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Manta Ray Gills Inspired Radially Distributed Nano-fibrous Membrane for Efficient and Continuous Oil-Water Separation

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Manta ray gills inspired super-hydrophilic membrane for efficient and continuous oil-water separation

Suspension feeding animals such as manta rays can separate water and food particles quickly and continuously through their special structured gill rakers via crossflow filtration. Inspired by this ecosystem engineering from nature, a facile membrane based set-up for oil-water separation mimicking the manta ray gill rakers was proposed in this paper. This crossflow process was fabricated using aligned electrospun nano-fibrous silk fibroin membrane. In this process, as the oil-water mixture travel in parallel manner across the membrane surface, water permeated through the membrane while oil was rejected by the membrane and collected in the middle pipe. Compared to traditional super-hydrophilic membrane separation conducted by gravity-driven dead-end approach, this method can avoid fouling issues and function continuously. Therefore, this nature-inspired method creates new opportunity for efficient oil-water separation. As an environmentally friendly

material, silk fibroin is naturally super-hydrophilic which demonstrated its potential in water treatment.

Environmental Significance Statement

Oil spill and oily wastewater have become great threats to ecosystem and human beings. Bio-inspired super-wetting surfaces have shown great potential in oil-water separation. Super-hydrophilic and underwater super-oleophobic membrane is developed widely for oil removal from water. However, traditional dead-end filtration set-up for oil-water separation is suffering from pore-blocking due to the accumulation of oil. Inspired by suspension feeding animals like manta ray, a facile crossflow membrane set-up is designed for efficient and continuous filtration. With this set-up, water is able to pass through the membrane, and oil will be collected. Silk fibroin as natural super-hydrophilic material is utilized for membrane fabrication.

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1. Introduction

Manta rays are large sea creatures which feed on suspended food particles in the ocean by filtering water rapidly and continuously[1]. Manta rays have never suffered from the clogging of food particles, even although they have to filter large amount of water all the time, and this phenomenon is owing to their special structured gill rakers[2]. As illustrated in Figure 1(a), manta rays separate the food particles from seawater via a crossflow filtration instead of dead-end filtration which prevents the clogging of their gill rakers[3-5]. As seawater and the suspended food particles enter its mouth, the stream travels across gill rakers. These rakers allow seawater to pass through but retains the suspended food particles. These suspended food particles are washed off the gill rakers to avoid clogging. Thereafter, the stream of seawater becomes more concentrated with suspended food particles and travels into the esophagus of manta rays. This crossflow filtration is beneficial as the particles and contaminants are less likely to be attached to the gill rakers of manta rays, compared with the dead-end filtration[6]. This unique filtering structure from nature is inspiring for water treatment, especially in oil-water separation.

The increasing consumption of fossil fuels and frequent oil spill produced oily wastewater has become a great threat to the ecosystem and sustainable development of human beings[7-9]. Traditional oil-water separation technologies, such as skimmers[10], absorbents[11], controlled burning[12] and biodegradation[13, 14], are suffering from low removal efficiency or secondary pollution[15]. Thus, facile materials with special wettability, especially material which enables the effective separation of water and oil, are widely studied[16-19]. Inspired from natural surfaces with special wetting behavior, materials are synthesized by manipulating the micro-/nano-structure or surface composition with the development of colloid and interface science[20-24]. Among them, super-hydrophilic and underwater super-oleophobic membranes have been widely investigated and effectively employed for the gravity-driven dead-end oil-water separation[25-28]. However, this method has intrinsic limitations, these membranes can be easily clogged by oil and the water flux will decrease significantly. Furthermore, the accumulation of oil on the membrane surface renders the separation process cannot be conducted continuously.

Inspired by the crossflow filtration of manta rays, we can solve this problem by combining membrane technology and the structure of manta ray gill rakers. By mimicking manta ray gills, a membrane based oil-water separation set-up was created. The membrane with aligned nanofiber was fabricated by electrospinning on a specially designed collector, as shown in Figure 1(c-d). During the oil-water separation process, water permeates through the membrane rapidly, while oil is repelled and collected in the inner iron pipe. Silk fibroin was chosen as the raw material to fabricate the nano-fibrous membrane due to its naturally super-hydrophilicity and underwater super-oleophobicity.

The laboratory scale experiments have verified that the membrane exhibits the ability to separate oil and water continuously and efficiently. Moreover, silk fibroin is a natural material which exhibits no hazard to the environment. This work provides a new perspective to achieve efficient and continuous oil-water separation. Additionally, silk fibroin has exhibited great potential as a novel material for water treatment.

2. Materials and Methods

2.1 Materials

Iron pipe (diameter 5 mm) were used as the electrode connecting to earth for electrospinning. Chemicals used includes sodium carbonate (Na_2CO_3), calcium chloride (CaCl_2), formic acid (FA) were purchased from Sigma-Aldrich. Deionized water (DI water, $18.4 \text{ M}\Omega\cdot\text{cm}^{-1}$ resistivity), ethanol (Chem-Supply Pty. Ltd., absolute) were used for posttreatment and cleaning. Olive oil, cooking oil, and silicon oil were used as test liquids.

2.2 Preparation of Silk Fibroin

After degumming in 5% Na_2CO_3 aqueous solution at 100°C for 1 hour, silk was dissolved in formic acid- CaCl_2 solution. Subsequently, the dissolved mixture is dried and washed by DI water to obtain the regenerated silk fibroin film.

2.3 Preparation of Electrospun Silk Fibroin Membrane

According to the results of our preliminary experiments, as shown in Figure S1, low concentration of silk fibroin (<10%) lead to the "beads-on-string" structure of electrospun nano-fibers, which influenced the quality of membrane. When the concentration reached 10%, uniform no-bead nano-fibers were obtained successfully, and therefore 10% was chosen for the fabrication our membrane in this research. 10% silk fibroin solution was produced by adding 1.0 g of solid silk fibroin into 7.54 mL of formic acid and was stirred for 6 hours until the solid silk fibroin was fully dissolved. The electrospinning was carried out at room temperature in a closed chamber. A 5mm iron pipe is used as the electrically conducted collector, with a plastic pipe surrounding the iron pipe for the silk fibroin fibers to attach itself. The silk fibroin fibers were then electrospun. The tip collector distance was kept at 20 cm and a voltage of 24 kV was supplied. The silk fibroin solution was placed in a syringe with a blunt-tip needle (nozzle diameter of 0.7 mm). Using a micro-syringe pump, the spinning solution was pushed through the needle at a feeding rate of 0.2 mL/h, 6 hours were required to produce the membrane by electrospinning.

Thereafter, the electrospun membrane was dipped in ethanol for 1 h to ensure that the fibers do not clump together when it come in contact with water. As shown in Figure S2, without any treatment, nano-fiber structure of the membrane was damaged

after immersing in water for 3hrs, while after ethanol treatment, nano-fiber structure was not influenced even immersing in water for 1 week.

2.4 Characterizations

The microstructures of prepared silk fibroin membrane were characterized by field emission scanning electronic microscopy (FESEM, JEOL JSM-7600F). The surface wettability of the membrane was tested by Video Contact Angle (VCA) device (AST Product Inc. Optima series). A video camera was used to determine the contact angle of each test. Thermogravimetric analyzer (TGA, Perkin Elmer TGA-7) measurement was performed from 30 °C to 700 °C, at a heating rate of 10 °C min⁻¹ in N₂ atmosphere. Fourier transform infrared (FTIR) spectra of the samples was recorded on a Perkin Elmer spectrum GX FTIR spectrometer.

2.4 Oil-water separation

In order to investigate the oil-water separation ability of the membrane, several types of oil-water mixture were prepared using vegetable oil, olive oil and silicon oil. The oil/water volume ratio was 1:9. Total organic carbon (TOC, Shimadzu VCSH) was used to analyze oil concentration. The membrane was pre-wetted by water at the beginning. Thereafter, oil-water mixture was continuously discharged into the filtration setup. Subsequently, water permeate through the membrane by gravity while concentrated oil-water mixture was collected via the iron pipe in the center.

The separation efficiency can be calculated by oil rejection ratio (R%):

$$R = \left(1 - \frac{C_p}{C_0}\right) \times 100\%$$

where C_0 and C_p are the oil concentration of the feed oil-water mixture and the permeate water.

3 Results and Discussions

3.1 Surface Morphology

By specially designing the collector of electrospinning as illustrated above, the nano-fibrous membrane setup could be obtained easily. Field emission scanning microscopy (FESEM) was utilized for the characterization of the microstructure of the as-prepared membrane. The radiate distribution of nano-fibers was proved by the FESEM image as shown in Figure 2(a). This fiber-radiate membrane was designed to mimic the manta ray gills for continuous oil-water separation. Figure 2(b) is the enlarged image of the nanofibers. It is clearly observed that the diameter of the fibers was around 100 nm. The average diameter of the fibers was 106 nm. The largest was 198 nm, while the smallest was 40.3 nm. The fiber diameter distribution

is shown in Figure S4. Therefore, a manta ray gills inspired nano-fibrous membrane was obtained by silk fibroin electrospinning.

3.2 FTIR and TGA

Figure 2(c) shows the FTIR spectrum of the silk fibroin membrane. Peaks were observed at 3300 cm⁻¹, 1630 cm⁻¹, 1530 cm⁻¹ and 1265 cm⁻¹. The point where the vibration is 3300 cm⁻¹ depicts adsorbed water in the silk fibroin membrane. The other three notable peaks or troughs are consistent with silk fibroin fibers that have undergone ethanol treatment[29, 30]. The thermogravimetric curve of as-prepared membrane is shown in Figure 2(d). The first stage of weight loss below 150 °C is due to the evaporation of water, while the second stage from 300 °C is associated with the degradation of silk fibroin[31, 32]. Silk fibroin fibers with these profiles exhibit better stability in water and better mechanical properties as compared to silk fibroin fibers that have not undergone ethanol treatment[33].

3.3 Wetting Behavior

Wetting Behavior of the membrane plays an important role in oil-water separation. As shown in Figure 3(a), during the contact angle testing process, when a water droplet contacted with the membrane surface, it quickly spread, and the water contact angle in air was 0°, which illustrated the super-hydrophilicity of the membrane. When the membrane was underwater, as shown in Figure 3(b), the oil contact angle was 154°, which illustrated the underwater super-oleophobicity of the membrane.

This wettability of the membrane is naturally from the abundant hydroxyl and amino groups on the surface of silk fibroin fiber. According to Wenzel model and Cassie-Baxter model, a hydrophilic surface can become more hydrophilic or super-hydrophilic with the increase of roughness[34, 35]. Due to the micro-/nano-structure of electrospun nano-fibers, this membrane possesses great roughness and thus super-hydrophilicity. Meanwhile, with the accordance of the wetting theories, the in-air-hydrophilic surface always shows oleophobicity underwater[36, 37], which is the same as the result of our test. With super-hydrophilicity in air and super-oleophobicity underwater, this membrane exhibits great potential in oil-water separation.

3.4 Separation of Oil and Water Mixtures

Continuous oil-water separation was conducted to test the efficiency of the membrane. The separation efficiency was evaluated using three types of oil, and the oil concentration was measured based on the total organic carbon. A certain volume of oil-water mixture was discharged into the set-up continuously. Water passed through the membrane quickly by gravity and was collected by the plastic tube, while rejected oil was collected through the inner pipe by a beaker as shown in Figure 4(a). Figure 4(d) illustrated that the separation efficiency

for three types of oil was at least 99.9%, showing efficient separation behavior (99.96% for olive oil-water mixture, 99.92% for silicone oil-water mixture, 99.96% for hexane-water mixture, 99.97% for vegetable oil-water mixture, 99.91% for diesel-water mixture and 99.91% for engine oil-water mixture).

Due to the super-hydrophilicity and underwater super-oleophobicity of the membrane, there will be a water film on the membrane surface, which is a stable underwater Cassie-Baxter wetting mode and can help achieve a robust water cushion between oil droplets and the membrane to prevent oil from permeating through [37-40]. Meanwhile, the radial arrays of nanofibers and the crossflow of oil-water mixture creates a continuously decreasing oil-water contact friction [41-43]. As a result, when an oil droplet is deposited on the surface, it will be driven to the center by both the wettability gradient and gravity as shown in Figure 5(a), rather than attaching on the membrane surface and blocking the pores. At the same time, when oil droplets are accumulated to the center, small droplets will converge to form big ones and finally be collected in the central pipe, just like the feeding process of manta rays. Therefore, this membrane setup is able to achieve efficient and continuous oil-water separation.

3.5 Long term filtration tests

In order to quantify the suitability of the membrane for long term filtration, separation tests were also conducted over time and permeate volume.

Firstly, to test the effectiveness of the membrane performance over a long period of time, the electrospun silk fibroin membrane subjected to constant filtration of a 1:9 oil-water mixture by volume. Samples are taken every hour over a period of 8 hours. These samples are then tested for its TOC concentration to calculate its separation efficiency over 8 hours. As seen from Figure 5(b), the membrane rejection performance remains high over a period of eight hours. This showed the effectiveness of the crossflow filtration that was adopted in the membrane setup. This ensures the membrane performance for oil water separation can be maintained at a high level after extended periods of time.

Secondly, the membrane was tested for its permeate quality after producing certain amounts of permeate water. Samples are taken from 50 mL to 700 mL of permeate water produced. As shown in Figure 5(c), the permeate quality remains high even after producing 700 mL of permeate. This demonstrated the effectiveness of the crossflow filtration that was utilized in the membrane setup. This ensures that permeate quality from oil water separation can be maintained at a high level after producing a substantial amount of permeate.

Conclusions

Inspired by the manta ray gill rakers, a novel silk fibroin membrane was successfully fabricated for the efficient oil-

water separation. By specially designing the collector of electrospinning, the crossflow nano-fibrous membrane setup could be obtained easily, which was able to achieve efficient and continuous oil-water separation. Water was collected in the outer cylinder, while oil was collected via the middle iron pipe. The membrane possessed super-hydrophilicity and underwater super-oleophobicity, which enabled the efficient oil-water separation, and the cross-flow design of the membrane also allowed continuous separation process. This investigation of bio-mimic designing and fabricating of nano-fibrous membrane for continuous and efficient oil-water separation provided great insights for water purification and water collection in different areas.

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Conflicts of interest

There are no conflicts to declare.

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Figure 1 Crossflow filtration in manta ray gills and bioinspired silk fibroin membrane. (a) Illustration of crossflow filtration in fish gills. (b) Gill structure of the manta rays. (c) Bioinspired electrospun silk fibroin membrane. (d) Illustration of bioinspired crossflow oil-water separation.

Figure 2 Characterization of electrospun silk fibroin membrane. (a)(b) FESEM images of nano-fibrous silk fibroin membrane. (c) FTIR image of the membrane. (d) TGA image of the membrane.

Figure 3 Contact angle of nano-fibrous silk fibroin membrane. (a) Water contact angle in air. (b) Oil contact angle in water.

Figure 4 Oil-water separation test of nano-fibrous silk fibroin membrane. (a) Separation setup. (b) Feed oil-water mixture. (c) Permeate water. (d) Separation efficiency of six types of oil (99.96% for olive oil-water mixture, 99.92% for silicone oil-water mixture, 99.96% for hexane-water mixture, 99.97% for vegetable oil-water mixture, 99.91 for diesel-water mixture and 99.91% for engine oil-water mixture).

Figure 5 (a) Schematic of the radially arrayed nanofibers for oil droplet self-transportation. (b) Separation efficiency over time. (c) Separation efficiency over permeate volume.