Research Article

Superhydrophobic Hair-Like Nanowire Membrane for the Highly Efficient Separation of Oil/Water Mixtures

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Water pollution caused by oil leakage and oily wastewater has become a serious environmental problem. Therefore, it is important to develop an efficient material to remove oil from water. Given the cost and efficiency, the membrane with superhydrophobicity is the most used material for the separation of oil/water mixtures. However, many works have been done through modification with a fluorinated reagent, causing high cost and damage to the environment. In this work, a simple and fast two-step method is employed to achieve a superhydrophobic hair-like nanowire membrane. Through the alkali-assisted oxidation process and modification with nonfluorinated low surface energy chemical, the so-obtained membrane (denoted as SHM), with the water contact angle of about 164°, exhibits excellent separation efficiency for binary mixtures of water and oils (toluene, hexane, gasoline, and so on). Meantime, this membrane also exhibits excellent durability and reusability in the long-term separation process, indicating its great potential for practical application in the future.

1. Introduction

Water pollution caused by oil leakage and oily wastewater has become a serious environmental problem and has endangered the health of human beings and wildlife. The oil/water separation as an efficient method has drawn considerable attention [1–4]. Among various oil/water separation methods, the membrane separation technology is considered as one of most effective methods to separate the oil and water [5, 6]. Various materials, such as meshes [7–12], polymer film [13–16], and foams [17–20], have been developed [21–25]. Among these materials, meshes are frequently used as the membrane materials, due to the mechanical workability, malleability, and relatively low cost.

Superhydrophobicity, with water contact angle (WCA) above 150° and sliding angle below 10°, was first discovered from plant leaves and also played an important role in the separation of oil/water mixtures [26–31]. Thanks to the study on the lotus effect, superhydrophobicity is successfully obtained through modification with a low surface energy reagent due to the strong water repellency of a nonpolar chemical surface to polar water [32, 33]. At the same time, according to the Cassie-Baxter model, a rough microstructure on the surface can be more hydrophobic due to the reservation of air beneath the water droplet [34, 35]. Based on this proper microstructure, through simple modification, superhydrophobicity can be obtained more feasibly. According to the above, many methods including chemical or electrochemical treatment, laser etching, and plasma processing have been reported [15, 36–41]. However, the most applied method to obtain superhydrophobicity is by introducing fluorinated low surface-energy chemicals on micro-/nanohierarchical structures [38–41]. But the high cost of fluorinated chemicals and the pollution to the environment limit the wide application. Meantime, it remains challenging to obtain large-scale superhydrophobic membranes by simple processes and be further used in practice.

Taking those factors into consideration, we synthesized a superhydrophobic membrane based on the unique hair-like microstructure. Due to the mechanical workability and relatively low cost, a copper mesh has been chosen as one of the most commonly used materials for the oil/water separation [42, 43]. Meantime, various morphologies are also reported on the copper substrate, such as needle-like, hair-like, arch-
like, and pine needle-like structures [40, 41]. But the superhydrophobic surface should be obtained after fluorination, which is more expensive and unfriendly to the environment. Given this, a simple and fast two-step method is employed to achieve superhydrophobicity (Scheme 1). The as-synthesized superhydrophobic hair-like nanowire membrane (denoted as SHM) with the water contact angle (WCA) above 150° can exhibit efficient separation for the oil/water mixtures. Furthermore, the low cost and fast preparation process of the membrane indicate its great potential for practical application.

2. Materials and Methods

2.1. Materials and Instrumentation. All chemical agents were obtained from commercial suppliers without further purification. The red copper mesh (purity > 99.97%, 200) was purchased from Anping Tairun Wire Mesh Co., Ltd., China. Sodium hydroxide, ammonium persulfate, and dodecanethiol were purchased from Shanghai Chemical Reagent Co., Ltd., China.

The powder X-ray diffraction (XRD) patterns were carried out with the Japan Rigaku DMax-γA rotation anode X-ray diffractometer. The scanning electron microscopy (SEM) images were obtained from the field emission scanning electron microanalyzer (Sigma 500, scanning electron microscope). The X-ray photoelectron spectroscopy (XPS) analysis was performed with the ESCALAB 250Xi high-performance electron spectrometer. The hydrophobic properties of the mesh were performed through a Kruss DSA30 contact angle analyzer.

2.2. Synthesis of Samples. The desired size of commercial Cu mesh (1.5 cm × 1.5 cm) was washed with diluted H2SO4 (5 vol%) and Milli-Q water to remove the surface oxide. The synthesis of the superhydrophobic mesh was realized via two room-temperature reactions including an alkali-assisted oxidation process. Briefly, the washed Cu mesh was soaked in 25 mL mixture solution containing 12.5 mL of 5 M NaOH, 2.5 mL of 1 M (NH4)2S2O8, and 10 mL of H2O for 45 min at room temperature to form a Cu(OH)2 microstructure on the mesh surface. Then, the Cu mesh was modified into a mixture solution of dodecanethiol and ethanol (v/v = 1 : 1000) for 20 min. Finally, the resulting mesh was dried in vacuum, and the superhydrophobic Cu mesh named SHM was obtained. The whole synthetic process can be taken as the following equations:

\[
2\text{Cu} + 6\text{NaOH} + 2(\text{NH}_4)_2\text{S}_2\text{O}_8 \rightarrow \text{Cu(OH)}_2 + \text{CuSO}_4 + 3\text{Na}_2\text{SO}_4 + 4\text{NH}_3 + 4\text{H}_2\text{O} \tag{1}
\]

\[
\text{Cu(OH)}_2 + 2\text{C}_{12}\text{H}_{25}\text{SH} \rightarrow \text{Cu(SC}_{12}\text{H}_{25})_2 + 2\text{H}_2\text{O} \tag{2}
\]

3. Results and Discussion

The preparation of SHM is schematically displayed in Scheme 1. The pretreated commercial Cu mesh was first soaked in the alkaline solution. Through the alkali-assisted oxidation process, the hair-like Cu(OH)2 nanowires (NWs) were grown on the surfaces of Cu wires. Subsequently, the Cu(OH)2 NWs were carefully modified with dodecanethiol, yielding the final superhydrophobic surface on the mesh. From the scanning electron microscopy (SEM) image, the Cu wires in the commercial Cu mesh are about 50 μm in diameter (Figure 1(a)). After the oxidation process, the hair-like Cu(OH)2 NWs were covered on the surface of Cu wires with similar diameter and length (Figures 1(b) and 1(c)). Through the cross-section picture inset in Figure 1(b), the length of nanowires is about 20 μm and the thickness is about 25 μm. Through modification, as shown in Figures 1(d) and 1(e), the obtained SHM well maintained the hierarchical structure, indicating that the hair-like Cu(OH)2 NWs are not completely destroyed by the dodecanethiol. Meantime, the X-ray diffraction (XRD) pattern of SHM can further confirm the existence of Cu(OH)2 due to the well-matched peaks. In addition, the peaks for the Cu can also be observed, indicating the existence of the Cu mesh (Figure 1(f)). The energy-dispersive X-ray spectroscopy (EDS) elemental analysis of the surface structure is performed (Figure 2). The signals of S and C in the pattern indicate that the alkyl thiol has formed a coating on the surface of the hair-like structure through the reaction with Cu(OH)2 NWs.

To further illustrate the chemical composition in SHM, X-ray photoelectron spectroscopy (XPS) analysis has been performed. As shown in Figure 3(a), the XPS survey spectrum clearly demonstrates the presence of Cu, O, H, S, and C on the surface. In the Cu 2p3/2 spectrum (Figure 3(b)),
The Cu\(^+\) also appeared except for the Cu\(^{2+}\). This may be explained that partial Cu\(^{2+}\) acted as a strong oxidizing agent to react with the dodecanethiol and turned to Cu\(^+\). Meantime, the dodecanethiol is turned to sulfate, which is further proven in the S 2p\(_{3/2}\) spectrum [43]. From the high-resolution S 2p\(_{3/2}\) spectrum (Figure 3(c)), two subpeaks can be fitted. The peaks at 162 eV and 163.5 eV are related to the sulfur of Cu(SC\(_2\)H\(_{25}\))\(_2\) and sulfur of free n-dodecanethiol, respectively [44, 45]. Accordingly, the surface Cu(OH\(_2\))\(_2\) has reacted with dodecanethiol and converted to copper thiolate with low surface energy, which is an important factor leading to the superhydrophobicity of the surfaces. At the same time, on the copper foil surface, the n-dodecanethiol molecules also exist in the free state due to the weaker reactivity with metallic copper and the porous structure.

The surface wettability of the as-synthesized SHM membrane was evaluated by the water contact angle (CA) measurements. Before any reaction, the contact angle of the copper mesh is 134.1° as shown in Figure 4(a). After the oxidation, the Cu(OH\(_2\))\(_2\) NWs are superhydrophilic with the contact angle about 0° (Figure 4(b)). However, through modification with dodecanethiol, the SHM exhibits superhydrophobicity. When a water droplet is placed on the surface of SHM in air, the water droplets remain spherical and unwetted on the membrane, as shown in Figure 4(e). Furthermore, the CA is measured ca. 163.9°, much better than the reported similar
Figure 2: The energy-dispersive X-ray spectroscopy elemental analysis of SHM.

Figure 3: (a) XPS survey spectrum of SHM. High-resolution XPS spectra of (b) Cu 2p, (c) S 2p, and (d) C 1s in SHM.
work of 151° [36], indicating the excellent water repellence and low adhesive force to water. For comparison, the CA of Cu mesh modified with dodecanethiol is also measured about 133° (Figure 4(c)). This result could demonstrate that geometrical microstructure and low surface energy can synergistically enhance the superhydrophobic property. Furthermore, by
changing the time of the oxidation process to 30 min and 60 min, respectively, the samples exhibit weak hydrophobic property than SHM (Figures 4(d) and 4(f)). Through the SEM shown in Figures 4(g)–4(i), the Cu(OH)$_2$ NWs obtained at 30 min are short and loose due to the lack of reaction time, while the Cu(OH)$_2$ NWs obtained at 60 min are more stubbed and aggregated into particles. The difference in the growth time leads to the changes of microstructure on the surface of the mesh, which influence the superhydrophobic property of each sample. The result indicates that the control of proper microstructure is important in order to obtain the superhydrophobicity.

At the same time, the impact of a water droplet with the SHM surface is also measured. As illustrated in Figure 5, the drop expands rapidly due to the large speed at the surface; subsequently, the drop retracts violently and rebounds from the surface. This phenomenon can further prove the superhydrophobicity of the SHM. Furthermore, the chemical stability of the surface superhydrophobicity was also tested by immersing SHM into HCl and NaOH aqueous solution. The surface wettability after immersion was measured and exhibited in Table 1. From the test, the SHM exhibits good chemical stability even after acidic or alkaline treatment.

The practical oil/water separation experiments were carried out with a self-made device. Five kinds of oils and organic solvents were used in this study. They were colored with oil red O and mixed with water that colored with methylene blue. As an example, 10 mL toluene dyed with oil red O

| Samples                                      | Water contact angle | Sliding angle |
|----------------------------------------------|---------------------|---------------|
| SHM                                          | $163.9 \pm 1.2^\circ$ | $8.0 \pm 0.5^\circ$ |
| Sample obtained by 30 min oxidation process  | $144.2 \pm 2.3^\circ$ | $13.2 \pm 0.7^\circ$ |
| Sample obtained by 60 min oxidation process  | $153.7 \pm 1.7^\circ$ | $10.5 \pm 0.4^\circ$ |
| SHM in 1 M HCl for 12 h                       | $159.0 \pm 1.4^\circ$ | $8.3 \pm 0.3^\circ$ |
| SHM in 1 M NaOH for 12 h                      | $158.0 \pm 1.6^\circ$ | $8.5 \pm 0.6^\circ$ |

Figure 5: The pictures of droplet movement on the surface of SHM. The droplet size is 5 μL.
and 10 mL water dyed with methylene blue are mixed and slowly poured into the separation device (Figure 6(a)). As shown in Figure 6(b), oil could pass through the SHM rapidly and drop into the tube beneath it by gravity, while water was retained on the top of the separation device, indicating an efficient separation for the mixture of oil and water. Subsequently, as shown in Figure 6(c), various immiscible oil/water mixtures were poured onto the membranes and immediately separated with a high separation efficiency, exhibiting a good flexibility in the separation process. The separation efficiency was calculated using the following equation:

$$\eta = \frac{V}{V_0} \times 100\%,$$

where $\eta$ represents the separation efficiency and $V$ and $V_0$ are the oil volume before and after the separation experiment, respectively. More importantly, the stability is a nonnegligible
factor in practice. For long-term oil/water separation, the separation efficiency of SHM during the 20 times continuous filtration did not present obvious change, indicating this membrane may be a potential option for practical oil/water mixture treatments (Figure 6(d)).

4. Conclusions

In summary, a facile two-step approach to synthesize a super-hydrophobic membrane is demonstrated. Based on the copper mesh, after oxidation and modification, the hair-like superhydrophobic nanowires are grown on the copper surface. Due to the rough microstructure and modification with low energy reagents, the as-prepared mesh exhibits superhydrophilicity with a high water contact angle up to 163.9° and high efficiency for the separation of oil/water mixtures. Impressively, the membrane also exhibits good stability without obvious changes in the efficiency even after 20 cycles. Thanks to the low cost, fast synthesis, and energy-efficient separation as well as good stability, this superhydrophobic membrane can be a promising candidate for many oil/water separation processes in the future.

Data Availability

The data used to support the findings of this study are included within the article and available from the corresponding author upon request.

Conflicts of Interest

The authors declare no competing financial interest.

Authors’ Contributions

All authors contributed equally in this work.

Acknowledgments

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References

[1] C. A. Kontovas, H. N. Psaraftis, and N. P. Ventikos, “An empirical analysis of IOPCF oil spill cost data,” Marine Pollution Bulletin, vol. 60, no. 9, pp. 1455–1466, 2010.

[2] A. Al-Futaisi, A. Jamrah, B. Yaghi, and R. Taha, “Assessment of alternative management techniques of tank bottom petroleum sludge in Oman,” Journal of Hazardous Materials, vol. 141, no. 3, pp. 557–564, 2007.

[3] F. Chen, J. Song, Z. Liu et al., “Atmospheric pressure plasma functionalized polymer mesh: an environmentally friendly and efficient tool for oil/water separation,” ACS Sustainable Chemistry & Engineering, vol. 4, no. 12, pp. 6828–6837, 2016.

[4] B. Doshi, M. Sillanpaa, and S. Kalliola, “A review of bio-based materials for oil spill treatment,” Water Research, vol. 135, pp. 262–277, 2018.

[5] W. Lv, Q. Mei, J. Xiao, M. Du, and Q. Zheng, “3D multiscale superhydrophilic sponges with delicately designed pore size for ultrafast oil/water separation,” Advanced Functional Materials, vol. 27, no. 48, article 1704293, 2017.

[6] J. Ge, D. Zong, Q. Jin, J. Yu, and B. Ding, “Biomimetic and superwettability nanofibrous skins for highly efficient separation of oil-in-water emulsions,” Advanced Functional Materials, vol. 28, no. 10, article 1705051, 2018.

[7] Y. Gao, M. Cheng, B. Wang, Z. Feng, and F. Shi, “Diving-facing cycle within a stimulus-responsive smart device towards developing functionally cooperating systems,” Advanced Materials, vol. 22, no. 45, pp. 5125–5128, 2010.

[8] S. Zhang, F. Lu, L. Tao et al., “Bio-inspired anti-oil-fouling chitosan-coated mesh for oil/water separation Suitable for broad pH range and hyper-saline environments,” ACS Applied Materials & Interfaces, vol. 5, no. 22, pp. 11971–11976, 2013.

[9] Q. Pan and M. Wang, “Miniature boats with striking loading capacity fabricated from superhydrophobic copper meshes,” ACS Applied Materials & Interfaces, vol. 1, no. 2, pp. 420–423, 2009.

[10] D. Tian, X. Zhang, J. Zhai, and L. Jiang, “Photocontrollable water permeation on the micro/nanoscale hierarchical structured ZnO mesh films,” Langmuir, vol. 27, no. 7, pp. 4265–4270, 2011.

[11] H. Li, X. Zhao, P. Wu, S. Zhang, and B. Geng, “Facile preparation of superhydrophobic and superoleophilic porous polymer membranes for oil/water separation from a polyarylester polydimethylsiloxane block copolymer,” Journal of Materials Science, vol. 51, no. 6, pp. 3211–3218, 2016.

[12] W. Fang, L. Liu, T. Li et al., “Electrosyn Pennituted polyurethane membranes with self-healing ability for self-cleaning and oil/water separation,” Chemistry, vol. 22, no. 3, pp. 878–883, 2016.

[13] W. Zhang, Z. Shi, F. Zhang, X. Liu, J. Jin, and L. Jiang, “Superhydrophobic and superoleophilic PVDF membranes for effective separation of water-in-oil emulsions with high flux,” Advanced Materials, vol. 25, no. 14, pp. 2071–2076, 2013.

[14] P.-C. Chen and Z.-K. Xu, “Mineral-coated polymer membranes with superhydrophilicity and underwater superoleophobicity for effective oil/water separation,” Scientific Reports, vol. 3, no. 6153, pp. 2779, 2013.

[15] M. Yue, B. Zhou, K. Jiao et al., “Switchable hydrophobic/hydrophilic surface of electrosynopn poly (l-lactide) membranes obtained by CF3 microwave plasma treatment,” Applied Surface Science, vol. 327, no. 1, pp. 93–99, 2015.

[16] X. Zhang, Z. Li, K. Liu, and L. Jiang, “Bioinspired multifunctional foam with self-cleaning and oil/water separation,” Advanced Functional Materials, vol. 23, no. 22, pp. 2881–2886, 2013.

[17] M. Cheng, Y. Gao, X. Guo, Z. Shi, J. F. Chen, and F. Shi, “A functionally integrated device for effective and facile oil spill cleanup,” Langmuir the Acs Journal of Surfaces & Colloids, vol. 27, no. 12, pp. 7371–7375, 2011.

[18] X. Gao, J. Zhou, R. Du et al., “Robust superhydrophobic foam: a graphdiyne-based hierarchical architecture for oil/water separation,” Advanced Materials, vol. 28, no. 1, pp. 168–173, 2016.

[19] X. Zhao, L. Li, B. Li, J. Zhang, and A. Wang, “Durable superhydrophobic/superoleophilic PDMS sponges and their applications in selective oil absorption and in plugging oil leakages,” Journal of Materials Chemistry A, vol. 2, no. 43, pp. 18281–18287, 2014.
