Durable Light-Driven Three-Dimensional Smart Switchable Superwetting Nanotextile as a Green Scaled-Up Oil–Water Separation Technology

Zahed Shami* and Parvin Holakooei

ABSTRACT: Stimuli-responsive polymer architectures are attracting a lot of interest, but it still remains a great challenge to develop effective industrial-scale strategies. A single-stage and cost-effective approach was applied to fabricate a three-dimensional (3D) smart responsive surface with fast and reversibly switchable wetting between superhydrophobicity and superhydrophilicity/underwater superoleophobicity properties induced by photo and heat stimuli. Commercially available PVDF and P25TiO2 as starting materials fabricated with a scaled-up electrospinning approach were applied to prepare 3D smart switchable PVDF-P25TiO2 nanotextile superwetted by both UV and solar light that is simply recovered by heat at a reasonable time. The superhydrophilic/underwater superoleophobic photo-induced nanotextile will act in "water-removing" mode in which water quickly passes through and the oil is blocked on the surface. An acceptable recycling, reusing, and superior antifouling and self-cleaning performance arising from a TiO2 photocatalytic effect makes it highly desired in a green scaled-up industry oily wastewater treatment technology. With these advantages, a large-scale industrial production process can be simply simulated by applying a conducting mesh-like collector substrate.

INTRODUCTION

Smart polymer membrane materials with controlled reversible wetting transitions can be highly desired to explore a unique solution for treatment of both oil-polluted water and water-polluted oil from complex sources.1−13 Such a remarkable ability of the controlled surface wettability including superhydrophobic/superoleophilic or superhydrophilic/underwater superoleophobic properties results from a synergistic effect of the chemical composition and the surface geometric structures, and it can be highlighted on the surface roughness.1,14−18 The surfaces with a well-tuned wetting property are considered to be fundamental in applications such as antimicrobial, antifogging, antifouling, and self-cleaning as well as oil-repelling performance required for an oil–water separation technology.4,10,19−21 Practically, self-cleaning superwettable surfaces can be of great use in a new green separation technology.22 Generally, self-cleaning superwettable materials are classified into two categories: Self-cleaning superhydrophobic surfaces, which can clean themselves through repelling the oily pollutants or by applying the photo-activated compounds, which degrade the organic pollutants to water and carbon dioxide via the photocatalytic effect.23−27 On the other hand, the self-cleaning property is achieved by the existence of the air pockets trapped onto the well-designed substrate, which facilitate forming of spherically shaped water droplets as effective pollutant carriers.19,28,29 So far, various approaches have been applied to produce the flexible polymeric substrates with a unique controlled wetting property.16,30−34 Both the intrinsic wettability and the surface roughness are considered as key factors for an excellent wetting behavior. Amongst, the electrospinning technique has become one of the most powerful approaches to fabricate three-dimensional (3D) hierarchical superwettable materials due to its simplicity and low cost, which provide not only various properties such as the ability to generate porous nanofibers with small and uniform diameters, large specific surface areas, and high structural alignment but also the multifunctional inorganic polymer nanocomposites can be simply prepared: Multifunctionalized inorganic materials will provide a special surface wetting behavior through the treatment of the surface roughness and energy.23,35−45 More importantly, the as-spun polymer nanofibers provide highly available functional groups suitable for selective interactions with special molecules to enhance the surface wetting behavior.43,46 It is believed that these achievements are still restricted by parameters such as high cost of reagents and equipment, time-consuming and complicated synthetic methods, low flux, and fast pore fouling as well as pore plugging caused by pollutant molecules, which all raise costs for treatment of large effluent volumes in a practical way as well as commercial purposes. Accordingly, the design of the novel and versatile materials with reversibly...
switchable wettability stimulated through external stimuli such as temperature, magnetic field, electric field, light irradiation, pH, and special chemicals are of significant interest.\textsuperscript{1,2,14,47–53} Nevertheless, such smart switchable materials may not be viable for device fabrication due to the production costs and reliability. Accordingly, it still remains a great challenge to develop facile and versatile strategies for the fabrication of reversibly switchable wettability of surfaces. In this regard, it is believed that in situ laboratory synthetic strategies so far reported for the preparation of the photo-induced smart superwettability materials, for example, hierarchical TiO\textsubscript{2} nanostructures, can be harsh and require long reaction times, and thus these approaches would be expensive and difficult to be industrially scaled-up.\textsuperscript{1,2,3,5,30,31,54}

We believe that the use of commercially available starting materials, poly(vinylidene fluoride) (PVDF) and P25TiO\textsubscript{2}, combined with the electrospinning technique as a versatile synthetic strategy for the production of 3D smart superwetting nanotextile would reduce costs and broaden the range of potential applications. Herein, we describe a simple and versatile way to fabricate a 3D photo-induced reversibly switchable superwetting material with the superior self-cleaning and anti-fouling property resulting from the TiO\textsubscript{2} photocatalytic effect. The synthetic strategy is simple, fast, and industrially scaled-up, and also starting materials, PVDF and P25TiO\textsubscript{2} are readily commercially available, which makes this work more and more interesting in the fundamental and applied research. Fast and effective UV/solar light-induced transferring of superhydrophobicity to superhydrophilicity/underwater superoleophobcity makes it excellent as a versatile self-cleaning technology in green industrial oil–water separation.

\textbf{RESULTS AND DISCUSSION}

Herein, 3D smart PVDF-P25TiO\textsubscript{2} superwetting nanotextile was prepared by a cost-effective and simply scaled-up electrospinning approach. Commercially available PVDF and P25TiO\textsubscript{2} as constructing materials of electrospinning solution were applied to produce laboratory-scale photo/heat-adjustable well-designed PVDF-P25TiO\textsubscript{2} nanotextile with a highly reversibly self-cleaning superwetting property, which can potentially be used for large-scale industrial production by applying a conducting mesh-like substrate as the collector of electrospinning setup (Scheme 1).\textsuperscript{35,56} The structural morphology of the as-spun nanofibers was investigated by SEM. In Figure 1b, various magnified SEM images of the as-spun PVDF-P25TiO\textsubscript{2} nanotextile clearly present a well-rough surface at nanoscale arising from the TiO\textsubscript{2}-shaped beads onto the nanotextile surface, providing low surface energy suitable for the enhanced superhydrophobicity with a water contact angle (WCA) of \textasciitilde154.9°\textpm0.8 compared with the as-spun pure PVDF nanotextile with a WCA of 113.6°\textpm1.2 (Figure 1a). As compared with pure PVDF electrospun nanostructures with an average diameter of \textasciitilde230 nm, the electrospun PVDF-P25TiO\textsubscript{2} fiber diameters are higher, confirming the presence of TiO\textsubscript{2} nanostructures onto the electrospun nanofibers. The average diameter of the as-prepared PVDF-P25TiO\textsubscript{2} nanofibers is \textasciitilde673 nm. Moreover, the observed peaks of Ti, O, C, and F elements in EDX analysis will present the as-spun PVDF-P25TiO\textsubscript{2} nanotextile characterizations (Figure 1c). The thermal stability of the as-spun nanotextile was investigated by TGA (Figure 1d), exhibiting that the as-spun thermally stable PVDF-P25TiO\textsubscript{2} nanotextile with the initial degradation temperature nearly 300 °C can be promising in the oil–water separation technology. More importantly, a high intrinsic chemical and mechanical resistance of the PVDF matrix to nearly all oils and organic solvents along with a TiO\textsubscript{2} photo-induced self-cleaning effect makes the as-spun 3D smart PVDF-P25TiO\textsubscript{2} nanotextile a versatile candidate in green scaled-up filtration industries (Figure S1).\textsuperscript{57,58}

To comprehensively investigate the photo-induced reversibly switchable wetting behavior of the as-prepared PVDF-P25TiO\textsubscript{2} nanotextile, both UV and solar light irradiation were applied as the irradiation source. Figure 2 shows the UV-induced superwetting behavior of the as-prepared PVDF-P25TiO\textsubscript{2} nanotextile. Before the photo-irradiation, the as-spun PVDF-P25TiO\textsubscript{2} nanotextile gives a WCA of 154.9°\textpm0.8, which is 41.3° higher than that of the pure electrospun PVDF nanotextile with a WCA of 113.6°\textpm1.2 (Figure 1), and thus such as-prepared PVDF-P25TiO\textsubscript{2} superhydrophobic nanotextile could be effectively used for the oil-polluted water removal (Video S1). After 50 min of UV light irradiation, the WCA was quickly decreased to 7.6°\textpm0.4, and then a nearly zero WCA was achieved after 55 min of irradiation. The reversibly switchable superwetting behavior of the solar light-induced PVDF-P25TiO\textsubscript{2} nanotextile is also exhibited in Figure 2. The effective transfer of superhydrophobicity to superhydrophilicity as well as underwater superoleophobicity was achieved after nearly 3 h of local solar light irradiation at a fixed time of 8:00 to 12:00 am in summer. These results confirm that the superior superwetting behavior can be simply achieved under both UV and solar light irradiation. Furthermore, as it can be seen in Figure 2, the reversibly cycling behavior of the photo/heat-induced PVDF-P25TiO\textsubscript{2} nanotextile after 10 cycles clearly confirms their effective superwetting ability. As it is shown in Figure 3a, a reversible superhydrophobicity with the WCA of 152.7° is achieved again when the photo-induced PVDF-P25TiO\textsubscript{2} superhydrophilic nanotextile is placed in an oven at 70 °C for 60 min. Again, the reversible super-
Figure 1. SEM images of the as-spun nanotextile (a) pristine PVDF and (b) PVDF-P25TiO$_2$ (photographs are static shapes of water droplets in air, displaying that the pristine PVDF nanotextile is hydrophobic, while the electrospun PVDF-P25TiO$_2$ nanotextile presents the superhydrophobicity with a water contact angle of more than 150°). (c) EDX curve of the as-spun PVDF-P25TiO$_2$ nanotextile. (d) TGA thermograms of the as-spun nanotextile.

Figure 2. Wetting behavior of the photo/heat-induced PVDF-P25TiO$_2$ nanotextile in air as a function of (a) photo-irradiation time and (b) cycle number.
hydrophilicity is achieved after the photo-irradiation, and now the heat-induced superhydrophobic material becomes superhydrophilic. Such a cyclic process of PVDF-P25TiO2 superwetting performance could be repeated many times. Figure 4 shows the affinity of oil and water spreading onto the photo-induced PVDF-P25TiO2 superwetting nanotextile. When a water droplet of nearly 4 μL is placed onto the photo-induced PVDF-P25TiO2 nanotextile surface in air, it quickly spreads, and a zero WCA is achieved. The whole process is completed within 0.43 s (Video S2). When an n-hexane droplet as the oil is placed onto the photo-induced superwetting surface in air, it also spreads quickly within 0.37 s (Videos S2 and S3). However, the oil droplet stays on the as-spun nanotextile without spreading with an oil contact angle (OCA) of 167° ± 0.6 when it is placed under water.49 These results confirm that the photo-induced PVDF-P25TiO2 superwetting nanotextile is simultaneously superhydrophilic and underwater superoleophobic. The oil and the water spreading behavior in air and water for the as-prepared PVDF-P25TiO2 nanotextile before the photo-irradiation/light irradiation or after heating treatment can be observed in Figure 4 too. A spherically shaped water droplet with a WCA of 153.8° ± 1.1 in air, a thoroughly disappeared oil droplet with an OCA of 0° in air for a whole time of 0.51 s, and a fast spreading of the OCA (chloroform as the oil) for the sample placed under water within a whole time of 0.39 s were achieved. This superior superwetting behavior is also observed when the hot water droplet at a temperature of about 95 °C was tested (Videos S2 and S4).1,5,16 Furthermore, a very weak contact of the underwater oil droplet placed on the photo-induced nanotextile confirms extremely low adhesion force of the oil droplet adhered to the nanofiber surface and thus can be featured as a superior underwater anti-oil adhesion nanostructure, especially for an oily wastewater separation technology, namely, “water-removing” process (Video S5). The ability of a special superwetting nanotextile is proved by the effective oil−water separation performance.50,60 Herein, the separation capability of the photo-induced PVDF-P25TiO2 nanotextile for oil-in-water emulsions, both surfactant-free and surfactant-stabilized emulsions, n-hexane-in-H2O, toluene-in-H2O, petroleum ether-in-H2O (petroleum/H2O), SDS-stabilized n-hexane-in-H2O, SDS-stabilized toluene-in-H2O, and SDS-stabilized petroleum ether-in-H2O (petroleum/SDS/H2O) with an oil/water volume ratio of 1:99 was tested. The as-prepared emulsions were then poured on the as-spun nanotextile to carry out the filtration driven by a high applied pressure (1 bar), a small applied pressure (0.1 bar), and also gravity only. All emulsions were successfully separated in one step (Video S6). The oil content in water after a one-time separation was measured by a total organic carbon (TOC) analyzer. As shown in Figure 5a, the oil content in the filtrates for the surfactant-free emulsions driven under a small applied pressure of 0.1 bar and only gravity force are all below 40 ppm. For the surfactant-free emulsions driven by a small applied pressure of 1 bar, the oil content in the filtrates is in the range of 85–123 ppm. For the SDS-stabilized emulsions driven under a high applied pressure of 1 bar, the oil content in the filtrates are in the range of 85–123 ppm. For the SDS-stabilized emulsions driven by a small applied pressure of 0.1 bar and only gravity force, the oil

Figure 3. Wetting behavior of the photo-induced PVDF-P25TiO2 nanotextile as a function of heating time after (a) UV light irradiation and (b) solar light irradiation.

Figure 4. (a) Static shape photographs of the oil and water droplets on the as-spun PVDF-P25TiO2 nanotextile surface in air and underwater. (b) Schematic illustration of the photo/heat-induced wetting behavior of the as-spun PVDF-P25TiO2 nanotextile.
content in the filtrates are all below 70 ppm, and under a high applied pressure of 1 bar, the oil content in the filtrates are in the range of 113−137 ppm. These results reveal a highly separation efficiency of the photo-induced PVDF-P25TiO₂ nanotextile. The higher oil content obtained for the emulsions driven under a high applied pressure of 1 bar can be resulted from the deformation of emulsified droplets, which will facilitate their passing through the pores of the textile. In comparison with the surfactant-free emulsions, for SDS-stabilized emulsions, the higher oil content in filtrates can be probably due to the presence of dissolved surfactants in the filtrate. As shown in Figure 5b, the fluxes obtained for the emulsions driven under gravity force only, n-hexane/H₂O, toluene/H₂O, petroleum/H₂O, n-hexane/SDS/H₂O, toluene/SDS/H₂O, and petroleum/SDS/H₂O are 4740, 5010, 4450, 3490, 3930, and 3720 Lm⁻² h⁻¹, respectively. The emulsions with 0.1 bar of applied pressure across the nanotextile exhibit the fluxes of 5270, 5600, 5350, 4950, 5260, and 4930 Lm⁻² h⁻¹ for n-hexane/H₂O, toluene/H₂O, petroleum/H₂O, n-hexane/SDS/H₂O, toluene/SDS/H₂O, and petroleum/SDS/H₂O, respectively. These values are somewhat higher than those observed for the emulsions driven by gravity only. For the separations driven by a high applied pressure of 1 bar, the corresponding fluxes are 28,560, 30,500, 28,300, 21,100, 22,750, and 19,900 Lm⁻² h⁻¹, which are several times higher than those of driven under a small applied pressure of 0.1 bar or gravity only (Table S1). Furthermore, as shown in Figure 5c, the separation capability of the photo-induced PVDF-P25TiO₂ nanotextile for oil-in-water emulsions with various amounts of oil was also investigated. Petroleum/H₂O emulsions with the different oil and water volume ratios from 1:99 to 10:90 were prepared, and the separation tests were investigated. The results show that all of the emulsions could be completely separated but with a decrease in flux with increasing the oil content in emulsion. To investigate the separation performance of the photo-induced PVDF-P25TiO₂ nanotextile, an optical microscope was used for displaying the appearance difference between the original emulsion and the corresponding collected filtrates. Figure 6a presents the separation performance of petroleum/H₂O emulsion and petroleum/SDS/H₂O emulsion. For both surfactant-free and SDS-stabilized emulsions, dense oil droplets of microscale are observed clearly in the original emulsions. Correspondingly, in the collected filtrates, no droplets are observed in the images, indicating the effectiveness of the as-prepared nanotextile for separating the oil-in-water emulsions. Furthermore, Figure 6b clearly displays that the as-spun photo-induced textile can be applied for separating the immiscible oil−water mixtures in which the textile acts in “water-removing” mode, where the water phase quickly passes through the mesh and the oil phase still remains on the surface (Video S7).

To further confirm the durability in the wetting behavior of the photo-induced PVDF-P25TiO₂ nanotextile, a set of separation cycling tests were performed, as it is shown in Figure 5d. The superhydrophilic/underwater superoleophobic photo-induced textile will act in “water-removing” mode in
which water quickly passes through and the oil is blocked on the surface. The wetting recovery is simply conducted by rinsing the textile with ethanol, drying at room temperature, and the textile again is used as a “water-removing” filter. The variation of the oil content in filtrates and their flux during this process were determined. It can be seen that after nine cycles, the flux slightly changes with time, and then it recovers almost to the starting flux only after cleaning with ethanol followed by light irradiation (Figure S2). These results indicate an excellent antifouling property and effective wetting storage stability of the as-spun PVDF-P25TiO2 nanotextile for long-term use in medium conditions.

Commercially, the “water-removing” technology always suffers from fouling issues arising from the oil adhesion onto the surface, which will seriously restrict this technology from again and long-term use. In this regard, the photo-activated materials such as TiO2 have been considered as significant candidates to effectively degrade the oily and organic compounds due to their photocatalytic effect. Herein, the TiO2 photo-induced self-cleaning capability of the as-spun PVDF-P25TiO2 nanotextile can be of significant importance in the oil—water separation technology, especially that such as-spun smart PVDF-P25TiO2 superwetting nanotextile will remain its superhydrophilicity and underwater superoleophobicity ability for long-time storage. To investigate the antifouling and self-cleaning performance, oleic acid as a non-volatile oily pollutant was selected and then exposed to UV light irradiation, and the variation of the WCA in air and underwater OCA of the as-spun smart superwetting nanotextile was investigated (Figure 7a).61 The photo-induced PVDF-P25TiO2 nanotextile presents a zero WCA in air. For oleic acid-adhered PVDF-P25TiO2 nanotextile, the WCA of

![Figure 6. Oil—water separation digital and optical photographs. (a) Petroleum ether/water and petroleum ether/SDS/water emulsions. (b) Immiscible n-hexane-water mixture, displaying that the photo-induced PVDF-P25TiO2 nanotextile acts in “water-removing” mode and a clean water can be obtained.](image)

![Figure 7. Antifouling and self-cleaning ability of the photo-induced PVDF-P25TiO2 nanotextile. (a) Water contact angle and underwater oil contact angle photographs. (b) FT-IR spectra. (c) UV—Vis curves, displaying that photo-activated TiO2 can degrade methylene blue dye present in the oil—water mixture.](image)
154.1° ± 0.6 is observed, proving the adhesion of oleic acid on the nanotextile. Interestingly, the superhydrophilicity and underwater superoleophobicity are recovered again after UV light irradiation for 2.5 h with the WCA of zero and the underwater OCA of 165.1° ± 0.3, respectively. To further confirm the antifouling and self-cleaning performance, the TiO2 photo-degradation of oleic acid was studied by FT-IR analysis, as it can be seen in Figure 7b.50,62 In the FT-IR spectrum of the as-spun PVDF-P25TiO2 nanotextile without oleic acid, any obvious peaks in the range of 2800−3000 cm$^{-1}$ are not observed. Nevertheless, oleic acid-adhered PVDF-P25TiO2 nanotextile presents three characteristic peaks at 2856, and 2929, and 1713 cm$^{-1}$ ascribed to the stretching vibration of $-\text{CH}_3$, $-\text{CH}_2$, and $\text{C}=\text{O}$ of the oleic acid, respectively. Such characteristic peaks ascribed to oleic acid in the FT-IR spectrum are not observed for the oleic acid-adhered PVDF-P25TiO2 nanotextile exposed to UV light irradiation for 2.5 h. Now, the FT-IR spectrum is similar to that of without oleic acid that displays a superior antifouling and self-cleaning capability of the photo-induced PVDF-P25TiO2 nanotextile, providing a versatile and effective strategy in green fundamental and applied research with large-scale manufacturing.

Furthermore, the capability of TiO2-induced degradation of organic pollutants was examined by immersing the photo-induced PVDF-P25TiO2 nanotextile into 10 mL of 500 μM methylene blue aqueous solution. As shown in Figure 7c, the absorption intensity corresponding to methylene blue decreases dramatically due to its decomposition by the photo-activated TiO2, and a clean water is achieved after UV treatment for 25 min.65 The additional water purification performance makes the as-prepared nanotextile more effective and promising in treating water pollution.

Eventually, our studies show that the superior reversibly switchable wetting behavior should be seriously dependent on the synthetic strategy and resulting product properties, namely, the surface chemistry and topography. For example, approximately, under the same processing conditions, such a reversibly switchable wetting ability cannot be achieved for the polymer film-like materials constructed by other methods except the electrospinning technique. Herein, it is believed that such a smart reversible superwetting property can be clearly ascribed to combined characteristics of both TiO2 well-distributed nanostructures and the as-spun hierarchical nanofibrous substrate; the electrospinning strategy can be preferred to provide a homogeneous distribution of TiO2 nanoparticles onto the nanoscaled porous PVDF fibers that will effectively provide the characterizations required for achieving the superior superwetting behavior.6 A simple mechanism is proposed to explain the switching behavior of the as-spun smart PVDF-P25TiO2 superwetting nanotextile (Scheme 2). Herein, the reversibly surface superwetting can be resulted from (a) the unique topography of the as-spun nanofibrous textile that will effectively provide both the surface roughness and 3D multiscale interconnected pores and (b) the unique chemical composition that can be ascribed to highly available oleophobic $-\text{CF}_2$ functional groups of PVDF and well-rough TiO2 nanostructures. Before the photo-irradiation, the air pockets entrapped in the 3D interconnected pores of the PVDF-P25TiO2 nanotextile as an effective hydrophobic medium cause the as-spun nanotextile to be a superior hydrophobic and oleophilic material (Video S1). After the heat treatment or before the photo-irradiation, the oil droplets are adsorbed by both highly available oleophobic oxygen bridges of TiO2 and the $-\text{CF}_2$ functional groups of PVDF (step 1), leading the surface to be well oil wetted (step 2). Now, the oil-spread layer is replaced with the air pockets entrapped into pores, and finally the oil passes through due to the 3D capillary effect (step 3). After the photo-irradiation, simultaneously, the oil and water filtration can be performed, the oleophilic $-\text{CF}_2$ groups of PVDF will provide the oil spreading, while highly available photo-induced hydrophilic hydroxyl groups of TiO2...
cause the surface to be well water wetted. The reason for the photo-induced underwater oleophobic wetting property can be resulted from the surrounding of the oleophilic regions by water that will act as an effective oil repellant material, and so it will induce the underwater superoleophobicity to the surface.

**CONCLUSIONS**

In summary, we present the preparation of photo (UV/solar light)-induced 3D smart reversibly superwettable PVDF-P25TiO2 nanotextile constructed by the electrospinning technique in a single step. Readily commercially available PVDF and P25TiO2 as starting materials fabricated with a versatile scaled-up electrospinning approach makes it possible to be significantly desired in the fundamental and applied research, especially as the filter in the industry-scale oily water treatment. Effective transfer to the superhydrophobic surface can be simply achieved by heat treatment. The transitions are easy to manipulate and reversible for many times. More importantly, such photo-induced smart PVDF-P25TiO2 superwetting nanotextile presents an excellent self-cleaning and antifouling property to remove the organic molecules through the TiO2 photocatalytic effect. With these advantages, a large-scale industrial production process can be simply simulated.

**EXPERIMENTAL SECTION**

**Materials.** Poly(vinylidene fluoride) (PVDF; Kynar 1000HD, Atokina Co), TiO2 (Degussa, P25), oleic acid, sodium dodecyl sulfate (SDS), acetone, N,N-dimethylacetamide (DMAC), n-hexane, chloroform, petroleum ether, toluene, oil red, and methylene blue were all purchased from Merck Chemical Company and were used as received. Stainless steel mesh (pore size: 1.8 cm) was cleaned with ethanol before use.

**Preparation of Electrospun 3D PVDF-P25TiO2 Nanotextile.** To obtain a proper electrospinning solution of PVDF-P25TiO2, 1.3 g of PVDF granules dried in a vacuum oven at 70 °C for 1 h was added into 10 mL of ultrasound acetone/DMAC (1/1, v/v) solvent mixture containing 7 wt % P25TiO2 with respect to the weight of the polymer and then magnetically stirred for 6 h at 60 °C. To prevent the solvent evaporation, the solution was prepared in a capped glass bottle. To fabricate the electrospun nanofibrous textile, an electrospinning setup (Fanavaran Nano-Meghyas, Iran) was used at room temperature with an applied voltage of 15 kV to the stainless steel needle with a gauge size of 24. The distance between the spinneret and collector was 25 cm, and the injection rate was 0.1 mL/h. The relative humidity was regulated to be more than 50% by the injection of steam stream into the electrospinning polymethylmethacrylate chamber. The as-spun PVDF-P25TiO2 nanofibers were dried at 50 °C for 12 h to remove the residual solvent. Pure PVDF nanofibers without TiO2 particles were prepared as a reference with the same PVDF concentration and the abovementioned operating conditions. For the preparation of the as-spun nanotextile coated on the stainless steel mesh, the stainless steel mesh was considered as the electrospinning collector.

**Preparation of Oil-in-Water Emulsions.** Surfactant-free oil-in-water emulsions were prepared by mixing water and oil (n-hexane, toluene, and petroleum ether) at 1:99 (v/v), and the mixtures were ultrasonicated for more than 2 h to obtain homogeneous emulsions. Within 1 h, no precipitation was observed in the emulsion solutions when placed in ambient conditions. Surfactant (SDS)-stabilized oil-in-water emulsions were prepared by adding the surfactant and oil into deionized water under rapid stirring and then sonicated. In detail, an SDS-stabilized petroleum ether-in-water emulsion (petroleum/SDS/H2O) was prepared by mixing petroleum ether and water (1:99, v/v) with addition of 0.02 mg of SDS per milliliter of emulsion under 3000 rpm mechanical stirring for 1 h followed by sonication for more than 1 h. The emulsions were investigated by optical microscopy observation. Based on the same abovementioned method, the oil–water emulsions at 2:98, 5:95, and 10:90 (v/v) ratios were also prepared. For all cycling tests, a certain volume of emulsion was poured on the photo-induced PVDF-P25TiO2 textile, and after the separation process, the used textile was simply rinsed with 10 mL of ethanol and dried at room temperature to recover the flux.

**Reversibly Switchable Oil–Water Separation.** To obtain the UV-induced PVDF-P25TiO2 nanotextile, the as-spun nanofibers were irradiated at a fixed distance of 30 cm by three parallel 15 W Hg lamps (Philips TL-D) placed in a wooden box equipped with air circulator. The solar light-induced wetting behavior of the-as spun sample was investigated under a local solar light at a fixed time of 8:00 to 12:00 am in summer. The oil–water separation was conducted by using the as-spun nanotextile fixed on a glass apparatus to separate oily water including immiscible oil–water (dyed with methylene blue), surfactant-free oil–water emulsions, and surfactant-stabilized oil–water emulsions, which passed through the nanotextile and collected by a flask placed under it. The flux was determined by calculating a certain volume of solution passed through the nanotextile. The oil content in the filtrate was measured by a using total organic carbon (TOC) analyzer.

**Characterization.** The morphology of the as-spun PVDF nanofiber with and without TiO2 loading was observed using a field emission scanning electron microscope (Hitachi S4160, Japan) equipped with an energy-dispersive X-ray spectroscopy (EDX) detector. The nanofibers’ diameters were measured from SEM images using the software Image J, and the average diameter was calculated from the measurements of 50 nanofibers. Fourier transform infrared spectroscopy (FT-IR, Bruker 27) was applied to evaluate the antifouling and self-cleaning performance of the as-spun smart nanotextile. TGA curves were obtained by using thermogravimetric analysis (TGA, Q50-TGA). Ultraviolet–visible spectrophotometry (UV–Vis, Varian) was used to study the photocatalytic effect of the as-spun nanotextile. Contact angles (CA) and corresponding measurements were measured with a homemade setup equipped with a Dino-lite digital microscope (AM7915MZTL, Taiwan). To measure underwater oil contact angles, the as-spun superwetting nanotextile was first immersed in water, and after that the oil droplet (nearly 4 μL of chloroform) (ρoil > ρwater) was carefully dropped onto the nanotextile surface from the bottom. For each value, five measurements per sample were done, and the average contact angle value was obtained using the software Photoshop and OriginPro.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03861.
Superhydrophobic TiO$_2$ nanotextile. (Video S1) Water contact angle measurement of the as-spun PVDF-P25TiO$_2$ nanotextile in air after photo-irradiation (AVI) (Video S2) Cool water (left), hot water (middle), and oil (n-hexane) contact angle measurement of the photo-induced PVDF-P25TiO$_2$ nanotextile in air (AVI) (Video S3) Oil (n-hexane) contact angle measurement of the photo-induced PVDF-P25TiO$_2$ nanotextile in air (AVI) (Video S4) Cool water (left), hot water (middle), and oil (n-hexane) contact angle measurement of the as-spun PVDF-P25TiO$_2$ nanotextile in air before photo-irradiation or after the heat treatment (AVI) (Video S5) Underwater oil (chloroform) contact angle measurement of the photo-induced PVDF-P25TiO$_2$ nanotextile (AVI) (Video S6) The separation ability of petroleum ether-in-water emulsion by the photo-induced PVDF-P25TiO$_2$ nanotextile driven under gravity only (AVI) (Video S7) Immiscible oil (n-hexane)-water separating ability of the photo-induced PVDF-P25TiO$_2$ nanotextile collected on a stainless steel mesh collector in air (AVI)

---

**AUTHOR INFORMATION**

**Author**

Zahed Shami — Department of Chemistry, Faculty of Science, University of Kurdistan, Sanandaj 66177-15175, Iran.

- orcid.org/0000-0001-6135-8784; Phone: (+9887) 33624133; Email: z.shami@uok.ac.ir

Author Parvin Holakooei — Department of Chemistry, Faculty of Science, University of Kurdistan, Sanandaj 66177-15175, Iran

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.9b03861

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was partly supported by Midea Chemi Co. (MCH). The authors would like to thank especially Dr. Bahrami for analysis and Ms. Barbara Ehrlichová for proofreading.

**ABBREVIATIONS**

- °, angle degree; °C, Celsius temperature; cm, centimeter; ρ, density; g, gram; h, hour; kV, kilovolt; m, meter; mL, milliliter; nm, nanometer; μL, microliter; μm, micrometer; min, minute; N, Newton; v, volume; wt, weight

**REFERENCES**

(1) Dang, Z.; Liu, L.; Li, Y.; Xiang, Y.; Guo, G. In Situ and Ex Situ pH-Responsive Coatings with Switchable Wettability for Controllable Oil/Water Separation. *ACS Appl. Mater. Interfaces* 2016, 8, 31281–31288.

(2) Li, J.-J.; Zhou, Y.-N.; Luo, Z.-H. Smart Fiber Membrane for pH-Induced Oil/Water Separation. *ACS Appl. Mater. Interfaces* 2015, 7, 19643–19650.

(3) Xu, Q. F.; Liu, Y.; Lin, F.-J.; Mondal, B.; Lyons, A. M. Superhydrophobic TiO$_2$—Polymer Nanocomposite Surface with UV-Induced Reversible Wettability and Self-Cleaning Properties. *ACS Appl. Mater. Interfaces* 2013, 5, 8915–8924.

(4) He, K.; Duan, H.; Chen, G. Y.; Liu, X.; Yang, W.; Wang, D. Cleaning of Oil Fouling with Water Enabled by Zwitterionic Polyelectrolyte Coatings: Overcoming the Imperative Challenge of Oil–Water Separation Membranes. *ACS Nano* 2015, 9, 9188–9198.

(5) Byun, J.; Shin, J.; Kwon, S.; Jang, S.; Kim, J. K. Fast and reversibly switchable wettability induced by a photothermal effect. *Chem. Commun.* 2012, 48, 9278–9280.

(6) Ghossoub, Y. E.; Schlenoff, J. B. Janus Nanofilms. *Langmuir* 2016, 32, 3623–3629.

(7) Su, B.; Tian, Y.; Jiang, L. Bioinspired Interfaces with Superwettability: From Materials to Chemistry. *J. Am. Chem. Soc.* 2016, 138, 1727–1748.

(8) Shami, Z.; Shariifi-Sanjani, N.; Khoei, S.; Faridi-Majidi, R. Triple Axial Coelectrosprun Multifunctional Double-Shell TiO$_2$@ZnO Carbon Hollow Nanofibrous Mat Transformed to C-Attached TiO$_2$ Brush-Like Nanotube Arrays: An Mo$^+$ Adsorbent Nonwoven Mat. *Ind. Eng. Chem. Res.* 2014, 53, 14963–14973.

(9) Wang, Y.; Shi, Y.; Pan, L.; Yang, M.; Peng, L.; Zong, S.; Shi, Y.; Yu, G. Multifunctional Superhydrophobic Surfaces Templated From Innately Microstructured Hydrogel Matrix. *Nano Lett.* 2014, 14, 4803–4809.

(10) Baidya, A.; Ganayee, M. A.; Jakka Ravindran, S.; Tam, K. C.; Das, S. K.; Rus, R. H. A.; Pradeep, T. Organic Solvent-Free Fabrication of Durable and Multifunctional Superhydrophobic Paper from Waterborne Fluorinated Cellulose Nanofiber Building Blocks. *ACS Nano* 2017, 11, 11091–11099.

(11) Li, D.; Li, Q.; Bai, N.; Dong, H.; Mao, D. One-Step Synthesis of Cationic Hydrogel for Efficient Dye Adsorption and Its Second Use for Emulsified Oil Separation. *ACS Sustainable Chem. Eng.* 2017, 5, 5598–5607.

(12) Duan, G.; Jiang, S.; Moss, T.; Agarwal, S.; Greiner, A. Ultralight open cell polymer sponges with advanced properties by PPX CVD coating. *Polym. Chem.* 2016, 7, 2759–2764.

(13) Mu, L.; Yang, S.; Hao, B.; Ma, P.-C. Ternary silicone sponge with enhanced mechanical properties for oil-water separation. *Polymer* 2015, 6, 5869–5875.

(14) Cheng, Z.; Wang, J.; Lai, H.; Du, Y.; Hou, R.; Li, C.; Zhang, N.; Sun, K. pH-Controlled On-Demand Oil/Water Separation on the Switchable Superhydrophobic/Superhydrophilic and Underwater Low-Adhesive Sulphorolophobic Copper Mesh Film. *Langmuir* 2015, 31, 1393–1399.

(15) Bielinski, A. R.; Boban, M.; He, Y.; Kazyak, E.; Lee, D. H.; Wang, C.; Tuteja, A.; Dasgupta, N. P. Rational Design of Hyperbranched Nanowire Systems for Tunable Superomniphobic Surfaces Enabled by Atomic Layer Deposition. *ACS Nano* 2017, 11, 478–489.

(16) Chu, Z.; Feng, Y.; Seeger, S. Oil/Water Separation with Selective Superantiwetting/Superwetting Surface Materials. *Angew. Chem., Int. Ed. Engl.* 2015, 54, 2328–2338.

(17) Luo, Z.-Y.; Chen, K.-X.; Wang, Y.-Q.; Wang, J.-H.; Mo, D.-C.; Lyu, S.-S. Superhydrophobic Nickel Nanoparticles with Core–Shell Structure To Decorate Copper Mesh for Efficient Oil/Water Separation. *J. Phys. Chem. C* 2016, 120, 12685–12692.

(18) Shami, Z.; Gharloghi, A.; Amininasab, S. M. Multifunctional pH-Switched Superwetting Copolymer Nanotextile: Surface Engineered toward on-Demand Light Oil–Water Separation on Superhydrophilic–Underwater Low-Adhesive Sulphorolophobic Nonwoven Mesh. *ACS Sustainable Chem. Eng.* 2019, 8917.

(19) Xu, Z.; Zhao, Y.; Wang, H.; Wang, X.; Lin, T. A Superantiprophobic Coating with an Ammonia-Triggered Transition to Superhydrophilic and Superoleophobic for Oil–Water Separation. *Angew. Chem. Int. Ed. Engl.* 2015, 54, 4527–4530.

(20) Wang, Y.; Lai, C.; Wang, X.; Liu, Y.; Hu, H.; Guo, Y.; Ma, K.; Fei, B.; Xin, J. H. Beads-on-String Structured Nanofibers for Smart and Reversible Oil/Water Separation with Outstanding Antifouling Property. *ACS Appl. Mater. Interfaces* 2016, 8, 25612–25620.
(21) Chatterjee, S.; Sen Gupta, S.; Kumaraswamy, G. Omniphic Polymeric Sponges by Ice Templing. Chem. Mater. 2016, 28, 1823–1831.

(22) Latthe, S. S.; Sudhagar, P.; Ravidhas, C.; Jennifer Christy, A.; David Kirubakaran, D.; Venkatesh, R.; Devadoss, A.; Terashima, C.; Nakata, K.; Fujishima, A. Self-cleaning and superhydrophobic CuO coating by jet-nebulizer spray pyrolysis technique. CrystEngComm 2015, 17, 2624–2628.

(23) Zhang, W.; Lu, X.; Xin, Z.; Zhou, C. A self-cleaning polybenzoxazine/TiO2 surface with superhydrophobicity and superoleophobicity for oil/water separation. Nanoscale 2015, 7, 19483.

(24) Kim, D.-Y.; Lee, J.-G.; Joshi, B. N.; Latthe, S. S.; Al-Deyab, S. S.; Yoon, S. S. Self-cleaning superhydrophobic films by supersonic-spraying polytetrafluoroethylene-titania nanoparticles. ACS Appl. Mater. Interfaces 2020, 12, 15169–15175.

(25) Park, C. B. Acid Base Polymeric Foams for the Adsorption of Micro-pollutants. Environ. Sci. Technol. 2016, 50, 11307–11314.

(26) Chen, Y.; Xie, A.; Cui, J.; Lang, J.; Yan, Y.; Li, C.; Dai, J. UV-Driven Anti-foiling Fiber Paper Fibers for Efficient Oil–Water Separation. Ind. Eng. Chem. Res. 2019, 58, 15180–15190.

(27) Liu, J.; Wang, L.; Guo, F.; Hou, L.; Chen, Y.; Liu, J.; Zhao, Y.; Jiang, L. A Robust Cu(OH)2 Nanoneedles Mesh with Tunable Wettability for Nonaqueous Multiphase Liquid Separation. Small 2017, 13, 1600499–1600507.

(28) Ge, D.; Yang, L.; Wang, C.; Lee, E.; Zhang, Y.; Yang, S. A multi-functional oil-water separator from a selectively pre-wetted superamphiphobic paper. Chem. Commun. 2015, 51, 6149–6152.

(29) Mukherjee, S.; Kansara, A. M.; Saha, D.; Gonnade, R.; Mullangi, D.; Manna, B.; Desai, A. V.; Singh, S. P.; Mukherjee, A.; Ghosh, S. K. An Ultrahydrophobic Fluorous Metal–Organic Framework Derived Recyclable Composite as a Promising Platform to Tackle Marine Oil Spills. Eur. J. Chem. 2016, 22, 10937–10943.

(30) Darmanin, T.; Guittard, F. Recent advances in the potential applications of bioinspired superhydrophobic materials. J. Mater. Chem. A 2014, 2, 16319–16359.

(31) Kuang, M.; Wang, J.; Jiang, L. Bio-inspired photonic crystals with superwettability. Chem. Soc. Rev. 2016, 45, 6833–6854.

(32) Long, Y.; Shen, Y.; Tian, H.; Yang, Y.; Feng, H.; Li, J. Superwettability Coprinus comatus coated membranes used toward the controllable separation of emulsified oil/water mixtures. J. Membr. Sci. 2018, 565, 85–94.

(33) Yang, J.; Chen, F.; Hua, J.; Fang, Y.; Yang, Q.; Bian, H.; Li, W.; Wei, Y.; Dai, Y.; Hou, X. Green, Biodegradable, Underwater Superoleophobic Wood Sheet for Efficient Oil/Water Separation. ACS Omega 2018, 3, 1395–1402.

(34) Ganesh, V. A.; Dinachali, S. S.; Nair, A. S.; Ramakrishna, S. Robust Superamphiphobic Film from Electrosprun TiO2 Nanostructures. ACS Appl. Mater. Interfaces 2013, 5, 1527–1532.

(35) Henke, P.; Kozak, H.; Artemenko, A.; Kubát, P.; Forstová, J.; Moser, J. Superhydrophilic Polystyrene Nanofiber Materials Generating O2(18)g: Postprocessing Surface Modifications toward Efficient Antibacterial Effect. ACS Appl. Mater. Interfaces 2014, 6, 13007–13014.

(36) Boo, C.; Lee, J.; Eilmeleck, M. Omniphic Polyvinylidene Fluoride (PVDF) Membrane for Desalination of Shale Gas Produced Water by Membrane Distillation. Environ. Sci. Technol. 2016, 50, 12275–12282.

(37) Zhang, C.; Li, P.; Cao, B. Electrosprun Microfibrous Membranes Based on PIM-1/POSS with High Oil Wettability for Separation of Oil–Water Mixtures and Cleanup of Oil Soluble Contaminants. Ind. Eng. Chem. Res. 2015, 54, 8772–8781.
fibrous Membranes for Membrane Distillation. ACS Appl. Mater. Interfaces 2015, 7, 21919–21930.

(58) Obaid, M.; Mohamed, H. O.; Yasin, A. S.; Yassin, M. A.; Fadali, O. A.; Kim, H.; Barakat, N. A. M. Under-oil superhydrophilic wetted PVDF electrospun modified membrane for continuous gravitational oil/water separation with outstanding flux. Water Res. 2017, 123, 524–535.

(59) Matsubayashi, T.; Tenjimbayashi, M.; Komine, M.; Manabe, K.; Shiratori, S. Bioinspired Hydrogel-Coated Mesh with Superhydrophilicity and Underwater Superoleophobicity for Efficient and Ultrafast Oil/Water Separation in Harsh Environments. Ind. Eng. Chem. Res. 2017, 56, 7080–7085.

(60) Shami, Z.; Amininasab, S. M.; Shakeri, P. Structure–Property Relationships of Nanosheeted 3D Hierarchical Roughness MgAl–Layered Double Hydroxide Branched to an Electrospun Porous Nanomembrane: A Superior Oil-Removing Nanofabric. ACS Appl. Mater. Interfaces 2016, 8, 28964–28973.

(61) Lai, Y.; Huang, J.; Cui, Z.; Ge, M.; Zhang, K.-Q.; Chen, Z.; Chi, L. Recent Advances in TiO2-Based Nanostructured Surfaces with Controllable Wettability and Adhesion. Small 2016, 12, 2203–2224.

(62) Li, L.; Liu, L.; Lei, J.; He, J.; Li, N.; Pan, F. Intelligent sponge with reversibly tunable super-wettability: robust for effective oil-water separation as both the absorber and filter tolerate fouling and harsh environments. J. Mater. Chem. A 2016, 4, 12334–12340.

(63) Wang, X.; Li, M.; Shen, Y.; Yang, Y.; Feng, H.; Li, J. Facile preparation of loess-coated membranes for multifunctional surfactant-stabilized oil-in-water emulsion separation. Green Chem. 2019, 21, 3190–3199.

(64) Shami, Z.; Delbina, S.; Amininasab, S. M. Wool-Like Fibrous Nonwoven Mesh with Ethanol-Triggered Transition between Antiwater and Antioil Supervetting States for Immiscible and Emulsified Light Oil–Water Separation. Langmuir 2019, 35, 10491.