Fabrication and Application of Superhydrophobic Multi-Stage Structure Separation Membranes

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Abstract. In this paper, the copper mesh was used as the base material, and the uniform nanowire structure was obtained by surface modification of the base material. The hydrophobic silica nanoparticles were grown in situ on the nanowires to obtain the prepared material with SiO\textsubscript{2} nanoparticles/Cu(OH)\textsubscript{2} nanowires (SiO\textsubscript{2}NPs/CuNWs) multi-stage structure. Fourier transform infrared spectroscopy (FTIR) showed that a large amount of methyl (-CH\textsubscript{3}) was present on the surface of the prepared material after modification of methyltrimethoxysilane (MTMS). Because of the existence of -CH\textsubscript{3}, the surface energy of the prepared material was reduced, so the hydrophilic substrate surface was changed into hydrophobic surface. Scanning electron microscopy (SEM) showed that the surface of the prepared material was uniformly distributed with SiO\textsubscript{2}NPs/CuNWs multi-stage structure, which improved the surface roughness of the base material, thus, the hydrophobic property was greatly improved. The contact angle (CA) of water droplet at the interface reaches 154°, indicating that the prepared material had excellent hydrophobic properties. Based on the porosity and surface hydrophobicity of the prepared material, it can be used to separate various oil-water mixtures efficiently.

1. Introduction

Oily wastewater and oil-pollution have been a serious problem in today's society. With the development of global industrialization and the improvement of people's living standards, there are kind of oily wastewater in our daily life [1]. At present, there are several methods for oil-water mixture separation [2, 3]. Such as centrifugal method[4, 5], chemical vapour deposition [6], electrospinning [7], spray coating method [8, 9] and so on [10, 11, 12]. Membrane material is a material with selective separation function. Membrane separation method has the advantages of high single-stage separation efficiency, large liquid flow, flexible and simple process, low environmental pollution, strong versatility and low energy consumption [13, 14]. In addition, the membrane material has selective for droplets. So it is feasible to use membrane separation method for oil-water separation.

In nature, there are many organisms with especial wettability, such as lotus leaf, water strider, mosquito eyes and so on [15,16,17], which provide inspiration for the preparation of special wetting property materials. The essence of oil-water separation is the interface science problem [18]. Inspired by nature, researchers have obtain superhydrophilic, superoleophobic or superhydrophobic superlipophilic oil-water separation membrane materials by designing a special wetting property of the membrane material surface, which undoubtedly greatly improves the oil-water separation efficiency. Oil-water separation materials with special wettability greatly promotes the development of oil-water separation materials. In general, there are two types of special wettable materials have been applied.
to oil-water separation: superhydrophilic or superoleophilic materials (oil removing) and superhydrophilic and underwater superoleophobic materials (water removing) [19, 20].

The first reported superhydrophobic material is the PTFE coated mesh fabricated by Jiang using spraying method for oil-water separation [21]. From then on, various superhydrophobic materials have been successively fabricated for oil-water separation. However, most reported methods exist several disadvantages such as high cost [22], dangerous materials [23] and complex devices [24]. In order to overcome above disadvantages, we first fabrication nanoparticles/nanowires multi-stage structure separation membranes. The copper mesh is used as a base material, and we first use the low temperature solution immersion method to modify the surface of the base material to obtain a uniform nanowire structure. The nanowire structure greatly improves the surface roughness of the base material. In the second step, we use methyltrimethoxysilane (MTMS) as hydrophobic modifier. The hydrophobic silica nanoparticles are then grown in situ on the nanowires. After 24h reaction, dried the mesh at 70 °C to obtain a copper mesh with SiO₂NPs/CuNWs structure. And the nanoparticle-nanowire composite multi-stage structure further increases the roughness of the material, thereby improving the hydrophobic properties of the material.

2. Experimental

2.1. Materials

Methyltrimethoxysilane (MTMS), ammonium persulfate ((NH₄)₂S₂O₈) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Sodium chloride (NaCl), sodium hydroxide (NaOH), ethanol, ammonia (NH₃·H₂O) were purchased from Sinopharm Chemical Reagent Co., Ltd. Acetone, hydrochloric acid (HCl) and absolute ethanol were purchased from Beijing Chemical Works. Dichloromethane, trichloromethane, bromobenzene, Sudan Red III were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Carbontetrachloride were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. The above reagents are all analytical pure and have not been further purified. Deionized water (H₂O) is ultrapure water (18.2MΩ/cm) treated by UHP Ultra Pure Water Machine.

![Figure 1. Schematic description of the preparation for SiO₂NPS-CuNWs copper mesh.](image)

2.2. Samples preparation

The SiO₂NPs-CuNWs copper mesh was synthesized by two-step method. As shown in Figure 1, the copper mesh was used as the base material, and cut into 3*3 cm squares. Ultrasonic cleaning the base material with acetone, absolute ethanol and H₂O for 20 minutes to remove surface stains. Mixed 0.3 mol/L (NH₄)₂S₂O₈ and 5 mol/L NaOH solution evenly. And then placed the base material into the mixed solution of (NH₄)₂S₂O₈ and NaOH at 5 °C for 30 min. After that, washed the base material with

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H₂O until PH = 7.0. In this step, the uniform Cu(OH)₂ nanowire (CuNWs) structure was obtained. In the second step, we used a magnetic stirrer to evenly mix 8ml of MTMS, 10ml of EtOH, 10ml of H₂O and 1ml of 1% HCl for 5min. Then we placed the mixed solution at 70 ° C for 1 hour. In this process, MTMS will undergo hydrolysis reaction. Then the CuNW scooper mash was placed in the MTMS hydrolyzate, and then add a certain amount of 1M NH₃•H₂O. The hydrophobic SiO₂ nanoparticles (SiO₂NPs) were grown on the nanowires in situ in the process. After 24h reaction, we took out the CuNWs copper mesh and then washed it with ethanol to remove excess SiO₂ particles on the surface. The mesh was dried at 70°C finally to obtain a copper mesh which having a SiO₂NPs-CuNWs structure.

2.3. Characterization
The morphologies of samples was analyzed by scanning electron microscope (SEM, HITACHI S-8000, Japan). The main parameters of the test are as follows: the working distance (WD) is set to 8 mm, the acceleration voltage is 5 kV, and the operating current is 10 uA. The contact angles (CA) measurements were made at room temperature with static contact angle measuring instrument (Zhongchen Powereach, JC2000C1, China). It should be noted that, in the measurement of the contact angle involved in the experiment, the volume of the droplets is 5 μL, and the measured values of the contact angles are average values of five points, and the errors are all within ±1°. The chemical composition of samples was analyzed via FT-IR spectroscopy (Bruker, TENSOR II, Germany). The spectra were recorded in the range of 4000~400cm⁻¹ at a resolution of 4cm⁻¹.

2.4. Oil/water separation
The micro-separating device for oil-water separation test is a barrel-type filter device. Superhydrophobic Membrane is fixed between the measuring barrel and the lower end interface (the inner diameter of the measuring barrel and the lower end interface is 1.5 cm) of the measuring barrel filter device. The three parts are fixed with the matching device clamp and placed vertically at the matching conical bottle mouth. The prepared oil-water mixture (in which the volume ratio of oil to water is 1:1 and the oil phase is dyed red with Sudan Red III) is poured 40 mL from the upper port of the micro oil/water separation device for oil-water separation test. After separation, the liquid in the conical bottle under the separation device is collected to detect the oil phase content in water. In this experiment, the oil phases used in oil-water separation test are dichloromethane, trichloromethane, bromobenzene and carbontetrachloride.

OIL480 infrared spectrophotometer was used to detect oil content in water phase after oil/water separation. The separation efficiency of oil-water separation membrane is explained by separation rate. The calculation formula of separation rate is as follows [21]:

\[ C(\%) = \left(1 - \frac{C_c}{C_0}\right) \times 100\% \]

Herein, \( C_0 \) and \( C_c \) are the concentration of oil phase before and after oil-water mixture. After 30 minutes of each separation, none oil droplets were visibly detected on the surface of the water before the oil-water separation membrane was considered to be successful. The final test value is the average calculated value of the three results.

3. Results and Discussion

3.1. The Surface morphology
After surface modification and hydrophobic modification, the microstructures of the original copper mesh changed greatly. The microstructures of the samples were observed by SEM. As shown in Figure 2a is the original copper mesh. We can see that the diameter of the copper mesh wire is about 25μm, the aperture is about 40μm, and the surface of the copper wire is smooth. After surface modification, the surface becomes rough (Figure 2b and Figure 2c). We can see that nanowires grow uniformly on the surface of copper mesh. The length of nanowires is about 5μm. At the same time,
nanowires structure greatly improves the roughness of copper mesh. Figure 2d is the hydrophobic SiO$_2$NPs-CuNWs structure copper mesh. SiO$_2$ nanoparticles (80-100 nm in diameter) grow uniformly on copper nanowires to form micron-nano multi-stage heterogeneous composite structure. Cassie study [25] shows that liquid can not completely wet the voids between the protrusions on the rough surface when it wets the heterogeneous surface. There is intercepted air under the droplet. In fact, the droplet is in a composite interface composed of solid and air. When droplets are placed on SiO$_2$NPs-CuNWs copper mesh, the grooves of SiO$_2$NPs-CuNWs multi-stage composite structure will intercept a large amount of air and form an air cushion structure, thus reducing the wettability of droplets.

![Figure 2](image)

**Figure 2.** SEM images of (a) the original copper mesh, (b)(c) copper mesh with nanowires, (d) the prepared materials and (e) FTIR spectra of prepared materials.

### 3.2. Chemical analysis of the prepared surface

In order to verify the existence of surface alkyl groups, the chemical constituents of the samples before and after modification were qualitatively analyzed by FTIR. Figure 2e shows the infrared spectrum of the material. At the wave number of 2980 cm$^{-1}$, 2896 cm$^{-1}$ and 1389 cm$^{-1}$, the stretching vibration peaks are -CH$_3$. The deformation vibration peak of methyl in -SiCH$_3$ with wave number 1237 cm$^{-1}$. Wave number 879 cm$^{-1}$ is the stretching vibration peak of Si-C. Wave number 1057 cm$^{-1}$ is the vibration peak of Si-O-Si and Si-O-C (chain). This is mainly attributed to the condensation reaction of MTMS monomer after hydrolysis. After MTMS hydrolysis, the molecule contains three silanol groups, which can bond with the hydroxyl groups on the surface of copper nanowires. At the same time, the silanol groups can also condense to form three-dimensional polysiloxane with network structure. Successful modification of MTMS can expose a large number of -CH$_3$ groups on the surface and inside of copper nanowires, which greatly reduces the surface energy of copper mesh and shows a certain hydrophobicity on the macro level. At the same time, MTMS self-condensation results in the formation of irregular micro-nano multi-stage structure particles on the copper nanowires and the internal surface, which increases the surface roughness of the copper mesh. And further increasing the hydrophobicity of the material.

### 3.3. Wettability of the prepared surface

We characterize the wettability of materials by contact angle. Figure 3a-d show the optical images of water, acid(1M HCl), salty(1M NaCl) and alkali(1M NaOH) droplets on the prepared surface. The water droplet contact angle is 154°, indicating that the prepared material has excellent hydrophobic property. The acid and alkali droplets contact angles are all above 140°. And the salty droplet contact angle decreases slightly, but it still reaches 150.5°. The material still exhibits excellent lyophobic properties under extreme conditions. It shows that the harmful ions such as H$^+$, OH$^-$ and Cl$^-$ can hardly reach the substrate and destroy the surface. Moreover, exposure to ultraviolet rays will reduce the
hydrophobicity of the materials, so we tested the contact angles of the material exposed to ultraviolet rays for different days in Figure 3c. The results show that even after 7 days exposure to ultraviolet rays, the contact angle of the material is still higher than 150°. Further illustrating that the material has excellent durability.

Figure 3. Images of droplets contact angles to (a) water, (b) 1M HCl, (c) 1M NaCl, (d) 1M NaOH and (e) water contact angles of prepared materials after being exposed to ultraviolet rays for different days.

Figure 4. (a) Separation process diagram of prepared materials to water and carbontetrachloride; (b) Separation efficiency of prepared materials for different heavy oils; (c) Separation efficiency of prepared materials for four types of heavy oil/water mixtures with 20 times of cycle; (d) Oil/water separation efficiency of prepared materials after being exposed to ultraviolet rays for different days.
3.4 Oil-water separation

Because of special wettability and excellent hydrophobicity of the materials, it can be used in the field of oil-water separation. We used a barrel-type oil-water separation device to carry out oil-water separation experiments. As shown in Figure 4a, we fixed SiO$_2$NPs-CuNWs copper mesh between the barrel and the conical bottle, and poured into the separation device a mixture of water and heavy oil with a volume ratio of 1:1, a total of 40 ml (in which heavy oil was dyed red with Sudan Red III beforehand). Heavy oil quickly passes through SiO$_2$NPs-CuNWs copper mesh, while water is trapped above the copper mesh. Four different heavy oils (dichloromethane, trichloromethane, bromobenzene and carbon tetrachloride) and water mixture were separated and tested. The separation efficiency of the four heavy oils were higher than 99.4% (Figure 4b). After 20 cycles of separation tests, the separation efficiency is still over 99% (Figure 4c). Moreover, the materials was exposed to ultraviolet rays for 1 to 7 days before separation tests. The results showed that the separation efficiency of the materials was 99.5% even after one week of exposure to ultraviolet rays (Figure 4e). The above results show that the material has excellent oil-water separation efficiency, high recycling efficiency and durability.

4. Conclusions

In summary, the superhydrophobic multi-stage structure membrane for oil-water separation was prepared via two-step method. The copper mesh was used as the base material, and the base material was surface-modified to obtain a uniform nanowire structure. The hydrophobic silica nanoparticles are grown in situ on the nanowires to obtain a separation membrane having a silica nanoparticle/copper nanowire multistage structure. A large amount of -CH$_3$ was present on the surface of the base material after modification of MTMS. The prepared material exhibits excellent hydrophobic properties and excellent lyophobic properties under extreme conditions such as water, acid, salty and alkali. The oil-water separation efficiency of different oil-water mixtures is over 99.4%. In addition, after 20 cycles of oil-water separation tests, the separation efficiency was still as high as 99%. It shows that the oil-water separation material has high separation efficiency and durability. Besides, the prepared material demonstrated good stability and durability for long time expose to ultraviolet rays.

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References

[1] He L, Lin F, Li X G, Sui H and Xu Z H 2015 Chem. Soc. Rev. 44 5446
[2] Chen P C and Xu Z K 2013 Sci. Rep. 3 2776
[3] Mark A S, Paul W B, Menachem E, John G G, Benito J. M and Anne M. M 2008 Nature 452 301
[4] Wei Q F, Mather R R, Fotheringham A F and Yang R D 2003 Mar. Pol. Bul. 46 780
[5] Ma Q, Cheng H, Fane A G, Wang R and Zhang H 2016 Small 12 2186
[6] Sasan R, Iraj M, Rostam M and Behzad P 2014 Chem. Eng. J. 252 11
[7] Manas K S, Kausik B, He F and Fan J T 2011 Appl. Surf. Sci. 257 7003
[8] Li J, Wu R N, Jing Z J, Yan L, Zha F and Lei Z Q 2015 Langmuir 31 10702
[9] Feng K Y, Hung G Y, Liu J S, Li M Q, Zhou C R and Liu M X 2018 Chem. Eng. J. 331 744
[10] Yuan S J, Chen C, Raza A, Song R X, Zhang T J, Pehkonen S. O and Liang B 2017 Chem. Eng. J. 328 497
[11] Zhang D G, Li L H, Wu Y L, Sun W J, Wang J P and Sun H W 2018 Col. Surf. A. 552 32
[12] Cheng Z J, Liu H W, Lai H, Du Y, Fu K W, Li C, Yu J X, Zhang N Q and Sun K N 2014 ACS Appl. Mater. Interfaces 6 636
[13] Xue Z X, Wang S T, Lin L, Chen L, Liu M J, Feng L and Jiang L 2011 Adv. Mater. 23 4270
[14] Du X, You S J, Wang X H, Wang Q R and Lu J D 2017 Chem. Eng. J. 313 398
[15] Wang B, Liang W X, Guo Z G and Liu W M 2015 Chem. Soc. Rev. 44 336
[16] Jiang L and Feng L 2010 Bioinspired Intelligent Nanostructured Interfacial Materials (World Scientific Publishing Co. Pte. Ltd. and Chemical Industry Press)
[17] Bharat B and Yong C J 2011 Pro. Mater. Sci. 56 1
[18] Gao X F, Xu L P, Xue Z X, Feng L, Peng J T, Wen Y Q, Wang S T and Zhang X J 2014 Adv. Mater. 26 1771
[19] Zhang J P and Seeger S 2011 Adv. Funct. Mater. 21 4699
[20] Xu Z G, Zhao Y, Wang H X, Wang X A and Lin T 2015 Angew. Chem. Int. Ed. 54 4527
[21] Feng L, Zhang Z Y, Mai Z H, Ma Y M, Liu B Q, Jing L and Zhu D B 2004 Angew. Chem. Int. Ed. 116 2046
[22] Xue Z X, Cao Y Z, Liu N, Feng L and Jiang L 2014 J. Mater. Chem. A. 2 2445
[23] Pan S J, Guo R, Björnmalms M, Richardson J. J, Li L, Peng C, Zieschang N.B, Xu W J, Jiang J H and Caruso F 2018 Nature Materials 17 1040
[24] Li L X, Hu T, Sun H X, Zhang J P and Wang A Q 2017 ACS Appl. Mater. Interfaces. 9 18001
[25] Cassie A B D 1944 Trans. Faraday Soc. 40 546