/water system, we take PF5 fibrous film sorbent as an example (Figure 4a−c). One-tenth of a gram samples were placed on the motor oil/water system (motor oil/water = 1:10 (w/w)).With higher buoyancy, the sorbent floats on the surface and keeps sucking the oil initially. After 15 min, at this quantity of oil spilled over water, almost the entire amount of added motor oil can be picked up by the PF5 sorbent. The adsorption rate is another important factor during the adsorption process. The relationship between the sorption capacity of sorbents films and contact time to the oil/water system (oil/water system is formed by the weight ration motor oil:water = 1:10. 0.1 g oil sorbents of each sample were dipped into the oil/water system) is shown in Figure 4d. After merely 3 min, all sorbents absorbed the red dyed colored motor oil quickly. The oil/water selective adsorption capacity is 9.7 ± 0.07, 9.2 ± 0.39, 8.6 ± 0.34, 7.5 ± 1.3, 7.4 ± 0.52, 6.3 ± 0.23, 5.3 ± 0.73, 4.6 ± 0.13, and 3.7 ± 0.25 g per 0.1 g of sorbents for PF5, F5, F6, PF7, F7, F9, PF12, F12, and F16, respectively. The fast sorption rate is due to the interconnected voids structure between these polymer fibers, which can hold oils in them with proper size. The thinner the

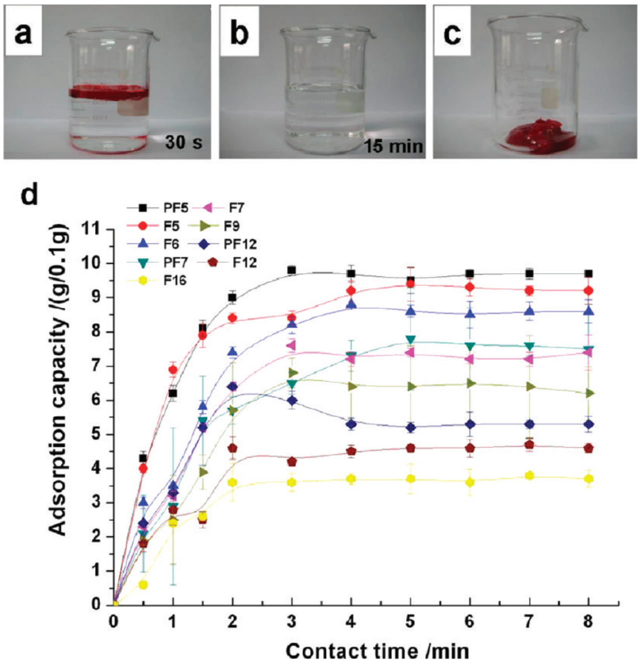

Figure 4. (a−c) Oil spill remove from water of PF5 sample (oil dyed with Oil Red, motor oil). (a) The PF 5 sorbent is placed on the motor oil initially. It floated on the oil surface with high buoyancy. (b) After 15 min, the sorbent adsorbed all given motor oil. The oil−water mixture becomes clear and transparent, only leaving water in the container. (c) The PF 5 oil sorbent sample after oil adsorption. (d) Sorption capacities of fibrous sorbents versus contact time with various oil pollutants. The PF5 fibrous film shows faster adsorption rate, and all samples can reach their maximum sorption capacity within 3 min.

fiber diameter, the faster the uptake rate and larger the adsorption capacity for the oil. The adsorption rate of PF5 is faster than any other samples. It is due to the larger specific surface area results from porous structure, i.e., increasing the specific surface areas of PS fibrous film can increase the efficiency and capacity of selective oil adsorption in oil/water system.

■ CONCLUSION

In the effort described above, we have successfully prepared the superhydrophobic and superoleophilic polystyrene fibrous sorbent films. By controlling the electrospinning condition, polystyrene films with different fibrous diameter and porous morphology can be obtained. These porous fibrous films show excellent oil adsorption capacity. Meanwhile, the oil adsorption capacity is also affected by the fibers' morphology. This work provides new insight to fabricate low-cost, high-efficiency oil absorption material through a convenient method for oil spill cleanup application.

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Notes

The authors declare no competing financial interest.

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