A Hierarchically-Nano Structured TiO_2-Carbon Nanofibrous Membrane for Concurrent Gravity-Driven Oil-Water Separation

Ming Hang Tai, Peng Gao, Benny Yong Liang Tan, Darren D. Sun, and James O. Leckie

Abstract—**A membrane with selective wettability and excellent thermal and chemical stability is required for effective oil-water separation. In this work, a novel TiO_2 nanosheet-anchored carbonnanofibers fabricated by using solvothermal method is presented. The hierarchical TiO_2 micro/nanostructure that grows on the surface of carbon nanofibers renders the membrane superhydrophilic and underwater superoleophobic. Coupled with the characteristic of high porosity and micron-scale pore size, the membrane is capable of separating oil from water by gravity. Thermal analysis show thatthe oil-water separation efficiency is greater than 99%. Furthermore, the membrane has an oil breakthrough pressure up to 3.63m which is the highest breakthrough pressure ever reported. Stability test indicates that the membrane is stable in ultrasonic, thermal and extreme pH conditions. Without compromising the separation efficiency, a permeate flux of 400-700L/m^2-hr can be achieved.**

Index Terms—**Carbonnanofiber, electrospinning, oil-water separation, titanium dioxide.**

I. INTRODUCTION

An efficient and cost-effective oil-water separation is of important issue in wastewater and water cleaning process due to the increasingly stringent regulations. Membrane-based separation [1]-[6] has been recently emerged as one of the alternatives to conventional oil-water separation methods such as skimming [7], gravity separation [8], and physical sorption [9]-[12]. However, membrane that is oleophilic and hydrophobic is easily prone to oil-fouling and a hydrophilic membrane is often permeable to both oil and water.

To resolve this problem, a membrane surface has to be modified toimpart hydrophilic (or superhydrophilic) and oleophobic (or superoleophobic) characteristics. This can be achieved through build-up of re-entrant surface texture in conjunction with roughness enhancement and hydrophilic modification [13]. Although many techniques such as in-situ polymerization [14]-[15], spray coating [16], layer-by-layer deposition [17]-[18], and etching [19]-[20] have been developed to manipulate the surface wettability of a substrate (mesh, membrane etc), only a few literatures reported solvothermal method [21], [22] which has been frequently used to synthesize hierarchically structured materials. This is so probably because solvothermal method involves high temperature and high pressure that is detrimental to the membrane, especially for polymeric membrane.

Carbonaceous materials such as carbon nanofibers are well known for their excellent mechanical and thermal stability property. Hence, they are able to withstand high temperature and pressure. A number of literatures [23], [24] have reported the growth of TiO_2 onto carbon fibers through hydrothermal method. Nevertheless, to the best of our knowledge, the growth of TiO_2 onto a free-standing carbonaceous membrane via solvothermal method for purpose of oil-water separation has yet to be demonstrated. The objective of the present work is to fabricate a TiO_2 nanosheet-anchored carbon nanofibrous membrane by using solvothermal method and explore its potential in oil-water separation.

II. MATERIALS AND METHODS

A. Preparation of Electrospun Carbon Nanofibrous Membrane

A precursor solution containing 7wt% polyacrylonitrile (PAN), 0.5wt% tetraethylorthosilicate (TEOS), dimethylformamide (DMF), and acetic acid was electrospun. During the process, the PAN nanofibers were self-assembled into a membrane. Subsequently, the PAN nanofibrous membrane was stabilized at 280 ℃ in air followed by carbonization at 900 ℃ in N_2 atmosphere. The holding time for both stabilization and carbonization is 2 hours.

B. Preparation of TiO_2 Nanosheet-Anchored Carbon Nanofibrous Membrane

DMF was first mixed with isopropyl alcohol (IPA) for 30 min. Subsequently, tetrabutylorthotitanate(TBOT) was added into the mixture and stirred for another 20 min. The volume ratio of DMF:IPA:TBOT was 1:1:0.067. The final mixture was then transferred into a Teflon-lined autoclave containing the carbon fibrous substrate and heated in an oven at 180 ℃ for 20 hrs. The final product was collected and washed thoroughly with ethanol to remove remnant TiO_2. Lastly, the product was dried overnight at 60 ℃.

C. Preparation of Oil-Water Mixture

Four types of oils (hexadecane, vegetable oil, olive oil and used pump oil) were selected. The emulsions were prepared by mixing water and oil in a volume ratio of 9:1. 6 drops of Triton X-100 were subsequently added to stabilize and to produce a milky mixture.

D. Gravity-Driven Separation Experiment

The as-prepared membrane, with effective surface area of

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$1.018\times10^{-3}m^2$, was sandwiched between a funnel and a volumetric flask. The mixtures were added onto the membrane and the separation was achieved by gravity. The time taken to filter the mixture with known volume was recorded to determine the permeate flux of the membrane.

E. pH and Thermal Stability

The pH of deionized water solutions were adjusted to pH 1, 7 and 14 by using 5M sodium hydroxide or 1M hydrochloric acid. Three pieces of the membrane were then separately immersed into the solutions for 7 days before the subsequent analyses. The membranes' thermal resistance was determined by performing thermo-gravimetric analysis (TGA, Perkin Elmer TGA-7). The sample was heated from 30 ℃ to 900 ℃ at a rate of 10 ℃/min and was immediately cooled down after reaching the pre-determined temperature.

F. Contact Angle Measurement

All the measurements (in air and water) were conducted by using a VCA instrument (AST products inc, Optima series). The measurements were repeated three times at different locations on the sample surface and the results were averaged. For a solid-oil-water system, the measurements were conducted by using DCM as oil. DCM is heavier than water so it sinks in water. Hence, underwater oleophobicity of the membrane could be easily determined by measuring the $CA_{o/w}$ formed between the three-phases (i.e. water, solid and oil).

G. Instrument and Characterization

The characterization of the fabricated membrane was performed by using field emission scanning electron microscopy (FESEM, JEOL JSM-7600F). Transmission electron microscopy (TEM) images were obtained by using a JEOL 2010-H microscope operating at 200kV. The crystal phase of the synthesized TiO_2 were confirmed by X-ray diffraction (XRD, Shimadzu XRD-6000) with monochromated high-intensity Cu Kα radiation (λ=1.5418 Å) operated at 40 kV and 30 mA.

H. Separation Efficiency Estimation

The purity of filtrate after separation was estimated by measuring the thermal loss in weight of water. Typically, a known mass of the filtrate was heated in oil bath from room temperature to 105 ℃ and the temperature was held constant for 1 hr. Note that all oils used in the experiment have boiling points higher than water. To further confirm the results, TGA was conducted. The sample was heated from 30 ℃ to 100 ℃ at a rate of 10 ℃/min and was held constant for 30 mins. We also carried out density measurement to estimate the degree of separation. The density of the filtrate was compared with the density calibration curves which were plotted by using the density of oil-water mixtures containing different oil compositions (0-2 wt%).

III. RESULTS AND DISCUSSION

Fig. 1a) shows the bare carbon nanofibrous membrane prepared by electrospinning. Prior to TiO_2 coating, the fibers are relatively thin with diameter of ~500nm. In addition, the surface has a smooth surface. After coating, as shown in Fig. 1b), the carbon nanofibers are wrapped by assemblies of TiO_2 nanosheets that make the surface very rough. The coating also doubles the nanofiber diameter to ~1μm. TEM observation reveals that the TiO_2 nanosheets wrap around the nanofiber and exhibits a structure similar to core/sheath structure. (Fig. 1c)) The TiO_2 nanosheets densely grown on the nanofiber are in polycrystalline phase.The lattice fringe has an interlayer distance of 0.35nm which can be assigned to the (101) plane in anatase TiO_2. (inset of Fig.1c)) This can be further confirmed by the XRD patterns shown in Fig. 1d). All the diffraction peaks are assigned to anatase TiO_2 (according to the JCPDS card file. 21-1272) except for the small peak at around 32 °that might be due tothe impurity of brookite TiO_2.The wetting behavior of the fabricated membrane was observed by measuring the contact angle in air ($CA_{w/a}$) and oil contact angle in water ($CA_{o/w}$). The results indicate that the membrane has a CAw/a close to zero and $CA_{o/w}$ of ~157 °, manifesting the superhydrophilicity and underwater superoleophobicity property of th membrane. Furthermore, the membrane possesses with high flexibility.As seen in Fig. 1f), the membrane can be bended at an angle of 90 ° without loss of structural integrity. This phenomenon can be attributed to the entanglement of the continuous and flexible carbon-silica nanofibers [25].

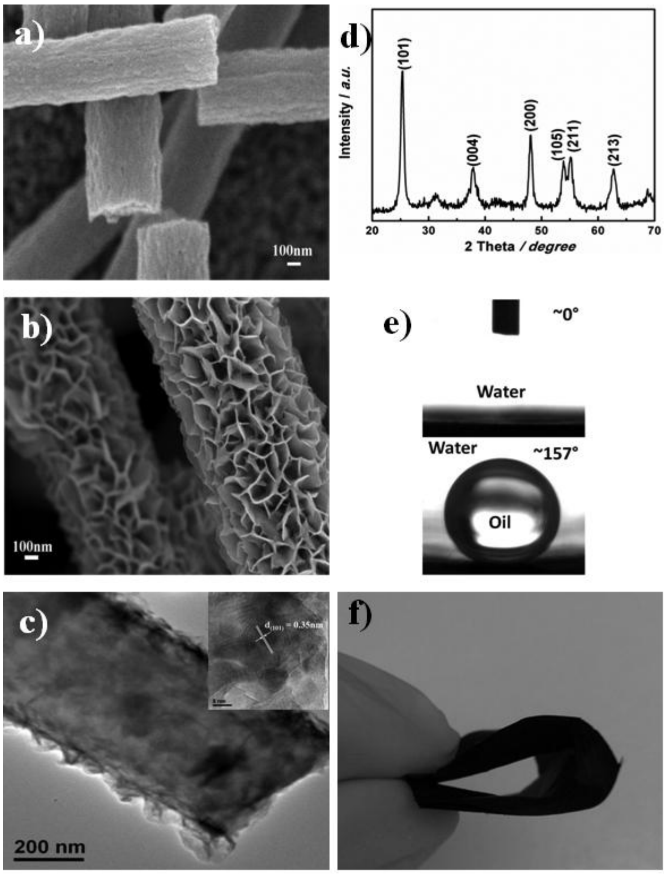

Fig. 1. Characterization of electrospun carbon nanofibrous membrane coated with TiO_2 nanosheets. a) and b) FESEM image of electrospun carbon nanofibers before and after TiO_2 nanosheets coating. c) TEM image showing TiO_2nanosheets are coated onto the surface of carbon nanofibers. d) XRD pattern of TiO_2 nanosheets. e) Photograph of a water droplet on the membrane in air (top) and oil droplet depositing on the membrane in water (Down). f) The digital photograph showing excellent membrane flexibility.

To further examine the wettability of the as-fabricated membrane, the spreading process of a water droplet is recorded by a VCA instrument operated in dynamic mode at a capture speed of 30 frames per second. As shown in Fig.

2a), the membrane shows a high affinity towards water (also due to the strong capillary effect with water) where the water spreads out rapidly at the moment it touches the membrane surface.This incident has resulted in a water contact angle close to zero. The entire wetting process only takes 132ms to complete, suggesting that the membrane is superhydrophilic.

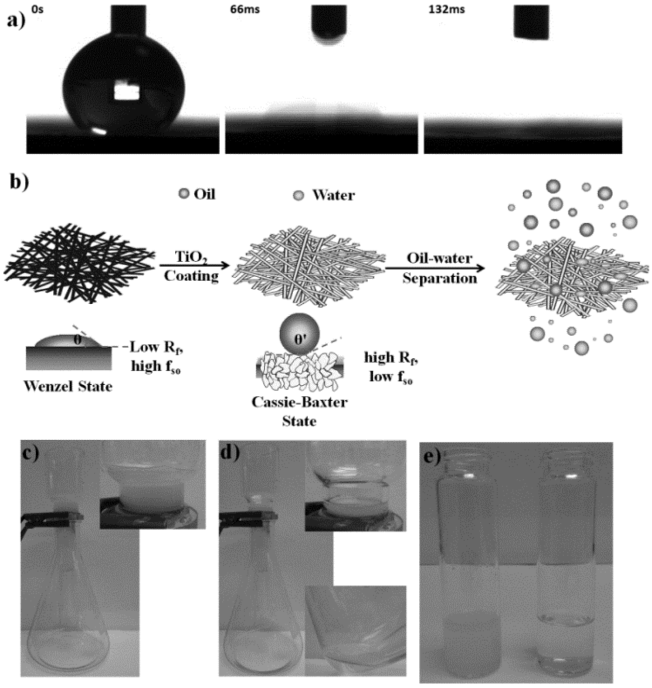

Fig. 2. a) Spreading and permeating process of a water droplet on the membrane. b) Illustration of wetting transition in underwater superoleophobic surface of aTiO_2-coated carbon nanofibrous membrane. Gravity-driven separation of oil-water mixture before c) and d) after separation. e) The oil-water mixture before and after separation.

The membrane also exhibited underwater superoleophobic character with very low adhesion to oil. Whendichloromethane (DCM) was injected onto the membrane that was immersed in methylene blue-dyed solution, we observed that DCM droplets rolled off the surface at highspeed. Themembrane has a tilting angle of ~10 °. We also observed that the DCM droplet could be readily detached from the surface, suggesting that the membrane has low adhesion to oil. This low adhesion to oil is due to the reduced liquid-solid contact area induced by roughened surface and the formation of water layer which will be discussed in the later section. In contrast, DCM droplets seeped into when came into contact with a pure carbon nanofiber membrane.

The change in wetting behavior of the membrane can be explained by the standard Wenzel and Cassie-Baxter model. The pristine carbonnanofibrous membrane with smooth surface is underwater oleophilic. In this case, the surface can be fully-wetted by oil and itfalls into the Wenzel state. However, after coating with TiO_2 nanosheets, the membrane becomes superhydrophilic and underwater superoleophobic. This is due to the micro/nanohierarchical structure arising from the dense array of vertically aligned, interconnected TiO_2 nanosheets thatroughen the surface as well as theintrinsic hydrophilic property of TiO_2. We hypothesized that the membrane with enhanced roughness can then trap water between oil droplet and the surface, yielding an oil-proof surface that prevents water wetting. As a result, the Cassie-Baxter state occurs. Such wetting transition from Wenzel to Cassie-Baxter regime can be described by the Cassie-Baxter model where the contact angle is given by$\cos\theta' = f_{so}(R_f\cos\theta + 1) - 1$, where $\cos\theta'$ is contact angle of oil in water for a rough surface, θ is contact angle of oil in water for a smooth surface, f_{so} is fractional solid-oil area, R_f is non-dimensional parameter of surface roughness. From the aboveequation, one can see that solely increasing the surface roughness is insufficient to change the sign of $\cos\theta$ from positive (oleophilic) to negative (oleophobic). However, it is possible if f_{so} is decreased to an extent that it results in a negative value on the left side in the equation. Therefore, the observed underwater superoleophobicity can be ascribed to the decreased f_{so}. The change in wetting behavior of membrane surface is illustrated in Fig 2b).

To verify the presence of oil-proof surface due to the formation of water barrier, we conducted a wetting test to the membrane with and without TiO_2 nanosheets. In the test, droplets of water was first dropped onto the membranes followed by olive oil. For pristine carbon nanofibrous membrane, we observed that the surface could be wetted by water beforeit contacted with oil. As oil came into contact with the membrane,oil replaced water and the membrane surface was turned into hydrophobic.This suggests that the membrane has a stronger affinity for oil than water. For TiO_2-coated carbon nanofibrous membrane, it exhibits a stronger affinity for water than oil becausethroughout the test, the membrane remained hydrophilic. The oil did not wet the surface and it could be easily washed away by rinsing with water. Hence, it is postulated that as the dry TiO_2-coated membrane contacts with the wetting phase, a liquid layer will beimmediately formed on the surface. This liquid layer serve as a repulsive barrier that prevents the membrane surface from being wetted by the next wetting phase. To verify this postulation, we repeated a similar wetting test where the TiO_2-coated membrane was first wetted by olive oil followed by water. We observed that the membrane became hydrophobic and oleophilic. The subsequent water wetting became unsuccessful. Combined with the earlier discussion, we suggest that the large cavities in the rough surface coupled with the hydrophilic property of TiO_2 facilitate the formation of water layer by trapping water between solid surface and oil droplet. By that, the chance for oil droplet to contact directly with the solid surface is lowered, as depicted in Fig. 2b). The membrane with such wetting behavior can be applied for control separation of oil and water.

Unlike those conventional pressure-driven membranes, we found that the as-fabricated TiO_2 nanosheet-anchored carbon nanofibrous membrane is capable of separating oil from water without applying pressure. For demonstration, free oil and water andoil-in-water mixture were poured into a home-made separation apparatus in which the as-prepared membrane was sandwiched between a funnel and a flask. We observed in both cases that, within a few seconds, the water passed through the membrane by gravity while the oil was retained above the membrane. (Fig. 2c)) Upon water contacted with the membrane, the surface is immediately wetted (as evidenced from the instantaneous water spreading behavior shown in Fig. 2a)) and a water barrier is formed. This incident has created a rough surface that further prevents the wetting of incoming oil. We observed that the oil retained on the membrane surface can be easily washed away by rinsing the membrane with water and the membrane can be reused. This is owing to the fact that the oil has low adhesion with the solid surface. On the contrary, oil retained on a pristine carbon nanofibrous membrane adhered to the surface after separation. Thepristine membrane eventually lost its water permeability and the separation was ceased after the separation was repeated 2-3 times.

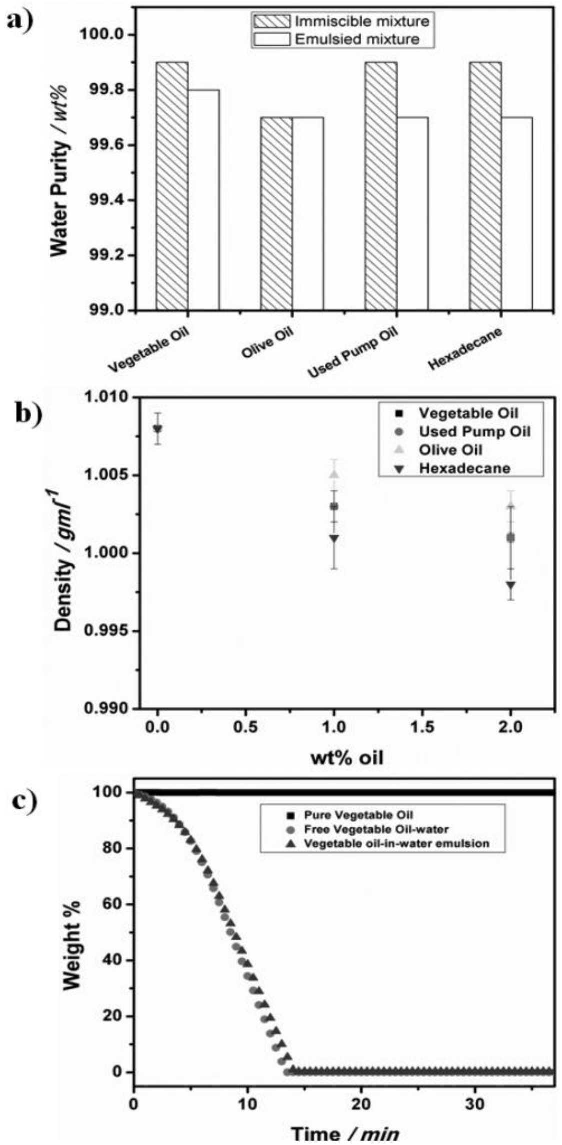

Fig. 3. The performance evaluation of the TiO_2-coated carbon nanofibrous membrane.a) The water purity in the filtrate after permeating a series type of oil-water mixtures through the as-fabricated membrane.b) Density of various oil-water mixtures as a function of oil composition. c) TGA data for the feed and the permeates after separation various mixtures (free water and oil and oil-in-water emulsion.

The separation efficiency of the membrane is characterized by measuring the water purity in the permeate. The water purity was estimated based on the weight loss of the permeateafter heating at 105 ℃.The results show that the permeates from oil-water separation have water purity higher than 99.5%. The water purity percentage of the permeates from the separation of various oils is shown in Fig. 3a). We estimate the separation efficiency by comparing the density of permeates with the density calibration curves. In the curve, different oil compositions (0wt%, 1wt%, 2wt%) in the oil-water mixtures are plotted against the corresponding densities of the mixtures. We measured the density of the permeates from the separation of free vegetable oil-water, olive oil-water, used pump oil-water and hexadecane-water to be 1.006±0.005 g/ml, 1.008±0.002 g/ml, 1.006±0.0004g/ml and 1.007±0.001 g/ml, respectively. Comparing these values with the calibration curves shows that the permeates have oil content significantly lower than 1wt% (Fig. 3b)). To further confirm, TGA was performed by using the permeates obtained from free vegetable oil and water as well as vegetable oil-in-water mixture. Pure vegetable oil was also used for comparison. As seen in Fig. 3b), after heating at 100 ℃ for 30 min, the weight of samples was decreased close to zero percent, revealing that almost all the water was boiled off. The results show that the permeates obtained from free vegetable oil and water and vegetable oil-in-water mixture contain only~0.001wt% and ~0.33wt% vegetable oil, respectively. These experimental results indicate that the membrane can separate oil from water with very high separation efficiency (>99%).

The breakthrough height ($H_{breakthrough}$), defined as the allowable maximum height of the liquid before it permeates through the separation medium, was used to further characterize the separation ability of the membrane. A superhydrophilic and superoleophobic membrane with large pore size usually results in low breakthrough height of oil oreven loss of oil-water separation capability. In practice, oil will gradually accumulate on a separator and exertcorresponding pressure to the beneath layer of wetting phase that could engender the permeation of oil through the membrane. Hence, design of a membrane with high breakthrough height of oil is favorable and more practical. Theoretically, $H_{breakthrough}$ can be obtained by using the relationship: $P_{breakthrough} = \rho g H_{breakthrough}$. To predict $P_{breakthrough}$, the equation derived by Kota *et al.* [26] was used in this work. According to the equation, for a membrane already saturated by the wetting phase, the required $P_{breakthrough}$ for the non-wetting phases is given by $(2R\gamma/D^2)*((1-\cos\theta)$ / $(1+2(R/D)*\sin\theta))$where R is the cylinder radius, γ the interfacial tension between the wetting phase and the non-wetting phase, D the half of the distance between fibers and θ the contact angle of the non-wetting phase on the solid surface. For the case of free olive oil (average density = 860g/ml) and water separation, $H_{breakthrough}$is predicted to be 3.88m ($P_{breakthrough}$=32724Pa) by substituting R=0.5μm, D=0.77μm, γ= 16.42mN/m and θ=152.6 ° into the equation. The D is estimated to be 0.77 μm (or $2D$ = 1.54 μm) based on the rejection efficiency of polystyrene particles by the membrane. Results showed that the membrane is capable of rejecting 96% of 2.061 μmparticles and 72.5 % of 1.025 μm particles basedon the TOC removal result. Hence, the membrane has a pore size range of 1.025 μm< x > 2.061 μm. For calculation, the average pore size (2D) of the membrane is estimated to be (2.061+1.025)/2 ≈ 1.54 μm.For comparison, the $H_{breakthrough}$ is experimentally measured by using free oil and water. We observed that olive oil started permeating through the membrane when a pumping pressure of around 30659kPa (230mmHg) was applied. This indicates that the experimental $H_{breakthrough}$ for olive oil is around 3.63m which closely match the theoretical value. To our knowledge, this isthe highest breakthrough height of oil ever reported. The high $P_{breakthrough}$ value implies that the membrane is highly resistant to pressure perturbations. The small pore diameter is expected to be the major contributing factor. The electrospun membrane used in our work are capable ofrejecting PS particles larger than 2.061μm(up to 96% rejection efficiency), implying that the membrane has small apparent pore size. Further, after TiO_2 nanosheets are grown on the fiber, the spacing between fibers (2*D*) is shortened owing to the increase in fiber diameter (*R*). This is illustrated in Fig. 4. According to Kota's equation, as D becomes smaller and R is larger, a greater $P_{breakthrough}$ will be resulted.

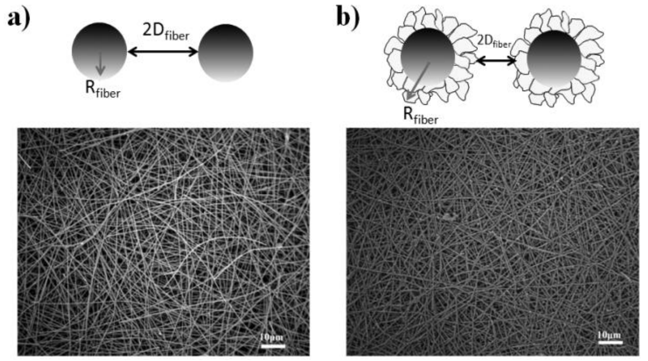

Fig. 4. The effect of TiO_2 coating to the effective fiber radius (R) and intercylinder spacing (2D). a) Before TiO_2 coating, the fiber diameter is approximately 0.5μm and the membrane has larger pore size (smaller R but larger D). b) After TiO_2 coating, the fiber diameter is increased to 1μm and the membrane pore size is considerably reduced (larger R but smaller D).

The chemical stability of the fabricated membrane was examined by investigating its changes with respecttothe structural morphology, permeate flux and surface wettability after immersed in different pH solution. Prior to the analysis, the membranes were separately immersed in solutions with pH of 1, 7, and 14 for 7 days. The membrane immersed in pH7 solution was used as a reference. Interestingly, the membrane is able to sustain a$CA_{o/w}$ above 150 ° after 7-day exposure to strong acid (pH 1) and strong alkaline (pH14) conditions. In addition, the membrane has $CA_{w/a}$ close to zero for all cases (Fig. 5a)). This observation study suggests that the superhydrophilic and underwater superoleophobic character of the membrane can be preserved under harsh chemical conditions. The permeate flux of the membranes was also determined. As seen in Fig.5a, all three membranes maintain high permeate flux between 400-700 L/m^2-hr.These valuesare comparable to other MF membranes reported elsewhere [27], [28]. The variation in permeate flux may be a consequence of the inconsistent membrane thickness. According to Hagen-Poiseuille equation, as the membrane thickness is small, the allowable flux of water permeate through the membrane is higher and vice versa. SEM observation reveals that the average thickness of membrane immersed in pH 1, 7, and 14 is 127.7±5μm, 188.7±5μm, and 124.3±2μm, respectively. This is in good agreement with the permeate flux result. Structurally, the membrane's morphology is also well-preserved. There is no noticeable change in the TiO_2 nanosheets coated on the fiber surface. The surface is remained porous and rough as seen in inset in Fig. 3b). To study the thermal stability of the fabricated membrane, TGA was performed. The result shows that the membrane is stable at a temperature up to 500 ℃ in air (beyond which it starts to degrade). We also investigated the wetting property after the membrane was heated at 500 ℃ in N_2. We found that the value of $CA_{o/w}$ is remained at above 150 °, showing that the membrane wett ability is thermally stable. Furthermore, we also found that the TiO_2 assembly remained stable after 20min ultrasonic irradiation, as seen in Fig. 5b).

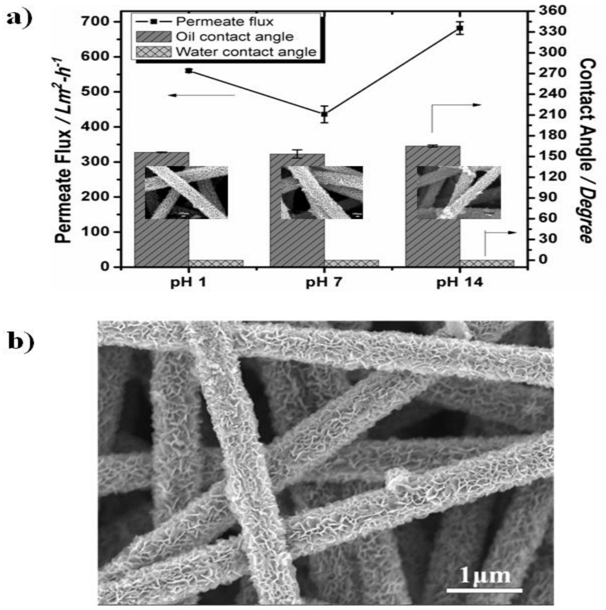

Fig. 5. a) The pH stability of the membranes in terms of permeate flux, water contact angle in air and oil contact angle in water. The inset shows the morphology of the membrane at each pHs. b) FESEM image of TiO_2-coated carbon nanofibrous membrane after ultrasonication for 20 min.

IV. CONCLUSION

In conclusion, by employing solvothermal method, a hierarchically structured TiO_2-carbon nanofibrous membrane was fabricated. The membrane possesses excellent oil-water separation efficiency and high chemical and thermal stability. We envision that this study will inspire the development of more advanced hierarchically-structured membranes for efficient membrane-based separation of oily water.

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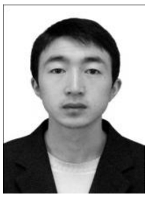

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