Efficient removal of oil from oil contaminated water by superhydrophilic and underwater superoleophobic nano/micro structured TiO₂ nanofibers coated mesh

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ABSTRACT

In this report, we investigated the TiO₂ nanofibers coated stainless steel mesh as a novel underwater superoleophobic membrane for the effective separation of contaminated oil-water mixtures. The membrane was fabricated by spray deposition of hydrothermally synthesized TiO₂ nanofibers on stainless steel mesh. The fabricated membrane exhibits superhydrophilicity and superoleophobicity properties in air and underwater respectively allowing the separation of oil-water efficiently. Randomly deposited TiO₂ nanofibers on mesh exhibit rough surface property and hence superhydrophilic nature. Water oil separation efficiencies of ~90 and ~99% were achieved with this filter for less viscous and highly viscous oil respectively. Additionally, the TiO₂ nanofibers coated mesh can degrade immiscible organic molecules due to photocatalytic activity of TiO₂ nanofibers under UV light. As a result of self-cleaning property of TiO₂ nanofibers coated mesh, the durability of the filter membrane was enhanced.

KEYWORDS: TiO₂ nanofibers, underwater superoleophobicity, oil-water separation, superhydrophilic, photocatalytic activity, super-wetting membrane

INTRODUCTION

Water pollution through immiscible and miscible oil is a major problem that each and every industrially revolutionized country has to face. Discharge of the oil polluted water to the environment without purification or pretreatment is a major threat to the human beings and to the whole ecosystem (Fosberg, 1974; Odeigah et al., 1997; Liu and Diamond, 2005; Olsson, 2015). Scientists anticipate new advanced techniques to clean up oil spills from water exceeding the traditional oil wastewater treatment methods such as coagulation and flocculation techniques (Bratby, 1980; Al-Shamrani et al., 2002; Inan et al., 2004), advanced chemical oxidation techniques (Munter, 2001; Schrank et al., 2004; Bautista et al., 2008; Xu et al., 2012), adsorption techniques (Balba et al., 1998; Mitchell et al., 2002; Gaya and Abdullah, 2008; Gur-Reznik et al., 2008; Fakhru'l-Razi et al., 2009; Pyrzynska, 2011), electrochemical/photocatalytic treatment methods (Ma and Wang, 2006; Chong et al., 2010) and biological treatment methods (Rosal et al., 2010; Xia et al., 2010).

On the other hand, currently, enormous demands do exist on the special wetting materials to fabricate oil water separating filter membranes due to their efficiency and the cost effectiveness (Yao et al., 2011; Xue et al., 2014; Dunderdale et al., 2015). These membranes can be integrated to the existing physical reactors of cleaning processes of the oil/water separating plants. In this respect, materials with superhydrophobic and superoleophilic properties have been intensively investigated in applying wastewater purification in last few decades (Wang et al., 2006; Lee et al., 2011; Xu et al., 2016). The major disadvantage of these gravity driven filter membranes with superhydrophobic and superoleophilic materials is that they easily get blocked and fouled by viscous/dense oil and affecting the oil-water separation and hence not suitable for the large scale oil water separation (Feng et al., 2004; Zhang et al., 2013). To overcome the

clogging and fouling of the oil-water separation filters, materials having superhydrophilic and underwater superoleophobic properties have been reported (Xue et al., 2011; Ding et al., 2012; Chen and Xu, 2013; Liu et al., 2013; Xu et al., 2013; Cai et al., 2014; Darmanin and Guittard, 2014; Manna and Lynn, 2015). Various underwater superoleophobic materials such as, titanium dioxide thin films (Sawai et al., 2013; Zhang et al., 2013; Gondal et al., 2014; Wang and Guo, 2014; Jo and Kim, 2015) polyacrylamide hydrogel coated mesh (Xue et al., 2011), silicates (Zhang et al., 2013), zinc oxide based mesh (Li et al., 2015), copper oxide covered mesh (Cheng et al., 2013; Liu et al., 2013), PANI nanowire films (Ding et al., 2012) etc. have been reported. Fabrication of superhydrophilic and underwater superoleophobic membranes is based on the coating of nano/micro hierarchical coating of highly polar material on a suitable substrate i.e. stainless steel (Bellanger et al., 2014; Cai et al., 2014; Darmanin and Guittard, 2014). According to the extended Young theories, (Young, 1805) it can be expected that underwater superoleophobic materials could be superhydrophilic in air (Bellanger et al., 2014; Cai et al., 2014) such that superhydrophilic materials in air should be suitable to prepare underwater superoleophobic solid surfaces.

Titanium dioxide is one of the heavily used inorganic materials in energy and environmental related applications (Hashimoto et al., 2005; Muneer et al., 2005; Thavasi et al., 2008). It is a well-known potential semiconductor photocatalyst which can degrade various organic pollutants with the aid of UV light (Turchi et al., 1990; Tayade et al., 2006; Choi et al., 2007). In the photocatalytic degradation process, the titanium dioxide surface functions as an adsorption midpoint to the organic molecules and the adsorbed molecules oxidize to CO₂ and H₂O with the aid of hydroxyl radicals (Nagaveni et al., 2004; Choi et al., 2007; Hathway, 2009; Pan et al., 2012). Hence, when the TiO₂ photocatalyst is fixed in a membrane, TiO₂ coated

membrane could have both light induced cleaning property as well as underwater superoleophobic property (Zhang et al., 2013).

For effective oil water separation, a membrane with a highly rough surface is necessary to achieve stable superhydrophilic property. Highly rough surfaces can be obtained by deposition of randomly oriented 1-D structures on suitable substrates (Marmur, 2003). Considering the hydrophilicity, TiO_2 with 1-D structures such as nanotubes, nanowires or fibrous TiO_2 structures are suitable materials for the fabrication of underwater superoleophobic filters. In this study, we fabricated superhydrophilic, nano-structured TiO_2 nanofibers on stainless steel mesh by the spray coating technique. The synthesis of TiO_2 nanofibers is simple and cost effective as well as TiO_2 nanofibers exhibit high repellency towards oil in under water. The micro/nanohierarchical coating of nano-structured TiO_2 fibers on mesh results in enhanced surface roughness and underwater superoleophobicity. The oil-water separation method is basically forward under gravity and shows excellent oil-water separation and the higher oil contact angle under water with a good recycling efficiency. Finally, the TiO_2 nanofibers coated stainless steel meshes possess both underwater superoleophobicity and self-cleaning properties.

EXPERIMENTAL SECTION

Preparation of TiO_2 nanofibers and fabrication of TiO_2 nanofibers coated stainless steel mesh

TiO_2 nanofibers were prepared by hydrothermal method. To prepare TiO_2 nanofibers, 2.0 g of TiO_2 nanoparticles (Degussa P25 TiO_2) was stirred with 30 ml of 10 mol/L $\text{NaOH}_{(\text{aq})}$ (Sigma Aldrich) solution for 1 h and the suspension was transferred to a 40 ml volume Teflon chamber until it filled 75% the volume of the chamber and the chamber was fixed into a hydrothermal

autoclave vessel. The vessel was allowed to heat at 170°C for 80 h in the furnace and the hydrothermally synthesized nano sodium-titanate suspension was collected at room temperature. The pH of the nanofibers was taken down to ~7.5-8.5 by washing with 1 mol/L HCl_(aq) and distilled water (Kim et al., 2006) and separated by centrifuging the suspension. These TiO₂ nanofibers were coated on the stainless steel mesh (#150 micron opening width, size 2''×2'' which were ultrasonically cleaned in acetone and then rinsed with ethanol and deionized water) by spraying the TiO₂ nanofiber suspension. To prepare TiO₂ nanofibers suspension, 10.0 g of nanofibers were suspended in 100 ml of 99.9% ethanol solution and sonicated for 10 min and stirred for 4 h. As prepared TiO₂ nanofibers suspension was sprayed to a pre-cleaned stainless steel by air brush spraying tool. The TiO₂ nanofibers coated mesh was sintered at 450°C for 45 min and cooled down to room temperature and finally it was rinsed with deionized water to remove excess or unbound TiO₂ nanofibers.

Oil/water separation experiments

The oil/water separation setup was prepared by fixing TiO₂ nanofibers coated stainless steel mesh into a PVC union setup as shown in Figure S1 in the supporting information. The water/oil mixture was prepared by mixing 15 g of engine oil (SAE 10W-30) and 40 g of water. The TiO₂ nanofibers coated mesh was pre-wetted with water before initiating the filtration and the water/oil mixture (8:3 w/w) was poured to the filtration set up (~ 20 cm² area of the mesh surface coated with ~6.0 mg of TiO₂ nanofibers having surface area of 37 m²/g) at the rate of 2.0 ml/s under the gravity. Water was collected into a beaker under the PVC union setup. The TiO₂ nanofibers coated mesh was rinsed with distilled water to remove the trapped oil droplets from the mesh after every filtration step. The separation efficiency (ϑ) was calculated by $\vartheta = (m_{\text{remains}})/(m_{\text{initial}}) \times 100\%$, where m_{remains} and m_{initial} are the mass of the oil before and after the

separation. The procedure for measurement of the oil mass in the experiment is given in the SI. The recycle efficiency was obtained by repeating the procedure for 20 cycles and the procedure was repeated for several oils (silicon oil, 1-octadecane, rapeseed oil and kerosene) to get the efficiency and stability of the filter for different oils.

Flow-down (membrane) photocatalytic activity

To check the flow through photocatalytic organic purification activity of TiO₂ nanofibers coated stainless steel mesh, TiO₂ nanofibers coated mesh was fixed between a union and 50 ml of 20 ppm methylene blue (MB, Aldrich) aqueous solution was subjected to flow at a rate of 1.6 ml/min from a peristaltic pump (Watson Marlow peristaltic pump 120S, 1-32 rpm, 102R single channel pump head, tube bore 0.8 mm, rate 1.6 ml/min) into the TiO₂ nanofibers coated mesh. UV light was irradiated on top of the union at 2520 J/m² by Atlas Suntest CPS plus UV range 300-800 nm. This procedure was applied to complete 20 cycles. The concentrations of the MB solutions during the cycles were obtained by measuring the maximum absorbance of the blue colored solution at 665 nm.

Instrumentation and characterization

Scanning electron microscope (SEM) images was taken by Carl Zeiss EVO LS15 scanning electron microscope, Fourier transform infrared spectroscopy (FTIR) was recorded from Thermo Nicolet 6700 FTIR machine, UV-Visible spectroscopy data were taken from Shimadzu 2450 UV-vis spectrophotometer. Contact angle images were taken from the JYSP-360 united test contact angle goniometer. Crystallographic data was taken from Ultima IV X-ray diffractometer.

RESULTS AND DISCUSSION

In this study, we fabricated 1-D TiO_2 nanofibers on stainless steel mesh to achieve superior superhydrophilicity properties. Nanofibers of TiO_2 were synthesised by hydrothermal method using TiO_2 powder and NaOH. In the process of formation of nanofibers, the TiO_2 powder reacted with NaOH to form sheet-like titanate (i.e. layered sodium titanate) and subsequently these nanosheets were transformed into other structures like nanotube, wires, fibers etc., by exfoliated from layered sodium titanate. The detail mechanism of formation of different TiO_2 structures can be found in previous studies (Bavykin et al., 2004; Tsai and Teng, 2004; Morgan et al., 2008). The SEM image of as synthesised TiO_2 nanofibers is shown in Figure 1a and the magnified SEM image of TiO_2 nanofibers is shown in Figure S2 of SI. The SEM image of as synthesized TiO_2 nanofibers reveals that the average length and diameter of the hydrothermally synthesized titania nanofibers are 20 μm and 150 nm respectively. A detailed analysis of nanofibers shown in Figure S2 indicates individually grown nanofibers are not connected to each other. Interestingly most nanofibers exhibit rigid structure. These TiO_2 nanofibers were coated on the stainless steel. The uncoated stainless steel mesh surface and TiO_2 nanofibers coated stainless steel meshes are illustrated in Figure 1b and 1c respectively. As shown in Figure 1c, the smooth stainless steel surface is completely covered with randomly oriented TiO_2 nanofibers resulting in a highly rough surface. The thickness of the coated TiO_2 nanofibers on stainless mesh can be estimated as follows; the pore diameter of bare mesh which is 150 μm (Figure 1b) has been reduced to $\sim 130 \mu\text{m}$ after coating of TiO_2 nanofibers (Figure 1c) on the mesh and hence it can be deduced a $\sim 10 \mu\text{m}$ thick TiO_2 layer on the surface of the mesh. The magnified SEM image of TiO_2 nanofibers coated mesh (Figure 1d) indicates that the TiO_2 nanofibers coated stainless steel mesh has both micro and nanoscale surface roughness which is

more important for manipulating the advance surface wettability. This type of micro/nano surface structure of the modified stainless steel mesh is more favorable to attract water and repel oil underwater which exhibits underwater superoleophobicity as a result of high surface roughness properties of these micro/nano surface structures (Wang et al., 2015).

It is known that the surface wetting behavior depends on chemical composition of the surface. Hence, in addition to the micro/nano morphological structure of the material, the wetting properties of a surface also highly depend on the chemical composition of the surface (Shin et al., 2016). Therefore, surface bonding properties of upper exposed layer of TiO₂ nanofibers were characterized by the FTIR analysis and shown in Figure 2. The broad band at the 3450 cm⁻¹ and a weak band at 1658 cm⁻¹ can be attributed to O-H vibrational stretching mode and the vibrational bending mode with the adsorbed water molecules respectively. These peaks reveal that the hydrothermally modified titanate surface has outer layered and interlayered O-H groups (Ferreira et al., 2006). Specially the broadening effect at the band near 3500 cm⁻¹ indicate the formation of different O-H groups on the Ti-OH surface due to adsorption of water molecules on hydrothermally synthesized TiO₂ nanofibers (Xu et al., 2014). The dominant intense band at 457 cm⁻¹ and 730 cm⁻¹ could be attributed to different types of Ti-O-Ti vibrations (Nikolić et al., 2008) and the peak at 920 cm⁻¹ indicates the Ti-O non bridging oxygen bonds and it may assign to Ti-O-Na bond types in the titanate structure (Nikolić et al., 2008). Such chemical composition and the bond polarity favor attraction of water easily on the surface of TiO₂ nanofibers coated mesh permitting it to acts as superhydrophilic membrane.

The X-ray diffraction patterns of TiO₂ nanofibers calcined at 450 °C were investigated and the results are given in the supporting information in Figure S3. XRD analyses indicate the existence of three possible crystals structures (anatase TiO₂, Ti₅O₉ and Na₂Ti₂₀O₂₅) in the

synthesized nanofibers and details of crystalline structures are given in SI. The binding property of TiO_2 nanofibers on to the mesh is an important parameter when fabricating filters. However, a clear bonding mechanism between TiO_2 and stainless steel mesh is unknown, but it has been proposed a diffuse bonding (it is a combination of mechanical compaction and chemical formation) between TiO_2 and steel mesh (Kliemann et al., 2011). Interestingly, adhesion test (see Figure S4) confirms that TiO_2 nanofibers are firmly bound to mesh and only loosely bound TiO_2 nanofibers are detached from the surface.

Wetting performance and underwater contact angel of the TiO_2 nanofibers coated membranes

For efficient oil-water separation, the wettability of the filter plays a big role and it is an important parameter. Despite the TiO_2 nanofibers coated mesh exhibits superhydrophilicity as well as oleophilicity in air, wetting rates of water and oil on the TiO_2 nanofibers coated mesh are different. i.e. water droplets spread completely on the TiO_2 nanofibers coated mesh instantly (with a static contact angle of $\sim 0^\circ$) while complete spreading of an oil droplet on the TiO_2 nanofibers coated mesh takes ~ 10 s in air. As shown in Figure 3a, the bare stainless steel mesh exhibits the water contact angle of $\sim 96^\circ$ in air and at the same time it exhibits underwater oleophilicity with a contact angle of $\sim 68^\circ$ (Figure 3d). As explained earlier and shown in Figure 3b and 3c, TiO_2 nanofibers coated mesh shows superhydrophilic as well as oleophilic natures respectively in air. Interestingly, the TiO_2 nanofibers coated mesh shows underwater oleophobic property as shown in Figure 3e. The underwater contact angle of 1,2- dichloroethane with TiO_2 nanofibers coated membrane is shown in the Figure 3f. As shown in Figure 3f, an underwater oil

contact angle of 162° confirms the superoleophobic property of the TiO_2 nanofibers coated mesh in underwater condition.

The Young's equation can be used to explain the contact angel of solid-air, solid-water, water-air, solid-oil, oil-air interfaces and this equation can be extended to an underwater oil droplets in solid surfaces as oil/water/solid systems (Cai et al., 2014). According to extended Young's equation, it can be expected that underwater superoleophobic materials could be hydrophilic in air. From contact angel measurements, it is clearly demonstrated the superoleophobic properties of the TiO_2 nanofibers coated mesh in underwater condition compared to bare mesh. As such, an efficient separation of oil and water with TiO_2 nanofibers coated mesh can be expected. In a very recent publication, Jo and Kim et al, reported oil water separation using TiO_2 nanopartciles on mesh (Jo and Kim, 2015). Yet our system is different as we have used TiO_2 nanofibers with nano/micro hierarchical behavior where a higher Cassie-Baxter state can be expected with TiO_2 nanofibers and hence enhanced liquid repelling material surface underwater. Especially here we have discussed the dual properties of underwater superoleophobicity and self-cleaning and photocatalytic activity of the membrane.

As described earlier, the TiO_2 nanofibers coated mesh has a great potential to repel oil under water due to superoleophobic properties in under water. In this study, water-oil separation efficiency was used to investigate the TiO_2 nanofibers modified mesh as an oil-water separation filter. The simple water/oil separation setup is illustrated in Figure 4a where the bare mesh (left) or TiO_2 nanofibers coated filter mesh (right) is fixed in a commercially available PVC union joint. Mixture of commercial engine oil (SAE 10W-30): water in 3:8 (w/w) ratio was passed through the pre-wetted filter under the gravity without any extra force. In this experiment, water is blue colored for clarity and the color of the oil is brown. As shown in Figure 4a, both water

and oil permeated through the bare mesh, while with the TiO_2 coated mesh, separation of engine oil (yellow-brown color) and the water (blue color) is clearly visible.

Different types of oil/water mixtures were passed through the TiO_2 coated mesh to check the feasibility of the separation including silicon oil, rapeseed oil, kerosene, 1-octadecene and engine oil and the individual separation efficiency of different oils can be seen in Figure 4b after one separation cycle. As shown in Figure 4b, separation efficiencies of ~99 and ~90% can be achieved with high viscous oil (silicon oil) and low viscous oil (kerosene) respectively. The filter made with TiO_2 nanofibers on the stainless steel mesh was tested for its durability by using the same filter for several separation cycles of oil-water mixture and the oil water separation efficiency with the separation cycles are shown in Figure 4c. From the Oil water separation results shown in Figure 4c, it is clear that at each separation cycle, over 97.5 (± 1.8)% separation efficiency was achieved where water in the mixture passed through the mesh quickly, and no visible oil was observed in the collected water.

Photocatalytic activity and self-cleaning property of the membrane

The TiO_2 nanofibers coated stainless steel mesh can function as a heterogeneous catalyst to degrade toxic organic matters at the same time with the oil water separation and hence it has the underwater self-cleaning property. To verify the photocatalytic property, MB solution was allowed to flow through the membrane under the gravity while the system was subjected to UV irradiation as shown in Figure 5a. The MB solution was passed through the mesh for few cycles to touch the MB solution on the semiconductor TiO_2 nanofibers to degrade the organic molecules more efficiently. The disappearance (or the degradation) of MB after passing through the membrane in the presence of UV light is clearly visible as shown in the image (right side) of Figure 5a. The degradation of MB with the reaction time was monitored by the UV visible

spectra and shown in Figure 5b. As shown in Figure 5b, the concentration of the MB solution was reduced from 20.0 ppm to 2.6 ppm within 20 cycles. The reduction of MB concentration could be due to both adsorption and degradation. The flow through process in the dark confirms that the concentration of the MB solution has dropped 20.0 ppm to 15.0 ppm within 20 cycles due to adsorption of MB on the surface of TiO₂ nanofibers. As well, a significant concentration drop (from 20 ppm to 0.6 ppm) is observed when the mesh allowed to retain in the 20.0 ppm static MB solution under UV light. In the degradation process of MB on TiO₂ photocatalyst, an electron can be promoted to the conduction band from the valence band at the photoexcitation which exceeding the energy of the band gap (3.23 eV), (Butler and Ginley, 1980; Nogueira and Jardim, 1993; Zhao et al., 1998) producing an e-h pair. The excited electron would react with adsorbed oxygen or reduce the adsorbed MB on TiO₂. While, the photo induced hole can react with adsorbed MB or form hydroxyl radical which is also a strong oxidative species. (Houas et al., 2001) The organic pollutant MB can be oxidized to CO₂, SO₄²⁻, NH₄⁺ and NO₃⁻ through several steps by hydroxyl radicals or holes. (Nogueira and Jardim, 1993)

Figure 5b indicates the degradation of the MB organic solution through the discoloration of the blue color. The degradation efficiency is highly depends on the MB adsorption rate on TiO₂ fibers, active area of the mesh and the intensity of the UV light. This underwater superoleophobic mesh can efficiently remove not only the immiscible oil but also organic contaminants in the water.

270 **CONCLUSION**

271 Superhydrophilic and underwater superoleophobic behavior of the hydrothermally synthesized
272 TiO₂ nanofibers coated stainless steel mesh is investigated. The TiO₂ nanofibers coated stainless
273 steel mesh shows the water contact angle of 0°-2° and the oil contact angle of 162° at the air and
274 under water respectively to prove the superhydrophilic and underwater superoleophobic
275 nature. The membrane can successfully separate different types of oil from water with a
276 separation efficiency of over ~99% and the photocatalytic effect of the membrane helps to
277 separate not only the immiscible oil but also the miscible organics from the water.

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283 REFERENCES

- 284 Al-Shamrani, A., James, A., Xiao, H., 2002. Destabilisation of oil–water emulsions and
 285 separation by dissolved air flotation. *Water Research* 36, 1503-1512.
- 286 Balba, M., Al-Awadhi, N., Al-Daher, R., 1998. Bioremediation of oil-contaminated soil:
 287 microbiological methods for feasibility assessment and field evaluation. *Journal of*
 288 *microbiological methods* 32, 155-164.
- 289 Bautista, P., Mohedano, A., Casas, J., Zazo, J., Rodriguez, J., 2008. An overview of the
 290 application of Fenton oxidation to industrial wastewaters treatment. *J. Chem. Tech. Biotech.* 83,
 291 1323-1338.
- 292 Bavykin, D.V., Parmon, V.N., Lapkin, A.A., Walsh, F.C., 2004. The effect of hydrothermal
 293 conditions on the mesoporous structure of TiO₂ nanotubes. *J. Mater. Chem.* 14, 3370-3377.
- 294 Bellanger, H., Darmanin, T., Taffin de Givenchy, E., Guittard, F., 2014. Chemical and physical
 295 pathways for the preparation of superoleophobic surfaces and related wetting theories. *Chemical*
 296 *reviews* 114, 2694-2716.
- 297 Bratby, J., 1980. Coagulation and flocculation. England: Uplands.
- 298 Butler, M., Ginley, D., 1980. Principles of photoelectrochemical, solar energy conversion. *J.*
 299 *Mater. Sci.* 15, 1-19.
- 300 Cai, Y., Lin, L., Xue, Z., Liu, M., Wang, S., Jiang, L., 2014. Filefish-Inspired Surface Design for
 301 Anisotropic Underwater Oleophobicity. *Advanced Functional Materials* 24, 809-816.
- 302 Chen, P.-C., Xu, Z.-K., 2013. Mineral-coated polymer membranes with superhydrophilicity and
 303 underwater superoleophobicity for effective oil/water separation. *Scientific reports* 3.
- 304 Cheng, Z., Lai, H., Du, Y., Fu, K., Hou, R., Zhang, N., Sun, K., 2013. Underwater
 305 Superoleophilic to Superoleophobic Wetting Control on the Nanostructured Copper Substrates.
 306 *ACS Applied Materials & Interfaces* 5, 11363-11370.
- 307 Choi, H., Stathatos, E., Dionysiou, D.D., 2007. Photocatalytic TiO₂ films and membranes for the
 308 development of efficient wastewater treatment and reuse systems. *Desalination* 202, 199-206.
- 309 Chong, M.N., Jin, B., Chow, C.W., Saint, C., 2010. Recent developments in photocatalytic water
 310 treatment technology: a review. *Water research* 44, 2997-3027.
- 311 Darmanin, T., Guittard, F., 2014. Wettability of conducting polymers: From superhydrophilicity
 312 to superoleophobicity. *Progress in Polymer Science* 39, 656-682.
- 313 Ding, C., Zhu, Y., Liu, M., Feng, L., Wan, M., Jiang, L., 2012. PANI nanowire film with
 314 underwater superoleophobicity and potential-modulated tunable adhesion for no loss oil droplet
 315 transport. *Soft Matter* 8, 9064-9068.
- 316 Dunderdale, G.J., Urata, C., Sato, T., England, M.W., Hozumi, A., 2015. Continuous, High-
 317 Speed, and Efficient Oil/Water Separation using Meshes with Antagonistic Wetting Properties.
 318 *ACS Applied Materials & Interfaces* 7, 18915-18919.
- 319 Fakhru'l-Razi, A., Pendashteh, A., Abdullah, L.C., Biak, D.R.A., Madaeni, S.S., Abidin, Z.Z.,
 320 2009. Review of technologies for oil and gas produced water treatment. *Journal of Hazardous*
 321 *Materials* 170, 530-551.
- 322 Feng, L., Zhang, Z., Mai, Z., Ma, Y., Liu, B., Jiang, L., Zhu, D., 2004. A super-hydrophobic and
 323 super-oleophilic coating mesh film for the separation of oil and water. *Angew. Chem. Int. Ed.*
 324 43, 2012-2014.
- 325 Ferreira, O.P., Souza Filho, A.G., Mendes Filho, J., Alves, O.L., 2006. Unveiling the structure
 326 and composition of titanium oxide nanotubes through ion exchange chemical reactions and
 327 thermal decomposition processes. *Journal of the Brazilian Chemical Society* 17, 393-402.

328 Fosberg, T., 1974. Method and apparatus for detecting oil pollution in water. Google Patents.
 329 Gaya, U.I., Abdullah, A.H., 2008. Heterogeneous photocatalytic degradation of organic
 330 contaminants over titanium dioxide: a review of fundamentals, progress and problems. *Journal of*
 331 *Photochemistry and Photobiology C: Photochemistry Reviews* 9, 1-12.
 332 Gondal, M.A., Sadullah, M.S., Dastageer, M.A., McKinley, G.H., Panchanathan, D., Varanasi,
 333 K.K., 2014. Study of Factors Governing Oil–Water Separation Process Using TiO₂ Films
 334 Prepared by Spray Deposition of Nanoparticle Dispersions. *ACS Applied Materials & Interfaces*
 335 6, 13422-13429.
 336 Gur-Reznik, S., Katz, I., Dosoretz, C.G., 2008. Removal of dissolved organic matter by granular-
 337 activated carbon adsorption as a pretreatment to reverse osmosis of membrane bioreactor
 338 effluents. *Water research* 42, 1595-1605.
 339 Hashimoto, K., Irie, H., Fujishima, A., 2005. TiO₂ photocatalysis: a historical overview and
 340 future prospects. *Japanese journal of applied physics* 44, 8269.
 341 Hathway, T.L., 2009. Titanium dioxide photocatalysis: studies of the degradation of organic
 342 molecules and characterization of photocatalysts using mechanistic organic chemistry.
 343 Houas, A., Lachheb, H., Ksibi, M., Elaloui, E., Guillard, C., Herrmann, J.-M., 2001.
 344 Photocatalytic degradation pathway of methylene blue in water. *Applied Catalysis B:*
 345 *Environmental* 31, 145-157.
 346 Inan, H., Dimoglo, A., Şimşek, H., Karpuzcu, M., 2004. Olive oil mill wastewater treatment by
 347 means of electro-coagulation. *Separation and purification technology* 36, 23-31.
 348 Jo, S., Kim, Y., 2015. Superhydrophilic–underwater superoleophobic TiO₂-coated mesh for
 349 separation of oil from oily seawater/wastewater. *Korean J. Chem. Eng.*, 1-4.
 350 Kim, G.-S., Seo, H.-K., Godble, V., Kim, Y.-S., Yang, O.-B., Shin, H.-S., 2006. Electrophoretic
 351 deposition of titanate nanotubes from commercial titania nanoparticles: application to dye-
 352 sensitized solar cells. *Electrochemistry Communications* 8, 961-966.
 353 Kliemann, J.-O., Gutzmann, H., Gärtner, F., Hübner, H., Borchers, C., Klassen, T., 2011.
 354 Formation of cold-sprayed ceramic titanium dioxide layers on metal surfaces. *J. Therm. Spray*
 355 *Technol.* 20, 292-298.
 356 Lee, C.H., Johnson, N., Drelich, J., Yap, Y.K., 2011. The performance of superhydrophobic and
 357 superoleophilic carbon nanotube meshes in water–oil filtration. *Carbon* 49, 669-676.
 358 Li, J., Yan, L., Li, W., Li, J., Zha, F., Lei, Z., 2015. Superhydrophilic–underwater
 359 superoleophobic ZnO-based coated mesh for highly efficient oil and water separation. *Mater.*
 360 *Lett.* 153, 62-65.
 361 Liu, J., Diamond, J., 2005. China's environment in a globalizing world. *Nature* 435, 1179-1186.
 362 Liu, N., Chen, Y., Lu, F., Cao, Y., Xue, Z., Li, K., Feng, L., Wei, Y., 2013. Straightforward
 363 oxidation of a copper substrate produces an underwater superoleophobic mesh for oil/water
 364 separation. *ChemPhysChem* 14, 3489-3494.
 365 Ma, H., Wang, B., 2006. Electrochemical pilot-scale plant for oil field produced wastewater by
 366 M/C/Fe electrodes for injection. *Journal of hazardous materials* 132, 237-243.
 367 Manna, U., Lynn, D.M., 2015. Synthetic Surfaces with Robust and Tunable Underwater
 368 Superoleophobicity. *Advanced Functional Materials*.
 369 Marmur, A., 2003. Wetting on hydrophobic rough surfaces: to be heterogeneous or not to be?
 370 *Langmuir* 19, 8343-8348.
 371 Mitchell, B.G., Kahru, M., Wieland, J., Stramska, M., 2002. Determination of spectral absorption
 372 coefficients of particles, dissolved material and phytoplankton for discrete water samples. *Ocean*
 373 *optics protocols for satellite ocean color sensor validation, Revision 3*, 231-257.

374 Morgan, D.L., Zhu, H.-Y., Frost, R.L., Waclawik, E.R., 2008. Determination of a Morphological
 375 Phase Diagram of Titania/Titanate Nanostructures from Alkaline Hydrothermal Treatment of
 376 Degussa P25. *Chem. Mater.* 20, 3800-3802.

377 Muneer, M., Qamar, M., Saquib, M., Bahnemann, D., 2005. Heterogeneous photocatalysed
 378 reaction of three selected pesticide derivatives, prothion, propachlor and tebuthiuron in aqueous
 379 suspensions of titanium dioxide. *Chemosphere* 61, 457-468.

380 Munter, R., 2001. Advanced oxidation processes—current status and prospects. *Proc. Estonian*
 381 *Acad. Sci. Chem* 50, 59-80.

382 Nagaveni, K., Sivalingam, G., Hegde, M., Madras, G., 2004. Photocatalytic degradation of
 383 organic compounds over combustion-synthesized nano-TiO₂. *Environmental science &*
 384 *technology* 38, 1600-1604.

385 Nikolić, L.M., Maletín, M., Ferreira, P., Vilarinho, P.M., 2008. Synthesis and characterization of
 386 one-dimensional titanate structure. *Processing and application of ceramics* 2, 109-114.

387 Nogueira, R.F., Jardim, W.F., 1993. Photodegradation of methylene blue: Using solar light and
 388 semiconductor (TiO₂). *J. Chem. Educ.* 70, 861.

389 Odeigah, P., Nurudeen, O., Amund, O.O., 1997. Genotoxicity of oil field wastewater in Nigeria.
 390 *Hereditas* 126, 161-167.

391 Olsson, G., 2015. Water and energy: threats and opportunities. *Water Intelligence Online* 14,
 392 9781780406947.

393 Pan, G., Wang, D., Liu, Y., 2012. Photocatalytic degradation pathways and adsorption modes of
 394 H-acid in TiO₂ suspensions. *Chin. Sci. Bull.* 57, 1102-1108.

395 Pyrzynska, K., 2011. Carbon nanotubes as sorbents in the analysis of pesticides. *Chemosphere*
 396 83, 1407-1413.

397 Rosal, R., Rodríguez, A., Perdigón-Melón, J.A., Petre, A., García-Calvo, E., Gómez, M.J.,
 398 Agüera, A., Fernández-Alba, A.R., 2010. Occurrence of emerging pollutants in urban wastewater
 399 and their removal through biological treatment followed by ozonation. *Water Research* 44, 578-
 400 588.

401 Sawai, Y., Nishimoto, S., Kameshima, Y., Fujii, E., Miyake, M., 2013. Photoinduced underwater
 402 superoleophobicity of TiO₂ thin films. *Langmuir* 29, 6784-6789.

403 Schrank, S., José, H., Moreira, R., Schröder, H.F., 2004. Elucidation of the behavior of tannery
 404 wastewater under advanced oxidation conditions. *Chemosphere* 56, 411-423.

405 Tayade, R.J., Kulkarni, R.G., Jasra, R.V., 2006. Transition metal ion impregnated mesoporous
 406 TiO₂ for photocatalytic degradation of organic contaminants in water. *Industrial & engineering*
 407 *chemistry research* 45, 5231-5238.

408 Thavasi, V., Singh, G., Ramakrishna, S., 2008. Electrospun nanofibers in energy and
 409 environmental applications. *Energy & Environmental Science* 1, 205-221.

410 Tsai, C.-C., Teng, H., 2004. Regulation of the physical characteristics of titania nanotube
 411 aggregates synthesized from hydrothermal treatment. *Chem. Mater.* 16, 4352-4358.

412 Turchi, C.S., Ollis, D.F., 1990. Photocatalytic degradation of organic water contaminants:
 413 mechanisms involving hydroxyl radical attack. *Journal of catalysis* 122, 178-192.

414 Wang, H., Guo, Z., 2014. Design of underwater superoleophobic TiO₂ coatings with additional
 415 photo-induced self-cleaning properties by one-step route bio-inspired from fish scales. *Appl.*
 416 *Phys. Lett.* 104, 183703.

417 Wang, J., Do-Quang, M., Cannon, J.J., Yue, F., Suzuki, Y., Amberg, G., Shiomi, J., 2015.
 418 Surface structure determines dynamic wetting. *Scientific reports* 5.

Wang, S., Song, Y., Jiang, L., 2006. Microscale and nanoscale hierarchical structured mesh films with superhydrophobic and superoleophilic properties induced by long-chain fatty acids. *Nanotechnology* 18, 015103.

Xia, S., Duan, L., Song, Y., Li, J., Piceno, Y.M., Andersen, G.L., Alvarez-Cohen, L., Moreno-Andrade, I., Huang, C.-L., Hermanowicz, S.W., 2010. Bacterial community structure in geographically distributed biological wastewater treatment reactors. *Environmental science & technology* 44, 7391-7396.

Xu, J., Zhang, H., Liu, T., Zhang, J., 2014. Fabrication and Characterization of Potassium and Sodium Titanate via a Hydrothermal Method. *J. Chem. Soc. Pak* 36, 388.

Xu, L.-P., Peng, J., Liu, Y., Wen, Y., Zhang, X., Jiang, L., Wang, S., 2013. Nacre-inspired design of mechanical stable coating with underwater superoleophobicity. *ACS nano* 7, 5077-5083.

Xu, P., Zeng, G.M., Huang, D.L., Feng, C.L., Hu, S., Zhao, M.H., Lai, C., Wei, Z., Huang, C., Xie, G.X., 2012. Use of iron oxide nanomaterials in wastewater treatment: a review. *Science of the Total Environment* 424, 1-10.

Xu, Z., Zhao, Y., Wang, H., Zhou, H., Qin, C., Wang, X., Lin, T., 2016. Fluorine-Free Superhydrophobic Coatings with pH-induced Wettability Transition for Controllable Oil–Water Separation. *ACS Applied Materials & Interfaces* 8, 5661-5667.

Xue, Z., Cao, Y., Liu, N., Feng, L., Jiang, L., 2014. Special wettable materials for oil/water separation. *J. Mater. Chem. A* 2, 2445-2460.

Xue, Z., Wang, S., Lin, L., Chen, L., Liu, M., Feng, L., Jiang, L., 2011. A Novel Superhydrophilic and Underwater Superoleophobic Hydrogel-Coated Mesh for Oil/Water Separation. *Advanced Materials* 23, 4270-4273.

Yao, X., Song, Y., Jiang, L., 2011. Applications of Bio-Inspired Special Wettable Surfaces. *Advanced Materials* 23, 719-734.

Young, T., 1805. An essay on the cohesion of fluids. *Philosophical Transactions of the Royal Society of London*, 65-87.

Zhang, L., Zhong, Y., Cha, D., Wang, P., 2013. A self-cleaning underwater superoleophobic mesh for oil-water separation. *Scientific reports* 3.

Zhao, G., Utsumi, S., Kozuka, H., Yoko, T., 1998. Photoelectrochemical properties of sol–gel-derived anatase and rutile TiO₂ films. *J. Mater. Sci.* 33, 3655-3659.

Table 01: Static contact angles of liquids in the medium of water and air

Medium	SS mesh water contact angle	TiO ₂ nanofibers coated membrane water contact angle	SS mesh oil contact angle	TiO ₂ nanofibers coated membrane oil contact angle
air	96°	0°	0°	0°
Underwater	-	0°	68°	162°

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Figure 1

Figure 2

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Figure 3

Figure 4

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Figure 5

Figure captions

Figure 1. SEM images of (a) TiO₂ nanofibers; (b) original bare stainless steel mesh; (c) low magnification scanning of TiO₂ nanofibers coated stainless steel mesh; (d) high magnification image of TiO₂ nanofibers

Figure 2. FTIR spectrum of TiO₂ nanofibers sintered at 450 °C

Figure 3. Air medium wetting properties of (a) water droplet on bare stainless steel mesh; (b) water droplet wetted TiO₂ nanofibers coated stainless steel mesh; (c) oil droplet wetted TiO₂ nanofibers coated stainless steel mesh. Underwater wetting properties of oil droplets on (d) bare stainless steel mesh; (e) TiO₂ nanofibers coated stainless steel mesh; (f) contact angle image of oil droplet on TiO₂ nanofibers coated stainless steel mesh underwater obtained by Goniometer.

Figure 4. (a) water-oil separation setup of uncoated (left side) and TiO₂ nanofibers coated mesh (right hand side) and separated oil-water from respective filters; (b) separation efficiencies of different oil types; (c) recyclable ability of the TiO₂ nanofibers coated membrane.

Figure 5. (a) Flow-down (membrane) photocatalytic activity set up where filter is fixed in the middle of PVC union and irradiated with Suntest CPS light source. The inset shows the color change of MB after irradiation; (b) Change of concentration of methylene blue (MB) with recycle time.

Graphical abstract

The TiO_2 nanofibers coated stainless steel mesh as a novel underwater superoleophobic membrane for the effective separation of contaminated oil-water mixtures is reported.