One-Step Solution-Immersion Process of Hydrophobic Octyl Graphene Oxide-Modified Nickel Foam for Highly Efficient Oil−Water Separation

Huayu Huang,*† Xingyu Wang,‡ Xin Liu,*† Yangzi Li,*† Haotian Sun,*† and Qi Li*†

†Shaanxi Key Laboratory of Earth Surface System and Environmental Carrying Capacity, College of Urban and Environmental Science, Northwest University, Xi’an 710127, China
‡Department of Civil and Environmental Engineering, University of Connecticut, Storrs, Connecticut 06269, United States

Supporting Information

ABSTRACT: Hydrophobic foam was prepared by immersing nickel foam in a dispersion of octyl group-grafted graphene oxide (GO) and used to clean up oil−water mixtures. Octyl graphene oxide (C8-GO) was synthesized using GO and triethoxyoctylsilane by a solvothermal method. The resulting coverage of the foam was characterized, and the surface morphology of the foam was also investigated. The static water contact angle (SWCA) was measured to evaluate the change in wettability of the developed foam. The pristine smooth microstructure of the nickel foam became rough after being covered with the C8-GO nanosheets. The SWCA of C8-GO nickel foam (C8-GO NF) surface was approximately 147°. The C8-GO NF can float on the surface of the water in contrast to the easy-sinking unmodified foam, demonstrating good hydrophobicity. Furthermore, the C8-GO NF showed outstanding performance in organic compound adsorption and excellent efficiency in oil−water separation. The reusability and durability of the obtained foam are evaluated to highlight its usability in more complicated scenarios. The use of C8-GO NF was proved to be a promising strategy for oil−water separation under harsh circumstance.

1. INTRODUCTION

The leakage of oil in water, especially in public waters, has had many negative effects on the economy and public health. These public hazards can lead to health risks to citizen’s lives. More seriously, some organic compounds are hard to decompose and cause long-term harm to humans. The highly efficient removal of oil in water is needed for more advanced disposal quality and lower cost. To date, there are several ways to prevent oil/organic leakage from spreading over a wide range, such as biodegradation, chemical dispersants, mechanical collection, and in situ burning. Nevertheless, these methods have the drawbacks of separation inefficiency, a long time requirement, and a high cost of operation. Moreover, secondary pollution is difficult to address in these processes. Thus, oil−water separation using sorbents is the most effective method for removing oils or organic solvents due to its recyclability and environmentally friendly properties. Various hydrophobic absorbents have been prepared for oil remediation, such as amine-modified clays, synthetic polymers, functionalized fly ash, and corn straw. However, these materials are limited for heavy oil separation because an oil barrier is formed on the material surface and prevents water permeation. Thus, an ideal absorbent material is urgently required. Porous materials are attractive for their facile preparation processes, large surface area, excellent stability, and good recyclability.

Foam can be used as a potential material for oil−water separation. Polymeric foams are widely used in the fields of oil spill cleanups. Hou et al. prepared the open-cell foam using polypropylene with a water contact angle of 151.5° and demonstrated an adsorption capacity of 48.9 g g⁻¹ for carbon tetrachloride. Zhang et al. used polypropylene by the melt
extrusion and leaching method to prepare the open-cell polymeric foam. However, the open-cell structures have the disadvantage of lower mechanical properties.13 Metal foam, a type of porous material, is flexible and has high malleability and mechanical strength. Metal foam is a potential substrate for oil–water separation after the coating or bonding of hydrophobic groups. Li et al. prepared CuO-coated foam with superhydrophobic properties by a solution-immersion process for heavy oil separation.11 Zhu’s group synthesized several hydrophobic copper foams by the in situ growth of Cu(OH)2 or ZnO nanomaterials on the skeleton.14 Nickel foam (NF) has a cellular structure consisting of solid metal and interconnected pores comprising a large portion of its volume. Various hydrophobic nickel foams have been fabricated and used to treat and clean oil and organic contaminants from water. To obtain the selectivity without sacrificing the huge surface area, the NF needs to be functionalized with hydrophobic groups. However, the ultrahigh hydrophobicity of the NF needs to be functionalized with water. To obtain the selectivity without sacrificing the huge surface area and adsorption capacity.

Herein, we developed an octyl GO-functionalized nickel foam using a one-step method. The hydrophobicity of the proposed foam was evaluated, and its adsorption capacity for several organics was also investigated. The hydrophobic foam was used to separate oil or organic compounds from oil–water mixture. The octyl GO-modified nickel foam showed high-efficiency absorption performance for the oil–water separation.

2. RESULTS AND DISCUSSION

2.1. Characterization. Figure 1A shows the Fourier transform infrared (FTIR) spectra of GO and octyl graphene oxide (C8-GO). It can be seen from the GO FTIR spectrum that there are OH stretching vibrations at 3594 cm−1, C=C stretching vibration at 1714 cm−1, C=C (unoxidized sp2CC bonds) stretching vibrations at 1610 cm−1, epoxy C–O vibrations at 1407 cm−1, and alkoxyl C–O vibrations at 1039 cm−1. After the GO was functionalized with octyl groups, the FTIR spectrum of C8-GO indicates methylene asymmetric and symmetric stretchings at 2915 and 2838 cm−1, respectively. These observed peaks proved that C8-GO was synthesized.

The X-ray powder diffraction (XRD) patterns of GO and C8-GO are illustrated in Figure 1B. The characteristic peaks of 11.6, 21.6, and 42.4° in GO correspond to the (001), (002), and (111) crystal planes, respectively. The pristine GO shows a (001) diffraction peak at 2θ = 11.6° with an interlayer distance of 0.79 nm. The interlayer distance of GO is higher than that of the corresponding graphite (0.34 nm), which is attributed to the oxygen-rich groups on GO nanosheets. However, the pores of these foams can be easily blocked due to the uncontrollable collapse defects of free-radical polymerization during recycling oil or water, influencing the efficiencies of the foam recycle and separation. It is important to develop promising candidates for foam surface modification to obtain hydrophobic properties and adsorption capacity.

Figure 1. (A) FTIR spectra of (a) GO and (b) C8-GO NF; (B) X-ray diffraction (XRD) patterns of (a) GO and (b) C8-GO NF; and (C) Raman spectra of (a) GO and (b) C8-GO NF.
and a dark transparent appearance, contributed to the reaction of the GO surface with octyl chains.

To characterize the surface morphology of the foam, scanning electron microscopy (SEM) images are shown in Figure 3. From Figure 3A, the pristine Ni foam has a porous and interconnected framework structure with a smooth surface. The skeleton of C8-GO nickel foam (C8-GO NF) became rough, and many nanomaterials were coated on the foam after the Ni foam was modified with C8-GO (Figure 3B). From the high-magnification SEM images of C8-GO NF (Figure 3C,D), the surface morphology and the thickness of C8-GO-coated Ni foam were observed, and a stable hydrophobic surface was formed.

2.2. Contact Angle. Figure 4A shows the photographs of the pristine Ni foam and C8-GO NF. The color of the Ni foam after treatment with C8-GO became black, in contrast to the original foam due to the amount of C8-GO coated on the Ni foam surface. Therefore, C8-GO NF maintained excellent hydrophobicity and oil–water separation capacity. Figure 4B shows four kinds of quasi-spherical droplets on the surface of C8-GO NF. The C8-GO NF demonstrated high hydrophobicity to acid solution, NaCl solution, basic solution, and water (droplets from left to right). The static water contact angle (SWCA) test indicated that the SWCA was approximately 147° ± 3° on the C8-GO NF plane (Figure 4C). Moreover, a cooking oil droplet could not be held on the plane and was immediately absorbed by the C8-GO NF. Figure 4D shows the SWCA on the C8-GO NF surface with increasing immersion time. The SWCA of the C8-GO NF did not change much and was maintained at approximately 145°. The SWCA result is a convincing proof of the water separation capacity. The pristine Ni foam tended to sink to the bottom of the water because of its high density and hydrophilicity. However, the C8-GO NF, with robust hydrophobicity, floated easily on the water surface (Figure 5).

2.3. Oil–Water Separation. A porous structure is beneficial to the adsorption of liquid. The C8-GO NF is a good sorbent for adsorbing oil or organic compounds due to its porous structure and the function of octyl GO. Figure 6 shows photographs of the oil–water separation process. Once the C8-GO NF was immersed in water containing a drop of trichloromethane (dyed with Oil Red O), the size of the red droplet clearly shrank and finally disappeared. The trichloromethane was quickly sucked into the C8-GO NF (the details can be found in the Supplemental Video).

The oil–water separation efficiency was investigated to evaluate the separation performance of the C8-GO NF. To make the measurement more precise, the experiment was performed in a stable closed zone to prevent disturbances from temperature, shaking, and airflow. As shown in Figure 7A, the C8-GO NF performed well in the adsorption of petroleum, dimethylbenzene, silicone oil, chloroform, diesel, and hexane in water, with a separation efficiency of no less than 96.5% for each. The results indicate that the C8-GO NF has high hydrophobicity and excellent adsorption ability for organic solvents owing to the porous structure of the Ni foam and the large surface area of GO.

2.4. Durability of C8-GO NF. The durability of the C8-GO NF was also investigated in separation efficiency experiments. The C8-GO NF can separate water and benzene effectively, and the separation efficiency was 97.6% for a water and benzene mixture. The C8-GO NF can be reused by heating the foam at 80 °C for oil–water separation. After 14 cycles of adsorption and desorption for benzene, the C8-GO NF still remained more than 95.3% separation efficiency. Moreover, when performing the separation efficiency test, the SWCA was recorded in each measurement. As shown in Figure 7B, the SWCA did not change much with the increasing separation time, and all of the SWCAs were above 145°. The results show that the C8-GO NF maintained high stable separation efficiency and hydrophobicity after 14 repeated cycles of use with a benzene–water mixture.

3. CONCLUSIONS

High hydrophobic C8-GO NF was prepared by coating octyl graphene on a Ni foam surface. The two-dimensional nanoscale octyl GO materials enhanced the surface roughness of the Ni foam and resulted in low water adhesion properties. The resultant surface of the C8-GO NF exhibits hydrophobicity with an SWCA of 147°. Furthermore, the C8-GO NF has excellent separation capacity with high selectivity for sorption from oil or organic solvent–water mixtures. Due to the excellent mechanical stability, facile preparation procedure,
and superior separation performance, the C₈-GO NF can be used as a very promising absorbent for the treatment of oil spills and oil-fouling problems.

4. EXPERIMENTAL SECTION

4.1. Materials. Ni foams were purchased from Anping Huirui Factory (China). Graphite and triethoxyoctylsilane were purchased from Sigma-Aldrich. N,N-Dimethylformamide (DMF), sulfuric acid, potassium permanganate, and hydrogen peroxide were purchased from Tianjin Sennics Co. Ltd. (China). All other chemicals were of analytical grade.

4.2. Synthesis of C₈-GO. GO was synthesized using the modified Hummer’s method.²⁶ Graphite powder was added to a mixture of concentrated H₂SO₄ and KMnO₄. The mixture was stirred at 80 °C for 5 h. Sulfuric acid (0.1 M) and hydrogen peroxide were added to the mixture in an ice bath. After the reaction proceeded for 2 h, the mixture was sonicated, centrifuged, and washed with HCl (10%). The GO was dried under vacuum.

Two grams of GO was ultrasonically dispersed into 300 mL of DMF and 5 mL of triethoxyoctylsilane. The reaction was kept at 80 °C for 24 h. The residue was washed with both ethanol and water. Then, the product was dried in a vacuum oven at 60°C, and C₈-GO was obtained.

4.3. Fabrication of C₈-GO NF. C₈-GO was dispersed into the DMF solvent. Ni foam was ultrasonically cleaned using acetone and water. The cleaned nickel foam was placed into the C₈-GO dispersion and ultrasonicated for 40 min. Then, the foam was dried under vacuum at 80 °C. The above operations were performed in a cycle and repeated four times to prepare C₈-GO-modified nickel foam.

4.4. Characterization. The structure of the samples was characterized by XRD patterns (D8 ADVANCE instrument, Bruker, Germany), FTIR spectroscopy (FTIR TENSOR 27 spectrophotometer, Bruker, Germany), and Raman spectroscopy (Labram HR800 Raman system, HORIBA, America). The morphologies of the samples were observed by SEM (Sigma 300 microscope, ZEISS, Germany) and TEM (Teccan F30G2 microscope, FEI, Netherlands). The static water contact angles (SWCA) of the samples were measured with a homemade apparatus. A 5 μL water droplet was carefully
dripped onto the samples, and the average SWCA value was obtained by measuring 10 different positions on the sample. **4.5. Measurement of Separation Efficiency.** The separation efficiency of the C₈-GO NF was measured for various oils and organic compounds. A weighted C₈-GO NF sample was placed into an oil–water mixture (5% v/v) and allowed to absorb at room temperature. The separation efficiency (η) was calculated from the ratio between the mass of the adsorbed oil (or organic compound) after separation and the mass of the original oil before separation. η was calculated according to the following equation

\[ \eta = \left( \frac{m_1}{m_0} \right) \times 100\% \]

where \( m_0 \) is the mass of the original oil before separation, and \( m_1 \) is the mass of the collected oil after separation. In addition, the above operation was repeated to measure the durability of the C₈-GO NF in the adsorption test.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03489. Supplemental video of trichloromethane adsorption of C₈-GO NF video; once the C₈-GO NF was immersed in the water containing a drop of trichloromethane (dyed with Oil Red O), the size of the red droplet clearly shrank and finally disappeared; the trichloromethane was quickly sucked into the C₈-GO NF (AVI).

**AUTHOR INFORMATION**

Corresponding Authors

*E-mail: huanghy@nwu.edu.cn. Tel: +86-29-88308417 (H.H.).
*E-mail: qili726@nwu.edu.cn. Tel: +86-29-88308427 (Q.L.).

ORCID

Huayu Huang: 0000-0003-1819-5515

Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the Program for Key Research and Development Plan in Shaanxi Province (No. 2019SF-243).

**REFERENCES**

(1) Zhang, Y.-L.; Wang, J.-N.; He, Y.; He, Y.; Xu, B.-B.; Wei, S.; Xiao, F. S. Solvothermal synthesis of nanoporous polymer chalk for painting superhydrophobic surfaces. Langmuir 2011, 27, 12585–12590.
(2) Kang, S. M.; You, I.; Cho, W. K.; Shon, H. K.; Lee, T. G.; Choi, I. S.; Karp, J. M.; Lee, H. One-step modification of superhydrophobic surfaces by a mussel-inspired polymer coating. Angew. Chem., Int. Ed. 2010, 49, 9401–9404.
(3) Atlas, R. M.; Hazen, T. C. Oil biodegradation and bioremediation: a tale of the two worst spills in US history. Environ. Sci. Technol. 2011, 45, 6709–6715.
(4) Chapman, H.; Purnell, K.; Law, R. J.; Kirby, M. F. The use of chemical dispersants to combat oil spills at sea: a review of practice and research needs in Europe. Mar. Pollut. Bull. 2007, 54, 827–838.
(5) Xu, Q. H.; Long, W.; Jiang, H.; Zan, C.; Huang, J.; Chen, X.; Shi, L. Hierarchical porous structures for superhydrophobic surfaces by a mussel-inspired polymer coating. Prog. Org. Coat. 2018, 124, 424–431.
(6) Li, J.; Yan, L.; Zhao, Y. Z.; Zha, F.; Wang, Q. T.; Lei, Z. Q. One-step fabrication of robust fabrics with both-faced hydrophobicity for the separation and capture of oil from water. Phys. Chem. Chem. Phys. 2015, 17, 6451–6457.
(7) Liao, C. Y.; Chou, J. Y.; Lin, J. J. Temperature-dependent oil absorption of poly (oxypropylene) amine-intercalated clays for environmental remediation. RSC Adv. 2015, 5, No. 100702.
(8) Wang, X. S.; Liu, J.; Bonefont, J. M.; Yuan, D. Q.; Thallapally, P. K.; Ma, S. Q. A porous covalent porphyrin framework with exceptional uptake capacity of saturated hydrocarbons for oil spill cleanup. Chem. Commun. 2013, 49, 1533–1535.
(9) Sakhivel, T.; Reid, D. L.; Goldstein, I.; Hench, L.; Seal, S. Hydrophobic high surface area zeolites derived from fly ash for oil spill remediation. Environ. Sci. Technol. 2013, 47, 5843–5850.
(10) Li, D.; Zhu, F. Z.; Li, J. Y.; Na, P.; Wang, N. Preparation and characterization of cellulose fibers from corn straw as natural oil sorbents. Ind. Eng. Chem. Res. 2013, 52, 516–524.
(11) Li, J.; Li, D.; Li, W.; She, H.; Feng, H.; Hu, D. Facile fabrication of three-dimensional superhydrophobic foam for effective separation of oil and water mixture. Mater. Lett. 2016, 171, 228–231.
(12) Hou, J.; Zhao, G.; Zhang, L.; Wang, G.; Li, B. High-expansion polypropylene foam prepared in non-crystalline state and oil adsorption performance of open-cell foam. J. Colloid Interface Sci. 2019, 542, 233–242.
(13) Zhang, X.; Wang, X.; Liu, X.; Lv, C.; Wang, Y.; Zheng, G.; Liu, H.; Liu, C.; Guo, Z.; Shen, C. Porous Polyethylene Bundles with Enhanced Hydrophobicity and Pumping Oil-Recovery Ability via Skin-Peeling. ACS Sustainable Chem. Eng. 2018, 6, 12580–12585.
(14) Zhu, H.; Gao, L.; Yu, X.; Liang, C.; Zhang, Y. Durability evaluation of superhydrophobic copper foams for long-term oil–water separation. Appl. Surf. Sci. 2017, 407, 145–155.
(15) Gao, R.; Liu, Q.; Wang, J.; Liu, J.; Yang, W.; Gao, Z.; Liu, L. Construction of superhydrophobic and superoleophilic nickel foam for separation of water and oil mixture. Appl. Surf. Sci. 2014, 289, 417–424.
(16) Liu, C. J.; Feng, X. Y.; Li, N.; Luo, C. W.; Chao, Z. S. Superhydrophobic Co3O4-loaded nickel foam with corrosion-resistant property prepared by combination of hydrothermal synthesis and PFAS modification. Surf. Coat. Technol. 2017, 309, 1111–1118.

(17) Wang, E.; Wang, H.; Liu, Z.; Yuan, R.; Zhu, Y. One-step fabrication of a nickel foam-based superhydrophobic and superoleophilic box for continuous oil–water separation. J. Mater. Sci. 2015, 50, 4707–4716.

(18) Zhao, F.; Liu, L.; Ma, F.; Liu, L. Candle soot coated nickel foam for facile water and oil mixture separation. RSC Adv. 2014, 4, 7132–7135.

(19) Lv, X.; Tian, D.; Peng, Y.; Li, J.; Jiang, G. Superhydrophobic magnetic reduced graphene oxide-decorated foam for efficient and repeatable oil–water separation. Appl. Surf. Sci. 2019, 466, 937–945.

(20) Fenner, B. R.; Zimmermann, M. V. G.; da Silva, M. P.; Zattera, A. J. Comparative analysis among coating methods of flexible polyurethane foams with graphene oxide. J. Mol. Liq. 2018, 271, 74–79.

(21) Feng, Z. Q.; Wu, F.; Jin, L.; Wang, T.; Dong, W.; Zheng, J. Graphene nanofibrous foam designed as an efficient oil absorbent. Ind. Eng. Chem. Res. 2019, 58, 3000–3008.

(22) Cao, C. F.; Zhang, G. D.; Zhao, L.; Gong, L. X.; Gao, J. F.; Jiang, J. X.; Tang, L. C.; Mai, Y. W. Design of mechanically stable, electrically conductive and highly hydrophobic three-dimensional graphene nanoribbon composites by modulating the interconnected network on polymer foam. Compos. Sci. Technol. 2019, 171, 162–170.

(23) Chen, C.; Zhu, X.; Chen, B. Durable Superhydrophobic/superoleophilic graphene-based foam for high-efficiency oil spill cleanups and recovery. Environ. Sci. Technol. 2019, 53, 1509–1517.

(24) Bai, W.; Huang, H.; Li, Y.; Zhang, H.; Liang, B.; Guo, R.; Du, L.; Zhang, Z. Direct preparation of well-dispersed graphene/gold nanorod composites and their application in electrochemical sensors for determination of ractopamine. Electrochim. Acta 2014, 117, 322–328.

(25) Singu, B. S.; Yoon, K. R. Exfoliated graphene-manganese oxide nanocomposite electrode materials for supercapacitor. J. Alloys Compd. 2019, 770, 1189–1199.

(26) Hummers, W. S.; Offeman, R. E. Preparation of graphitic oxide. J. Am. Chem. Soc. 1958, 80, No. 1339.