***Supporting Information for:***

**Enhanced superhydrophobicity of electrospun carbon nanofiber membranes by hydrothermal growth of ZnO nanorods for oil-water separation**

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**Text 1.** The calculation method for the density and porosity of membrane.

The *porosity* (%) of the membrane was calculated by the following formula (Xu et al., 2021; Fu et al., 2021):

where *m2* is the weight of the wetting membrane (g), *m1* is the weight of the drying membrane (g), *ρ* is the density of n-butanol (0.811 g/cm3), and *V* is the volume of the membrane (cm3).

The formula for calculating the membrane density *(ρ)* was as follows:

where *m* is the weight of the membrane (g), *V* is the volume of the membrane (cm3).

**Text 2.** Details of emulsion separation experiments.

To prepare the water-in-oil emulsion, carbon tetrachloride and water were mixed with a ratio of 99:1. Then, 0.2 mg/mL Span-80 was added as a surfactant stabilization emulsion. Finally, the mixture was mechanically stirred at 1300 rpm/min for 3h to obtain a milky emulsion. The separation efficiency (*f*) of emulsion was determined by the following formula (*Xu et al., 2021*):

*(3)*

where *C0* and *C* were the water content in the emulsion and filtrate, respectively.

Xu, H., Liu, H., Huang, Y., Xiao, C., 2021. Three-dimensional structure design of tubular polyvinyl chloride hybrid nanofiber membranes for water-in-oil emulsion separation. *J. Membr. Sci.* 620, 118905. https://doi.org/10.1016/j.memsci.2020.118905.

Fu, Q., Zhang, W., Muhammad, I.P., Chen,X., Zeng, Y., Wang, B., Zhang, S., 2021. Coaxially electrospun PAN/HCNFs@PVDF/UiO-66 composite separator with high strength and thermal stability for lithium-ion battery. *Micropor. Mesopor. Mater.* 311, 110724. https://doi.org/10.1016/j.micromeso.2020.110724.

**Table S1.** Possible formation mechanism of ZnO nanorods.

|  |  |
| --- | --- |
| **Chemical reaction** | **Order** |
|  | *(1)* |
|  | *(2)* |
|  | *(3)* |
|  | *(4)* |
|  | *(5)* |

**Table S2.** The density and porosity of the F/ZnO/CNF-x membrane.

|  |  |  |
| --- | --- | --- |
| **Materials** | **Density(g/cm3)** | **Porosity(%)** |
| CNF | 0.1139 | 63% |
| F/ZnO/CNF-1 | 0.1426 | 57% |
| F/ZnO/CNF-2 | 0.1608 | 45% |
| F/ZnO/CNF-3 | 0.1923 | 37% |
| F/ZnO/CNF-4 | 0.2040 | 29% |

**Table S3.** Comparison of separation efficiency of the F/ZnO/CNF-3 with other membrane materials reported in the literature.

|  |  |  |  |
| --- | --- | --- | --- |
| **Materials** | **Oil-water mixture** | **Efficiency (%)** | **Ref.** |
| TiO2–PVA sponge | CCl4/water mixture | 97.8 | (He et al., 2022) |
| PCL/ph-LPSQ membranes | CCl4/water mixture | 99.3 | (Wang et al., 2022) |
| Biomimetic membrane | Chloroform/water mixture | 98 | (Chen et al., 2022) |
| Janus–CA Fiber Membrane | water-in-toluene emulsion | 98.7 | (Yu et al., 2021) |
| n-hexane/water mixture | 97.1 |
| CNF grafted PU | Hexane/water mixture | 97.8 | (Baig et al., 2019) |
| PPS membrane | Water-in-CCl4 emulsions | 99 | (Kou et al., 2021) |
| CNFM | Chloroform/water mixture | 99.4 | (Kong and Xin, 2022) |
| Water-in-CCl4 emulsions | 98.7 |
| F/ZnO/CNF | CCl4/water mixture | 99.7 | This work |
| Water-in-CCl4 emulsions | 99.2 |

He, Z., Wu, H., Shi, Z., Kong, Z., Ma, S., Sun, Y., Liu, X., 2022. Facile Preparation of Robust Superhydrophobic/Superoleophilic TiO2-Decorated Polyvinyl Alcohol Sponge for Efficient Oil/Water Separation. *ACS Omega* 7, 7084-7095. https://doi.org/10.1021/acsomega.1c06775.

Wang, F., Liu, K., Xi, Y., Li, Z., 2022. One-step electrospinning PCL/ph-LPSQ nanofibrous membrane with excellent self-cleaning and oil-water separation performance. *Polymer* 249, 124858. https://doi.org/10.1016/j.polymer.2022.124858.

Chen, Y., Quan, Z., Song, W., Wang, Z., Li, B., Mu, Z., Niu, S., Zhang, J., Han, Z., Ren, L., 2022.Hierarchically structured biomimetic membrane with mechanically/chemically durability and special wettability for highly efficient oil–water separation. *Sep. Purif. Technol.* 300, 121860. https://doi.org/10.1016/j.seppur.2022.121860.

Yu, X., Zhang, X., Xing, Y., Zhang, H., Jiang, W., Zhou, K., Li, Y., 2021. Development of Janus Cellulose Acetate Fiber (CA) Membranes for Highly Efficient Oil–Water Separation. *Materials* 14(20), 5916. https://doi.org/10.3390/ma14205916.

Baig, N., Alghunaimi, F. I., Dossary, H. S., Saleh, T. A., 2019. Superhydrophobic and superoleophilic carbon nanofiber grafted polyurethane for oil-water separation. *Process Saf. Environ.* 123, 327-334. https://doi.org/10.1016/j.psep.2019.01.007.

Kou, X., Han, N., Zhang, Y., Tian, S., Li, P., Wang, W., Wu, C., Li,W., Yan,X., Zhang, X., 2021. Fabrication of polyphenylene sulfide nanofibrous membrane via sacrificial templated-electrospinning for fast gravity-driven water-in-oil emulsion separation. *Sep. Purif. Technol.* 275, 119124. https://doi.org/10.1016/j.seppur.2021.119124.

Kong, F. and Xin, B., 2022. Three-dimensional and flexible carbon nanofiber mat by one-step electrospinning for efficient oil/water separation. *Colloid. Surf. A* 652, 129824. https://doi.org/10.1016/j.colsurfa.2022.129824.



**Fig. S1.** Schematic diagram of fluorination.



**Fig. S2.** The EDS result of F/ZnO/CNF-3.

**Fig. S3**

**Fig. S3.** Strain-stress curves (a) and Young's modulus (b) of F/ZnO/CNF-x membrane at different hydrothermal time.

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**Fig. S4.** Optical microscope images and digital photographs of the emulsion and filtrate (a), flux and separation efficiency of F/ZnO/CNF-x membranes(b), cycle separation performance of F/ZnO/CNF-3 membrane for emulsion (c).



**Fig. S5.** WCAs and separation efficiency (carbon tetrachloride/water mixture) of F/ZnO/CNF-3 before and after soaking in different pH solution.

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