One-step preparation of GO/SiO2 membrane for highly efficient separation of oil-in-water emulsion

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A B S T R A C T

The development of filtration membranes with ultrahigh water flux for separation of oil-in-water emulsions by low energy consumption approach is currently an urgent demand. A novel nanocomposite membrane with superhydrophilic and underwater superoleophobic properties has been successfully prepared by one-step vacuum filtration of an aqueous graphene/SiO2 dispersion on a microfiltration substrate. Owing to the addition of SiO2 nanoparticles, the interlayer space of graphene oxide (GO) layers is expanded, enabling this composite membrane to separate a variety of oil-in-water emulsions with ultrahigh water flux (> 4550 L m\textsuperscript{-2} h\textsuperscript{-1} bar\textsuperscript{-1}), a 2-order-of-magnitude improvement as compared to pure GO membrane, and also superior compared to most commercialized membranes. The proposed convenient, time-saving (< 10 min) and low cost strategy endows possibility of massive production and shed light on commercial applications of water treatment of oil-in-water wastes in industry and daily life.

1. Introduction

Today, with increased global industrialization, the pollution of water resources is one of the major problems that commands urgent attention \cite{1,2}. In particular, petrochemical industry, oil fields and related machine operations generate large quantities of oil-contaminated waste water every day \cite{3}. A direct discharge of this wastewater into water bodies poses serious threat to both people and environment \cite{4,5}. This danger is all the more severe for oil-in-water emulsions when compared to other types of waste, and the challenging problem of separating emulsified oil from wastewater needs to be addressed urgently \cite{6}. Traditional techniques using coalescing agents, oil skimmers, settling tanks, centrifuges, magnetic separations and flotation technologies have been found to be sufficient only for the separation of immiscible oil/water mixtures. However, these methods are ineffective when used to treat emulsified oil/water mixtures. Thus, more research is needed to develop improved separation methods to treat oil-contaminated waste water \cite{7-9},

Membrane filtration, especially microfiltration and ultrafiltration, is a promising tool to address this problem. Due to their microporous structure, membranes can be used to continuously remove dispersed oil drops from oily wastewater \cite{10-13}. However, a major problem in this technique is its low flux, one to two orders of magnitude lower than the separation flux of the free oil-water mixture \cite{6}. Besides, certain membranes are designed oleophilic, invariably resulting in serious fouling caused by oil permeation. The viscosity of the oil can also lead to performance degradation to some extent. Therefore, super-hydrophobic materials are unsuitable for the separation of oil-in-water mixtures or emulsions.

GO consists of oxygenated graphene sheets having oxygen-containing functional groups on their basal planes as well as at the edges. GO is thus hydrophilic, with a high chemical activity and forms a uniform dispersion in water and hence, is being considered a promising material of surface modification of membranes \cite{14-16}. However, pure GO membranes often have a smooth and compact stacked-structure and have only limited improvement on the performance of the membrane. According to Cassie-Wenzel theory, one of the effective methods to overcome these drawbacks is to introduce hydrophilic nanoparticles to improve surface roughness \cite{17}. Inspired by previous literatures, we have proposed an underwater superoleophobic GO/SiO2 membrane prepared by filtering SiO2 nanoparticles together with GO suspension. Amorphous SiO2 nanoparticle is chosen for the following reasons. First of all, SiO2 carries a substantial amount of hydroxyl groups and the concentration of hydroxyl groups is directly proportional to the specific
surface area of the amorphous silica. SiO₂ nanoparticles that naturally own high specific surface can be quite hydrophilic, which may benefit the water flux of the composite membrane. In addition, on the SiO₂ surface there are also abundant siloxane groups or ≡Si−O−Si≡ bridges with oxygen atoms, resulting in structurally bound water inside the silica skeleton and very fine ultramicropores [18]. To the best of our knowledge, no previous attention has been paid on separation of oil-in-water emulsions by GO/SiO₂ composite materials. A few reports have depicted methods using GO/SiO₂ for the purpose of desalination or absorbing toxic/hazardous materials from water, but most of them used two-step method to fabricate membranes [19–21]: first depositing GO on the substrates, and then modifying GO-coated substrate with SiO₂ particles. Although the strategy is shown effective on enhancing the surface roughness, the inner part of the membranes remained unchanged and the performance improvement by the addition of SiO₂ was therefore limited. In this paper, we propose a one-step method to

Fig. 1. Characterization of membrane morphology. (a) SEM image of the surface of pure GO membrane, showing a smooth structure. (b) SEM image of the GO/SiO₂ membrane and the macroscopic optical photograph (b, inset). (c) Cross-sectional SEM image of GO membrane, and (d) Cross-sectional SEM image of GO/SiO₂ membrane. (e)-(f) Schematic of the comparative formation of GO and GO/SiO₂ membrane.
prepare GO/SiO2 membranes by vacuum filtration. The combination of superhydrophilicity and superoleophobicity prevents oil from permeating through the membrane and also minimizes pore blockage by the viscous oil. At the same time, filtration process enables the insertion of SiO2 nanoparticles in between the GO layers, so the vertical spacing between GO layers dramatically expands, allowing water to permeate more effortlessly through the layered membrane structure. To the best of our knowledge, pure GO membrane will lose the separation ability after drying because of the decrease of the intersheet spacing of laminar GO [22]. As for GO/SiO2 membranes, the interlayer spacing were determined by SiO2 nanoparticles while the decrease of the interlayer spacing could be neglected. Therefore our membrane can maintain the separation performance no matter being used freshly or after being dried, meaning that the membrane can be used whenever needed after a long-time storage. Since SiO2 nanoparticles can be found not only on the surface of GO membrane, but also everywhere at interlayer space from top to bottom, the resistance to oil fouling is further enhanced. Its filtration performance towards various oil-in-water emulsions was studied in detail. Additionally, fabrication time and cost have also been investigated.

2. Experimental

2.1. Materials

Silicon dioxide (specific surface area 400 m² g⁻¹, Aladdin, Shanghai, China). Mixed cellulose ester (MCE) membranes (pore size 220 nm. Xinya Purification equipment Co., LTD, Shanghai, China). Dodecane (98%, Aladdin, Shanghai, China). Carbon tetrachloride (99.5%, Aladdin, Shanghai, China). Gasoline (Sinopac, China). Engine oil (5W-30, Mobil, China). Rapeseed oil (Shijiliangyou Import & Export Co. Ltd, Qingdao, China).

2.2. Fabrication of GO/SiO2 membrane

The schematic of the equipment is given in Fig. S1. GO/SiO2 membrane were specifically designed for high flux nanofiltration. A commercial MCE membrane was used as the supporting substrate. GO was prepared by Hummer’s method as previously reported [23]. While higher water permeability requires the membrane to be as thin as possible, a very small amount of only 6 μg GO was introduced into the composite membrane. Besides, SiO2 nanoparticles with a diameter of 30 nm were introduced into GO nanosheets at the same time. The optimal dosage of SiO2 nanoparticles was determined to be 12 mg. SiO2 nanoparticles can enhance the hydrophilicity and increase water permeation flux. However, over-dosage of SiO2 nanoparticles may block the pores of the substrate and thereby reduce the flux. The optimized process to prepare GO/SiO2 membrane is as follows; firstly, 3 μL 2 mg mL⁻¹ GO was diluted to 100 mL by deionized water, and afterwards 12 mg of hydrophilic silica was added to the dispersion, sonicating for 5 min to form a stable and uniform dispersion (no particles can be observed in solution). A MCE substrate (with 220 nm apertures) was rinsed by deionized water for three times. A thin GO/SiO2 membrane was obtained when the suspension was filtered on MCE substrate under vacuum of 1 bar. GO layers stack up to form a horizontally layered structure. The filtration process can be finished in less than 1 min. The whole filtration process was recorded by a video in Mov. S1, demonstrating its rapidity.

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2.3. Preparation of oil-in-water emulsion

Oil-in-water emulsion was prepared by mixing water and oil in a volume ratio of 9:1 [24] and sonicating (power 2 kW) the mixtures for over 10 h to form a milky white emulsion. Dodecane, gasoline, engine oil and rapeseed oil were used as oil components, respectively. All the emulsions were stable for more than six days.

2.4. Characterization of the membrane

The surface morphology and cross section of the membrane were characterized by scanning electron microscopy (Ultra Plus, Zeiss, Germany). XRD was measured on SmartLab 3 Multipurpose X-ray Diffractometer with built-in intelligent guidance. FT-IR spectrometer (Nicolet is 50, Thermo, Germany, resolution 4 cm⁻¹) was used to obtain the FTIR spectra. Samples were prepared by mixing with KBr and the measurements were carried out at room temperature, signal-averaging a minimum of 32 scans. The surface composition of the membranes was confirmed by X-ray photoelectron spectroscopy (Escalab 250Xi, Thermo, Germany) using Mg Kα (1254.0 eV) as the radiation source. Survey spectra were taken in the binding energy range of 0–1400 eV. The optical microscopy images of the oily emulsion samples were observed by optical microscopy (Olympus BX 60). Emulsion separation efficiencies were obtained with the help of a Fischer Moisture Titrator (Mettler Toledo Karl V30S, Switzerland). For each cycle, the flux was determined by calculating volume (V) of the filtrate within 3 min (Δt). The area of a GO/SiO2 membrane contacted with the emulsions was 11.3 cm² (A). The flux (P) was calculated according to the following equation:

\[ P = V \times \frac{10000}{A} \times \frac{60}{\Delta T} \text{L m}^{-2} \text{h}^{-1} \] (1)

The separation efficiency was calculated by oil rejection coefficient R as follows [25]:

\[ R(\%) = \left(1 - \frac{C_p}{C_o}\right) \times 100\% \] (2)

Where \( C_p \) and \( C_o \) represent oil concentration of the original emulsion and the collected liquid after filtration, respectively.

3. Results and discussion

3.1. Membrane Morphology and composition analysis

The SEM images of the GO and GO/SiO2 membrane are shown in Fig. 1, from which an enhancement of surface roughness due to SiO2 nanoparticles is clearly observed (Fig. 1a and b. Inset 1b: the photo-graph of GO/SiO2 membrane). Similarly, stacked and compact GO layers become rougher as shown in cross-sectional images (From Fig. 1c to d). In addition, the thickness of the membrane is measured to be 1.96 μm, which is two orders of magnitude greater than that of the pure GO membrane. The thickness increased due to the insertion of SiO2 nanoparticles, and the increased interlayer spacing enables water to permeate more effortlessly and significantly improves water flux. In order to collect more information on interlayer spacing, X-Ray Diffraction (XRD) has been taken before addition of SiO2. The spectra was shown in Fig. S4 in Supporting Information and the spacing value was calculated to be 0.82 nm. After introducing SiO2 nanoparticles, the XRD peaks reflecting membrane structure was diminished by the non-crystalline SiO2. Therefore, XRD test was not suitable for determining the membrane structure. However, since SiO2 nanoparticles were well distributed between two adjacent layers (the new Fig. 1d), the average interlayer spacing could be deduced as the same as the average particle size (which is around 40 nm). Moreover, the presence of SiO2 increases the surface roughness, as well as the roughness of each of the stacked GO layers in the membrane bulk. Based on Cassie- Wenzel
theory, such nanoscale protrusions enhance the hydrophilicity of the entire laminated structure [17]. Therefore better hydrophilic property is expected, compared to surface modification with SiO2. A schematic image of this effect is given in Fig. 1e and f. To further investigate its pore size and thermal properties, BJH adsorption cumulative pore volume test and thermo-gravimetric analysis were conducted and the result is shown in Fig. S5.

The interaction of GO with SiO2 nanoparticles was confirmed by FTIR and XPS spectra, showing the presence of certain bands assigned to various vibrations in the solSiO2 network. As shown in Fig. 2a and b, signals due to introduction of SiO2 can be noted both in IR and XPS spectra of GO/SiO2 membrane, while the bands caused by other elements are similar to that in the GO membrane. The analysis of FTIR spectra in Fig. 2a reveals bands centered at around 792–802 cm$^{-1}$ and 456–472 cm$^{-1}$ corresponding, respectively, to the symmetric stretching vibrations of Si-O-Si and their bending mode. The intense and broad band observed at 1092–1100 cm$^{-1}$ is mainly due to Si-O-Si asymmetric stretching vibrations [26]. XPS spectra curve fitting of the C 1s, O 1s, and Si 2p spectra were performed in Fig. 2c-e. C 1s which assigned to C=O, C=O and O=O-C-OH (appearing at 284.8 eV and 278.9 eV), as well as O 1s which contributions from C=O and O=C-OH groups (appearing at 531.0 eV) kept same in GO and GO/SiO2 membranes. Due to the

Fig. 2. Composition analysis. (a) FTIR spectra and (b) XPS spectra of GO and GO/SiO2 membranes, together with GO/SiO2 membranes that after separating repeseed oil, engine oil, and gasoline. (c)-(f) Curve fitting of the C 1s, O 1s, Si 2s, and Si 2p respectively.
The existence of SiO₂, Si 2s and Si 2p binding energies can be observed at 150.5 eV and 103.1 eV, respectively. Furthermore, the GO/SiO₂ membranes after separating rapeseed oil, engine oil, and gasoline were also inspected. This series of tests confirmed that no chemical changes were incurred during the separation process, consolidating the stability of GO/SiO₂ membrane.

3.2. Hydrophilicity and underwater oleophobicity measurement

The hydrophilicity and underwater oleophobicity of the GO/SiO₂ membrane show significant enhancement compared to pure GO membrane, as highlighted in Fig. 3. In the process of experiment, all membranes were placed in water, and carbon tetrachloride stained with Sudan Red 5B was used as a model because its density is higher than water and easy to form droplet in the bottom of aqueous phase. Here, substrate, substrate with only GO and with only SiO₂ were used for comparison (Fig. 3a–c). It can be clearly seen that the MCE substrate without any coating is weakly oleophobic under water, with carbon tetrachloride contact angle of ~ 105 ± 1°. Therefore, pure MCE membrane is not capable of separating the oil/water mixture. The oleophobicity is improved when the MCE substrate is coated with either silica nanoparticles or GO. The contact angle increased to 129 ± 1° and 135 ± 1°, respectively, as GO and SiO₂ coatings showing superior oleophobicity to enable oil/water separation. However, this performance may not be satisfying, when processing emulsified oil in waste water. In contrast, when a carbon tetrachloride droplet was placed on the GO/SiO₂-modified membrane, it completely sit on the surface to form a sphere, typical anti-wetted interface (Fig. 3d). The underwater contact angle of ~ 165 ± 1° demonstrated the GO/SiO₂-modified membrane is superhydrophilic and underwater superoleophobic. Furthermore, water droplet permeated more rapidly through the GO/SiO₂ membrane than on its counterparts, indicating appreciable hydrophilicity (Fig. 3 (right panel), Fig. S6, Mov. S2 in Supporting Information).

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3.3. Measurement of permeation flux, separation effect and retention

To intuitively understand the separation effect, optical microscopy was used to observe the difference between the original emulsions and their corresponding collected filtered liquid. Emulsions stayed stable without stratification for at least six days (Fig. S7, Supporting Information), proving their high stability. Fig. 4a–c (left column) show optical microscopy images of emulsified dodecane, engine oil and gasoline in water. In contrast, no oil droplet is observed in the collected filtrate (right column), indicating the effectiveness of the GO/SiO₂ membrane for separating different types of oil-in-water emulsions. Mov. S3 exhibits the process of filtering 60 mL dodecane-in-water emulsion. The process was finished within 1 min, showing high flux and separation efficiency. Regardless of different components, extremely high flux of 4550, 4124, 3724 and 3890 L m⁻² h⁻¹ bar⁻¹ for dodecane-in-water, gasoline-in-water, engine oil-in-water and rapeseed oil-in-water emulsions, respectively, was measured respectively (Fig. 4d). The results are 2–3 orders of magnitude higher than pure GO membrane [27]. The trivial difference of flux observed corresponding to different emulsions is most probably due to the disparity of the viscosity. Basically, an oil-in-water emulsion with a lower oil viscosity will have a higher flux.

In order to evaluate the durability of the membrane, 30 cycles of separation test were conducted to investigate whether oil are able to permeate the membrane, block the pores, and accordingly deteriorate membrane performance. The results shown in Fig. 4e proved that the separation performance of the membrane remains essentially unchanged even after 30 cycles. More details can be found in Fig. S8. In addition, dodecane, with a low volatility, was chosen to “pollute” the membrane first and then dried in the oven at 30 °C. Underwater contact angle was monitored afterwards and the whole process was repeated for 10 times. Fig. S9 shows the small fluctuations in contact angle, which demonstrates its excellent antifouling performance to some extent. This may due to the superoleophobicity of the membrane, preventing the oils from permeating the surface. To confirm whether there happened SiO₂ leakage, ICP test was conducted to detect silicon content in filtrate. The result showed that the content of Si in pure water was 3.8 ppb, and when water passed through the GO/SiO₂ membrane, the Si content became 6.2 ppb, only with a slightly rise.

Moreover, in order to investigate the mechanical property of this membrane, the intrusion pressure, which represents the maximum height of liquid that the membrane can support, was studied. The oil passed through the membrane when the pressure was higher than being...
exerted, despite the membrane is oleophobic. The intrusion pressure of GO/SiO$_2$ membrane was measured by pouring oil onto a water-immersed membrane to the maximum height. The results have been shown in Fig. S10 and Mov. S4- S5, indicating that the membrane had more than 9 kPa intrusion pressure for oils, which is superior to many separation membranes [24]. Therefore, the durability of the GO/SiO$_2$ membrane has demonstrated its huge potency of industrial applications.

Fig. 4. Separation results of different oil/water emulsions. (a)–(c) Optical microscopy images of the emulsions before and after separation. The emulsions are (a) dodecane in water, (b) gasoline in water, and (c) engine oil in water. All the emulsions stay emulsified and no stratification was observed for at least six days. (d) Water permeation flux of the GO/SiO$_2$ membranes for oil-in-water emulsions containing gasoline, dodecane, engine oil, and rapeseed oil under 1 bar pressure. (e) Flux retention with number of cycles for dodecane separation. Negligible decline in flux performance is observed after 30 cycles.
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The emulsion separation efficiencies of the four kinds of emulsions were quantified according to Eq. (2). The significant decline in oil content in all cases confirms the excellent separation efficiency of the membrane (~99.3%). It should be noted that the GO/SiO2 deposited membranes can also be used under low pressures (0.2–0.8 bar) to separate oil-in-water emulsions, as shown in Fig. S11, Supporting Information. For example, the water permeation flux reached 760 Lm−2 h−1 for dodecane/water emulsion under an outside pressure of 0.2 bar. The performance allows to expand the scope of applications of the membrane to the environment where high pressures cannot even be applied.

3.4. Comparison with other emulsion separation membranes

Fig. 5 shows the comparison of the proposed GO/SiO2 membrane with other membranes made from different materials, reported in the literature [24,28–39]. Despite the high separation efficiency (>99%, not shown in the figure) which they have in common, other critical parameters, such as water flux, fabrication time and cost, may determine the practical application potential of the membranes. It should be noticed here, that the cost listed includes only the cost of raw materials (prices of the reagents quoted by Sigma as reference), which means that instrument, energy and labor costs have not been taken into account. Besides, the time needed during fabrication was calculated by summing all time which has been listed in experimental section.

It is found that few previous membranes have satisfying answer performance with regard to all the flux/time/cost at the same time, and energy intensive steps such as high temperature calcination, many hours dehydration or long-time ultrasonication are always required during fabrication.

Table S1 shows the data of these three parameters and at the same time points out the high energy consumed steps during fabrication. In dramatic contrast to these membranes, our proposed GO/SiO2 membrane substantially enhance the water flux and meanwhile saves both time and cost (0.16 h and 39 $ per m2). Fig. S12 shows a radar graph comparing GO-based membranes, which confirms that the membranes reported in this work can be practically beneficial to treat emulsified industrial wastewater, as well as for waste water purification in everyday applications.

4. Conclusions

In conclusion, we have successfully developed a one-step method based on a GO/SiO2 nanocomposite framework to prepare flexible membranes for the separation of oil-in-water emulsion. The incorporation of SiO2 nanoparticles between GO layers expands the vertical interlayer nanochannel and therefore and enhance the water permeability. Meanwhile, SiO2 nanoparticles also interact with single GO layers to endow the membrane more hydrophilicity and oleophobicity, which prevents oil droplets from permeating through the membrane. As a result, the composite membranes show high water permeation flux (4550 L m−2 h−1 bar−1) and oil rejection (>99%) for different types of oil-in-water emulsions. While retaining the unique properties of GO, the GO/SiO2 membrane significantly improved the water flux by two orders of magnitude, the major drawback by using conventional materials. Moreover the one-step strategy is easy to apply and the process of membrane fabrication plus nanoparticle in corporation can be completed by vacuum filtration within 10 min. Therefore, the performance of the GO/SiO2 membrane developed in this work stands as a milestone and shows great potential of massive production and waste water treatment applications.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.memsci.2018.02.029.

References
