

Superhydrophilic-underwater superoleophobic TiO₂-coated mesh for separation of oil from oily seawater/wastewater

Sunhee Jo and Younghun Kim[†]

Department of Chemical Engineering, Kwangwoon University, Kwangwoon-ro 20, Nowon-gu, Seoul 01897, Korea

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Abstract—Oil/water separation is a topic of interest worldwide because of increasing release of industrial oily wastewater and frequent leakage of crude oil. Superhydrophilic and underwater superoleophobic meshes were fabricated by simple and fast dip-coating of nanosized TiO₂ on a stainless steel mesh with a 50 μm pore size. The coated mesh was used for oil/water separation by gravity-driven filtration without additional energy. After acid treatment and TiO₂ coating of the mesh, its surface property was altered from hydrophobic to superhydrophilic and superoleophobic. Oil/water separation was achieved in 3 s with an efficiency of 98–99%, irrespective of oily water type (seawater or wastewater). Initial separation efficiency was maintained during a test involving 20 recycles. Therefore, the as-made TiO₂-coated mesh can be used in practical applications such as for wastewater purification, and in the petroleum industry.

Keywords: Oil Separation, Superhydrophilic, Superoleophobic, Wettability, Mesh

INTRODUCTION

Due to the increase in industrial oily wastewater volume and frequency of accidental oil spills, the development of effective and inexpensive methods for oil/water separation has become an important issue environmentally and economically [1]. Although several oil/water separation methods, such as adhesion, membrane filtration, and absorbance, have been developed and are widely used [2], achieving an energy- and cost-effective oil/water separator with high separation efficiency remains challenging. Because oil/water separation is governed by the interfacial features of the substrate, the fabrication of preferential wettability materials toward oil or water would be desirable and effective [3,4].

Novel materials with both hydrophobic/oleophilic “oil-removing” surfaces and hydrophilic/oleophobic “water-removing” surfaces have been developed to facilitate the spread and penetration of the oil or water phase through the materials readily, while the other phase is repelled [2–6]. However, the oil-removing surface is easily fouled and blocked by oils due to its oleophilicity, which influences the recyclability and separation efficiency [5]. In addition, among the most prominent membrane-filtration techniques, the gravity-driven method is preferred due to its high cost-efficiency and permeability, compared to cumbersome and expensive cross-flow filtration [2,6]. Therefore, a water-removing membrane with a superhydrophilic/superoleophobic surface is more effective for gravity-driven filtration. To date, various materials such as TiO₂ [2], palygorskite [3], Cu(OH)₂ [4], ZnO [5], or hydrogels [6] have been investigated to achieve underwater superoleophobicity, and showed effective oil-water separation. However, a method for the separation of oil from oily seawater or wastewater with high separation efficiency has yet to be developed.

Therefore, separation efficiency and stability in the complex oily seawater or wastewater environment should be evaluated to facilitate practical applications.

We fabricated superhydrophilic ($\theta_{\text{water}} < 0^\circ$) surfaces that exhibit underwater superoleophobicity ($\theta_{\text{oil}} > 170^\circ$) by the dip-coating of nanosized TiO₂ onto stainless steel meshes (50, 75, 150, and 300 μm pore size). The as-made TiO₂-coated mesh exhibited excellent water affinity and underwater oil repellency. Thus, the superhydrophilic/superoleophobic TiO₂-coated mesh was used for gravity-driven separation of oils (n-hexane, decane, hexadecane, and vegetable oil) from oily water, seawater, and wastewater. In addition, the separation efficiency and stability was evaluated after multiple recycles.

EXPERIMENTAL

TiO₂ nanoparticles of ca. 20 nm diameter were purchased from Evonik (Degussa) and dispersed in ethanol to prepare a 0.03 g/mL coating solution. Stainless steel meshes with pore diameters of 50 to 300 μm were pretreated by immersion in a cleaning solution containing H₂SO₄ and saturated sodium dichromate solution for 30 min at 65 °C [7], followed by washing with deionized water (DW). The mesh substrates were immersed in the coating solution for 10 s and subsequently withdrawn vertically and then dried at 65 °C. The resulting coating mesh was subjected to heat treatment at 500 °C for 2 h to render the surface more mechanically robust [2]. Artificial seawater (35‰) and synthetic wastewater (460 mg/L COD and 44 mg/L TN) were prepared using a method described previously [8,9]. The surface morphology of meshes was analyzed by field emission scanning electron microscopy (FE-SEM, S-4800). The contact angles (CA) were measured using a home-made goniometer [10], and the volume of the individual water and oil droplets was 10 μL . To visualize oil/water separation, water and oil were colored with methylene blue and Sudan red 3, respectively. When water was dropped onto the TiO₂-coated mesh, it sponta-

[†]To whom correspondence should be addressed.

E-mail: korea1@kw.ac.kr

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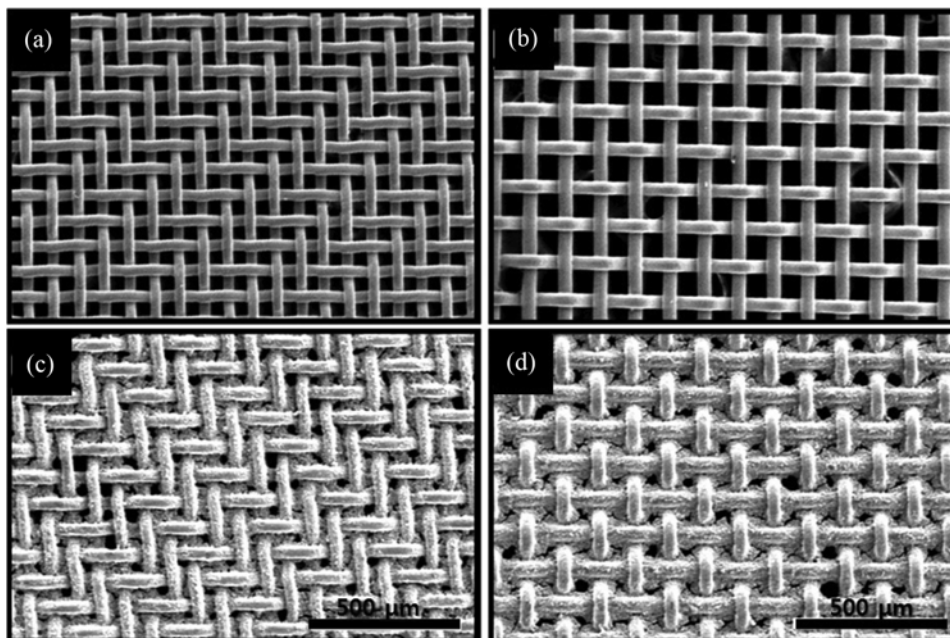


Fig. 1. SEM images of the original stainless steel mesh with (a) 50 and (b) 75 μm pores and the TiO_2 -coated mesh with (c) 50 and (d) 75 μm pores.

neously spread over and penetrated the mesh; therefore, the water-spreading rate (m^2/s) was measured as spread-area per unit time. The separation efficiency was calculated from the mass difference between the oil in the initial oil-water mixture and that in the penetrated water phase.

RESULT AND DISCUSSION

We selected nanosized TiO_2 to prepare a superhydrophilic/superoleophobic surface due to its stability, cost efficacy, and intrinsic superhydrophilicity. As shown in Fig. 1, meshes were uniformly covered with TiO_2 nanoparticles by dip-coating. The coating thickness of TiO_2 on the mesh was 6 μm in a cross-sectional view. As-made mesh exhibited both micro- and nano-scale surface roughness (Fig. 1(c) and 1(d)), which is crucial for controlling surface wettability [2]. TiO_2 coating of the stainless steel induced pore-opening to a greater degree with increasing mesh pore size (Fig. S1).

When pre-wetted in an aqueous phase, coated mesh surfaces become superoleophobic for various oils, such as n-hexane, decane, hexadecane, and vegetable oil. We used hexane as a representative oil to characterize the underwater wettability of the meshes. As shown in Fig. 2(a) and Fig. S2(a), the contact angle of water in air (θ_{water}) of uncoated meshes increased from 70° to 130° with increasing mesh pore size. As reported by Chen et al. [7], pretreatment of mesh with acid enhanced the surface hydrophobicity with increasing pore size. TiO_2 -coated meshes showed an almost zero degree of contact angle. However, the TiO_2 coating process dramatically altered the surface wettability from hydrophobic to superhydrophilic. While the contact angle of oil in water (θ_{oil}) of uncoated mesh with 50 μm pores was $<110^\circ$, that of the coated mesh was $>170^\circ$, indicating that the TiO_2 -coated mesh has underwater superoleophobicity (Fig. 2(b) and Fig. S2(b)). Annealing promotes the

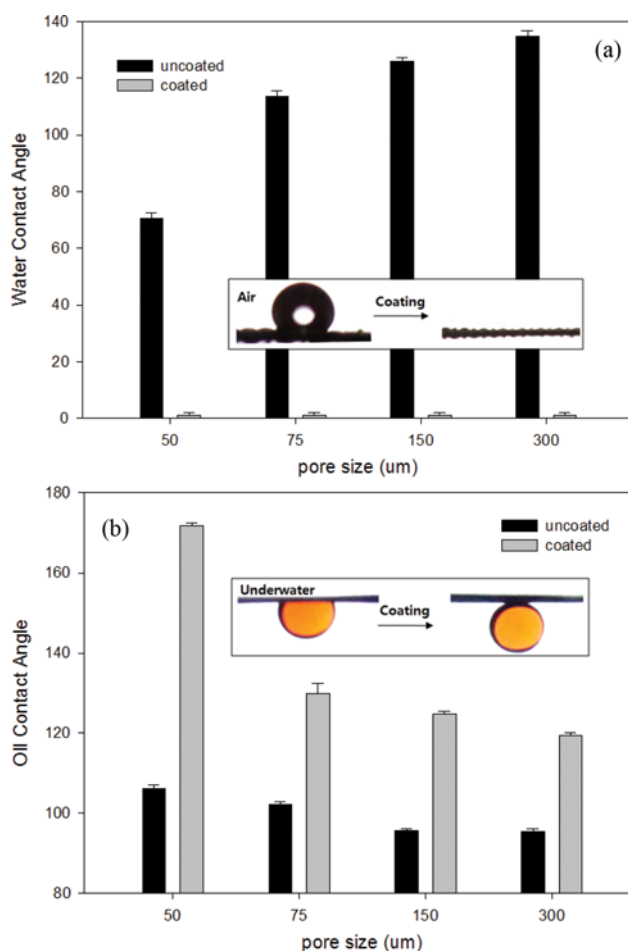


Fig. 2. Contact angle change in (a) air and (b) water according to pore size of the original and coated mesh.

formation of hydrogen bonds, and consequently enhances the surface hydrophilicity and underwater oleophobicity [2,7].

The water-spreading rate on the TiO₂-coated mesh increased with decreasing pore size, which enabled determination of a suitable pore size to achieve superwetting (Fig. S3). Since mesh hydrophilicity, underwater oleophobicity, and spreading rate decreased with decreasing mesh pore size, a mesh pore size of 50 μm resulted in the highest spreading rate (superwetting) [11] and the highest oil contact angle underwater.

If an oil droplet is carefully placed on the coated mesh, the porous mesh can withstand the hydrostatic pressure of the oil column (Fig. S4). At a critical height (h_{max}), the oil begins to flow downward and penetrate the TiO₂-coated mesh. The intrusion pressure (P_i) is expressed as $P_{\text{int}} = \rho g h_{\text{max}}$ (Fig. S5), and the coated mesh with the smallest pores showed the highest P_{int} value of 2 kPa, which was two-fold that reported previously [2]. The higher the intrusion pressure,

the higher the oil-permeation resistance. Therefore, the high intrusion pressure for oil on the mesh might enhance oil/water separation and recyclability. The as-made TiO₂-coated mesh with 50 μm pores is thus the most suitable for oil/water separation applications.

The unique superhydrophilicity and underwater superoleophobicity of the as-made meshes are desirable for oil/water separation. Oil/water separation was performed as shown in Fig. 3. A 100 mL volume of oil/water mixture (3 : 7 v/v) was poured onto the water-pre-wetted TiO₂-coated mesh, which was fixed between two glass funnels. Water permeated through the coated mesh rapidly; no visible oil was observed in the collected water (Fig. 3(b)). Other oil/water mixtures, such as decane, hexadecane, and vegetable oil, were also successfully separated by the same process and showed almost 99% separation efficiency (Fig. S6). The separation process was completed within 3 s (see the Supporting video). The water flux (F) penetrating the mesh was calculated as $F = V/St$, where V is the volume permeated through the mesh, S is the area of mesh, and t is the time required for water permeation. Here, the water flux reached 25 L/m²s, which is greater than reported previously [3]. Notably, the as-made TiO₂-coated mesh exhibited a very high separation rate for oily water.

To evaluate the practical applicability of TiO₂-coated mesh, separation tests of oil from oily seawater and wastewater were carried out. The separation efficiency of both oily seawater and wastewater was >98% (Fig. 3(c)). The ionic strength of the artificial seawater and synthetic wastewater used here was 0.493 M and 0.047 M, respectively. The high concentration of ions in artificial seawater and synthetic wastewater may alter the interfacial tension between the oil and water, as compared to fresh water. As reported by Ábrahám et al. [12], the surface tension of water at a non-equilibrated interface decreased as the ion concentration in solution increased. Therefore, the decrease in the surface tension of water influenced the wettability of the surface, resulting in slightly lower separation efficiency.

In addition, the coated meshes retained underwater superoleophobicity after 20 separation cycles with 98% separation efficiency for a hexane/seawater mixture (Fig. 4). The slight decrease (2%) in

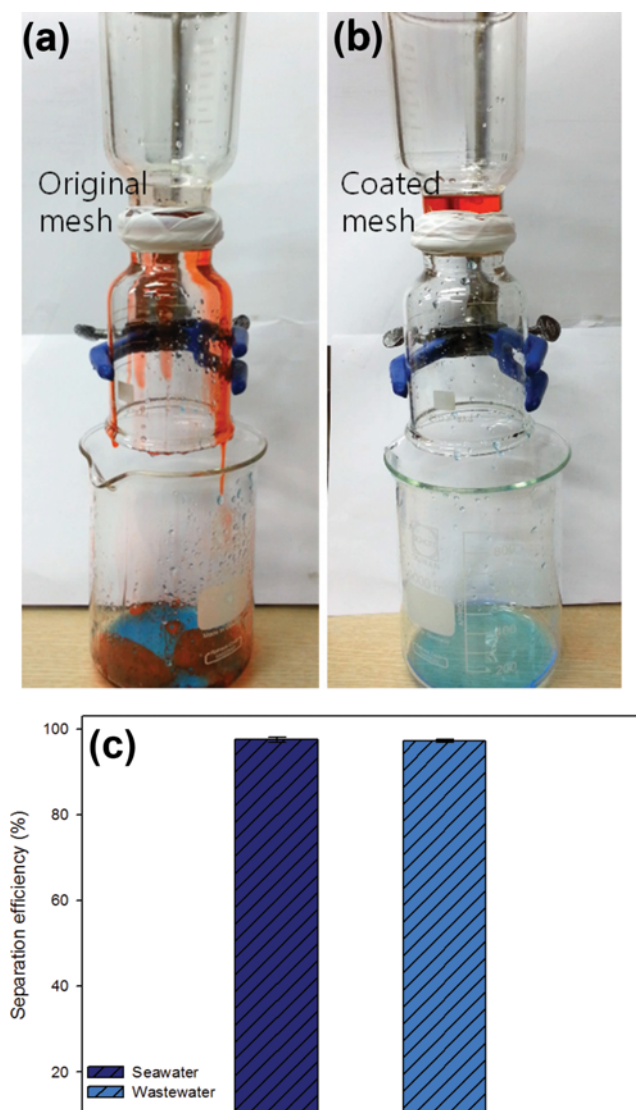


Fig. 3. Separation of a hexane/water mixture using the (a) original and (b) coated mesh. (c) Separation efficiency of hexane from oily seawater and wastewater.

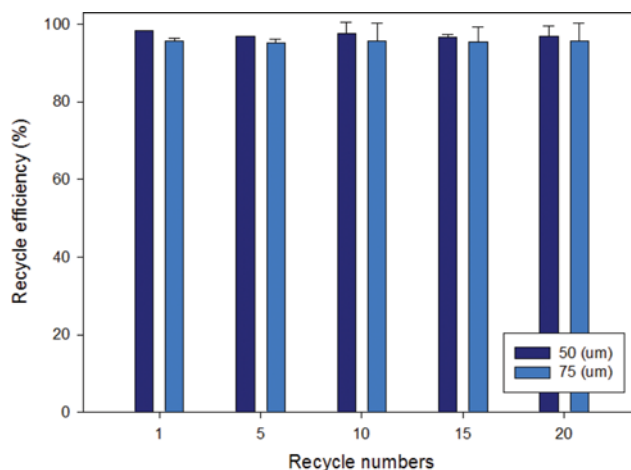


Fig. 4. Separation efficiency of hexane in seawater according to recycle number.

separation efficiency might be due to the fouling of oil and the removal of TiO₂ nanoparticles from the coated mesh. The type water of (seawater or wastewater) in the oil/water mixture had an only slight influence on oil separation, and so the as-made TiO₂-coated mesh can be applied for oil/water separation in the field.

CONCLUSIONS

Robust superhydrophilic and underwater superoleophobic TiO₂-coated meshes were prepared by a simple dip-coating method and successfully applied to separate oil from oily water (seawater and wastewater). While acid treatment of mesh increased its hydrophobicity, TiO₂ coating of the mesh dramatically changed its surface properties to be superhydrophilic/superoleophobic. The as-made meshes could selectively and rapidly separate oil from oily water with a separation efficiency of up to 99%, which was maintained over 20 separation cycles. Since the mesh pore size is a key factor in oil/water separation, the TiO₂-coated mesh with a 50 µm pore size was most suitable for use in oil/water separation applications.

ACKNOWLEDGEMENTS

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SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at <http://www.springer.com/chemistry/>

journal/11814.

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Supporting Information

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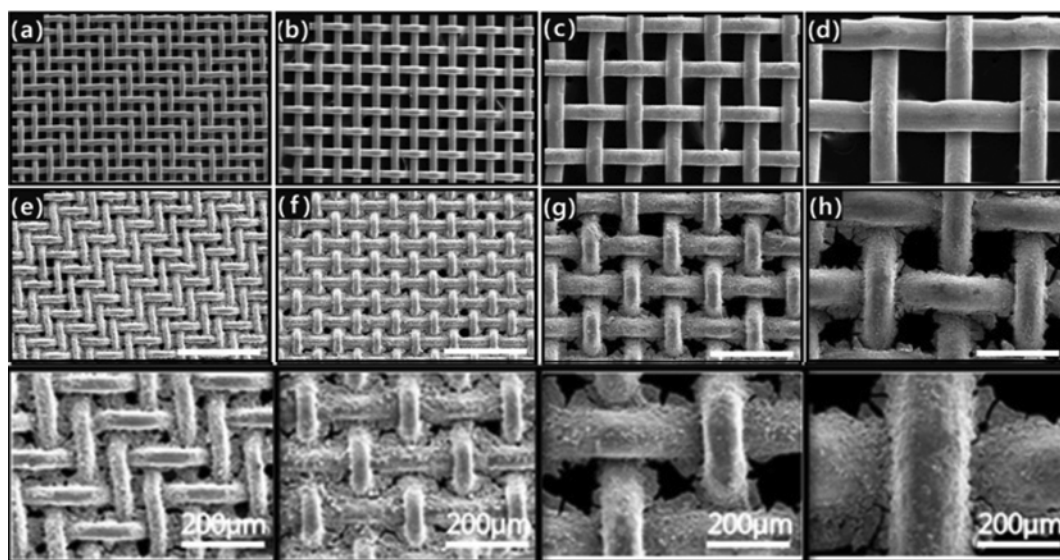


Fig. S1. SEM images of original meshes with (a) 50, (b) 75, (c) 150, and (d) 300 μm , and (e)-(h) TiO_2 -coated meshes of (a)-(d) (scale bar: 500 μm).

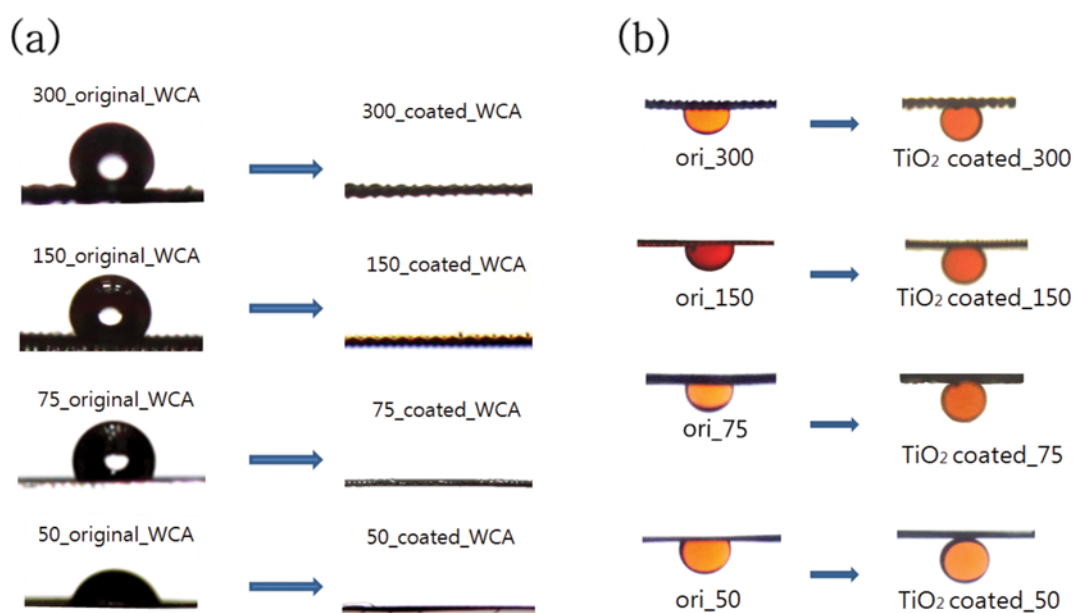


Fig. S2. Contact angle measurement in (a) air and (b) water for original and TiO_2 -coated meshes.

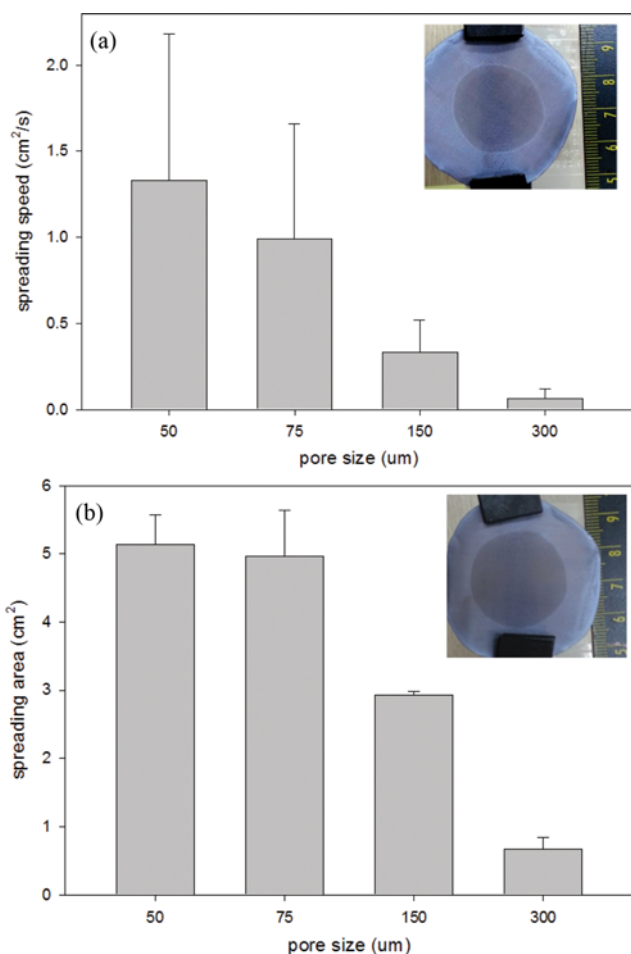


Fig. S3. Water spreading speed and area on the TiO_2 -coated meshes with different pore size.

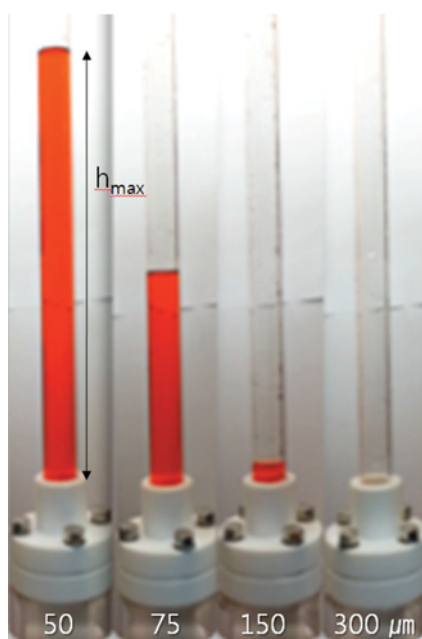


Fig. S4. Measurement of maximum critical height of oil for the TiO_2 -coated meshes with different pore size.

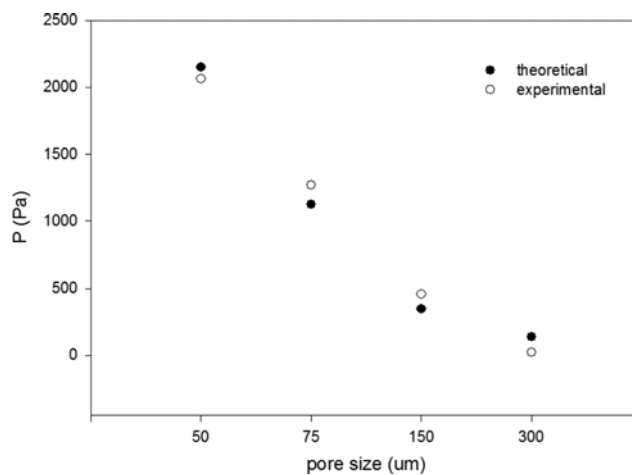


Fig. S5. Oil breakthrough pressures of TiO_2 -coated meshes.

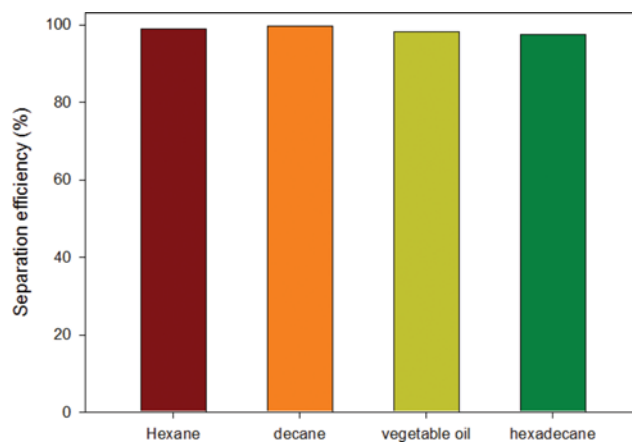


Fig. S6. Separation efficiency of various oils in water using TiO_2 -coated mesh of 50 μm pore.