Fabrication of Superhydrophobic Surface on Stainless Steel Meshes for Oil-Water Separation

Xiaohui Wang*, Zhuo Han and Shan Huang
Technical Test Centre of Sinopec Shengli OilField, Shandong, Dongying 257000, China

*Corresponding author e-mail: wxhui583@126.com

Abstract. In this paper, a superhydrophobic surface for oil-water separation were fabricated by grafting polymer on 3D hierarchical polydopamine-graphene (PDA-graphene) aerogel modified stainless steel mesh (SSM). The chemical compositions and surface morphology of the as-prepared composite were characterized by HNMR, FTIR and SEM. The results show that polymer/PDA-graphene/SSM exhibits unique interfacial properities, including hierarchically porous structure, large specific surface area, hydrophilicity and oleophobicity, hence it could work as excellent oil-water separation material. Oil-water separation experiments indicate that the average water permeation of the film is 1155 L h⁻¹m⁻²bar⁻¹, and the separation efficiency is 99.1%, which identifying the excellent performance of polymer/PDA-graphene/SSM.

1. Introduction
Oil-bearing wastewater pollution has noxious effects on human health and the ecological environment [1], hence it is urgent to develop new technologies for water purification and treatment. Membrane separation technology which possesses many advantages like low energy consumption, high single-stage separation efficiency, low environmental pollution and versatility, is widely used in oil-water separation [2]. In recent years, membrane with special wettability surface including superhydrophilic, superhydrophobic and superamphiphatic surface etc have been created rapidly [3]. Among various interfaces, superhydrophilic and under-water superhydrophobic surface is urgent needed for oil-water separation, as oil-bearing water can quickly infiltrate and penetrate downward, and oil would be blocked on the surface of the membrane, thus achieving the effect of high-throughput and rapid separation of oil-water mixture in dynamic fluids [4]. Designing special wettability of the material to obtain superhydrophilic or super-hydrophobic separation material is undoubtedly the most effective means to improve oil-water separation performance. To create novel interface materials for oil/water separation, the micro/nano surface morphology, along with the interaction of hydrophilic and hydrophobic groups should be delicately designed to achieve simultaneous superhydrophilicity and superoleophobicity [5].

Among variety of materials, Graphene and its composites are promising candidates for water treatment because of its low cost, high durability and interesting physical properties. 3D porous graphene gel with large contact area is an ideal material for oil-water separation [6]. In this paper, graphene hydrogel will firstly be functionalized by adhesive, hydrophilic polydopamine. After that the graphene gel will be further modified by polymer to fabricate a hydrophilic/oleophobic membrane on stainless steel mesh (SSM). Random copolymer of 2-(2-methoxyethoxy) ethyl methacrylate (MEO₂MA) oligo
(ethylene glycol) methyl ether methacrylate and 2, 2'-dithiobis [1- (2-bromo-2-methyl-propionyloxy)]s ethane (DTBE) were synthesized by atom transfer radical polymerization (ATRP). 3D PDA-graphene aerogel modified stainless steel mesh (SSM) was prepared by hydrothermal treatment. Thereafter, a super hydrophobic surfaces is manufactured by grafting polymer on the PDA-graphene modified via Michael addition. In this reaction, the polymers with –SH as nucleophile agent were anchored to aromatic ring of PDA. The chemical compositions and surface morphology of as-prepared composite were characterized by HNMR, FTIR and SEM, and oil-water separation efficiency of the film was investigated.

2. Experimental

2.1. Chemicals

2, 2’-dithiobis [1- (2-bromo-2-methyl-propionyloxy)]s ethane (DTBE) was purchased from J&K Chemical Ltd. 2-(2-methoxyethoxy) ethyl methacrylate (MEO2MA), oligo(ethylene glycol) methyl ether methacrylate (475 g/mol, OEGMA475) macromer, copper (I) bromide, 2,2-bipyridyl, tributyl phosphine (TBUP) were purchased from Sinopharm Chemical Reagent Co., Ltd. Stainless steel mesh (800 mesh) was offered by Taobao Trade Co. Ltd.

2.2. Synthesis of P(MEO2MA-co-Omega475-SH)

P (MEO2MA-co-Omega475-SH) were synthesized by atom transfer radical polymerization as demonstrated in Figure 1. Briefly, MEO2MA (941mg, 5mmol), OEGMA475 (119mg, 0.25mmol) and DTBE (21.6 mg, 0.05 mmol) were dissolved in 5 mL anhydrous methanol and transferred into a Schlenk tube sealed with a septum, then the tube was degassed for 15 minutes by Nitrogen. Then 2 mL methanol
containing copper (I) bromide (28.8 mg, 0.2 mmol) and 2,2-bipyridyl (52.0 mg, 0.30 mmol) were added into the system with a syringe, and degassed for another 15 mins. The mixture was heated at 50 °C for 10 h, after that the experiment was stopped by opening the flask and exposing the catalyst to air. The final mixture was diluted in ethanol and passed through a short silica column (60-200 mesh) in order to remove copper catalyst. Then, the most of the filtered solution was removed and the final product was obtained by precipitating with hexane.

To reduce the disulfide bond, 1.0 g of the as prepare MEO2MA-co-OEGMA475-S-S-MEO2MA-co-OEGMA475 was first dissolved in 15.0 mL of DCM at 25 °C, then 400 µL of tributyl phosphine was added as the reduction catalyst. Subsequently, the mixture was stirred for 30 min and evaporated to obtain P (MEO2MA-co-OMEGA475-SH).

2.3. Preparation of polymer/PDA-graphene/SSM

Graphene oxide (GO) was prepared according to Hummers’ method with slight modifications [7]. Dopamine (1.0 mg mL$^{-1}$) was added into GO aqueous dispersions (2.0 mg mL$^{-1}$) with pH adjusted to about 7.0, and the mixture was transfer into beaker with a piece of SSM (5×5 cm). The beaker was heated at 60 °C for 6 h without any disturbance to produce PDA-graphene/SSM.

1g P (MeO 2MA-co-OEGMA475-SH) was dissolved into 200mL 0.1 M Bicine buffer, then PDA-graphene/SSM was immersed in the solution and stirred in 24h in air at room temperature. After drying, polymer/PDA-graphene/SSM was obtained.

3. Results and Discussion

3.1. Characterization

Figure 2A displays the H NMR spectrum of P (MeO2MA-co-OEGMA475-SH). Multiple peaks at 0.8-1.2 ppm are attributed to the methyl protons in polypropylene (C-CH$_3$). Peaks at 1.7-2.0 ppm are ascribed to methylene protons in the main chain (-C-CH$_2$-C-). Strong single peak at 3.4 ppm reveals methyl proton of ester groups (-O-CH$_3$). Peaks at 3.5-3.8 ppm are ascribed to methylene protons in the ether group (-O-CH$_2$-CH$_2$-O-), Peaks at 4.3 ppm are ascribed to methylene protons connected to ester group (-CH$_2$-OOC-). Figure 2B shows the FTIR spectrum of PDA-graphene and polymer/PDA-graphene. In the spectrum of PDA-graphene, the peak at 1628 cm$^{-1}$ is ascribed to C=C stretching vibration of graphene [9]. The peaks at 1514 cm$^{-1}$ reveals the existence of indole or indoline structures. After Michael addition with P (MeO2MA-co-OEGMA475-SH), two characteristic peaks at 2925 cm$^{-1}$ and 2853 cm$^{-1}$ appears, which are ascribed to the stretching vibration of methyl and methylene at the backbone of random copolymer [10]. Peaks at 1458 cm$^{-1}$ and 1376 cm$^{-1}$ are characteristic for polypropylene structure.
The appearance and micro-morphology changes of SSM before and after surface modification are demonstrated in Figure 3. After surface modification, the colour of SSM changes from grey to dark brown (Figure 3A, B). From SEM images, it can be seen that bare SSM shows a metal wire grid structure with smooth surface (Figure 3C). Polymer/PDA-graphene filled the space of metal grid after hydrothermal treatment and grafting of polymer (Figure 3C). High magnification images indicate polymer/PDA-graphene forms a 3D hierarchical structure (Figure 3E, F), which greatly increase the contact area in the oil-water separation. According to the abovementioned characterization technology, polymer/PDA-graphene/SSM has been successfully fabricated.

The water contact angle of polymer/PDA-graphene/SSM is 72º, indicating the hydrophilicity of the membrane surface. The under-water oil contact angle is about 143º, which reveal under water oleophobicity of the membrane surface. Both properties are essential for oil-water separation for the composite membrane.

3.2. Oil-water separation test

Since polymer/PDA-graphene/SSM exhibits unique interfacial properties, including hierarchically porous structure, large specific surface area, hydrophilicity and oleophobicity, it is considered as excellent oil-water separation material. Here, oil field waste water from Sinopec Shengli OilField was taken as research object to test its separation capacity. In our experiment, five parallel wastewater samples were investigated. During oil/water separation process, water passed quickly through the membrane and oils were retained above the membrane (Figure 4). Table 1 shows the results of the oil-water separation parallel experiments using polymer/PDA-graphene/SSM. It can be seen that the average flux is 1155 L h⁻¹ m⁻² bar⁻¹, and the separation efficiency is 99.1%, which identifying the excellent performance of the as-prepared polymer/PDA-graphene/SSM.

Figure 3. The photos and SEM images of SSM before and after modification.

Figure 4. The photo of polymer/PDA-graphene/SSM before and after wastewater treatment.
Table 1. Parallel experiments for oil-water separation.

| sample | Flux (L h\(^{-1}\) m\(^{-2}\) bar\(^{-1}\)) | Separation efficiency (%) |
|--------|------------------------------------------|---------------------------|
| 1\#    | 1187                                     | 99.2                      |
| 2\#    | 1143                                     | 99.1                      |
| 3\#    | 1154                                     | 99.0                      |
| 4\#    | 1126                                     | 99.0                      |
| 5\#    | 1163                                     | 99.1                      |
| average| 1155                                     | 99.1                      |

4. Conclusion

In conclusion, a facile method for manufacturing super hydrophobic surfaces is presented using the stainless steel wire mesh as support, and polymer modified 3D hierarchical polydopamine-graphene aerogel as surface modifier. This hydrophobic surfaces possesses hierarchically porous structure, large specific surface area, hydrophilicity and oleophobicity, hence, it works as excellent oil-water separation material. Oil-water separation experiments indicate the average flux is 1155 L h\(^{-1}\) m\(^{-2}\) bar\(^{-1}\), and the separation efficiency is 99.1%. Therefore, the as-prepared polymer/PDA-graphene/SSM would be a good candidate for oil/water separation to meet emerging needs in practical applications.

References

[1] H. Shao, X.-L. Liu, D.-W. Wang, W.-W. Xu, Study of Oil-bearing Wastewater Treatment by Chitosan-bentonite and PDMDAAC-bentonite, Rock Miner Anal. 33 (2014) 426-432.
[2] D. Xu, S. Hein, K. Wang, Chitosan membrane in separation applications, Mater Sci Technol. 24 (2008) 1076-1087.
[3] L. Zhang, N. Zhao, J. Xu, Surfaces with special wettability: Applications in oil/water separation, Chinese Sci Bull. 58 (2013) 3372-3380.
[4] Z. Xue, S. Wang, L. Lin, L. Chen, M. Liu, Y. Feng, L. Jiang, A Novel Superhydrophilic and Underwater Superoleophobic Hydrogel-Coated Mesh for Oil/Water Separation, Adv. Mater. 23 (2011) 4270-4273.
[5] J. Yang, L. Yin, H. Tang, H. Song, X. Gao, K. Liang, C. Li, Polyelectrolyte-fluorosurfactant complex-based meshes with superhydrophilicity and superoleophobicity for oil/water separation, Chem. Eng J. 268 (2015) 245-250.
[6] Y. Cheng, P. Xu, W. Zeng, C. Ling, S. Zhao, K. Liao, Y. Sun, A. Zhou, Highly hydrophobic and ultralight graphene aerogel as high efficiency oil absorbent material, J. Environ. Chem. Eng. 5 (2017) 1957-1963.
[7] Y. Sun, S. Luo, H. Sun, W. Zeng, C. Ling, D. Chen, V. Chan and K. Liao, Engineering closed-cell structure in lightweight and flexible carbon foam composite for high-efficient electromagnetic interference shielding, Carbon. 136 (2018) 299-308.
[8] H.-Y. Lv, S.-X. Liu, C. Xu, R. Tian, L. Wang, Synthesis and Characterization of Temperature-Sensitivity P (ME2MA-co-OEGMA) Copolymers, Acta Phys.-Chim. Sin. 28 (2012) 2683-2689.
[9] Y. Sun, H. Zheng, C. Wang, M. Yang, A. Zhou, H. Duan, Ultrasonic-electrodeposition of PtPd alloy nanoparticles on ionic liquid-functionalized graphene paper: towards a flexible and versatile nanohybrid electrode, Nanoscale 8 (2016) 1523-1534.
[10] Y. Sun, W. Zeng, H. Sun, S. Luo, D. Chen, V. Chan, K. Liao, Inorganic/polymer-graphene hybrid gel as versatile electrochemical platform for electrochemical capacitor and biosensor, Carbon. 132 (2018) 589-597.