

A FACILE WAY TO PREPARE A SPONGE/CELLULOSE FIBER COMPOSITE AND ITS APPLICATION IN OIL/WATER SEPARATION

YABING CUI,* XING WU,** WENXUAN HU,** JIA FENG,* ZHIGUO LI,*
GUOWEI ZHOU,* YIMING CAI,** WEIYANG LV*** and MIAO DU**

*State Grid Zhejiang Electric Power Co., Ltd., Hangzhou 310014, China

**MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

***School of Materials Science and Engineering, Zhejiang Sci-Tech University, Hangzhou 310018, China

Y. Cui and X. Wu contributed equally to this work and should be considered co-first authors

✉ Corresponding author: M. Du, dumiao@zju.edu.cn

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Developing efficient filtering materials, with both high permeation flux and rejection, by a low-cost and facile way, for oil/water separation has been the goal that mankind pursues. In this paper, we report a porous poly(melamine formaldehyde) (PMF) sponge with superwettability and controlled pore size obtained simply, by introducing hydrophilic fibers, *i.e.* cellulose fibers. Driven by concentration or pressure difference, the fibers diffuse into the sponge body, and the pore size of the sponge can be regulated by changing only the fiber content. These hydrophilic fibers endow the sponge with inherent superhydrophilicity and underwater superoleophobicity. The resulting modified sponges, with varied pore sizes, can effectively separate a wide range of oil/water mixtures (including layered oil/water mixtures, surfactant-free oil/water emulsion and the surfactant-stabilized emulsion) solely by gravity, with high permeation flux and satisfactory oil rejection. It is expected that such a facile way will provide a low-cost and easily scaled-up method to construct a series of filtering materials for highly efficient separation of target oil/water mixtures.

Keywords: cellulose fiber, sponge, composite, oil/water separation

INTRODUCTION

Cellulose, one of the essential constituents of the cell wall of lignocellulosic biomass, has been widely used in industries and daily life, as in paper and packaging, pharmaceuticals and cosmetics, textiles and foods, as well as in the adhesive industries, for many years.¹⁻⁴ Nevertheless, research efforts have been made to adapt cellulose to nanotech applications in the last decades due to its outstanding properties, *e.g.* advanced mechanical strength, high crystallinity, high surface area, advanced hydrophilicity, biodegradability, biocompatibility, optical transparency, among others.⁵⁻⁶

Cellulose nanomaterials (nano-CMs), alone or in combination with other polymers in the production of composites, have been extensively used in different areas, including composite films, packaging, paper, tissue engineering, regenerative medicine, optoelectronics, environmental remediation, cosmetics *etc.*⁷⁻¹⁰ Among them, nano-CMs play an important role in environmental governance owing to their natural origin, advanced hydrophilicity, biodegradability and versatility.

Oil/water separation has been a worldwide challenge due to the increasing exploitation of

crude oil and frequent oil spill accidents, as well as the release of oily wastewater in industrial processes, such as textile, leather, metallurgy and petrochemical ones.^{11,12} Traditional cleanup technologies, like gravity degreasing, air flotation, *in-situ* burning, bioremediation, centrifuging and oil skimming, still suffer from low efficiency and high cost.¹³ To date, interfacial superwetting materials with substrates of metallic meshes, fabrics and polymeric membranes have been successfully developed to meet this demand.^{14,15} Membrane filtration technology, including ultrafiltration and microfiltration, has been extensively investigated and a variety of membranes have been fabricated via the rational control of chemical compositions and surface structures.^{16,17} Nevertheless, the conventional two-dimensional membranes, with small pore sizes and short permeation channels, are easily contaminated during long-term operation because of surfactant adsorption and pore blocking, leading to an obvious decline in flux and separation efficiency.¹⁸ Thus, the strategy of using three-dimensional (3D) porous structures, with tunable pore size and interconnected permeation path, for realizing excellent oil/water separation performance has been developed recently. To design a 3D filter for effective oil-polluted water separation, suitable pore size and wettability are the two key characteristics that should be carefully considered.¹⁹ Two methods are generally used to fabricate 3D filters. One is constructing a bulk substrate by bottom-up assembly, like the process used to fabricate graphene monoliths. Si *et al.* prepared a nanofiber-assembled cellular aerogel with tunable porous structure for emulsion separation; SiO₂ nanoparticles were introduced to control the pore size.²⁰ He *et al.* prepared a cellulose nanofiber aerogel by cross-linking between cellulose nanofibers and polyamideamine-epichlorohydrin.²¹ Note that these approaches have some disadvantages, such as high cost, complicated modification, and being time-consuming. The other strategy is to use directly commercial sponges and metal foams with 3D structures (most of them with pore size from 100 μm to 500 μm) as substrates,^{22,23} followed by a post-modification to achieve the

required pore structure and wettability.

We have reported a robust porous poly(melamine formaldehyde) (PMF) sponge with superwettability and controlled pore size through introducing layered double hydroxides (LDH) nanoscrolls and SiO₂ electrospun nanofibers.²⁴ The LDH nanoscrolls endow the sponge with inherent superhydrophilicity and the SiO₂ nanofibers act as pore size regulators by overlapping the PMF mainframe. Our approach allows the intrinsic large pores in the pristine sponge to decrease quickly from 109.50 μm to 23.35 μm , while maintaining porosity above 97.8%. The resulting modified sponges with varied pore sizes can effectively separate a wide range of oil/water mixtures solely by gravity, with ultrahigh permeation flux. However, the preparation method possessed sophisticated and time-consuming multiple steps, such as electrospinning, calcination at high temperature and hydrothermal treatment. A facile way to substitute the present method of oil/water separation materials with high flux and separation effectiveness needs to be developed.

Owing to the superhydrophilicity, cellulose materials have been widely used to fabricate oil/water separation materials. Cellulose nanofiber sponges with asymmetric wettability and strong mechanical property exhibited excellent separation efficiency for oil-water emulsions.^{25,26} Besides, cellulose nanocrystals, bacterial cellulose and other nanofibers have been employed to prepare ultralight, robustly compressible and superwetable oil/water separation materials.²⁷⁻²⁹ In this paper, we have made an attempt to construct a 3D multiscale structure by a facile and time-saving way. Several kinds of cellulose fibers were introduced into a PMF sponge to endow it with superhydrophilicity and underwater superoleophobicity. As shown in Figure 1, the hydrophilic cellulose fibers with suitable diameter and length were directly inserted into the porous PMF substrate to tune the pore size by diffusion or vacuum suction/filtering. Through glutaraldehyde (GA) vapor curing,³⁰ the fibers could be fixed on the mainframe of the PMF sponge. Combining with the conventional hydrophilic modification,²⁴ the PMF composites

exhibit superhydrophilicity and underwater superoleophobicity by this low-cost and easily scaled-up method. With the advantages of superwetting property and tunable pore size, these modified sponges can effectively separate layered oil/water mixtures, surfactant-free oil/water

emulsions and surfactant-stabilized oil/water emulsions, solely by gravity, with high fluxes that were dozens of times higher than those of filtration membranes. We hope to provide a facile way to prepare oil/water separation materials with high flux and oil rejection.

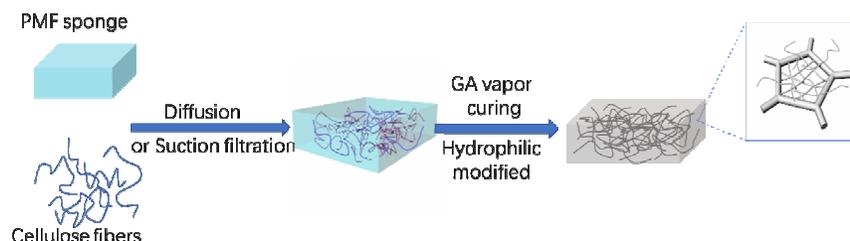


Figure 1: Schematic diagram of the PMF sponge modified by cellulose fibers

EXPERIMENTAL

Materials

Five kinds of cellulose fibers were selected. Xuan paper was purchased from China Xuan Paper Co., Ltd. Two cellulose nanofibrils (1 wt%, CNF-1, CNF-2) and cellulose nanocrystals (CNCs) were obtained from Zhejiang Agriculture and Forestry University. Bacterial nanocellulose (BC) dispersion (1 wt%) was purchased from Guilin Qihong Technology Co., Ltd. The poly(melamine formaldehyde) (PMF) sponge was purchased from Clean Wrap Company. Tween-80, *n*-hexane, 1,2-dichloroethane, ethanol and glutaraldehyde (GA) were supplied by the Sinopharm Chemical Reagent Co., Ltd, China. Distilled water was used in the experiments. All the reagents were used as received, without further purification.

Preparation of sponge/cellulose fiber composites

A certain amount of Xuan paper was cut into small pieces and soaked in 100 mL of water for several hours. After homogenizing the mixture for 30 min at 13000 rpm using a high-speed homogenizer (T25 D S25, IKA, Germany), a Xuan paper fiber (XPF) dispersion was obtained. Subsequently, the PMF sponge block, cut into 2.0 cm × 2.0 cm × 0.4 cm, was immersed into the uniform XPF dispersion or other cellulose fiber aqueous dispersion for 12 h of adsorption. For comparison, the sponge/cellulose fiber composites were also prepared by a vacuum suction filtration method. Firstly, the PMF sponge, with the size of 4.0 cm × 5.0 cm × 0.5 cm, was put onto the filter of a funnel. Then, 10 mL of cellulose nanofibril dispersions with different concentrations was poured into the funnel, and an air pump was used to realize rapid filtration. Because the diameter of cellulose fibers was smaller than the pore size of PMF, most fibers could enter the sponge body.

The sponge containing cellulose fibers was then frozen at $-30\text{ }^{\circ}\text{C}$ for 12 h and freeze-dried at $-50\text{ }^{\circ}\text{C}$ for 24 h. In order to fix the adsorbed cellulose fibers onto the sponge mainframe, the sponge composites were exposed to GA vapor at room temperature for 6 h, where GA reacted with the hydroxyl group on the cellulose fiber and the amino group on the PMF sponge, so as to ensure that cellulose fibers would not fall off during future use.³⁰ During GA crosslinking treatment, the hydrophilic hydroxyl groups on the cellulose fiber participated in the reaction and reduced the wettability of the sponge surface to water to some extent. In order to improve the wettability, the sponge needs to be conventionally modified to be hydrophilic again.²⁴ That is, it needs to be immersed with cellulose fibers in the buffer solution dissolved with dopamine and polyethyleneimine (pH = 8.5), under shaking at room temperature for about 6 hours, washed with clean water several times, and then vacuum dried to obtain a sponge with cellulose fiber regulated pore size. The ultimate modified sponges were denoted as PMF/XPF, PMF/CNF-1, PMF/CNF-2 and PMF/BC, respectively.

Characterization

The morphology of the modified sponges with different cellulose fibers were observed by scanning electron microscopy (SEM, Hitachi S-4800, Japan). The contact angle was measured via a contact angle system (Harke-SPCA, Peking Harke Experimental Instrument Factory, China). In order to reduce the experimental error, three areas of each sponge were taken for measuring the contact angle and the average value was calculated. Optical microscopy images were taken on a NIB900 (USA) by dropping an emulsion on a glass slide. The concentration of pollutants remaining in the solution was analyzed by a Lambda

35 UV-Vis absorption spectrometer at room temperature.

The modified sponge is mainly used for oil-water separation. Since oil generally exists in water in the form of small droplets, the surface of the sponge in water should show oil repellency to these oil droplets in order to prevent the oil droplets from passing through. Therefore, the underwater oil contact angle was also measured in this paper. Underwater oil contact angle test procedure: water was added to a certain height in a square glassware, and the modified sponge was placed at the bottom of the glassware. Dichloroethane with higher density than water was used as the test oil phase. 6 μL dichloroethane oil droplets were extruded on the surface of the sponge with a syringe. According to the shape of the oil droplets on the surface of the modified sponge, the underwater oil contact angle was analyzed.

Separation of oil/water mixture

Several oil/water mixtures, such as a layered oil/water mixture, a surfactant-free emulsion and a surfactant-stabilized emulsion, were used to test the separation efficiency of the modified multiscale sponges. The layered oil/water mixture was a mixture of *n*-hexane and water (*v:v* = 1:1). To prepare the oil-in-water surfactant-free emulsion, 1 mL of *n*-hexane was added into 99 mL of distilled water. Then, the mixture was emulsified by a high-speed homogenizer (5000 rpm for 10 min). Besides, two oil-in-water emulsions (1 mL of sunflower oil or olive oil and 99 mL of water), with 1.5 mg of Tween-80 as surfactant, were also prepared by using the high-speed

homogenizer (600 rpm for 10 min). The separation process was carried out in a home-made filtration unit, where the modified sponges were sandwiched between two silica gaskets. The freshly prepared mixtures could go through the sponge simply by gravity. During the experiments, the height of the mixture column was maintained at 10 cm and the real-time flux was determined every 30 s. The oil rejection was determined by measuring the oil content in the feed and in the corresponding filtrate with the UV-Vis absorption spectrometer (the oil was dyed with Oil Red O).

The treatment capacity of the oil-water mixture to pass through a circular hole area channel with a radius (*R*) was calculated according to $\frac{V}{t \cdot \pi R^2 \cdot \Delta P}$, in which *V* is the volume of the mixture, ΔP is the liquid column pressure, *t* is the passing time. The unit of treatment capacity, or flux, is $\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$.

RESULTS AND DISCUSSION

Morphology of several cellulose fibers and modified sponges

Cellulose fibers are generally categorized into three basic groups related to their production process, *i.e.*, normal cellulose fiber, cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs).³¹ Five kinds of cellulose fibers were selected in this paper and their morphology is shown in Figure 2.

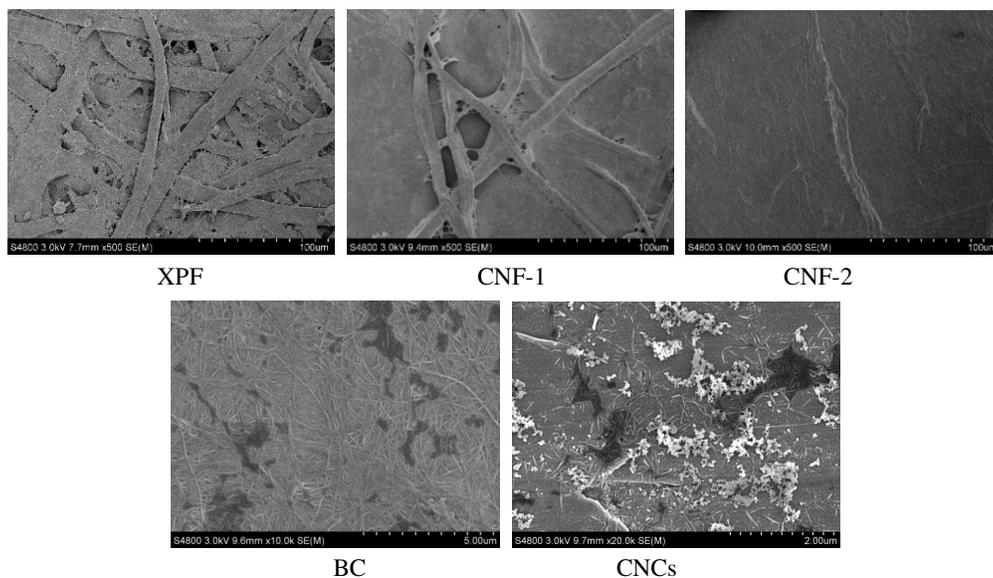


Figure 2: Morphology of five cellulose fibers

The XPF has a diameter of 10 μm and a length of several hundred micrometers. CNF-1

and CNF-2 have smaller diameter and length than those of XPF. The diameter of CNF-2 is about 3.9

μm . Bacterial cellulose (BC) is a natural nano-structured material produced by microorganisms. The diameter of BC is only 20-50 nm, which is much lower than others. The

diameter of CNCs is also 20-50 nm, but their length (0.2-0.5 μm) is much shorter than that of the BC.

Table 1
Parameters of five cellulose fibers

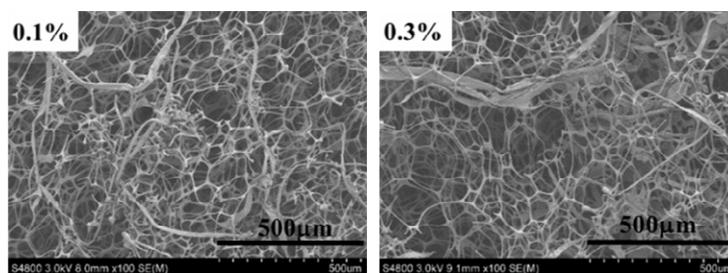
| Sample | Diameter (μm) | Length (μm) |
|--------|----------------------------|--------------------------|
| XPF | 16.7 \pm 3.1 | 100-500 |
| CNF-1 | 13.8 \pm 3.7 | 100-500 |
| CNF-2 | 3.9 \pm 1.3 | 100-500 |
| BC | 20-50 nm | 20-100 |
| CNC | 20-50 nm | 0.2-0.5 |

Although the CNCs could easily diffuse into the PMF body, they are very easy to be washed out because of their small size. Therefore, CNCs were not further utilized in this work. The parameters of the five cellulose fibers are summarized in Table 1.

The commercially available PMF sponges, with pore sizes of 100-200 μm , were selected as porous substrate due to their low cost, high porosity and robustness.^{32,33} The morphology of the PMF sponge modified by the four cellulose fibers is shown in Figures 3-6. When the concentration of XPF aqueous suspension is 0.1% (mass percent), only a few fibers are distributed on the surface of the PMF sponge (Fig. 3). The interior of the sponge represents an interconnected network architecture, with a smooth and flat mainframe surface, in which XPFs were not observed. As the concentration increases, more fibers diffuse into the sponge. When the concentration of XPF is up to 0.7%, XPF of large size adheres to the surface, and

some small-sized XPFs enter the sponge interior. Thus, the pore architecture of the sponges is regulated by changing the concentration of the XPF aqueous dispersion.

The morphologies of PMF/CNF-1 and PMF/CNF-2 are shown in Figures 4 and 5, respectively. Compared with PMF/XPF, more cellulose nanofibrils enter the sponge at the same concentration due to their smaller diameter. When the concentration of CNF-1 aqueous dispersion is as high as 0.5%, a large number of CNF-1 nanofibrils can be seen in the sponge. As the diameter of CNF-2 nanofibrils is much smaller, more nanofibrils are observed inside the sponge or on the surface of the sponge. When the concentration is 0.5%, some CNF-2 nanofibril films even form between sponge skeletons, confirming the ease in the fabrication of films with CNF-2. These films close some pores of the PMF sponge, which would decrease the flux remarkably.



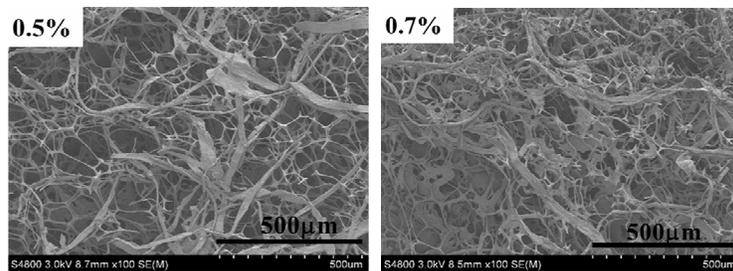


Figure 3: Morphology of PMF sponges modified with XPF aqueous dispersion

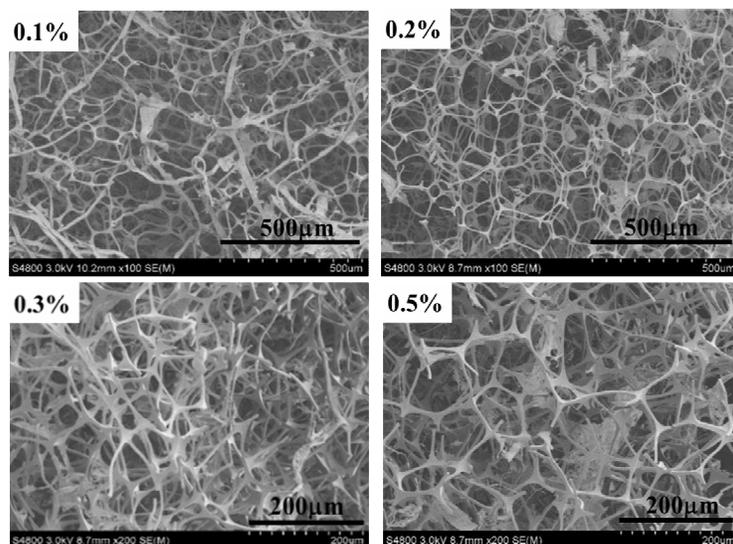


Figure 4: Morphology of PMF sponges modified with CNF-1 aqueous dispersion

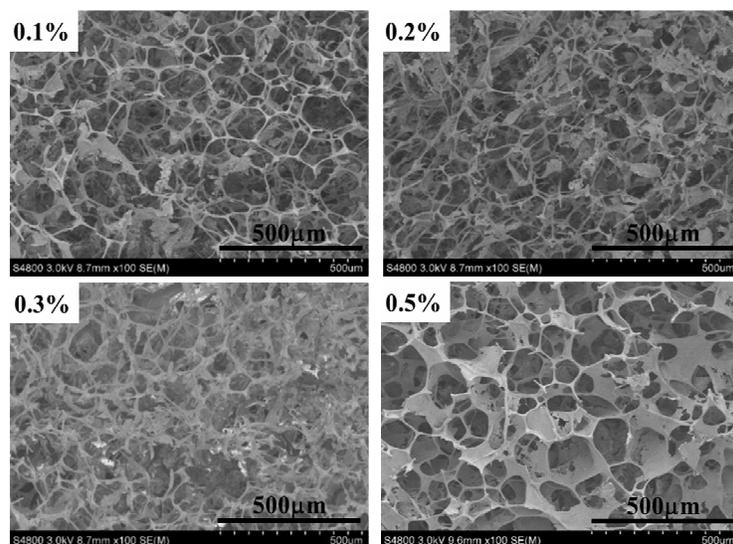


Figure 5: Morphology of PMF sponges modified with CNF-2 aqueous dispersion

The diameter of BC fiber is only 20-50 nm, and it can easily enter the sponge, even at low

concentration (Fig. 6). At a concentration of 0.1%, more BC fibers can get into the sponge body,

compared with other cellulose fibers. In the case of 0.15%, there are a large number of BC nanofibers inside the sponge. The final modified sponge exhibits diverse microstructures, from micrometers to nanometers: the matrix sponge possesses a major pore size of 100-200 μm , and

these pores are highly overlapped by numerous BC nanofibers, which form minor pores of 5-50 μm . Large flakes of BC films begin to form at 0.2% and plenty of sponge pores are blocked. This will lead to a sharp decrease of the flux, despite the promotion of oil rejection.

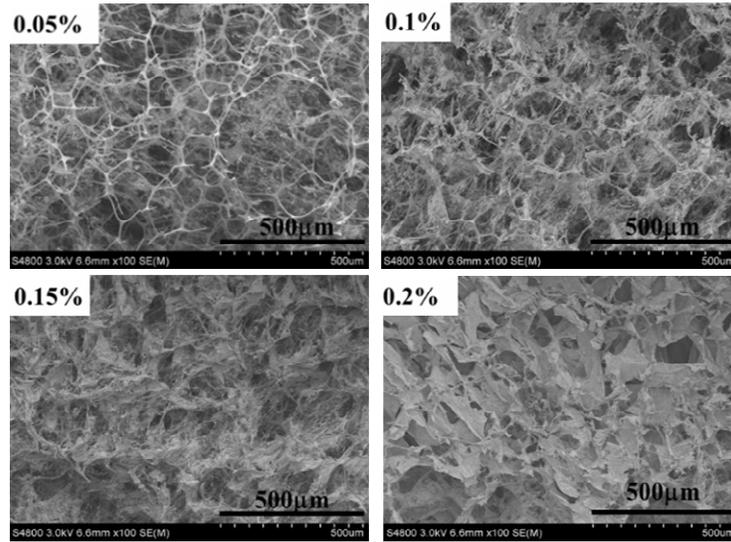


Figure 6: Morphology of PMF sponges modified with BC aqueous dispersion

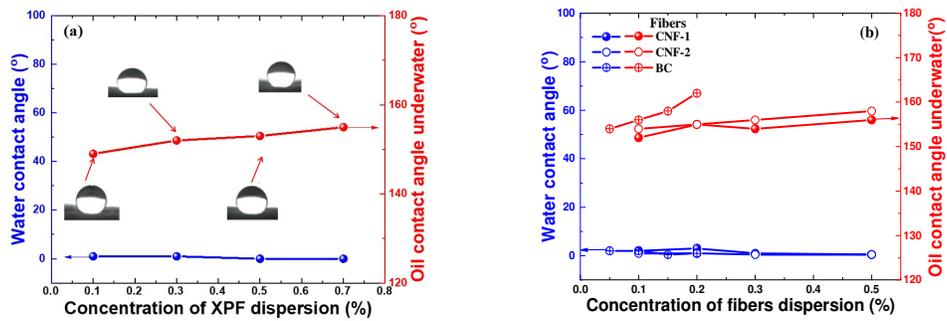


Figure 7: Effects of different cellulose fiber concentration on water contact angle and underwater oil contact angle of the modified sponge surface

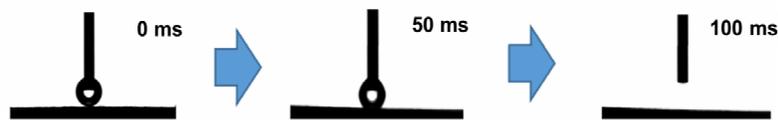


Figure 8: Photographs of dynamic measurements of water permeation on the surface of PMF/BC sponge

Hydrophobicity and oil repellency of the modified sponge

The cellulose nanofibers, in combination with

the high surface energy of numerous inherent O-H groups, endow the modified sponges with superhydrophilic and underwater

superoleophobic properties. As shown in Figure 7, all the modified sponges show extremely small water contact angle (WCA) of nearly 0° in air. A high-speed camera system was used to record the permeation process of a water droplet (Fig. 8). When a 2 μL water droplet contacted the PMF/BC composite surface, it permeated the sponge quickly and the whole process was completed within 50 ms, which suggested the prominent water-wetting property of the modified sponges.

In addition, the superhydrophilic samples generally exhibited underwater superoleophobic properties, according to the developed Young's and Cassie equations.^{34,35} Here, 1,2-dichloroethane was selected as a model oil, due to its higher density than that of water. The underwater oil contact angle (OCA) of the sponge modified with 0.5% XPF was 153° , and negligible deformation was observed during the dynamic contact test (Fig. 7a). This result reveals the pretty low oil adhesion of the modified sponge surfaces. With increasing concentration of the cellulose nanofiber dispersion, the OCA increased slightly. The PMF sponge modified with other cellulose fibers also exhibited high OCA and small WCA values (Fig. 7b). When the sponge was modified by 0.5% CNF-2 or 0.2% BC dispersion, the OCA is as high as 160° , showing excellent underwater superoleophobic properties. The formation of cellulose films is beneficial to improve the oil repellency underwater. Moreover, an *n*-hexane jet could bounce off the PMF/BC surface under water with no trace left, and the viscous sunflower oil adhered on the sponge could also be simply removed by immersing the sample in water, which further confirmed the feasibility of the modified sponges for practical anti-oil-fouling applications in an aqueous environment.

Separation of oil-water mixture with the modified sponge

Several oil/water mixtures, such as layered oil/water, surfactant-free emulsion and surfactant-stabilized emulsion, were used to test the separation efficiency of the modified multiscale sponges (pre-wetted by water). The

inset of Figure 9(a) shows the separation process for layered *n*-hexane/water mixtures ($v:v = 1:1$) driven only by gravity. The mixtures were poured onto the modified sponge and the water quickly permeated through the sponge, while *n*-hexane was retained above. The pristine PMF and the modified PMF sponges have water flux as high as $1 \times 10^7 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, which could be attributed to their superhydrophilic property and high porosity. Although pristine PMF can separate the layered oil/water mixture, there are some oil droplets in the separated water. While for the modified PMF, all the dyed oil was retained above the sponge. For 60 mL of layered oil/water mixture, the separation can be completed in only several seconds with the PMF modified with 0.5% XPF dispersion, and finally 30 mL of water was obtained. With the increase of cellulose fiber concentration, the oil/water separation capacity of the four modified sponges decreases gradually, which is related to the smaller pore size of the modified sponge. Compared with the sponge modified with XPF, the oil/water separation capacity of the BC fiber modified sponge declines remarkably, indicating that the pore size changed more obviously. Especially, the two modified sponges containing cellulose films (PMF/CNF-2, 0.5% CNF-2 dispersion; PMF/BC, 0.2% BC dispersion) exhibit lower flux. Nevertheless, compared with the ordinary oil-water separation membrane, the oil-water treatment capacity of the above modified sponge is still 10-1000 times higher (the treatment capacity of the separation membrane is generally $10^4 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$).^{36,37}

For surfactant-free *n*-hexane/water emulsion ($v:v = 1:99$) with the average oil droplet size of twenty microns, the water flux was about $2 \times 10^7 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ for the pristine PMF and then showed a sharp decrease with increasing cellulose nanofiber content for the PMF sponge modified by the four cellulose fibers, whereas the oil rejection gradually increased (as displayed in Fig. 10). The oil rejection was 80% for the PMF modified with 0.05% BC dispersion and reached 95% for the PMF modified with 0.2% BC aqueous dispersion. The rejection of the BC modified sponge for the oil-water emulsion is

about 80-95%, while that of the XPF modified sponge is only 75-90%. It is worth noting that the surfactant-free emulsions could be effectively separated, even when the sizes of oil droplets were smaller than the pore size of the modified sponge ($\sim 40 \mu\text{m}$), implying that the separation process for the modified sponges was a combination of size-sieving surface filtration and coalescence of oil droplets in the tortuous microchannels.^{38,39}

A surfactant-stabilized emulsion tends to form

small droplets with high stability and complex structure,⁴⁰ which is still a great challenge in remediation by commercial porous materials. In this study, Tween-80 was used as surfactant to prepare a stable emulsion with an average oil droplet size of $12.02 \mu\text{m}$. The configuration method of the oil water emulsion is: the volume ratio of oil (sunflower oil or olive oil) to water is 1:99 (100 mL), the surfactant is Tween 80 (1.5 mg).

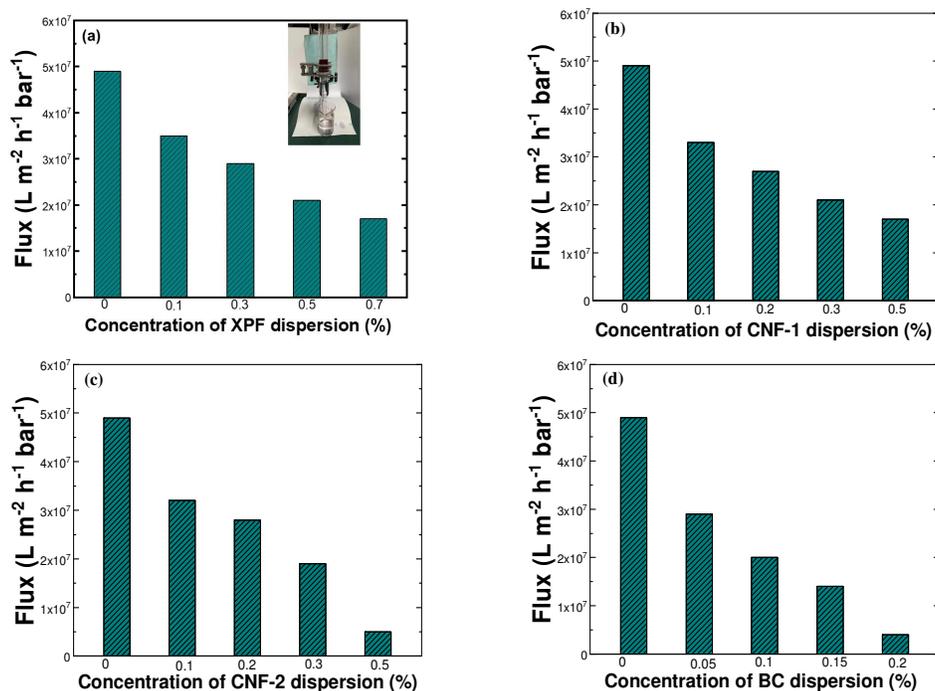
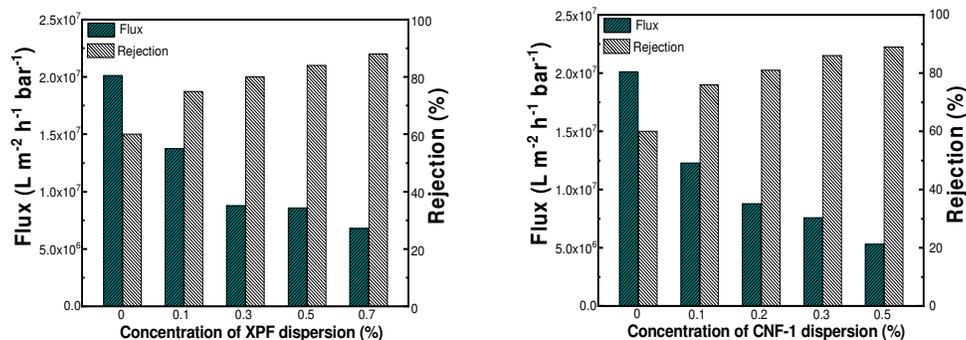


Figure 9: Flux of layered oil/water mixture for sponges modified with different cellulose fibers



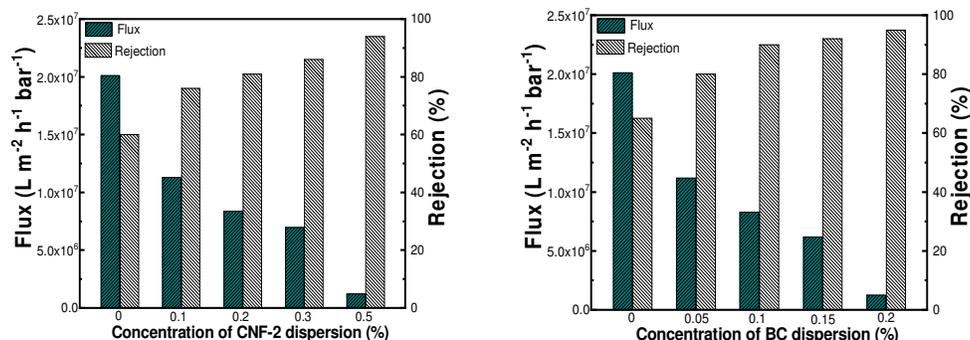


Figure 10: Separation effect of sponges modified with different cellulose fibers on oil-water emulsion without surfactant

Four modified sponges (PMF/XPF, 0.7% XPF dispersion; PMF/CNF-1, 0.5% CNF-1 dispersion; PMF/CNF-2, 0.3% CNF-2 dispersion; PMF/BC, 0.15% BC dispersion) were selected to verify the efficiency of oil/water separation. The separation behaviors were similar to that of the surfactant-free one, whereas the highest rejection was only about 90% (for the sponge modified by 0.15% BC dispersion, Fig. 11). The smaller oil droplets in the emulsion and their higher stability

in resisting coalescence during the separation process could be attributed to this phenomenon. Considering that the coalescence of droplets in sponges plays a key role in emulsion separation, it might be helpful in achieving higher oil rejection by increasing the number of sponges, *i.e.*, prolonging the permeation path of emulsion in sponges. As expected, the oil rejection of emulsion was significantly improved when three sponges were stacked to perform the separation.

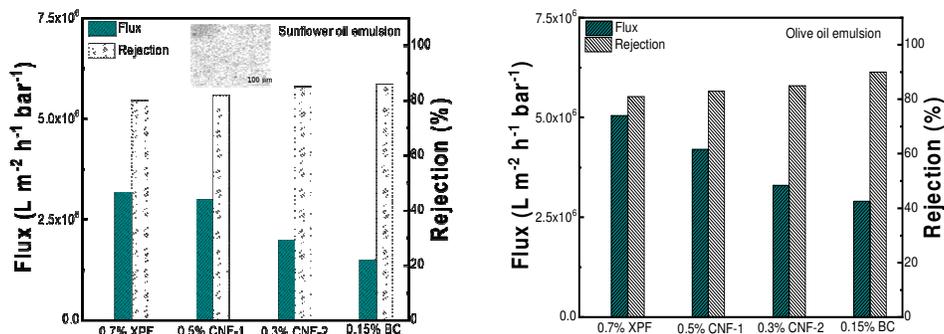


Figure 11: Separation effect of different cellulose fibers modified sponges on oil-water emulsion containing surfactant

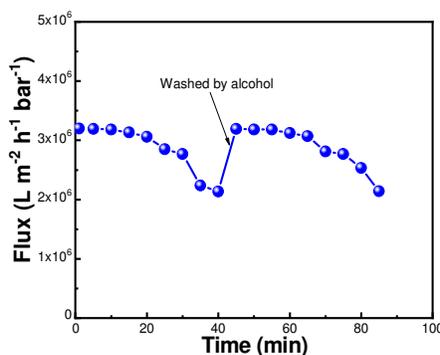


Figure 12: Time evolution of water flux and flux recovery of the PMF sponge modified by 0.15% BC dispersion for sunflower oil emulsion

The water permeation flux was above $1 \times 10^5 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ for three PMF/BC sponges (0.15% BC dispersion), with oil rejection of about 96%, which was almost one order of magnitude higher than that of filtration membranes with similar oil rejection.⁴¹

Reuse of the modified sponge

The water permeation flux with the evolution of filtration time was measured to further assess the practical application of the modified sponges in emulsion separation. Sunflower oil/water emulsion was stabilized by Tween-80. The reusability of the BC nanofiber modified sponge was investigated. As shown in Figure 12, the water flux decreased gradually for the emulsion due to the accumulated oil droplets within the modified sponges. After continuous treatment for 40 min, the treatment capacity of oil-water separation decreased slightly, which was caused by the enrichment of oil droplets on the sponge surface. Nevertheless, its treatment capacity was still much higher than that of the separation membrane. After washing with ethanol, the

permeation flux recovered completely to its starting value, suggesting the good stability and excellent antifouling property of the multiscale structures.

Sponge/fibers composite prepared by suction filtration

The diffusion process of cellulose nanofibers into PMF took a long time owing to the relatively small pore size. For the sake of comparison, suction filtration was used to prepare fast the composite sponge, which took slightly more than ten minutes. The composite sponge was the PMF modified by 0.3% CNF-2 aqueous dispersion. As shown in Figure 13, the CNF-2 film formed on the upper surface, while fewer CNF-2 fibers were found on the lower surface of the sponge. There was a gradient distribution from upper to lower surface. Compared with Figure 5, there were more CNF-2 fibers distributed on the upper surface, but fewer fibers on the lower surface. This led to a smaller flux, but higher rejection than that of normal PMF modified through concentration difference diffusion.

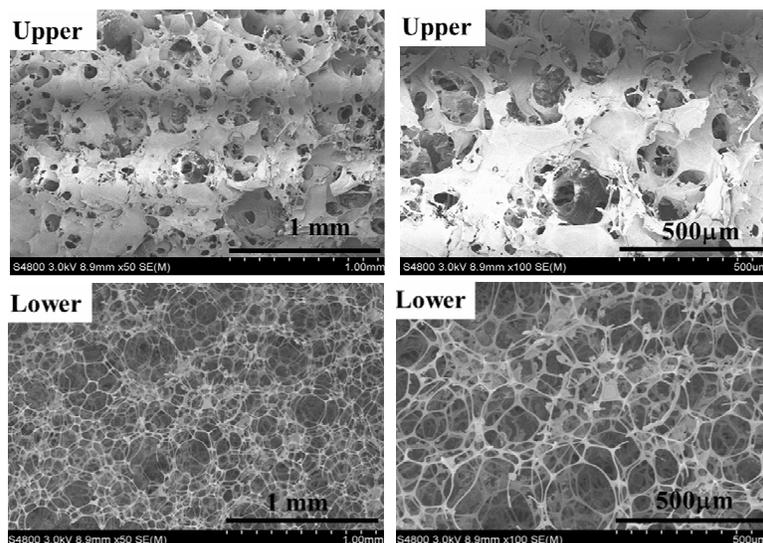


Figure 13: Upper and lower surface morphology of 0.3% CNF-2 dispersion modified PMF by suction filtration

CONCLUSION

In summary, we have constructed 3D porous PMF composite sponges simply by introducing common and easily available natural cellulose

fibers. All four cellulose fibers could diffuse into the sponge body and regulate the pore size of the sponge through concentration or pressure difference, which allows the intrinsic large pores

of the pristine sponge to decrease quickly, while maintaining high porosity. These hydrophilic cellulose fibers endow the sponge with inherent superhydrophilicity and underwater superoleophobicity. The modified sponges, with varied pore sizes, can effectively separate a wide range of oil/water mixtures (including layered oil/water mixtures, surfactant-free oil/water emulsions and surfactant-stabilized emulsions) solely by gravity, with high permeation flux and satisfactory oil rejection. The modified sponges show good reusability, after washing with ethanol. It is expected that such a pore size tuning technology can provide a low-cost and easily scaled-up method to construct a series of filtering materials for highly efficient separation of target oil/water mixtures.

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