

One-Step Breaking and Separating Emulsion by Tungsten Oxide Coated Mesh

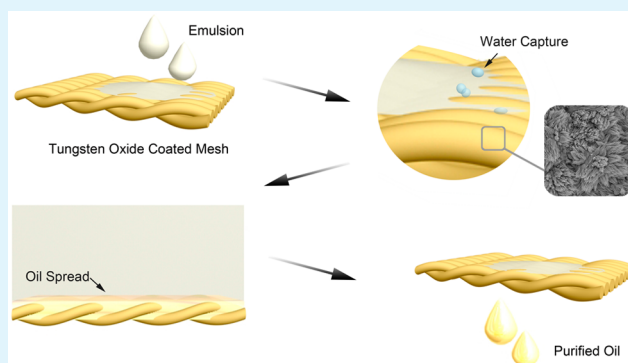
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S Supporting Information

ABSTRACT: Tungsten oxide coated mesh has been fabricated by a simple and inexpensive method. This coated mesh has a dual structure on the surface, consisting of microscale “flower” and nanoscale acicular crystal as the “petal”. Combining the micro/nano structure of the surface and the native hydrophilic property of tungsten oxide, the coated mesh shows special wettability: superhydrophilic in air and superoleophobic under water. Because of the special wettability, such a mesh can be used to separate oil/water mixtures as well as emulsions. Attributed to the good water adsorption capacity of tungsten oxide, the abundant grooves of the micro/nanostructure, and the microsized pores of the surface, this coated mesh can accomplish the demulsification process and the separation process in one single-step, and no further post treatment is needed. As an “emulsion breaker and separator”, this kind of mesh gives another idea of emulsion separation, which has prospective application in industrial fields such as water treatment and petroleum refining.

KEYWORDS: tungsten oxide, micro/nanostructure, in-air superhydrophilic and underwater superoleophobic, one-step process, oil/water separation, emulsion separation



INTRODUCTION

Water pollution is happening every day since industrial waste, household waste, and leakage accidents such as petroleum spills keep doing damage to our environment, thus making water treatment an important and urgent issue in the present world.^{1–5} Among several methods for solving water pollution,⁶ materials with special wettability used for oil/water separation are widely developed, since the first mesh with superhydrophobic and superoleophilic surface was used to separate oil/water mixtures,⁷ which provides a new idea for making use of the special wettability in polluted water remediation.^{8–23} Many materials were found to have the special wettability of its nature, and for the sake of much broader applications, more and more materials have been designed and synthesized to accomplish a particular combination of special wettabilities, such as superhydrophilic and superoleophobic.^{24–28} Most of these materials are organic hydrogel and polymers, such as polyacrylamide, which was first introduced as a water-favoring material. But there is a main disadvantage of this kind of material: as the hydrating process going on, the hydrogel becomes soft and easily swept by liquid flow, and the mesh lost its water-favoring property. Inorganic material was then taken into consideration. Metallic oxide, for example, a $\text{Cu}(\text{OH})_2$ nanowire coated copper mesh, was prepared with a surface oxidation method.²⁹ The water-favoring property of such a material is based on the hydrophilicity and the nanoscale structure. Compared with organic hydrogel, inorganic metallic

oxide coated meshes show no shape change between water adsorption and desorption. Thus, they will be stronger than polymer hydrogel, making the mesh more stable in liquid flow. After several cycles of separation, the mesh could still maintain its water-favoring property. More and more novel materials with potential for special wettability, like graphene, have also been used for water/oil separation.^{30–32}

However, these kinds of separations are based on the phase separation mechanism, according to which water and oil are totally in different phases, and there is always a clear interface between them. Therefore, separation of an emulsion, a complex oil/water mixture without a clear interface, is still a challenge.^{33–36} Among the traditional demulsification methods, powderlike demulsifier is often used, where the process usually contains three steps: mixing, breaking, and separating. The powder is first mixed with the emulsion to break it, and then the powder is separated from the solution by centrifugation or gravity. These steps make the demulsification and the separation process very complex, especially in the treatment of a large amount of emulsion. Meshes that can be used in emulsion filtration will reduce the steps of separation and simplify the after-treatment process. Different from the mesh used in oil/water separation, a smaller pore size is required and

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the surface structure becomes a much more important factor for separation of emulsions. Therefore, the preparation of such a mesh, whether using organic or inorganic material,^{37,38} is always a complicated process.

Here we've prepared a tungsten oxide coated mesh with a simple hydrothermal method. This coated mesh has pores of near 10 μm , on which the tungsten oxide crystal has formed a hybrid flowerlike microstructure and a petal-like nanostructure. The mesh shows good water-favoring property with a water contact angle (WCA) of 0° and an underwater–oil contact angle (OCA) above 150° , indicated that the mesh has the property of superhydrophilic and underwater superoleophobic. This special wettability offered the mesh possibility in application of oil/water separation. As a result, water could pass through the mesh smoothly while oil could not. Furthermore, tungsten oxide has good ability in demulsification of water–oil emulsion, where the emulsion was broken after permeating through the mesh. Turbid emulsion was poured upside the mesh and clear solution was collected downside. This emulsion separating process just contains one step, which gives a more efficient tool to be used for water treatment.

EXPERIMENTAL SECTION

Materials. Ethanol and acetone (Dongfanglongshun Co. Ltd., Beijing, China), sodium tungstate and oxalic acid (Sinopharm Chemical Reagent Co., Ltd., Beijing, China) were used as purchased. All the reagents were of analytical grade.

Preparation of Tungsten Oxide Coated Steel Mesh. The original steel mesh as substrate was rinsed sequentially with deionized water and acetone, and dried at room temperature. Then the mesh was cut into $5 \times 5 \text{ cm}^2$ pieces. 0.025 mol sodium tungstate were first dissolved in 25 mL deionized water. Hydrochloric acid (2 mol/L) was added into the solution drop by drop until the pH reached 2.0. The solution was then diluted to 250 mL, and 3.15 g of oxalic acid was dissolved in the solution to form a stable tungsten oxide colloidal suspension. This suspension was to be used as reaction liquid in further hydrothermal process. The steel mesh as prepared was immersed in the tungsten oxide colloidal suspension, and moved into a high pressure reactor, heated to 180°C for 4 h. After the reaction, the mesh sample was picked from the mixture and rinsed with deionized water and acetone. Finally, the mesh was dried at room temperature for further characterization and experiment.

Instrumentation and Characterization. SEM images were taken with JEOL JSM-7500 scanning electron microscope. XPS pattern was characterized with a Thermo Escalab 250Xi spectrometer using an Al $K\alpha$ X-ray source with 1486.6 eV voltage, and XRD pattern was characterized with a Bruker D8-advanced X-ray diffractometer with 40 kV voltage and 40 mA current. Contact angle was measured using a Dataphysics OCA-20 contact angle analyzer, 3 μL of 1,2-dichloroethane was used as the oil droplet.

Oil/Water Separation Experiments. The oil/water separation experiments were performed by the as-prepared tungsten oxide coated mesh. The mesh was predrying before fixed. The mesh was fixed by two polytetrafluoroethylene (PTFE) clamps, and two glass tubes were fixed on each side. The mixture of oil (*n*-hexane dyed by oil red) and deionized water (50 v/v%) was poured into the glass tube. The separation process was driven by gravity only.

Emulsion Separation Experiments. The one-step breaking and separating experiments were performed by the as-prepared tungsten oxide coated mesh, using the same devices in the oil/water separation experiment above. Toluene and water were first mixed with an ultrasonic cleaner (100:1 v/v) to form a stable water-in-oil (W/O) type emulsion, and then poured into the glass tube. The separation process was also driven by gravity only.

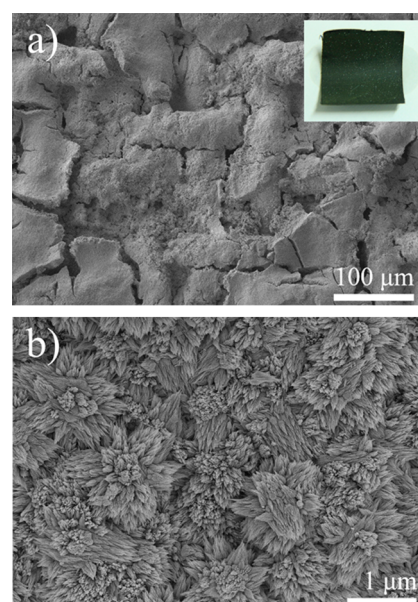


Figure 1. SEM images of the tungsten oxide coated mesh: (a) steel mesh covered with tungsten oxide; the inset is a typical photograph of the mesh; (b) high-magnification view of the flowerlike micro/nanostructure of the as-prepared mesh.

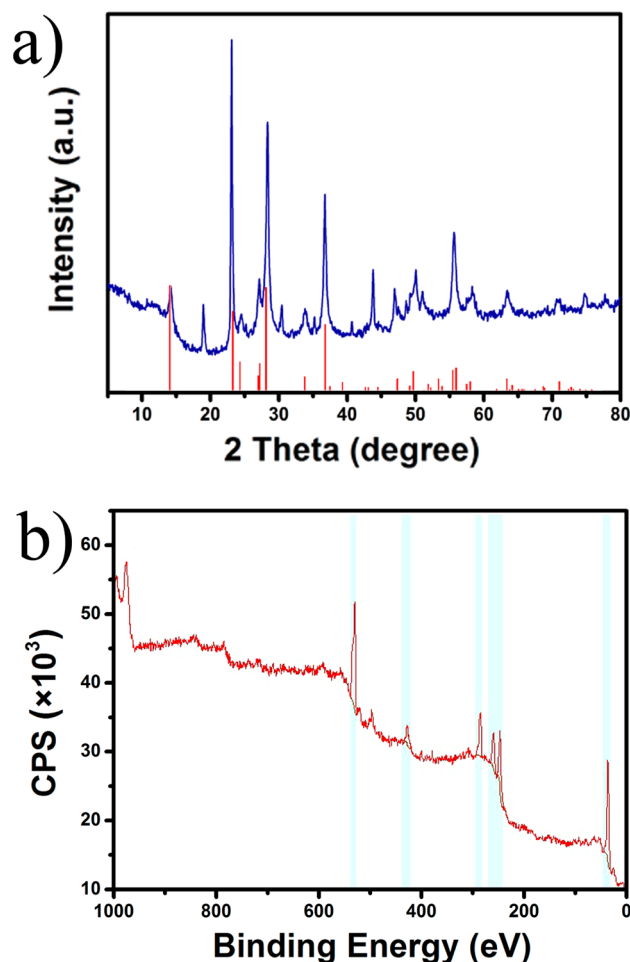


Figure 2. XRD spectrum and XPS pattern of the tungsten oxide coated mesh: (a) XRD spectrum of the tungsten oxide coated mesh; (b) XPS pattern tungsten oxide coated mesh.

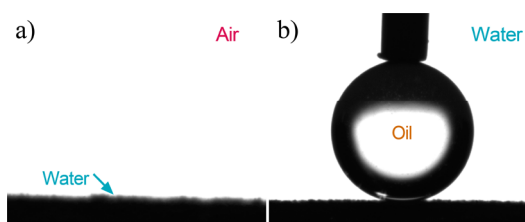


Figure 3. Contact angle of the tungsten oxide coated mesh: (a) photographs of water droplets on the surface of the mesh in air; (b) photographs of oil droplets on the surface of the mesh under water.

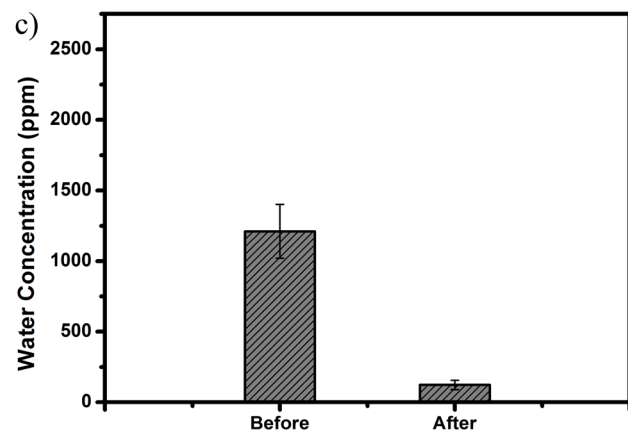
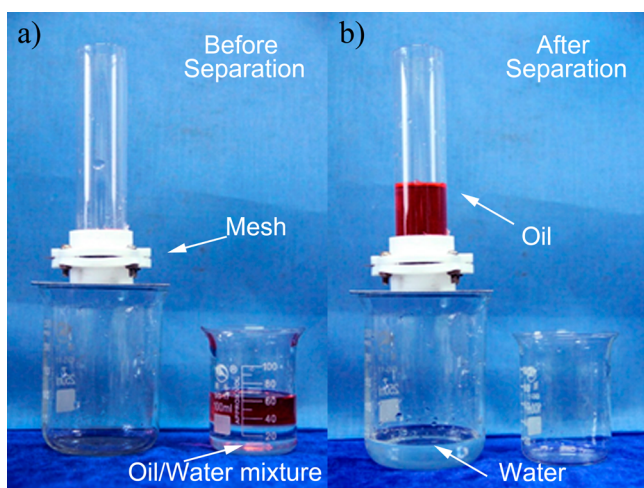


Figure 4. Oil/water separation studies of the tungsten oxide coated mesh: (a) deionized water and *n*-hexane dyed with oil red was mixed before separation; (b) water penetrated the mesh while *n*-hexane was blocked in the upper tube after separation; (c) water concentration of the oil/water mixture before separation and the oil filtered after separation.

RESULTS AND DISCUSSION

Morphology of the Tungsten Oxide Coated Mesh. As the scanning electron microscopy (SEM) image shows (Figure 1a, b), the surface of the steel wire was nearly blocked by tungsten oxide. The original line texture of the steel wire could not be observed, which means near 100% percent of the surface was covered. The photograph in Figure 1a shows a typical image of the mesh, which indicates that the stainless steel mesh was thoroughly covered by tungsten oxide, and we could hardly observe pores in a macro view of the mesh. The pore size of the as prepared mesh was about 10 μm , which was slightly larger than traditional microporous membrane. The small pore size

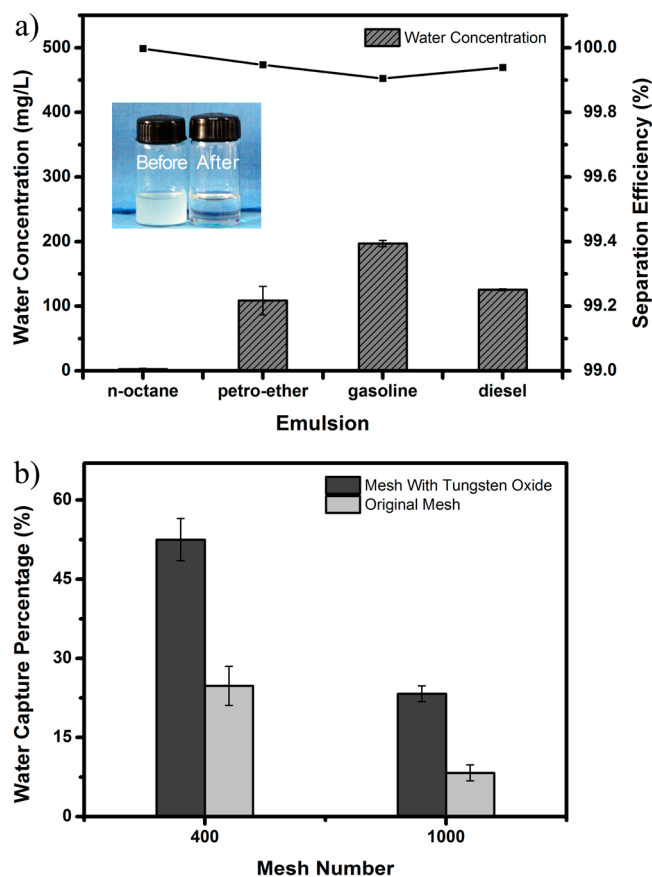


Figure 5. Breaking and separating emulsion experiment of the tungsten oxide coated mesh: (a) Water concentration of the clear filtered and the separation efficiency of tungsten oxide coated mesh for a selection of oils; the inset is the W/O emulsion formed by toluene and water before separation and the purified filtrate after separation. (b) Water capture percentage of tungsten oxide coated mesh and original bare mesh as a function of mesh number.

made it easy for the mesh to adsorb small water droplet in the emulsion. In a smaller scale (Figure 1b), the tungsten oxide nanocrystal has formed flowerlike structure with needlelike petals. Microscale flowers and nanoscale needles have combined to form a micro/nano hybrid structure on the mesh's surface. This kind of structure was the main reason for the mesh's special wettability.

Chemical Composition of the Tungsten Oxide Coated Mesh. To verify the composition of the mesh's surface, an X-ray diffraction (XRD) characterization was performed. In the XRD pattern (Figure 2a), the peaks highly match the values of the standard card (JCPDS card No. 85-2459), with space group *P63/mcm* and lattice parameters of $a = 7.3242 \text{ \AA}$, $b = 7.3242 \text{ \AA}$, $c = 7.6624 \text{ \AA}$, $\beta = 90.000^\circ$, and no other diffraction peaks were observed, which indicates that the mesh is well-covered by tungsten oxide crystal. An X-ray photoelectron spectroscopy (XPS) was also performed. In the XPS pattern (Figure 2b), peaks of tungsten, oxygen, and pollutant carbon were observed by scanning bonding energy from 0 to 1000 eV. The two main peaks at 284.8 and 530.4 eV are marked with C 1s, O 1s, and other four main peaks at 36.80, 260.4, 246.8.9, and 426.8 eV are marked with W 5p, W 4d_{3/2}, W 4d, and W 4p, respectively, which also indicates that the steel mesh was covered by tungsten oxide instead of other components. Furthermore, there is no iron's peak in the XPS pattern, and

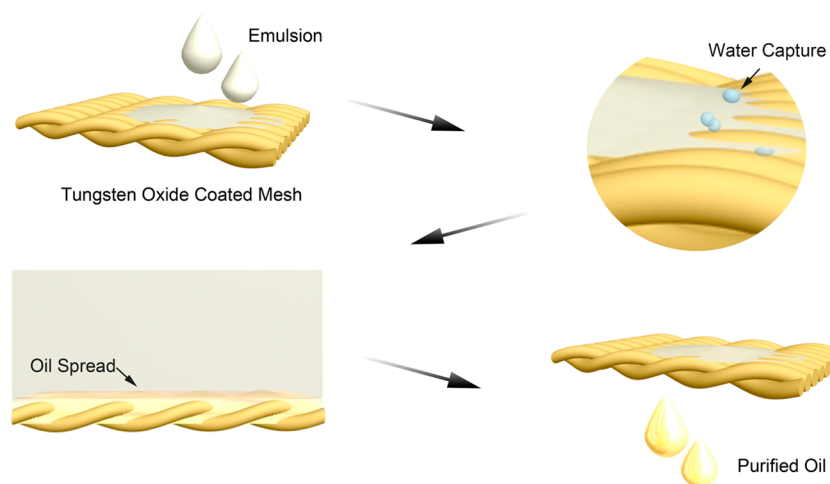


Figure 6. Schematic process of one-step breaking and separating emulsion by tungsten oxide coated mesh.

XPS has a scanning depth less than 10 nm commonly, from which we could speculate that the surface of the steel mesh was thoroughly covered by tungsten oxide crystal.

Wettability Properties of the Tungsten Oxide Coated Mesh. As reported,³² a rough surface composed of micro and nanostructures could significantly amplify the wettability, which could make a hydrophilic surface superhydrophilic as well as make a hydrophobic surface superhydrophobic. In our work, tungsten oxide is hydrophilic as a traditional metallic oxide. After the micro/nano hybrid structure was formed, the mesh achieved its superhydrophilic property. In the contact angle (CA) measurement, when a water droplet touched the mesh, it could quickly spread in less than one second, showing a water contact angle (WCA) of 0° (Figure 3a), which is a proof of the mesh's superhydrophilic property. To examine the mesh's wettability of oil, it was first immersed in water, then a 1,2-dichloroethane droplet was moved vertically downward until it was contacted the mesh. The oil droplet could totally not infiltrate into the mesh, and the result showed an oil contact angle (OCA) of 160° (Figure 3b), larger than 150° , which means that the mesh was superoleophobic underwater.

This superoleophobic property is believed to be attributed to the water-favoring property of the tungsten oxide coated mesh. After the mesh was immersed in water, water could be trapped in the hierarchical structure. The trapped water acted as the repulsive phase to prevent the oil droplet from contacting with the mesh directly, thus the oil droplet could not spread. In summary, the superoleophobic property of the mesh is contributed by both the micro/nanohybrid structure and the hydrophilicity of tungsten oxide. For this kind of system, the oil contact angle could be expressed by the Cassie–Baxter equation

$$\cos \theta' = f \cos \theta + f - 1$$

It could be obtained by dividing the visual surface area by the actual surface area (including the surface area in the hierarchical structure). f is a function of the surface roughness. θ' is the oil contact angle on a smooth surface underwater and is the oil contact angle on a rough surface underwater. In our work, the surface of the mesh is very rough because of the hierarchical structure of tungsten oxide. Thus, f could be very small near 0, and $\cos \theta'$ is near -1 , which means θ' could be very large. When θ' is larger than 150° , the surface is superoleophobic under water.

Oil/water Separation Using the Tungsten Oxide Coated Mesh. Because of the mesh's special wettability of superhydrophilic and underwater superoleophobic, it could be utilized for oil/water separation. The water-favoring property guaranteed that water could quickly spread and pass through the mesh. The superoleophobic property also infers that oil will be retarded after water flows down. Our experimental result confirmed this assumption. As shown in Figure 4a, b, the mixture of oil (*n*-hexane dyed with oil red) and water was poured into the glass tube. Because of a higher density, water phase first permeated through the mesh and the mesh was totally soaked with water. The oil phase was then retarded upside the mesh, and the whole separation process was successfully completed. After the separation, water was collected in the beaker downside, while oil was retarded in the glass tube upside. The water concentration of the filtered oil is less than 130 ppm, as shown in Figure 4c, which indicated a high efficiency of the oil/water separation.

Emulsion Separation Using the Tungsten Oxide Coated Mesh. The as-prepared tungsten oxide coated mesh was further used for breaking and separating stable water-in-oil (W/O) type emulsion. Using the same device shown in Figure 4a, the emulsion (formed of toluene and water) was poured into the glass tube. With no repulsive water phase, toluene could spread and pass through the mesh slowly. During the permeation process, the small water droplets in the emulsion were captured by the flowerlike structure tungsten oxide with hierarchical structure, and clear toluene flowed down and passed through the mesh. As shown in Figure 5a, the emulsion was successfully broken and separation by the mesh just in one step. A series of emulsion were prepared to test the separation capability. The water concentration is below 240 ppm for all results, indicating a separation efficiency higher than 99.90%. The water-favoring property was characterized by measuring the increased weight tungsten oxide, a steel mesh with a mesh number of 400 could maintain water more than half of its weight, whereas a bare stainless steel mesh could only maintain 25% (Figure 5b). The growth of tungsten oxide has significantly increased the mesh's water-favoring property. This property makes the mesh easily capture small water droplets. As shown in Figure 6, when the emulsion passed by, water droplets were captured by the micro/nanostructure formed of tungsten oxide, whereas oil spread on the mesh's surface, and the emulsion was then broken. The efficiency of

demulsification benefited from both the water favoring property and the hierarchical structure on the mesh's surface.

CONCLUSION

We've successfully prepared a tungsten oxide coated stainless steel mesh with a simple hydrothermal method. Tungsten oxide has formed flowerlike structure on the steel wire's surface with microscale flower and nanoscale petal. This structure attributes the mesh with good water-favoring property. It is super-hydrophilic in the air and superoleophobic under water. This special wettability makes the mesh able to be applied in oil/water separation, in which water could pass while oil could not. Furthermore, the mesh could also be used in emulsion separation. After permeating through the mesh, turbid emulsion becomes clear. This mesh has prospective applications in water treatment, especially in oil purification and demulsification.

ASSOCIATED CONTENT

Supporting Information

Movie of the emulsion breaking and separating process. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

- WCA, water contact angle
- OCA, underwater-oil contact angle
- PTFE, polytetrafluoroethylene
- SEM, scanning electron microscopy
- XRD, X-ray diffraction
- XPS, X-ray photoelectron spectroscopy
- W/O, water-in-oil

REFERENCES

- (1) Gossen, L. P.; Velichkina, L. M. Environmental Problems of the Oil-and-gas Industry. *Pet. Chem.* **2006**, *46*, 67–72.
- (2) Bayat, A.; Aghamiri, S. F.; Moheb, A.; Vakili-Nezhaad, G. R. Oil Spill Cleanup from Sea Water by Sorbent Materials. *Chem. Eng. Technol.* **2005**, *28*, 1525–1528.

- (3) Osuji, L. C.; Onojake, C. M. Trace heavy metals associated with crude oil: A Case Study of Ebocha-8 Oil-spill-polluted Site in Niger Delta, Nigeria. *Chem. Biodivers.* **2004**, *1*, 1708–1715.

- (4) Baker, J. M. Ecological Effectiveness of Oil Spill Countermeasures: How Clean is Clean? *Pure Appl. Chem.* **1999**, *71*, 135–151.

- (5) Nordvik, A. B.; Simmons, J. L.; Bitting, K. R.; Lewis, A.; StromKristiansen, T. Oil and Water Separation in Marine Oil Spill Clean-up Operations. *Spill Sci. Technol. Bull.* **1996**, *3*, 107–122.

- (6) Shannon, M. A.; Bohn, P. W.; Elimelech, M.; Georgiadis, J. G.; Marinas, B. J.; Mayes, A. M. Science and Technology for Water Purification in the Coming Decades. *Nature* **2008**, *452*, 301–310.

- (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) Cao, Y.; Chen, Y.; Liu, N.; Lin, X.; Feng, L.; Wei, Y. Mussel-inspired Chemistry and Stober method for Highly Stabilized Water-in-oil Emulsions Separation. *J. Mater. Chem. A* **2014**, *2*, 20439–20443.

- (9) Long, Y.; Hui, J.; Wang, P.-p.; Xiang, G.-l.; Xu, B.; Hu, S.; Zhu, W.-c.; Lu, X.-Q.; Zhuang, J.; Wang, X. Hydrogen Bond Nanoscale Networks Showing Switchable Transport Performance. *Sci. Rep.* **2012**, *2*, 612–617.

- (10) Liang, H. W.; Guan, Q. F.; Chen, L. F.; Zhu, Z.; Zhang, W. J.; Yu, S. H. Macroscopic-Scale Template Synthesis of Robust Carbonaceous Nanofiber Hydrogels and Aerogels and Their Applications. *Angew. Chem., Int. Ed.* **2012**, *51*, 5101–5105.

- (11) Kwon, G.; Kota, A. K.; Li, Y.; Sohani, A.; Mabry, J. M.; Tuteja, A. On-Demand Separation of Oil-Water Mixtures. *Adv. Mater.* **2012**, *24*, 3666–3671.

- (12) Lee, C. H.; Johnson, N.; Drelich, J.; Yap, Y. K. The Performance of Superhydrophobic and Superoleophilic Carbon Nanotube Meshes in Water-oil Filtration. *Carbon* **2011**, *49*, 669–676.

- (13) Gui, X.; Wei, J.; Wang, K.; Cao, A.; Zhu, H.; Jia, Y.; Shu, Q.; Wu, D. Carbon Nanotube Sponges. *Adv. Mater.* **2010**, *22*, 617–621.

- (14) Li, H. J.; Wang, X. B.; Song, Y. L.; Liu, Y. Q.; Li, Q. S.; Jiang, L.; Zhu, D. B. Super-"amphiphobic" Aligned Carbon Nanotube Films. *Angew. Chem., Int. Ed.* **2001**, *40*, 1743–1746.

- (15) Feng, X.; Jiang, L. Design and Creation of Superwetting/antiwetting Surfaces. *Adv. Mater.* **2006**, *18*, 3063–3078.

- (16) Yuan, J.; Liu, X.; Akbulut, O.; Hu, J.; Suib, S. L.; Kong, J.; Stellacci, F. Superwetting Nanowire Membranes for Selective Absorption. *Nat. Nanotechnol.* **2008**, *3*, 332–336.

- (17) Manna, U.; Carter, M. C. D.; Lynn, D. M. "Shrink-to-Fit" Superhydrophobicity: Thermally-Induced Microscale Wrinkling of Thin Hydrophobic Multilayers Fabricated on Flexible Shrink-Wrap Substrates. *Adv. Mater.* **2013**, *25*, 3085–3089.

- (18) Cao, Y.; Zhang, X.; Tao, L.; Li, K.; Xue, Z.; Feng, L.; Wei, Y. Mussel-Inspired Chemistry and Michael Addition Reaction for Efficient Oil/Water Separation. *ACS Appl. Mater. Interfaces* **2013**, *5*, 4438–4442.

- (19) Tsujii, K.; Yamamoto, T.; Onda, T.; Shibuichi, S. Super oil-repellent Surfaces. *Angew. Chem., Int. Ed.* **1997**, *36*, 1011–1012.

- (20) Nicolas, M.; Guittard, F.; Geribaldi, S. Synthesis of Stable Super Water- and Oil-repellent Polythiophene Films. *Angew. Chem., Int. Ed.* **2006**, *45*, 2251–2254.

- (21) Zhang, J.; Seeger, S. Superoleophobic Coatings with Ultralow Sliding Angles Based on Silicone Nanofilaments. *Angew. Chem., Int. Ed.* **2011**, *50*, 6652–6656.

- (22) Aulin, C.; Netrval, J.; Wagberg, L.; Lindstrom, T. Aerogels from Nanofibrillated Cellulose with Tunable Oleophobicity. *Soft Matter* **2010**, *6*, 3298–3305.

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

- (24) Jin, M.; Wang, J.; Yao, X.; Liao, M.; Zhao, Y.; Jiang, L. Underwater Oil Capture by a Three-Dimensional Network Architected Organosilane Surface. *Adv. Mater.* **2011**, *23*, 2861–2864.

(25) Liu, M.; Zheng, Y.; Zhai, J.; Jiang, L. Bioinspired Super-antiwetting Interfaces with Special Liquid-Solid Adhesion. *Acc. Chem. Res.* **2010**, *43*, 368–377.

(26) Bobji, M. S.; Kumar, S. V.; Asthana, A.; Govardhan, R. N. Underwater Sustainability of the "Cassie" State of Wetting. *Langmuir* **2009**, *25*, 12120–12126.

(27) Tian, D.; Zhang, X.; Tian, Y.; Wu, Y.; Wang, X.; Zhai, J.; Jiang, L. Photo-induced Water-oil Separation Based on Switchable Superhydrophobicity-superhydrophilicity and Underwater Superoleophobicity of the Aligned ZnO Nanorod Array-coated Mesh Flms. *J. Mater. Chem.* **2012**, *22*, 19652–19657.

(28) Deng, D.; Prendergast, D. P.; MacFarlane, J.; Bagatin, R.; Stellacci, F.; Gschwend, P. M. Hydrophobic Meshes for Oil Spill Recovery Devices. *ACS Appl. Mater. Interfaces* **2013**, *5*, 774–781.

(29) Zhang, F.; Zhang, W. B.; Shi, Z.; Wang, D.; Jin, J.; Jiang, L. Nanowire-Haired Inorganic Membranes with Superhydrophilicity and Underwater Ultralow Adhesive Superoleophobicity for High-Efficiency Oil/Water Separation. *Adv. Mater.* **2013**, *25*, 4192–4198.

(30) Crick, C. R.; Gibbins, J. A.; Parkin, I. P. Superhydrophobic Polymer-coated Copper-mesh; Membranes for Highly Efficient Oil-water Separation. *J. Mater. Chem. A* **2013**, *1*, 5943–5948.

(31) Dong, Y.; Li, J.; Shi, L.; Wang, X.; Guo, Z.; Liu, W. Underwater Superoleophobic Graphene Oxide Coated Meshes for the Separation of Oil and Water. *Chem. Commun.* **2014**, *50*, 5586–5589.

(32) Song, J.; Huang, S.; Lu, Y.; Bu, X.; Mates, J. E.; Ghosh, A.; Ganguly, R.; Carmalt, C. J.; Parkin, I. P.; Xu, W.; Megaridis, C. M. Self-Driven One-Step Oil Removal from Oil Spill on Water via Selective-Wettability Steel Mesh. *ACS Appl. Mater. Interfaces* **2014**, *6*, 19858–19865.

(33) Salager, J. L.; Maria Forgiarini, A. Emulsion Stabilization, Breaking, and Inversion Depends upon Formulation: Advantage or Inconvenience in Flow Assurance. *Energy Fuels* **2012**, *26*, 4027–4033.

(34) Rayat, K.; Feyzi, F. Estimation of the Electric Field Strength Required for Breaking the Water-in-oil Emulsion: A Thermodynamic Approach Considering Droplets Deformation and the Effect of Interfacial Tension. *Fluid Phase Equilib.* **2012**, *316*, 156–163.

(35) Bakircioglu, D.; Topraksever, N.; Kurtulus, Y. B. Determination of Zinc in Edible Oils by Flow Injection FAAS after Extraction Induced by Emulsion Breaking Procedure. *Food Chem.* **2014**, *151*, 219–224.

(36) Feng, L.; Li, S. H.; Li, Y. S.; Li, H. J.; Zhang, L. J.; Zhai, J.; Song, Y. L.; Liu, B. Q.; Jiang, L.; Zhu, D. B. Super-hydrophobic Surfaces: From Natural to Artificial. *Adv. Mater.* **2002**, *14*, 1857–1860.

(37) Howarter, J. A.; Youngblood, J. P. Amphiphile Grafted Membranes for the Separation of Oil-in-water Dispersions. *J. Colloid Interface Sci.* **2009**, *329*, 127–132.

(38) Zhang, W.; Zhu, Y.; Liu, X.; Wang, D.; Li, J.; Jiang, L.; Jin, J. Salt-Induced Fabrication of Superhydrophilic and Underwater Superoleophobic PAA-g-PVDF Membranes for Effective Separation of Oil-in-Water Emulsions. *Angew. Chem., Int. Ed.* **2014**, *53*, 856–860.