Biocompatible Meshes with Appropriate Wettabilities for Underwater Oil Transportation/Collection and Highly Effective Oil/Water Separation

Chih-Feng Wang,[*,†] Wen-Ning Wang,[‡] Shiao-Wei Kuo,[§] Yeo-Wan Chiang,[§] Jui-Hsiang Hung,[∥] and Kuo-Jung Lee[‡]

[†]Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei 106, Taiwan
[‡]Department of Materials Science and Engineering, I-Shou University, Kaohsiung 840, Taiwan
[§]Department of Materials and Optoelectronic Science, National Sun Yat-Sen University, Kaohsiung 804, Taiwan
[∥]Department of Biotechnology, Chia Nan University of Pharmacy and Science, Tainan 717, Taiwan

S *Supporting Information*

ABSTRACT: In this study, we prepared biocompatible superhydrophilic and underwater superoleophobic tannic acid (TA)/polyvinylpyrrolidone (PVP)-coated stainless-steel meshes that mediated extremely efficient separations of mixtures of oil and water. These TA/PVP-coated stainless-steel meshes displayed excellent antifouling properties and could be used to separate oil/water mixtures continuously for up to 24 h. Moreover, a funnel-like TA/PVP-coated stainless-steel mesh device could be used for underwater oil transportation and collection. In conjunction with our continuous oil removal system, this device allowed for the continuous collection and removal of oil pollutants from underwater environments. The high performance of these TA/PVP-coated stainless-steel meshes and their green, low-energy, cost-effective preparation suggests great potential for practical applications.
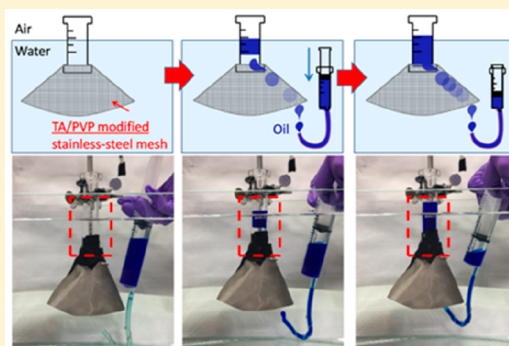
INTRODUCTION

Rapid developments in offshore oil production and transportation come with the cost of greater potential for oil spills and accidents.[1−3] In 2010, an estimated 210 million gallons of oil was released into the Gulf of Mexico after the explosion of BP's Deepwater Horizon oilrig, one of the largest offshore oil spills in history and an unprecedented environmental disaster. A report from the International Tanker Owners Pollution Federation (ITOPE) reveals that over 1800 accidents occurred with large oil tankers from 1970 to 2016, resulting in the loss of approximately 5.73 million tons of oil. Currently implemented techniques for oil/water separations require high energy consumption and proceed with low separation efficiencies and high costs. As a result, the development of new methods for the collection and removal of large amounts of organic pollutants from water remains an attractive global challenge.

Materials possessing special wettabilities have attracted a great amount of commercial and academic attention.[4−6] The use of such materials is one of the most promising approaches for effective oil/water separation. In the past decade, oil removal techniques using superhydrophobic/superoleophilic (oil-removing) materials have allowed for effective and facile oil/water separations, through either selective oil filtration,[7−10] transportation,[11] or absorption.[12−18] The first example of an

oil/water separation system using a superhydrophobic and superoleophilic polytetrafluoroethylene (PTFE)-coating mesh was reported in 2004.[7] Although such special wettable materials can be effective agents for oil/water separations, they are readily fouled or even blocked up by oils (especially high-viscosity oils) because their intrinsic oleophilicity affects the separation efficiency. Inspired by the wetting behavior of fish scales, materials exhibiting superhydrophilic and underwater superoleophobic behavior are of interest because they allow water to pass, thereby alleviating the issue of oil-fouling.[19] Following this strategy, several materials exhibiting both superhydrophilic and underwater superoleophobic properties have been prepared with the aim of applying them in efficient separations of oil/water mixtures.[20−32] Song and co-workers developed cement-coated mesh films that displayed suitable superhydrophilicity and underwater superoleophobicity for the effective separation of immiscible oil/water mixtures. Their cement-coated meshes were also highly reusable and stable throughout repeated oil/water separation tests using alkali, salt, and boiling water.[33] Zeng et al. used konjac glucomannan (KGM) and tolylene-2,4-diisocyanate (TDI) to

Scheme 1. Schematic Representation of the Preparation of the Eco-friendly TA/PVP Coating
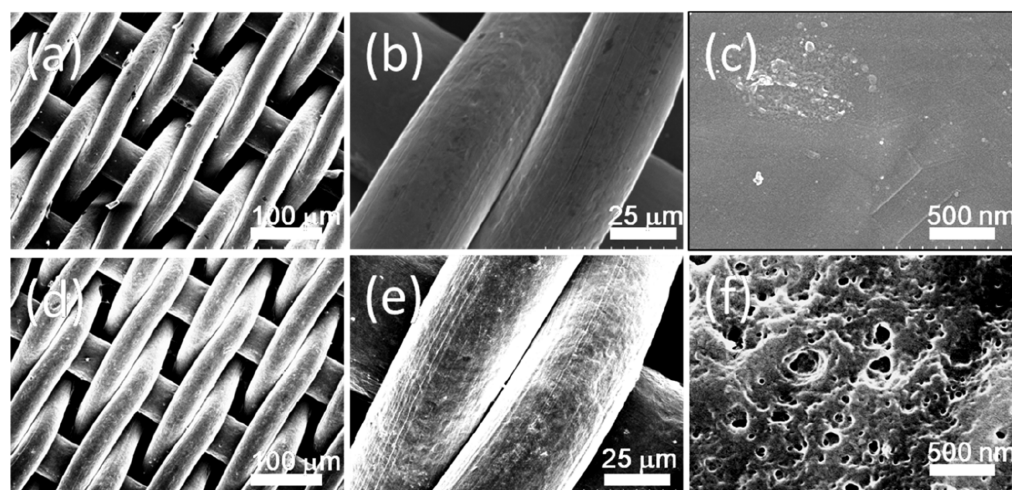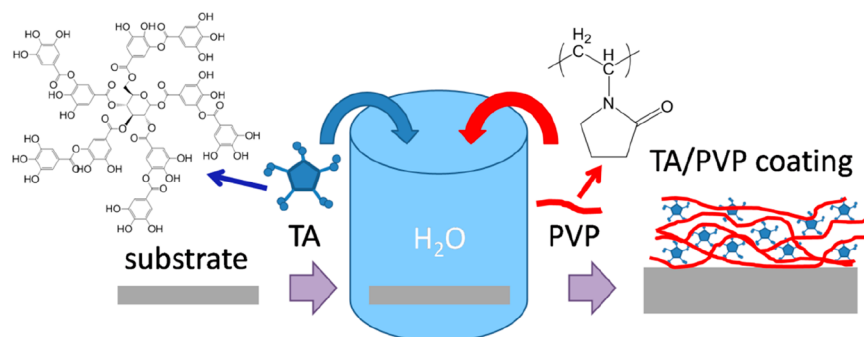
Figure 1. SEM images of the (a–c) pristine and (d–f) TA/PVP-modified stainless-steel meshes.

prepare highly biocompatible, underwater superhydrophilic, and multifunctional biopolymer membranes that were applicable in the separations of oil/water mixtures and the adsorption of water-soluble pollutants.[34] Zhang and co-workers reported the preparation of inorganic membranes wrapped with cupric phosphate nanosheets. The as-prepared membranes displayed superior superhydrophilic and underwater anti-oil- and anti-bio-fouling properties that allowed for efficient oil/water separation.[35] Nevertheless, all of these methods require multistep processes, stringent preparation specifications, and the use of harmful chemicals, thereby limiting their practical applications.

In this paper, we present a simple and eco-friendly method for the fabrication of superhydrophilic and underwater superoleophobic tannic acid (TA)/polyvinylpyrrolidone (PVP)-coated stainless-steel meshes. TA is a naturally available, water-soluble, fully biodegradable, high-molecular-weight polyphenolic compound, mostly extracted from plants and microorganisms; accordingly, it has already been approved by the U.S. Food and Drug Administration. TA is capable of complexing or cross-linking macromolecules at multiple binding sites through multiple non-covalent interactions, including hydrogen-bonding, ionic, and hydrophobic interactions. It can also coordinate with metal ions to form TA–metal networks.[36,37] Furthermore, PVP has attracted great interest from academia and industry for its nontoxicity, facility at forming complexes, high biological compatibility, strong adhesiveness, and resistance to thermal degradation in solution. It has found wide use in many fields, for example,

in aerosol products, as a food additive, as a dispersing agent providing colloid stability, and as a blood plasma substitute. Previous studies demonstrated that naturally derived and inexpensive TA can be an efficient gelation binder for hydrogel formation with commercially available water-soluble PVP polymers.[38−40] In this present study, we found that TA/PVP-coated stainless-steel meshes prewetted with water displayed superhydrophilicity and underwater superoleophobicity and could be used in effective oil/water separations. Our as-prepared TA/PVP-coated stainless-steel meshes exhibited high separation capacity, allowing for the separation of oil/water mixtures continuously for up to 24 h without any increase in the oil content in the filtrate. In addition to oil spills on water surfaces, deepwater oil spills are also catastrophic for marine and other aquatic ecosystems and the health of local residents. Thus, as part of this study, we also fabricated a simple device for underwater oil transportation and collection using the TA/PVP-coated stainless-steel meshes. In conjunction with our continuous oil removal system,[13] this device allowed for the continuous collection and removal of oil pollutants from an underwater environment. The excellent performance of our TA/PVP-coated stainless-steel mesh films in oil/water separations and underwater oil collection and their preparation through an eco-friendly process suggest great potential for their applicability in real oil/water separations and oil spill cleanups.

■ RESULTS AND DISCUSSION

TA is a water-soluble, high-molecular-weight, polyphenolic compound containing a central carbohydrate (glucose) core esterified by phenol (gallic acid) units. Previous studies have indicated that TA assembles with PVP through hydrogen bonding to form low-toxicity, non-ionic, biocompatible, and high-pH-stable complexes. In this study, we prepared TA/PVP complexes on glass slides through an eco-friendly one-step process without the need for any harmful chemical agents (Scheme 1). The water contact angle (CA) of the TA/PVP coatings was $31 \pm 2°$ (Figure S1 of the Supporting Information); although hydrophilic, this value is too high for the materials to be classified as superhydrophilic.

The wettability of a solid surface depends upon two factors: its chemical composition and its topographical microstructure. Merging the TA/PVP coatings with a stainless-steel mesh provided us with superhydrophilic surfaces. Panels a−c of Figure 1 present scanning electron microscopy (SEM) images of the pristine stainless-steel mesh. SEM images of the TA/PVP-coated stainless-steel mesh (panels d−f of Figure 1) revealed that the TA/PVP complexes had uniformly coated the mesh fibers, with no complexes observed in the pores of the mesh, potentially allowing for free passage of water through the membrane during the oil/water separation process. We observe nanoscale roughness in the magnified SEM image of a single-coated mesh fiber (Figure 1f). When a water droplet came into contact with the surface, it instantly spread out and permeated into the TA/PVP-coated stainless-steel meshes (the process was complete within 5 s), resulting in a CA of less than 3° (Figure 2a). The superhydrophilicity of the TA/PVP-coated stainless-steel mesh resulted from a combination of the hydrophilicity of the TA/PVP complex and the nanoscale

roughness of the microscale mesh structure. A similar phenomenon occurred when adding a droplet of oil as a detecting probe, suggesting that the TA/PVP-coated stainless-steel mesh also possessed superoleophilicity (CAs of n-hexane, n-hexadecane, isooctane, and diesel all close to 0°) in air.

Remarkably, the TA/PVP-coated stainless-steel meshes become superoleophobic when immersed in water. Underwater oil droplets on the mesh surface were nearly spherical (Figure 2b) with high CAs (>150°; Figure 2c). When the TA/PVP-coated stainless-steel mesh was immersed in water, some water became trapped within its rough microstructure because of the superhydrophilicity of the material; subsequently, in the presence of oil, it formed an oil/water/solid composite interface. The trapped water layer inside the mesh structure decreased the contact area of the solid−oil interface, resulting in high underwater superoleophobicity. Gratifyingly, the TA/PVP-coated stainless-steel meshes exhibited excellent stability toward corrosive aqueous liquids. Initially, we immersed the TA/PVP-coated stainless-steel meshes in acidic (pH 2) and saline (3.5 wt % NaCl) solutions for as long as 24 h and then examined their underwater oil wettability and morphology. Underwater, n-hexadecane droplets were nearly spherical on the TA/PVP-coated stainless-steel meshes in the acidic (pH 2) and NaCl (3.5 wt %) solutions, with oil CAs of 158° and 161°, respectively, confirming the stable underwater superoleophobicity of the TA/PVP-coated stainless-steel meshes in these corrosive liquids. We also tested the storage stability of the superhydrophilic TA/PVP-coated stainless-steel meshes in the 3.5 wt % NaCl solution. After 30 days, the TA/PVP-coated stainless-steel meshes retained high superoleophobicity, with a CA of approximately 160°. Low underwater oil adhesion is preferred for efficient oil/water separation. Thus, we examined the underwater oil adhesive behavior by positioning oil droplets through a steel needle onto the mesh surface. Figure 2d reveals that the adhesive force was negligible, suggesting that we would observe excellent performance in subsequent tests of oil/water separation.
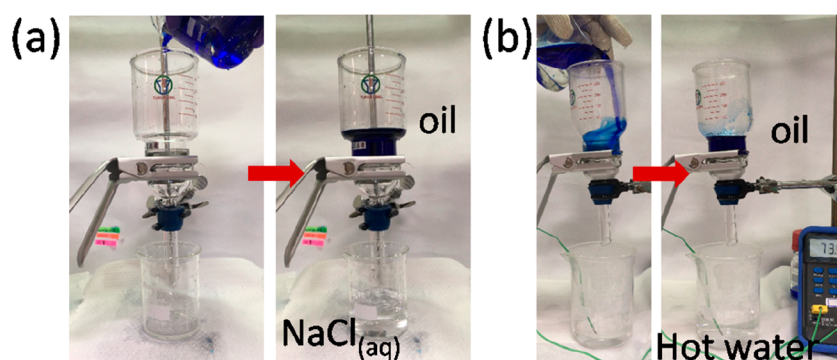
Because the TA/PVP-coated stainless-steel meshes exhibited both underwater superoleophobicity and water permeability, they facilitated separations of oil/water mixtures with high efficiency. We performed a series of oil/water separation experiments to determine the oil/water separation capability of our TA/PVP-coated stainless-steel mesh. Prior to pouring the oil/water mixture, we prewetted the separating membrane with water; this step was necessary for successful oil/water separation. Initially, we poured mixtures of toluene and water (1:1, v/v) into two glass tubes, between which the coated mesh was set (Figure 3a). The water passed quickly through the prewetted TA/PVP-coated stainless-steel mesh and entered the beaker below. In contrast, all of the oil was retained above the TA/PVP-coated stainless-steel mesh as a result of its underwater superoleophobicity. This separation was solely gravity-driven and, consequently, highly energy-efficient. Other oils and organic solvents (i.e., hexane, petroleum ether, and oleic acid) were also separated from water in the same manner. We used a gas chromatography system with flame ionization detection (GC/FID) to measure the oil contents of the various filtrates. Each of the oil/water mixtures was separated with high efficiency during these separation tests; the n-hexane/water, isooctane/water, n-hexadecane/water, and diesel/water mixtures provided oil contents of 1.0, 0.97, 0.05, and 1.53 ppm, respectively.
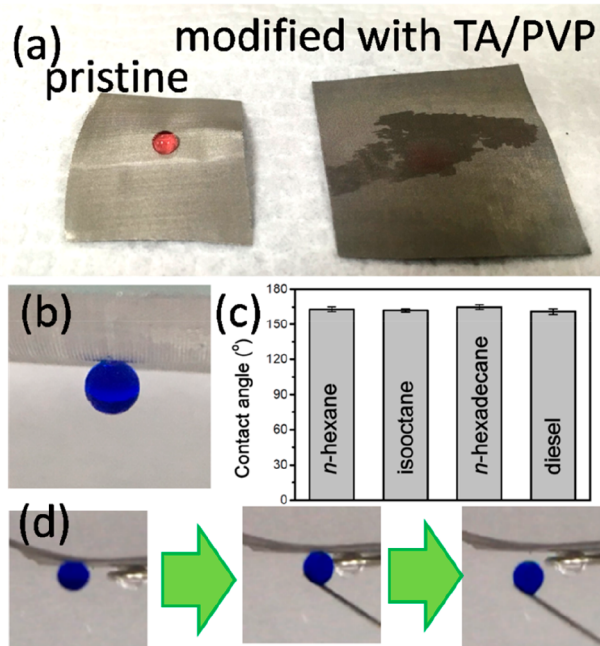
Figure 2. (a) Photograph of water droplets on the pristine and TA/PVP-modified stainless-steel meshes. (b) Photograph of an oil droplet (n-hexadecane) beneath a TA/PVP-modified stainless-steel mesh in water (CA of 162°). (c) Underwater CAs of a series of oils. (d) Dynamic contact of an oil droplet on a TA/PVP-modified stainless-steel mesh, demonstrating its low underwater oil adhesiveness.
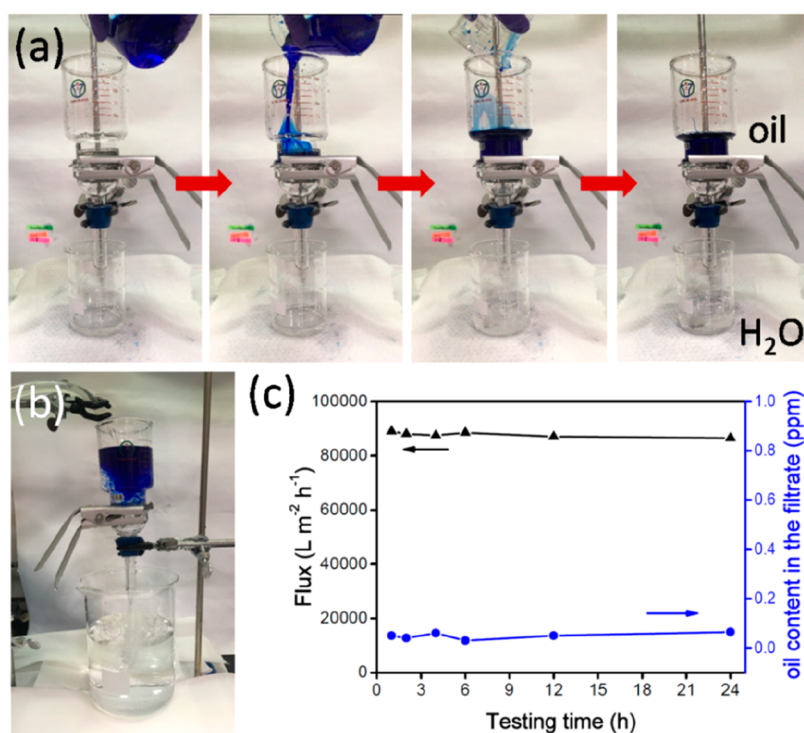
Figure 3. (a) Solely gravity-driven separation of oil/water mixtures performed through the TA/PVP-modified stainless-steel mesh. (b) Continuous separation test of diesel/water mixtures performed using the TA/PVP-modified stainless-steel mesh. (c) Real-time monitoring of the variation of the flux and the oil content in the filtrate, plotted with respect to time, during 24 h of separation of *n*-hexadecane/water mixtures, performed using a TA/PVP-modified stainless-steel mesh.

Figure 4. Solely gravity-driven separations of (a) oil/aqueous NaCl and (b) oil/hot water (92 °C) mixtures, performed through the TA/PVP-modified stainless-steel mesh.

Next, we tested the TA/PVP-coated stainless-steel mesh for its suitability for use in continuous oil/water separation and to further study its robustness and antifouling properties. In the continuous oil/water separation test (Figure 3b), we added water to the upper glass tube continuously while maintaining the height of the oil/water mixture at 6.5 cm. Initially, a *n*-hexadecane/water mixture was separated through this continuous separation test over a period of at least 1 h. The water flux and the oil contents in the filtrate during the continuous separation test were 86 000 L m⁻² h⁻¹ and 0.07 ppm, respectively. Furthermore, when we performed the continuous separations of *n*-hexadecane/water mixtures for up to 24 h through the TA/PVP-coated stainless-steel mesh, we observed no visible oil in the collected water at any time during the testing process, confirming the high effectiveness of this separation process. Notably, the decrease in the flux was negligible, and the oil contents in both filtrates remained at less

than 0.08 ppm (Figure 3c). Thus, because of the excellent antifouling properties of this system, we suspect that it should be possible to use TA/PVP-coated stainless-steel meshes to treat larger volumes of oil/water mixtures over longer periods of time. The TA/PVP-coated stainless-steel meshes not only separated free oil/water mixtures with high efficiency but also displayed high performance under briny and hot environments. Here, we prepared two kinds of oil/water mixtures,, combining *n*-hexadecane with 3.5 wt % NaCl$_{(aq)}$ and hot water (91 °C), respectively, and separated them through the prewetted TA/PVP-coated stainless-steel mesh (panels a and b of Figure 4). Both of these aqueous solutions passed quickly through TA/PVP-coated stainless-steel mesh, but again the oil was repelled and, thereby, retained in the upper glass tube, confirming the durable underwater superoleophobicity of the TA/PVP-coated stainless-steel mesh.
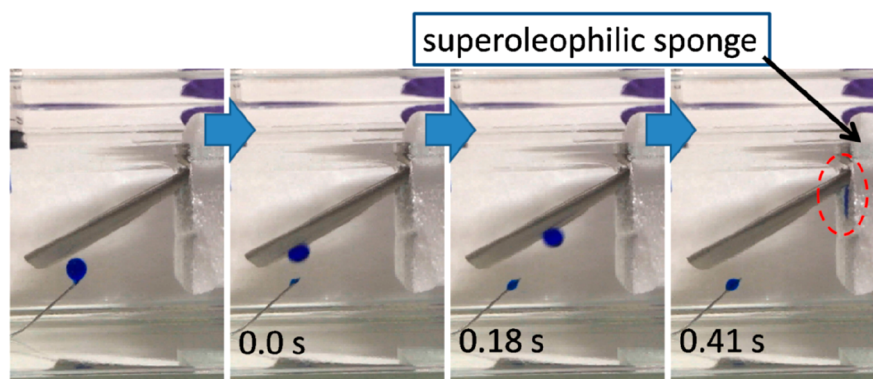
Figure 5. Time sequence of snapshots of an oil droplet rolling along the TA/PVP-modified stainless-steel mesh.
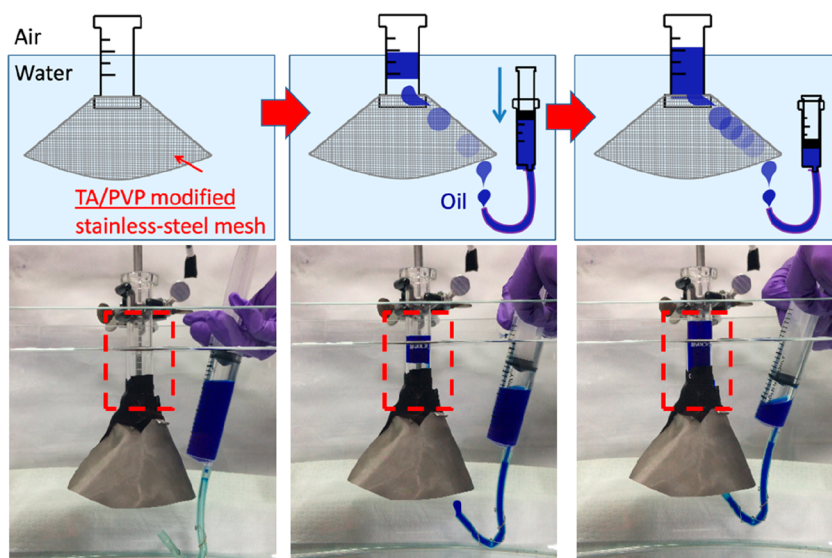

Figure 6. Schematic representations and photographs of the process of continuous transportation and collection of oil from an underwater environment.
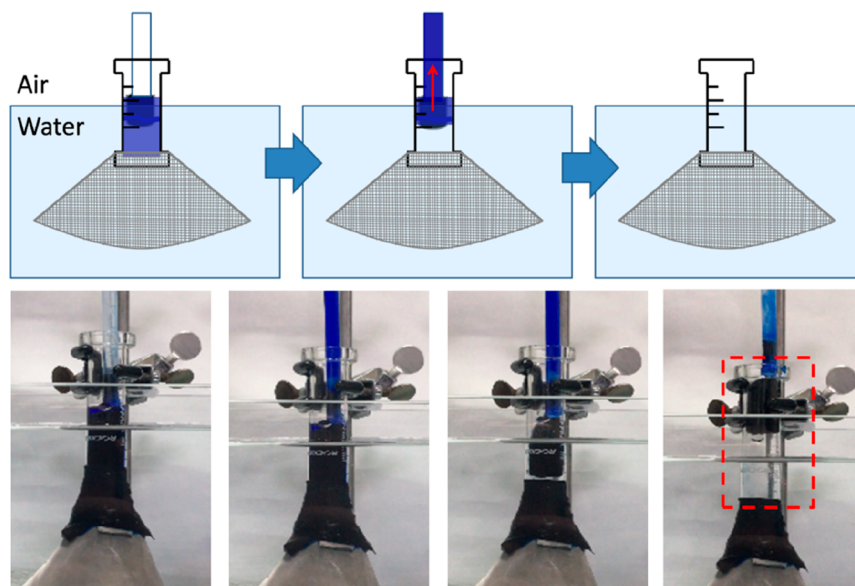

Figure 7. Schematic representations and photographs of the process of continuous absorption and removal of an organic solvent from a water surface.

To study the applicability of this system to handling deepwater oil spills, we also examined the underwater oil transportation and collection processes using the TA/PVP-coated stainless-steel mesh. Figure 5 reveals the process of an underwater oil droplet rolling off a 23°-tilted TA/PVP-coated stainless-steel mesh. Here, a droplet of oil was injected into the TA/PVP-coated stainless-steel mesh; after its release from the needle, the droplet floated toward the mesh but rolled off as soon as it made contact. Subsequently, the oil droplet was absorbed by a superoleophilic sponge. Inspired by this behavior, we used the TA/PVP-coated stainless-steel mesh to fabricate an "underwater oil capture system" for transporting and collecting oil droplets in water. Figure 6 illustrates the application of the TA/PVP-coated stainless-steel mesh in an underwater oil capture process. The TA/PVP-coated stainless-steel mesh was worked into the shape of a funnel and connected to a glass tube to form an oil capture device. This device was first immersed in water. Because of the super-hydrophilicity of the TA/PVP-coated stainless-steel mesh, some water became trapped within its rough microstructure. Next, we injected oil droplets into the device; they rolled along the surface of the TA/PVP-coated stainless-steel mesh. Finally, we collected the injected oil droplets in a glass tube. The collected oil could then be removed using our continuous oil removal system.[13] We connected a superhydrophobic/super-oleophilic sponge to a tube and placed it at the oil−water interface (Figure 7). We then employed a vacuum system to remove the oil from the water surface in a continuous manner. Finally, we removed the oil completely from the water surface, leaving only transparent and clean water in the beaker.

CONCLUSION

We have fabricated a biocompatible, low-toxicity, superwetting material from a naturally water-soluble polyphenolic compound (TA) and a highly biocompatible polymer (PVP). Resulting TA/PVP-coated stainless-steel meshes exhibited superhydrophilicity and underwater superoleophobicity; such materials would appear to have practical applicability in separations of water-rich immiscible oil/water mixtures, even mixtures of oil with corrosive aqueous solutions or hot water, with extremely high separation efficiencies. Furthermore, our TA/PVP-coated stainless-steel meshes displayed excellent antifouling properties during long-term use. Accordingly, we fabricated a simple device for underwater oil transportation and collection through TA/PVP-coated stainless-steel meshes. In conjunction with our continuous oil-removing system, this funnel-like TA/PVP-coated stainless-steel mesh device facilitated the continuous collection and removal of oil pollutants in underwater environments. Thus, TA/PVP-coated stainless-steel meshes have great potential for use in purifying immiscible oil/water mixtures and collecting oil pollutants from underwater environments.

ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.8b01901.

Experimental section and image of a water drop on the

TA/PVP-modified glass slide (Figure S1) (PDF)

AUTHOR INFORMATION

Corresponding Author
*Telephone: 886-2-27301210. Fax: 886-2-27303733. E-mail: cfwang@mail.ntust.edu.tw.

ORCID 🄾
Chih-Feng Wang: 0000-0002-0758-7153
Shiao-Wei Kuo: 0000-0002-4306-7171
Yeo-Wan Chiang: 0000-0002-5409-102X

Notes
The authors declare no competing financial interest.

REFERENCES

(1) Yip, T. L.; Talley, W. K.; Jin, D. The effectiveness of double hulls in reducing vessel-accident oil spillage. *Mar. Pollut. Bull.* **2011**, *62*, 2427−2432.

(2) Dalton, T.; Jin, D. Extent and frequency of vessel oil spills in US marine protected areas. *Mar. Pollut. Bull.* **2010**, *60*, 1939−1945.

(3) Li, Q. X.; Kang, C. B.; Zhang, C. K. Waste water produced from an oilfield and continuous treatment with an oil-degrading bacterium. *Process Biochem.* **2005**, *40*, 873−877.

(4) Wang, P.; Zhao, T.; Bian, R.; Wang, G.; Liu, H. Robust Superhydrophobic Carbon Nanotube Film with Lotus Leaf Mimetic Multiscale Hierarchical Structures. *ACS Nano* **2017**, *11*, 12385−12391.

(5) Meng, L.; Bian, R.; Guo, C.; Xu, B.; Liu, H.; Jiang, L. Aligning Ag Nanowires by a Facile Bioinspired Directional Liquid Transfer: Toward Anisotropic Flexible Conductive Electrodes. *Adv. Mater.* **2018**, *30*, 1706938.

(6) He, M.; Wang, P.; Xu, B.; Jiang, L.; Liu, H. The Flexible Conical Lamella: A Bio-Inspired Open System for the Controllable Liquid Manipulation. *Adv. Funct. Mater.* **2018**, *28*, 1800187.

(7) Feng, L.; Zhang, Z. Y.; Mai, Z. H.; Ma, Y. M.; Liu, B. Q.; Jiang, L.; Zhu, D. B. A super-hydrophobic and super-oleophilic coating mesh film for the separation of oil and water. *Angew. Chem., Int. Ed.* **2004**, *43*, 2012−2014.

(8) Liu, C. T.; Su, P. K.; Hu, C. C.; Lai, J. Y.; Liu, Y. L. Surface Modification of Porous Substrates for Oil/Water Separation using Crosslinkable Polybenzoxazine as An Agent. *J. Membr. Sci.* **2018**, *546*, 100−109.

(9) Siddiqui, A. R.; Maurya, R.; Balani, K. Superhydrophobic self-floating carbon nanofiber coating for efficient gravity-directed oil/water separation. *J. Mater. Chem. A* **2017**, *5*, 2936−2946.

(10) Wang, C. F.; Chen, L. T. Preparation of Superwetting Porous Materials for Ultrafast Separation of Water-in-Oil Emulsions. *Langmuir* **2017**, *33*, 1969−1973.

(11) Wang, C. F.; Tzeng, F. S.; Chen, H. G.; Chang, C. J. Ultraviolet-Durable Superhydrophobic Zinc Oxide-Coated Mesh Films for Surface and Underwater-Oil Capture and Transportation. *Langmuir* **2012**, *28*, 10015−10019.

(12) Feng, Y.; Wang, Y.; Wang, Y.; Yao, J. Furfuryl alcohol modified melamine sponge for highly efficient oil spill clean-up and recovery. *J. Mater. Chem. A* **2017**, *5*, 21893−21897.

(13) Wang, C. F.; Lin, S. J. Robust Superhydrophobic/Super-oleophilic Sponge for Effective Continuous Absorption and Expulsion of Oil Pollutants from Water. *ACS Appl. Mater. Interfaces* **2013**, *5*, 8861−8864.

(14) Chen, F.; Lu, Y.; Liu, X.; Song, J.; He, G.; Tiwari, M. K.; Carmalt, C. J.; Parkin, I. P. Table Salt as a Template to Prepare Reusable Porous PVDF−MWCNT Foam for Separation of Immiscible Oils/Organic Solvents and Corrosive Aqueous Solutions. *Adv. Funct. Mater.* **2017**, *27*, 1702926.

(15) Li, J.; Chen, Y.; Gao, J.; Zuo, Z.; Li, Y.; Liu, H.; Li, Y. Graphdiyne Sponge for Direct Collection of Oils from Water. *ACS Appl. Mater. Interfaces* **2018**, DOI: 10.1021/acsami.8b01207.

(16) Ju, G.; Liu, J.; Li, D.; Cheng, M.; Shi, F. Chemical and Equipment-Free Strategy To Fabricate Water/Oil Separating Materials for Emergent Oil Spill Accidents. *Langmuir* **2017**, *33*, 2664−2670.

(17) Cao, N.; Yang, B.; Barras, A.; Szunerits, S.; Boukherroub, R. Polyurethane sponge functionalized with superhydrophobic nano-diamond particles for efficient oil/water separation. *Chem. Eng. J.* **2017**, *307*, 319−325.

(18) Xu, Z.; Miyazaki, K.; Hori, T. Dopamine-Induced Super-hydrophobic Melamine Foam for Oil/Water Separation. *Adv. Mater. Interfaces* **2015**, *2*, 1500255.

(19) Xue, Z. X.; Wang, S. T.; Lin, L.; Chen, L.; Liu, M. J.; Feng, L.; Jiang, L. A Novel Superhydrophilic and Underwater Superoleophobic Hydrogel-Coated Mesh for Oil/Water Separation. *Adv. Mater.* **2011**, *23*, 4270−4273.

(20) Wang, K.; Han, D. S.; Yiming, W.; Ahzi, S.; Abdel-Wahab, A.; Liu, Z. A Windable and Stretchable Three-Dimensional All-Inorganic Membrane for Efficient Oil/Water Separation. *Sci. Rep.* **2017**, *7*, 16081.

(21) Wang, C.-F.; Huang, H.-C.; Chen, L.-T. Protonated Melamine Sponge for Effective Oil/Water Separation. *Sci. Rep.* **2015**, *5*, 14294.

(22) Wang, C.-F.; Yang, S.-Y.; Kuo, S.-W. Eco-Friendly Superwetting Material for Highly Effective Separations of Oil/Water Mixtures and Oil-in-Water Emulsions. *Sci. Rep.* **2017**, *7*, 43053.

(23) Zhang, L.; Gu, J. C.; Song, L. P.; Chen, L.; Huang, Y. J.; Zhang, J. W.; Chen, T. Underwater Superoleophobic Carbon Nanotubes/core-shell Polystyrene@Au Nanoparticles Composite Membrane for Flow-through Catalytic Decomposition and Oil/Water Separation. *J. Mater. Chem. A* **2016**, *4*, 10810−10815.

(24) Cao, Y. Z.; Liu, N.; Zhang, W. F.; Feng, L.; Wei, Y. One-Step Coating toward Multifunctional Applications: Oil/Water Mixtures and Emulsions Separation and Contaminants Adsorption. *ACS Appl. Mater. Interfaces* **2016**, *8*, 3333−3339.

(25) Luo, C.; Liu, Q. Oxidant-Induced High-Efficient Mussel-Inspired Modification on PVDF Membrane with Superhydrophilicity and Underwater Superoleophobicity Characteristics for Oil/Water Separation. *ACS Appl. Mater. Interfaces* **2017**, *9*, 8297−8307.

(26) Li, J.; Yan, L.; Li, H.; Li, W.; Zha, F.; Lei, Z. Underwater Superoleophobic Palygorskite Coated Meshes for Efficient Oil/Water Separation. *J. Mater. Chem. A* **2015**, *3*, 14696−14702.

(27) Li, J.; Li, D.; Yang, Y.; Li, J.; Zha, F.; Lei, Z. A Prewetting Induced Underwater Superoleophobic or Underoil (Super) Hydro-phobic Waste Potato Residue-Coated Mesh for Selective Efficient Oil/Water Separation. *Green Chem.* **2016**, *18*, 541−549.

(28) Li, J.; Zhao, Z.; Li, D.; Tian, H.; Zha, F.; Feng, H.; Guo, L. Smart Candle Soot Coated Membranes for On-Demand Immiscible Oil/Water Mixture and Emulsion Switchable Separation. *Nanoscale* **2017**, *9*, 13610−13617.

(29) 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 OilWater Separation Membranes. *ACS Nano* **2015**, *9*, 9188−9198.

(30) Huang, K. T.; Yeh, S. B.; Huang, C. J. Surface Modification for Superhydrophilicity and Underwater Superoleophobicity: Applications in Antifog, Underwater SelfCleaning, and Oil−Water Separation. *ACS Appl. Mater. Interfaces* **2015**, *7*, 21021−21029.

(31) Huang, S.; Wang, D. A Simple Nanocellulose Coating for Self-Cleaning upon Water Action: Molecular Design of Stable Surface Hydrophilicity. *Angew. Chem., Int. Ed.* **2017**, *56*, 9053−9057.

(32) Lei, L.; Zhang, Q.; Shi, S.; Zhu, S. Highly Porous Poly(high internal phase emulsion) Membranes with "Open-Cell" Structure and CO_2-Switchable Wettability Used for Controlled Oil/Water Separation. *Langmuir* **2017**, *33*, 11936−11944.

(33) Song, J.; Li, S.; Zhao, C.; Lu, Y.; Zhao, D.; Sun, J.; Roy, T.; Carmalt, C. J.; Deng, X.; Parkin, I. P. A superhydrophilic cement-coated mesh: An acid, alkali, and organic reagent-free material for oil/water separation. *Nanoscale* **2018**, *10*, 1920−1929.

(34) Zeng, M.; Echols, I.; Wang, P.; Lei, S.; Luo, J.; Peng, B.; He, L.; Zhang, L.; Huang, D.; Mejia, C.; Wang, L.; Mannan, M. S.; Cheng, Z. Highly Biocompatible, Underwater Superhydrophilic and Multifunctional Biopolymer Membrane for Efficient Oil−Water Separation and Aqueous Pollutant Removal. *ACS Sustainable Chem. Eng.* **2018**, *6*, 3879−3887.

(35) Zhang, S.; Jiang, G.; Gao, S.; Jin, H.; Zhu, Y.; Zhang, F.; Jin, J. Cupric Phosphate Nanosheets-Wrapped Inorganic Membranes with Superhydrophilic and Outstanding Anticrude Oil-Fouling Property for Oil/Water Separation. *ACS Nano* **2018**, *12*, 795−803.

(36) Ejima, H.; Richardson, J. J.; Liang, K.; Best, J. P.; Van Koeverden, M. P.; Such, G. K.; Cui, J.; Caruso, F. One-Step Assembly of Coordination Complexes For Versatile Film and Particle Engineering. *Science* **2013**, *341*, 154−157.

(37) Guo, J.; Ping, Y.; Ejima, H.; Alt, K.; Meissner, M.; Richardson, J. J.; Yan, Y.; Peter, K.; Von Elverfeldt, D.; Hagemeyer, C. E.; Caruso, F. Engineering Multifunctional Capsules Through The Assembly of Metal−Phenolic Networks. *Angew. Chem., Int. Ed.* **2014**, *53*, 5546−5551.

(38) Fan, H.; Wang, L.; Feng, X.; Bu, Y.; Wu, D.; Jin, Z. Supramolecular Hydrogel Formation Based on Tannic Acid. *Macromolecules* **2017**, *50*, 666−676.

(39) Erel-Unal, I.; Sukhishvili, S. A. Hydrogen-Bonded Multilayers of a Neutral Polymer and a Polyphenol. *Macromolecules* **2008**, *41*, 3962−3970.

(40) Kozlovskaya, V.; Kharlampieva, E.; Drachuk, I.; Cheng, D.; Tsukruk, V. V. Responsive Microcapsule Reactors Based on Hydrogen-Bonded Tannic Acid Layer-By-Layer Assemblies. *Soft Matter* **2010**, *6*, 3596−3608.