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Underwater Self-Cleaning Scaly Fabric Membrane for Oily Water Separation

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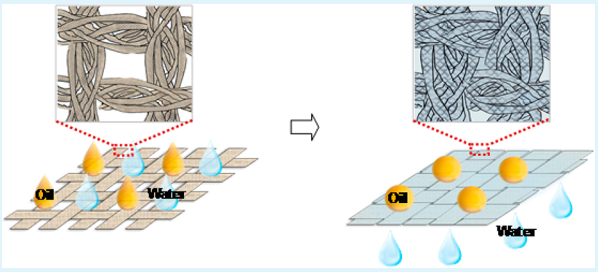
Supporting Information

ABSTRACT: Oily wastewater is always a threat to biological and human safety, and it is a worldwide challenge to solve the problem of disposing of it. The development of interface science brings hope of solving this serious problem, however. Inspired by the capacity for capturing water of natural fabrics and by the underwater superoleophobic self-cleaning property of fish scales, a strategy is proposed to design and fabricate micro/nanoscale hierarchical-structured fabric membranes with superhydrophilicity and underwater superoleophobicity, by coating scaly titanium oxide nanostructures onto fabric microstructures, which can separate oil/water mixtures efficiently. The microstructures of the fabrics are beneficial for achieving high water-holding capacity of the membranes. More importantly, the special scaly titanium oxide nanostructures are critical for achieving the desired superwetting property toward water of the membranes, which means that air bubbles cannot exist on them in water and there is ultralow underwater−oil adhesion. The cooperative effects of the microscale and nanoscale structures result in the formation of a stable oil/water/solid triphase interface with a robust underwater superoleophobic self-cleaning property. Furthermore, the fabrics are common, commercially cheap, and environmentally friendly materials with flexible but robust mechanical properties, which make the fabric membranes a good candidate for oil/water separation even under strong water flow. This work would also be helpful for developing new underwater superoleophobic self-cleaning materials and related devices.



KEYWORDS: *superwetting, underwater superoleophobic, scaly, micro/nanoscale hierarchical structure, water/oil separation*

INTRODUCTION

The frequent occurrences of oil spills and increasing industrial oily water and chemical leakage have become major environmental problems, which always pose a threat to biological and human safety, so that there a worldwide challenge to find solutions.[1−3] How to separate oily wastewater effectively has always been the goal for us. The development of interface science, especially with respect to the special surface wettability of liquid/air/solid, liquid/liquid/solid, and even liquid/liquid/air/solid interfaces, has brought hope of solving this serious problem.[4−13] Through rational design of surface structure and chemical composition, more and more multifunctional materials with special wettability have been fabricated and developed for oily wastewater separation.[14−23]

By constructing the materials' surfaces with superhydrophobicity and superoleophilicity simultaneously, "oil-removal" type materials, such as organic polymer materials,[24−31] inorganic materials,[32−36] and other organic/inorganic hybrid materials,[37−42] have been developed for oily wastewater separation. However, these "oil-removal" materials membranes are easily fouled, blocked up and even damaged by oils because of their intrinsic oleophilicity, resulting in a quick decrease in separation efficiency, flux, and membrane life, and even secondary pollution. These drawbacks have dramatically limited their practical applications for mass production. Considering the practical applications, superoleophobic and superhydrophilic material surfaces may be more suitable for effective oily wastewater separation and long-term use, although oleophobic surfaces are often hydrophobic because of the water surface tension being higher than that of oil in air.[8−10] Recently, material surfaces with underwater superoleophobicity have been proposed and investigated.[43−47] Polymer and hydrogen-coated materials were broadly applied to achieve superhydrophilic and underwater superoleophobic characteristics, and the "water-removal" method has been developed for effective water and oil separation based on these character-

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istics.[48−57] Despite much progress in this field, some of these polymeric materials are vulnerable under severe environmental conditions, which can cause them to fall off the substrate due to their characteristic of swelling in water and/or metamorphosis of the polymeric membrane under long-term scouring by water, thus resulting in the reduction of flux and membrane life. From a practical perspective, new strategies to realize stable, efficient, and antifouling water and oil separation membranes through economical, practical, and facile approaches are highly desirable.

To design superhydrophilic and underwater superoleophobic oil/water separation membranes, the size of the surface porosity and the water capture capacity are two important factors.[48,49] A suitable pore size can effectively separate oil/water emulsions,[26,52] and high water capture capacity can maintain the stable underwater superoleophobicity of the membranes and high breakthrough pressure. Natural fabrics such as cotton fabrics can absorb and hold large amounts of water, which makes us comfortable when we wear cotton clothes on hot days, but the water absorption rate of the fabrics is not very fast. In the meantime, fish are resistant to being contaminated by plankton or endangered around oil pollution areas at sea, because of the underwater self-cleaning property of their scales.[43] The special structures of fish scales with fast-spreading superhydrophilicity and underwater superoleophobicity are critical for their self-cleaning property.

Inspired by the high capacity for capturing water of the natural cotton fabrics and the self-cleaning fish scales, herein, we report a strategy to fabricate superhydrophilic and underwater superoleophobic micro/nanoscale hierarchical-structured fabric membranes by coating scaly titanium oxides onto the fabrics, which can efficiently separate oil/water mixtures. The micro/nanoscale hierarchical-structured membranes can absorb water quickly owing to the superwetting property of the scaly nanostructured titanium oxide, and have high water-holding capacity due to the microstructure of the fabric fibers and their spacing, which lead to the formation of a stable triphase interface in the fabrics with a robust underwater self-cleaning property. This work provides an effective strategy for oil/water separation and would be beneficial for accelerating the treatment of oily wastewater.

EXPERIMENTAL SECTION

Preparation of the Scaly Titanium-Oxide-Coated Fabric Membranes with Micro/Nanoscale Hierarchical Structures. A sol−gel method was used to coat scaly nanostructured titanium oxide on cotton fabrics (purchased from the Qingdao Hengye Textile Co., Ltd.). The fabrics grown with the titanium oxide membranes were prepared through being soaked in a titanium-oxide−ethanol sol−gel solution. First, tetrabutyl titanate solution was prepared by dissolving tetrabutyl titanate in ethanol in a volume ratio of 1:5, respectively, and some glacial acetic acid was added into the solution to ensure that its pH was ∼5. Then, a solution prepared from ultrapure water and ethanol with a volume ratio of 1:1 (with the volume of the ultrapure water as five times that of the tetrabutyl titanate mentioned above) was slowly poured into the tetrabutyl titanate ethanol solution under stirring. After mixing, the solution was aged for 48 h under seal at room temperature, and then the titanium oxide sol solution was prepared. Next, a piece of fabric was soaked after plasma treatment in the titanium-oxide−ethanol sol solution for 2 h. Finally, the fabrics were coated with the titanium oxide sol by dip-coating three times and were dried at 60 °C for 2 h, completing the preparation of the micro/nanoscale hierarchical-structured scaly titanium-oxide-coated fabric membranes.

Instruments and Characterization. Scanning electron microscope (SEM) images were collected using a JEOL JSM-6700F SEM at 10.00 kV. Contact angles (CAs) were measured on a Dataphysics OCA20 CA system at room temperature. A 3 μL water droplet (surface tension, γ_{LV} = 72 mN m^{-1}) or oil droplet was used in all the water/oil CA measurements. The CA value was obtained by averaging the CAs at five different positions. The oil adhesion forces were measured according to the literature.[48] Gasoline was taken as an example for oil detection. The pore sizes of the wetted and dried fabrics were measured from photographs taken with an optical microscope (UM200i of Chongqing UOP Photoelectric Technology Co., Ltd.).

RESULTS AND DISCUSSION

Fabrication and Static Wetting Behavior of the Scaly Fabric Membranes. To achieve self-cleaning membranes for effective oil/water separation, a special functional material membrane with stable superhydrophilic and superoleophobic properties is necessary. The scaly titanium-oxide-coated fabric surface with micro/nanoscale hierarchical structures is a good candidate for this purpose, because titanium oxide exhibits superhydrophilicity with fast water-spreading velocity, and the natural fabrics have good water capture capacity. In this study, we first grew the scaly titanium oxide on the fabric surface after plasma treatment. The scanning electron microscope (SEM) images show that the titanium oxide is well coated on the fibers of the fabric and that micro/nanoscale hierarchical structures are formed in the titanium-oxide-coated fabrics, which are composed of intrinsic microscale holes (with pore sizes of 40−80 μm), microscale strips (with diameters 10−20 μm), and the scaly nanoscale titanium oxide membrane (with thickness of 60−200 nm) on the strips (Figure 1a−d). The micro/nanoscale hierarchical structures have a great influence on the wettability property, i.e., the micro/nanoscale structures can enhance both the hydrophilic and the underwater oleophobic properties of the fabrics. For the original fabrics in air, the fabric surface is temporarily hydrophobic to a water droplet to some extent, with a CA of ∼136° (Figure 1e), because of some natural impurities such as pectin, waxy substances, and fats on the cotton fibers; the fabric surface is superoleophilic to an oil droplet, with a CA of ∼0° (Figure 1f), whereas either a water droplet or an oil droplet can spread on the titanium oxide-coated fabric membrane with CAs of ∼0° in air (Figure 1g), although the fabric membrane surface underwater is superoleophobic to an oil droplet with a CA of ∼165° (Figure 1h). The results indicate that the titanium-oxide-coated fabric membrane is superhydrophilic and underwater superoleophobic. The wettability of the fabric surface has noticeably changed from unstable temporary hydrophobicity to superhydrophilic after it is coated with titanium oxide, since the water droplet can soak into the titanium-oxide-coated fabric very quickly and prevent oil fouling (Figures S1 and S2 in the Supporting Information).

Dynamic Wetting Behavior of the Scaly Fabric Membranes. The dynamic wetting behaviors of water and oil on the scaly titanium-oxide-coated fabric membranes play a critical role in the process of water and oil separation. As mentioned above, the titanium-oxide-coated fabric membranes are both superhydrophilic and superoleophilic in air, but the water and oil spreading speeds on the fabrics vary widely. The measurement results for the water and oil spreading speeds on the fabrics show that a water droplet spreads completely on the titanium-oxide-coated fabric membrane surface within 100 ms after the water droplet comes into contact with the coated fabric membrane (Figure 2a), whereas the required time for an oil droplet to completely spread on the same fabric surface is up

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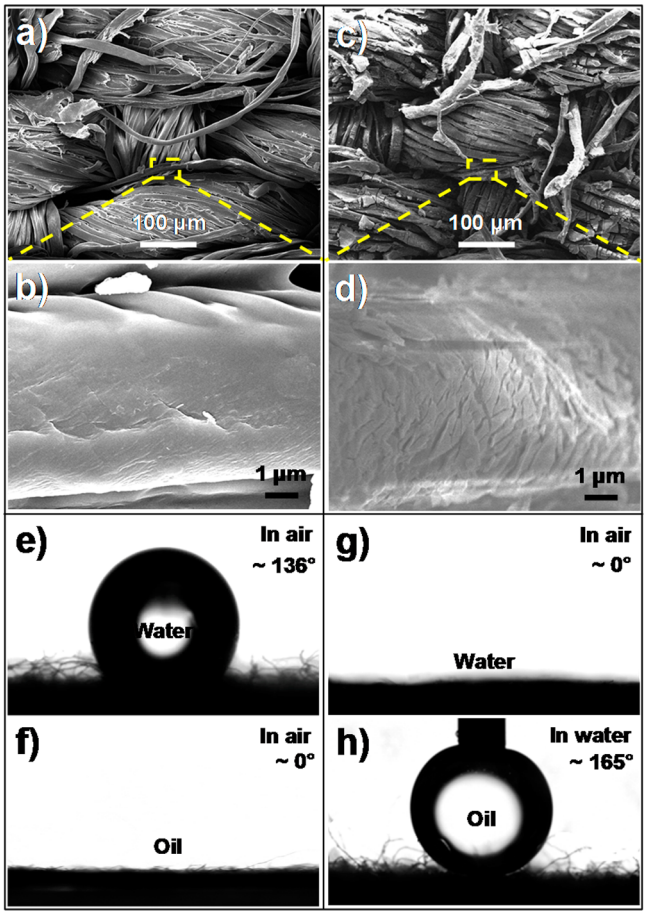

Figure 1. Scanning electron microscope (SEM) images and contact angle (CA) images of the fabrics. Low-magnification and magnified SEM images of (a, b) original cotton fabric and (c, d) titanium-oxide-coated fabric membrane. The SEM images show that the micro/nanoscale hierarchical structures of the titanium-oxide-coated fabric membranes are composed of microscale holes, microscale diameter strips, and nanosized scales on the strips. Photographs of a liquid droplet on the original fabric in air: (e) water with a CA of ~136°; (f) oil (gasoline) with a CA of ~0°. Photograph of a liquid droplet on the titanium-oxide-coated fabric membrane: (g) water with a CA of ~0° in air; (h) oil (gasoline) with a CA of ~165° in water. The results indicate that the titanium-oxide-coated fabric membrane is superhydrophilic and underwater superoleophobic.

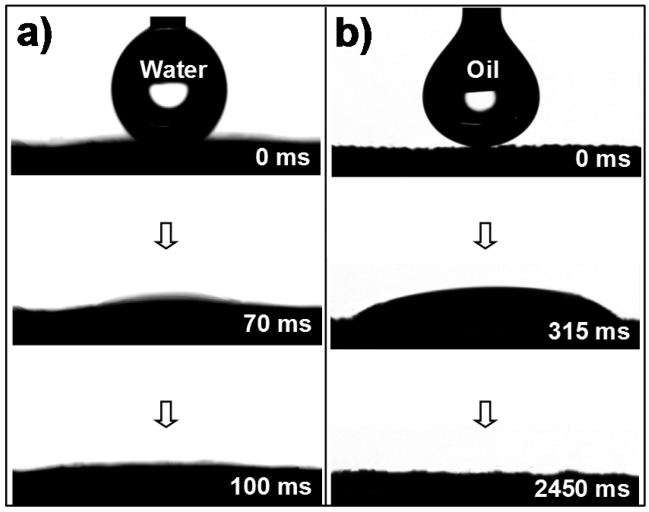

Figure 2. Photographic sequences of a liquid droplet spreading on the titanium-oxide-coated fabric membrane. (a) Water droplet spreads on the titanium-oxide-coated fabric membrane surface completely within 100 ms. (b) The required time for an oil (gasoline) droplet to completely spread on the same fabric membrane surface is up to 2450 ms. The results indicate that water spreading speed is much faster than that of oil on the titanium-oxide-coated fabric membrane.

to 2450 ms after the oil droplet is brought into contact with the coated fabric membrane (Figure 2b). Thus, the water spreading speed is much faster than that for oil on the micro/nanoscale hierarchical-structured titanium-oxide-coated fabric membrane, which provides the chance that water can occupy the entire surface structure of the fabric, and accordingly, robust underwater superoleophobicity of the membrane can be achieved. Further work also demonstrated this. As shown in Figure 3a, the original fabrics with different pore sizes showed similar temporary hydrophobicity to water, whereas all the fabric membranes became superhydrophilic after coating with the scaly titanium oxide. Moreover, the water spreading speed on the titanium-oxide-coated fabric membranes increases with decreasing pore size, which can help us to choose a suitable pore size to achieve superwetting. The underwater–oil CAs, corresponding to the underwater superoleophobicity, also increase with decreasing pore size after the fabrics are coated with scaly titanium oxide (Figure 3b). Thus, the fabrics with average pore size of 84 μm can meet the conditions of both the fastest spreading speed, i.e., superwetting, and the highest oil CA underwater. It is worth noting that the underwater–oil CAs of the original fabrics and the titanium-oxide-coated fabric membranes with different pore sizes show that the oil CAs of the original fabrics are lower than on the titanium-oxide-coated fabric membranes, because there are many air bubbles on the original fabrics and oil can partly intrude into the structure of the fabrics, so that these fabrics have higher oil adhesion and a weaker self-cleaning property (Figures S3 and S4 in the Supporting Information).[8]

To achieve stable superhydrophilic and underwater superoleophobic membranes, the water capture capacity and the pore size of the fabric surface are two important factors. A suitable pore size can effectively release the water and prevent oil penetration, and high water capture capacity can maintain the stable superoleophobicity of the membrane through forming a strong water layer because of the underwater superoleophobicity of the coated fabrics.[48,49] The water-holding capacities of the fabrics with different pore sizes before and after coating with titanium oxide indicate that the water-holding capacity increases with increasing pore size of the fabric, which could be attributed to greater absorption of water by the fabrics with larger pore size, and vice versa (Figure 4a). At the same time, the pore sizes of the titanium-oxide-coated fabric membranes after wetting increases as the original pore size increases (Figure 4b). Among them, there are no apparent holes on the fabric with the pore size of 84 μm after wetting by water. Considering these two aspects, the titanium-oxide-coated fabric membranes with the statistical pore size of 84 μm can meet the requirements of water penetration and stable superoleophobicity for further oil and water separation.

Underwater–Oil Adhesion Property of the Scaly Fabric Membranes. During the water/oil mixture separation process, one of the most important problems is membrane fouling by oil. This problem can be solved by reducing the underwater–oil adhesion on the separation membrane. The

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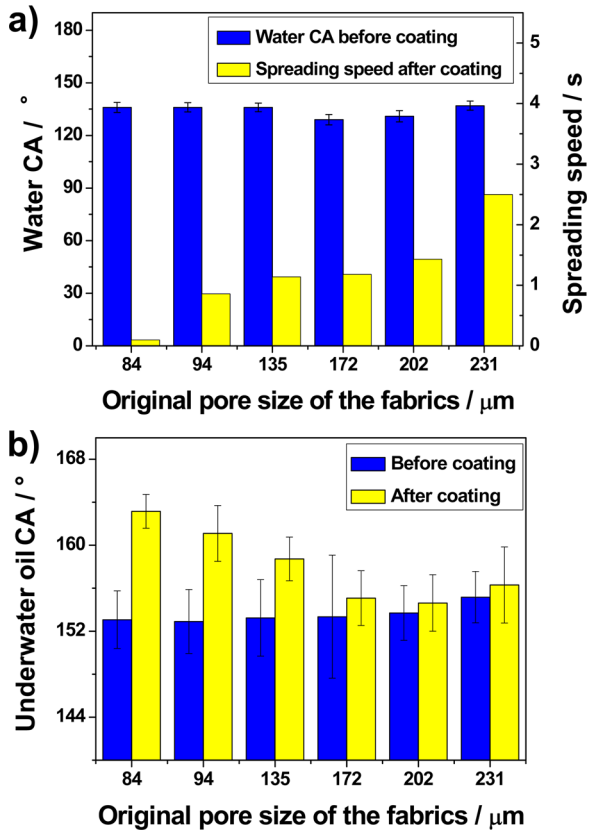

Figure 3. Wettability characterization of the fabrics. (a) Water CAs of the original fabrics and the water spreading speed on the titanium-oxide-coated fabric membranes with different pore sizes. (b) Underwater–oil (gasoline) CAs of the original fabrics for the titanium-oxide-coated fabric membranes with different pore size. Oil CAs on the original fabrics are lower than on the titanium-oxide-coated fabric membranes, because there many air bubbles exist on the original fabrics and oil can partly intrude into the structure of the fabric, so that these uncoated fabrics have higher oil adhesion and a weaker self-cleaning property.

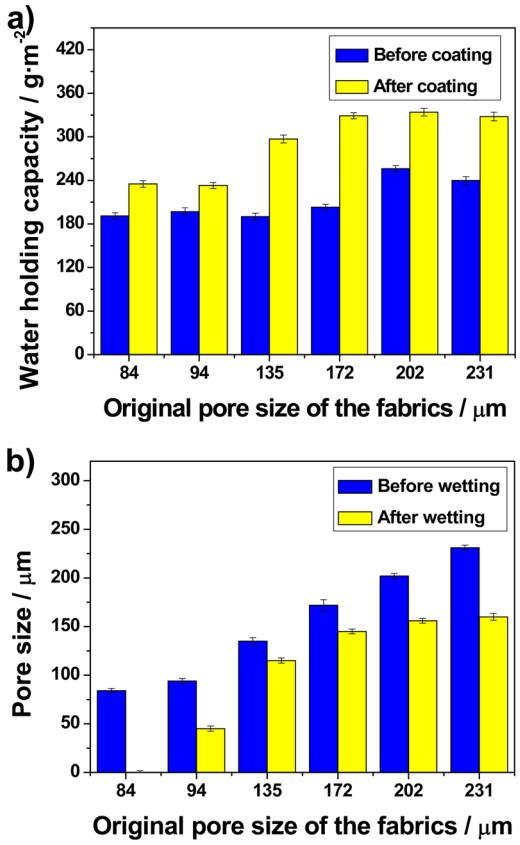

Figure 4. Water capturing ability (through comparing the weights of the wet and dried titanium-oxide-coated membranes) and pore size change of the fabrics. (a) Water-holding capacities of the fabrics with different pore sizes before and after coating by titanium oxide. With increasing pore size of the fabric, the water-holding capacity is increased, which could be attributed to the greater absorption of water by the fabrics with larger pore size, and vice versa. (b) Pore sizes of the titanium-oxide-coated fabric membranes before and after wetting. The thickness of all the fabrics is about 25 μm.

scaly nanostructures provide the possibility of achieving a self-cleaning underwater superoleophobic surface with low oil adhesion. To illustrate the oil adhesion of the titanium-oxide-coated fabric membranes in water, we investigated the oil-adhesion force–distance curves of the fabrics with the original pore size of ~84 μm. In the oil-adhesion force measurement process, an oil droplet was brought into contact with the membrane, pressed down, and left on the surface of the titanium-oxide-coated fabric membrane to move at a constant speed of 0.005 mm s^{-1} (Figure 5a). If we take the oil adhesion force of a 5 μL droplet of gasoline as an example, the adhesion force of the oil droplet on the coated fabric membrane changes with different droplet pressing distances (0–0.4 mm). The testing results indicate that the oil droplet adhesion force of the titanium-oxide-coated fabric membrane increases from ~1 to ~6.5 μN when the droplet pressing distance increased from 0 to 0.4 mm. The oil droplet adhesion force is less than 7 μN, even when the droplet pressing distance is up to 20% of the diameter for an oil droplet (Figure 5b). Therefore, the scaly titanium-oxide-coated fabric membranes have low underwater–oil-adhesion force characteristics, which can slow down fouling of the membrane. As a result, the self-cleaning property of the fabric membranes can lengthen the functional fabric life for separation and maintain the separation velocity and flux.

Oil/Water Separation of the Scaly Fabric Membranes.

To test the oily water separation capability of the micro/nanoscale hierarchical-structured titanium-oxide-coated fabric membranes, three types of oil/water mixtures (gasoline/water, liquid paraffin/water, and soybean oil/water) that stand for the main oily wastewater problems of the industrial, chemical, and food industries, respectively, were used in the separation experiment. A schematic diagram of the water/oil mixture separation process is shown in Figure 6. In this separation process, the titanium-oxide-coated fabric membrane is saturated with water before being fixed under a glass funnel. The reason for the saturation of the coated fabric membrane is to ensure the accuracy of the separation efficiency and the success of the separation. The oil/water mixtures are prepared through stirring the oil and water (e.g., gasoline as oil, with the gasoline content 30 wt %) for 6 h under sealed conditions with an oil droplet diameter of ~20 μm, which is between an emulsion and liquid stratification. When the oil/water mixture is poured straight into the setup, water goes through the coated fabric membrane quickly and is separated into the receiving container, while oil stays over the fabric membrane. Thus, the oil and water mixture is separated successfully, and the separation efficiency of the three types of oily water is very high. Even the separation efficiency of edible oil in water, which is difficult to

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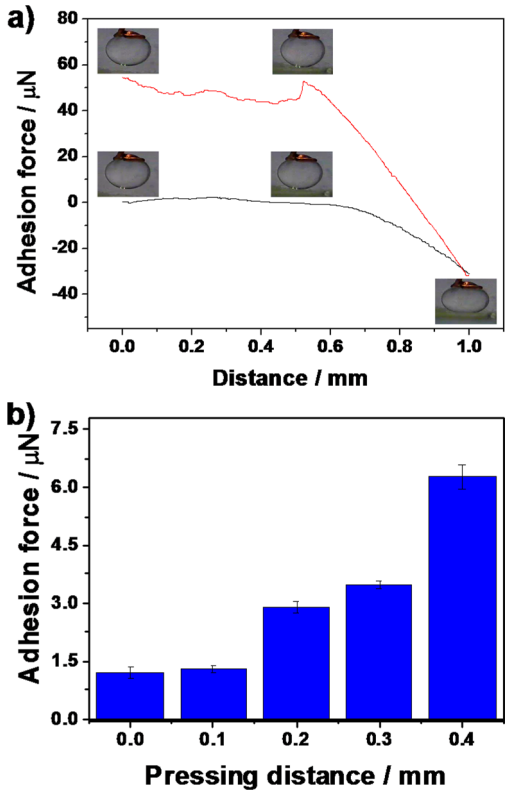

Figure 5. Underwater−oil adhesion measurement of the titanium-oxide-coated fabric membrane with a pore size of 84 μm. (a) Force−distance curve of the underwater−oil (gasoline) droplet adhesion force on the micro/nanoscale hierarchical-structured titanium-oxide-coated fabric membrane. The red and the black lines are the pressing and relaxing process, respectively. Insets are photographs of the corresponding states of the pressing droplets during the testing process. (b) The adhesion force of the oil on the titanium-oxide-coated fabric membrane changes with different pressinging distances of the oil (gasoline) droplet. The results indicate that oil droplet adhesion force of the titanium-oxide-coated fabric membrane is less than 7 μN, even when the pressing distance is up to 20% of the diameter of an oil droplet.

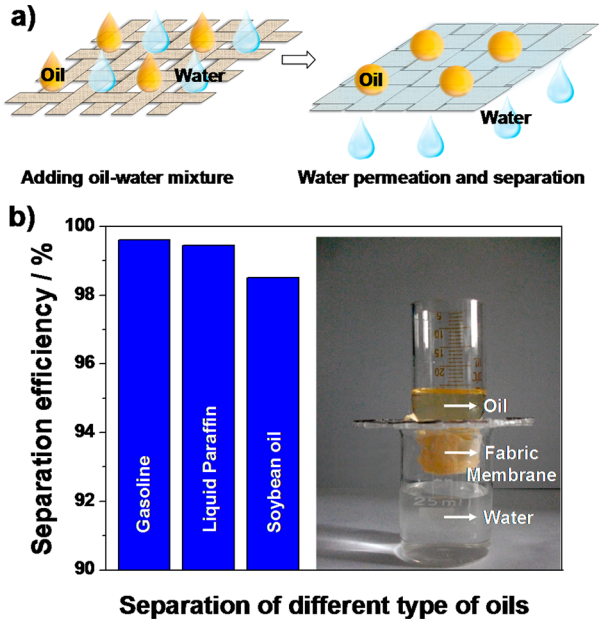

Figure 6. Schematic diagrams of the water/oil mixture separation and the separation results. (a) When the mixture of oil and water (e.g., gasoline as the oil with content of 30 wt %) is poured into the setup, the water goes quickly through the coated fabric membrane and is separated into the receiving container, whereas oil stays over the coated fabric membrane. (b) The oil separation efficiency of the three different types of oils is very high. Inset is the water/oil separation experimental setup.

separate, is higher than 98.5% (The separation efficiency is detected through comparing the weight of water before and after separation.) This oil/water separation process is driven solely by gravity for superhydrophilicity and underwater superoleophobicity. The fast spreading of water and easy saturation that are important features of the titanium-oxide-coated fabric membranes promote the rapid separation of water/oil mixtures with water penetration flux of 4.72 L s^{-1} m^{-2}, which is much faster than for the original fabrics with water penetration flux of 0.95 L s^{-1} m^{-2} after wetting. The water penetration flux is obtained by calculating the volume of the penetration water through a certain size of the coated fabric membrane within a certain period of time and doing this several times. The results indicate that the oil and water separation based on the scaly titanium-oxide-coated fabric membranes is very efficient and promising for application in practical oily wastewater treatment. Moreover, because many oxygen vacancies exist on the surface of the TiO_2, which cause the exposure of Ti ions, the −OH and −C−O−C− groups, which are the main groups of cellulose (raw material of the cotton fabric) can easily coordinate with Ti ions to steadily anchor the titanium oxide onto the cellulose surface.[58] The strong interactions between the substrate and the TiO_2 coating make the fabric membrane stable and resistant to significant performance degradation, even after 100 cycles. Although the water CA of the titanium-oxide-coated membranes would increase after long-term storage, this problem can be solved through an ultraviolet (UV)-irradiation process because the titanium oxides can become more hydrophilic under UV-irradiation, and this can ensure that the membranes keep their favorable separation efficiency after long-term storage.[59]

Mechanism of Oil/Water Separation for the Scaly Fabric Membranes. To further understand the oil/water mixture separation mechanism of the micro/nanoscale hierarchical-structured titanium-oxide-coated fabrics, the microscopic water and oil wetting states of the fabrics before and after coating with titanium oxides are modeled in Figure 7. In the dry state, the fabrics before and after coating with titanium oxide have similar pore structure and size, and the fiber strips are similar except for the scaly nanostructured titanium oxide on the fabric membrane (Figure 7a, b). When the fabrics are fully wetted by water, the fabrics before and after coating with titanium oxide can both absorb and hold some quantities of water, which lead to the expansion of the fabrics. The original fabrics need a very long time to be wetted because of their temporary hydrophobicity, which can form some air bubbles on the fabrics underwater (Figure 7c and Figure S5a in the Supporting Information). Because the scaly titanium-oxide-coated fabrics are superhydrophilic, water spreads quickly on the fabric membrane, and there is almost no pore structure in the fabrics, because the microstructures of the fabric membrane are full of water and air bubbles cannot exist on them in water (Figure 7d and Figure S5b).[8] When the water/oil mixture is poured onto the fabric membrane, the superhydrophilic scaly titanium-oxide-coated fabric can absorb water and be quickly

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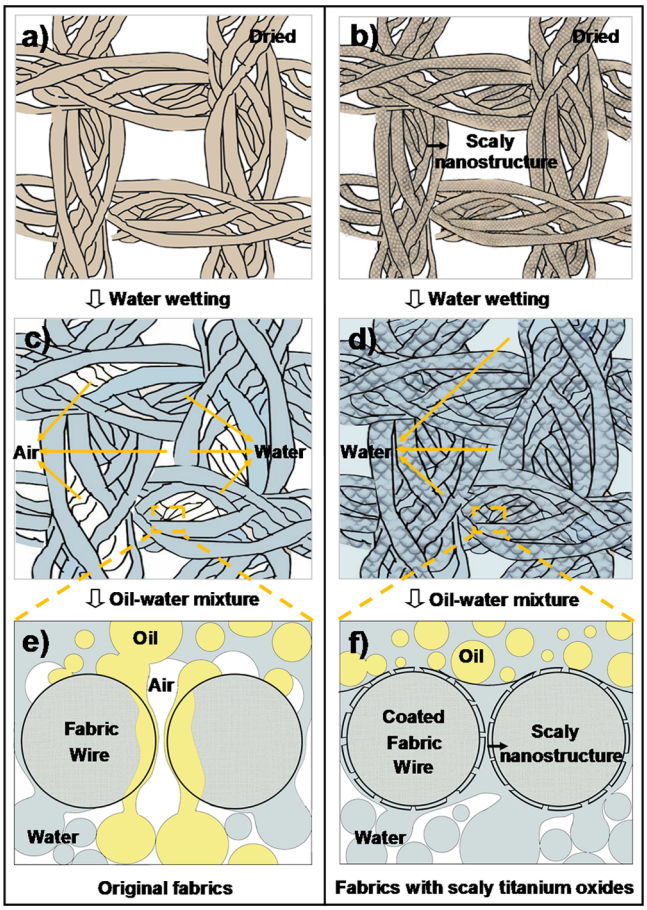

Figure 7. Schematic wetting mechanism diagrams of the water/oil mixture separation based on the micro/nanoscale hierarchical-structured titanium-oxide-coated fabrics. (a, c, e) Original fabrics. (b, d, f) Titanium-oxide-coated fabric membranes. (a, b) Dry fabrics. (c, d) Wetted fabrics. The results indicate that the scaly nanostructured titanium oxide membrane is superhydrophilic, so that water can spread on the fabric membrane quickly and there are almost no air bubbles on the fabric, while the original fabric needs a much longer time to be wetted because of its temporary hydrophobicity, which can lead to some air bubbles on the fabric underwater. (e, f) Cross-sectional views of of original and coated fabrics in the process of oil/water separation. When the water/oil mixture is poured onto the fabric membrane, the scaly fabric membrane can absorb water and be saturated quickly in all the contact areas before the oil can wet the membrane, so that the water goes through the membrane quickly, while the oil stays over the membrane because of the stable superoleophobicity in water. Thus, the scaly titanium-oxide-coated fabric membranes can separate the oil/water mixture effectively. In the case of the original fabrics, however, some air bubbles are present on the fabrics underwater, so the oil can wet the fabrics where there are air bubbles and penetrate through these areas owing to the superoleophilicity of fabrics in air. During the oil/water competitive wetting process, both the oil and the water can wet and penetrate the original fabrics, so the fabrics could not separate the oily water effectively.

saturated by the water in all the contact areas before the oil can wet the coated fabric membrane, resulting in a stable triphase interface. Thus, water goes through the coated fabric membrane quickly because of the microstructured fabric fibers and their spacing, whereas the oil stays over the coated fabric membrane because of the scaly nanostructured titanium-oxide-induced stable underwater superoleophobicity, so that the micro/nanoscale hierarchical-structured titanium-oxide-coated fabric membrane can separate the oil/water mixture effectively. In the case of the original fabrics, however, some air bubbles still exist on the fabric underwater and form an unstable four-phase interface, so that oil can wet the fabric areas with air bubbles and penetrate through these areas because of the superoleophilicity of the fabric in air.[8] During the process of oil/water competitive wetting of the fabrics, both the oil and the water can wet and penetrate the original fabric, so that the fabric could not separate the oil/water mixture effectively (Figure 7e, f and Figure S6 in the Supporting Information). Therefore, successful oily water separation can be achieved only through the micro/nanoscale hierarchical-structured titanium-oxide-coated fabric membranes, which also have an underwater self-cleaning property due to the underwater superoleophobicity with ultralow adhesion.

CONCLUSIONS

In summary, inspired by the water capturing capacity of natural cotton fabrics and self-cleaning fish scales, a strategy was proposed to design and fabricate micro/nanoscale hierarchical-structured fabric membranes with superhydrophilicity and underwater superoleophobicity by coating scaly titanium oxide onto the fabrics, which can efficiently separate oil/water mixtures. The special micro/nanoscale hierarchical structures of the fabric membranes are critical for the separation process because such structures can enhance the hydrophilicity and underwater oleophobicity. The scaly titanium oxide nanostructures can make the fabric membranes absorb water quickly, i.e., superwetting. With the intrinsic high water-holding capacity of the microstructures of the fabrics, the scaly titanium-oxide-coated fabrics can be saturated by water completely, i.e., air bubbles cannot exist on the membrane in water, and a stable oil/water/solid triphase interface is formed. On the other hand, the ultralow underwater−oil adhesion force results in a robust self-cleaning property. Therefore, with the superwetting and the underwater oleophobic self-cleaning property, these membranes are suitable for the separation of different oil/water mixtures. Moreover, the natural fabrics, not limited to cotton, bamboo fiber, and hemp fabrics, are common, commercially cheap, and environmentally friendly materials with flexible but robust mechanical properties, which make the fabric membranes a good candidate for oily wastewater separation, even under strong water flow. This work would also be helpful for the design and application of new underwater superoleophobic self-cleaning materials and related devices.

ASSOCIATED CONTENT

Supporting Information

Photographs of the fabrics after immersion in water for different times before and after titanium oxide coating. Wetting state of the titanium-oxide-coated fabric membrane in the water/oil interface. Photographs of the water wetting states on the fabrics. Sequence of oil (gasoline) wetting of fabric area with an air bubble on the original fabric. Optical microscope images of the water-saturated fabrics. Photographs of the oil/water mixture separation based on the original cotton fabric after water saturation. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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