Supplementary Information

The efficient separation of surfactant stabilized oil/water emulsions with a flexible and superhydrophilic graphene/TiO_2 composite membrane

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Methods

Synthesis of GO and SGO: GO sheets were prepared according to the modification of Hummer's method,[1] and the procedure was reported in the previous work.[2] SGO sheets were prepared by a sulfonation reaction.[3] Typically, 200 mg of GO, 3 g of sodium 2-chloroethanesulfonate hydrate ($ClCH_2CH_2SO_3H$) and 1.6 g of NaOH were added into 500 mL of deionized (DI) water. The mixture was put under ultrasonication condition for 3 h and then 2 mL of HNO_3 was added into the mixture. Finally, the mixture was washed with ethanol for three times and put into vacuum drier for 2 days.

Synthesis of hierarchical TiO_2 sphere: Hierarchical TiO_2 spheres were

prepared according to the slight modification of previous reported method.[4] In a typical procedure, 3 mL of TBT was added the mixture of 45 mL of DMF and 45 mL of IPA drop by drop. Then, the mixture was transferred to a Teflon-lined stainless-steel autoclave (volume: 125 mL), which was then heated to 200°C and kept for 20 h. The product was collected by centrifugation after the autoclave cooled to room temperature and followed by ethanol washing. Finally, the material was dried at 60°C for 24 h and calcined at 450°C for 2 h with a ramping rate of 5°C min^{-1}.

Supplementary Information

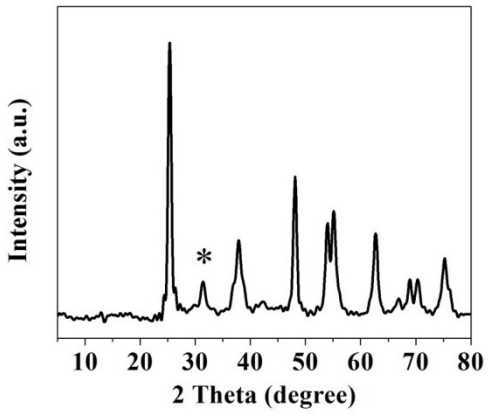

Figure S1 | XRD spectrum of SGO-TiO_2 membrane.

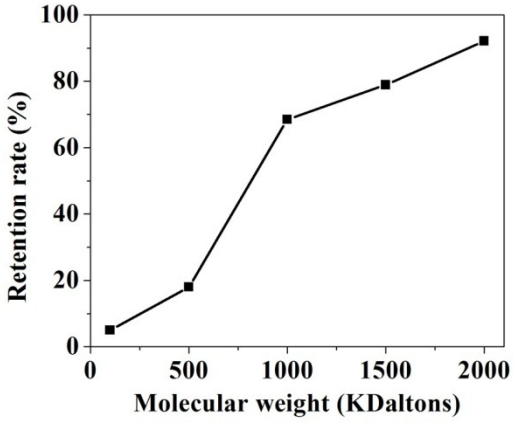

Figure S2 | Retention rates of dextran of different molecular weights by the SGO-TiO_2 membrane.

Determination of pore size of the SGO-TiO_2 membrane: The molecular weight cut-off (MWCO) is adopted to characterize the pore size of membrane. Here, the MWCO of the SGO-TiO_2 membrane was evaluated by filtering different molecular weights of dextran aqueous solution (0.1 g/L). The dextran concentrations of feed (C_{feed}) and filtrate ($C_{filtrate}$) were

determined by total organic carbon (TOC) measured by a Shimadzu TOC-VCSH TOC analyzer. The retention rate (R) was calculated by the following equation:

$$R=(1-\frac{C_{filtrate}}{C_{feed}})*100\%$$

Fig. S2 shows that the retention rates of dextran increase with increasing the molecular weight of dextran. The molecular weight of dextran with 90% retention was less than 2000 kDa. This means the corresponding pore size of the SGO-TiO_2 membrane is less than 60 nm.[5]

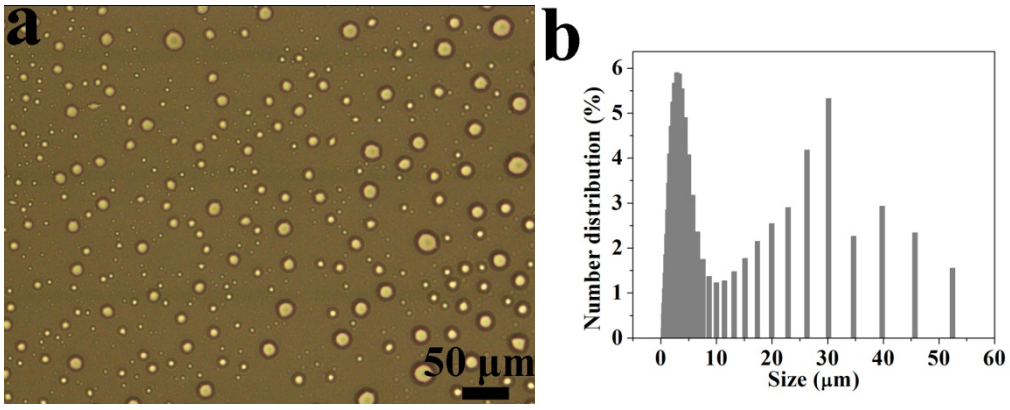

Figure S3 | (**a**) Optical microscopy images of toluene-in-water emulsions without surfactant showing the size of the oil droplets is in the range of 1-50 μm. (**b**) DLS data of toluene-in-water emulsions without surfactant confirming the size of the oil droplets is between 1 and 50 μm.

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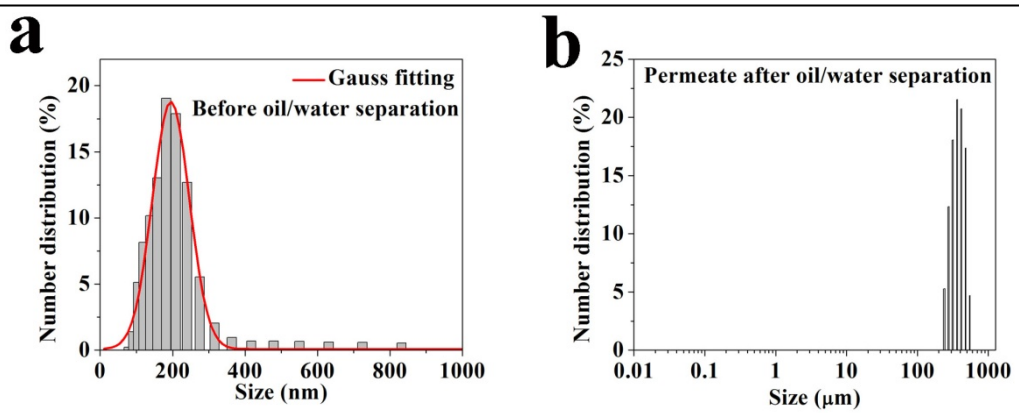

Figure S4 | (**a**) DLS data of the feed emulsions for surfactant-stabilized emulsions of toluene-in-water showing the oil droplet size is around 200 nm; (**b**) DLS data of the corresponding filtrate for surfactant-stabilized emulsions of toluene/water showing no oil droplets around these ranges are observed (the peak around 400 μm is an error singal caused by the machine).

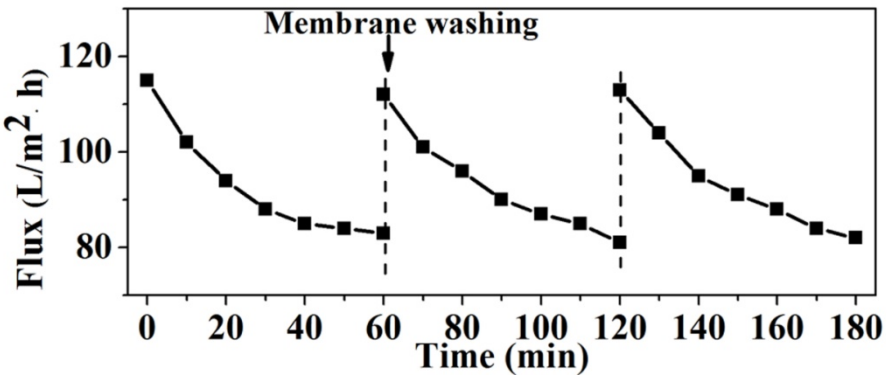

Figure S5 | The permeate flux of the membrane as the function of running time, and there is a membrane washing per 60 min to remove the oil residual.

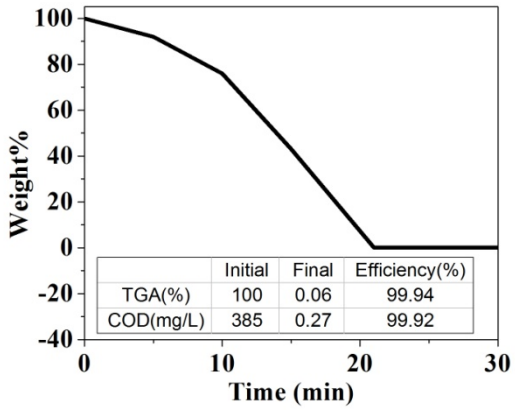

Figure S6 | TGA curve of crude oil-in-water emulsion after oil/water separation and COD results of crude oil-in-water emulsion before and after oil/water separation.

Explanation of oil/water separation efficiency: Fig. S6 shows the TGA analysis of the permeate of crude oil-in-water emulsion after oil/water separation. After heating at 110 °C for about 30 min, around 99.94% of water in the permeate was evaporated, which indicated the high oil removal efficiency of this novel membrane. In addition, the inset of Fig. S6 shows the results of the chemical oxygen demand (COD) experiments. The results showed that COD of permeate is about 0.27 mg/L, which is significantly lower than the initial COD of crude oil-in-water emulsion (385 mg/L), demonstrating that the crude oil has been removed efficiently. Hence, considering the results of TGA and COD, our flexible and superhydrophilic graphene/TiO_2 composite membrane is highly efficient to separate oil-in-water emulsions.

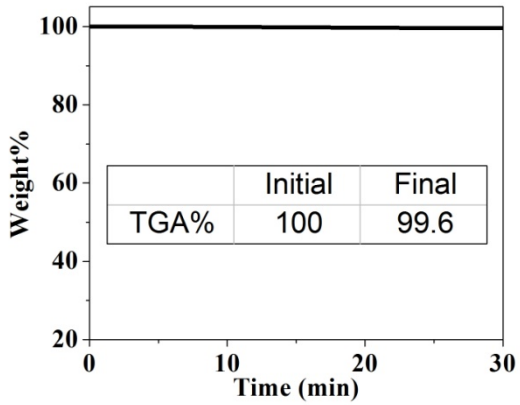

Figure S7｜ TGA curve of separated crude oil after oil/water separation.

Characterization of separated oil phase: Fig. S7 shows the TGA analysis of separated crude oil after oil/water separation. The TGA results indicate that the majority part of the separated oil phase is crude oil, and only around 0.4% is water, which can be attributed to the superhydrophilic and superoleophobic properties of the membrane.

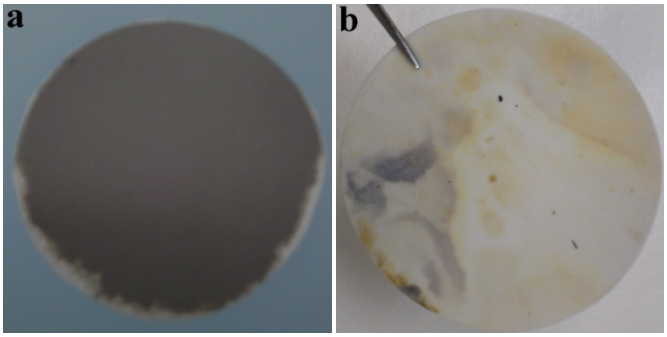

Figure S8｜ Photos of graphene/TiO_2 membrane (a) and commercial PES membrane (b) after washing by water.

Characterization of membrane after oil/water separation: Fig. S8a shows that the graphene/TiO_2 membrane after crude oil/water separation was

washed simply by water. It was found that no oil residues were on the surface of the graphene/TiO_2 membrane due to the superhydrophilic and superoleophobic properties of the membrane. However, for commercial PES membrane (Fig. S8b), a clear oil fouling layer could be found, which would affect the long-term stability. Hence, this novel membrane is better for oil/water separation than commercial PES membrane.

Reference

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