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REVIEW ARTICLE OPEN

Carbon-based polymer nanocomposite membranes for oily wastewater treatment

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Increasing oil contaminants in water is one of the major environmental concerns due to negative impacts on human health and aquatic and terrestrial ecosystems. The objective of this review paper is to highlight recent advances in the application carbon-based polymer nanocomposite membranes for oily wastewater treatment. Carbon-based nanomaterials, including graphene and graphene-oxide (GO), carbon nanotubes (CNTs), and carbon nanofibers (CNFs), have gained tremendous attention due to their unique physicochemical properties, such as excellent chemical and mechanical stability, electrical conductivity, reinforcement capability, and their antifouling properties. This review encompasses innovative carbon-based membranes for effective oil–water separation and provides a critical comparison of these membranes regarding the permeation flux, wettability, and flux recovery. The current challenges for the successful development of carbon-based nanocomposite membranes and opportunities for future research are also discussed.

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INTRODUCTION

In recent years, with growing oil production industries, the amount of oil-contaminated wastewater has also increased.[1] Oily wastewater originates from many sources, such as crude oil production, petroleum refining, petrochemical, textile, leather, food, and metal industries, in the form of discharge effluent.[2–4] Since oil contamination negatively affects human health and other living organisms, finding efficient and cost-effective methods for its removal from wastewater has been the focus of numerous studies.[5]

To date, different methods have been used for oil–water separation, such as coagulation/flocculation, gravity separation, skimming, and flotation.[5–9] Although these methods are found to be effective for the removal of free oil, with oil droplet size >150 µm, they are relatively inefficient for the separation of dispersed oil in the range of 20–150 µm.[10] This low efficiency along with high operating costs and incompatibility with small oil–water droplets are the main restrictions of these methods.[11] Physical separation of oil from the oil–water mixture by using membrane technology has gained many interests, as it can effectively separate much smaller oil droplets.[11–13] However, some major limitations such as fouling and long-term structural degradation have limited the sustainable application of membrane technology for oily wastewater treatment.[5,14]

Currently, most oil–water separation membranes are made of polymeric materials, which are grouped into two categories, based on their surface properties: hydrophobic and hydrophilic.[15] Hydrophobic membranes repel water and allow oil droplets to permeate freely, which might lead to fouling issues.[2,16,17] These membranes are fabricated by two main methods, (i) chemical modification of rough surface with low surface energy materials, and (ii) creating micro/nanoscale roughness on low surface energy materials. Superhydrophobic surfaces have self-cleaning and anti-contamination properties that is called the Lotus effect.[18] On the other hand, hydrophilic membranes allow water droplets to transfer through the membrane and repel oil droplets. These membranes exhibit better antifouling properties as compared with the hydrophobic membranes.[19]

To enhance the performance of the polymeric membranes in terms of permeability, thermomechanical stability, and antifouling property, advance inorganic nanomaterials with tunable pore size, high surface area, and unique surface chemistry, are typically incorporated into the membrane matrix.[5,15,20] Among available nanomaterials, carbon-based nanomaterials have gained a great interest, as they provide significant improvement in aforementioned properties.[2,5,18,21–23] Three main carbon-based nanomaterials which are investigated in the literature are graphene and graphene oxide (GO),[24,25] carbon nanotubes (CNT),[26] and carbon nanofibers (CNF).[13,16] In this review, recent advances of utlizing GO, CNT, and CNF to fabricate nanocomposite membranes for oil–water separation are discussed. The performance of developd carbon-based nanocomposite membranes are reviewed and compared regarding permeation flux, separation effciency, and antifouling properties.

CARBON-BASED NANOMATERIALS

The structure of carbon-based nanomaterials is presented in Fig. 1. Graphene is the individual layers of graphite which is the most stable form of carbon in standard condition. Carbon atoms in graphene are arranged in a hexagonal lattice structure. GO is a by-product of graphite oxide, which is produced by dispersing graphite oxide in basic solutions or in polar solvents to yield a monomolecular layer, known as GO. Graphite oxide itself is produced by treating graphite with strong oxidizers. The main difference between GO and graphite oxide is the interplanar spacing between the individual atomic layers of the latter compound. Moreover, reduced graphene oxide (RGO) is produced by the deoxygenation of GO following chemical and physical processes. The main reason for the reduction of GO is to restore

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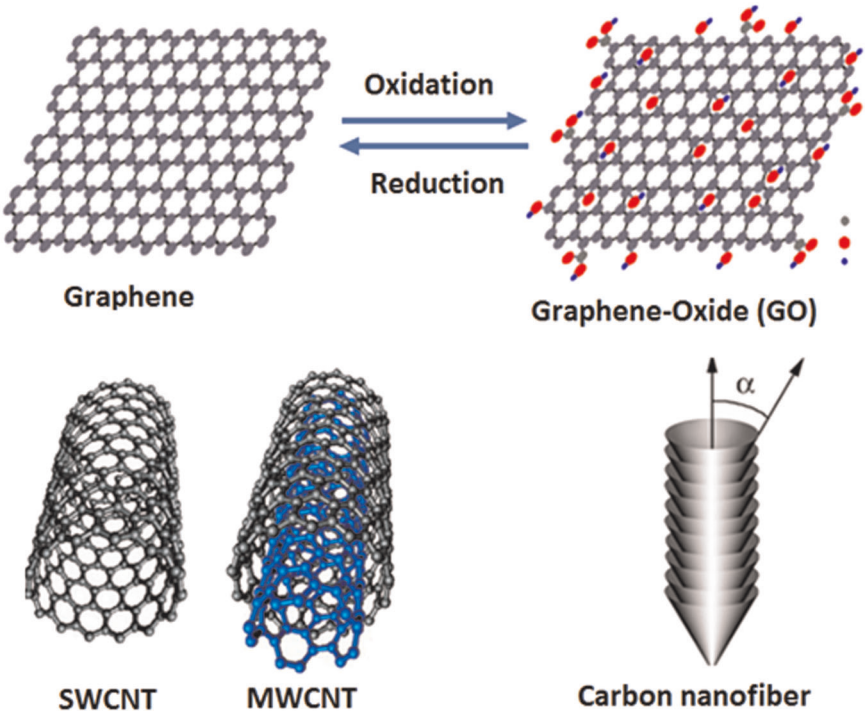

Fig. 1 The structure of carbon-based nanomaterials, adapted with permission from refs. [31,44,56]

the conductivity of graphene.[5,27] CNT has a hollow structure, which consists of folded graphene layers. These layers are arranged in a cylindrical hexagonal lattice structure. They can be assembled as either one single graphene layer with cylindrical form (single-walled CNT, SWCNT) or multilayers (multiwalled CNT, MWCNT)[22–29] CNFs are similar to MWCNT, but graphene layers in CNFs are assembled in a stacked cone structure.[30] The internal structure of CNFs can be characterized by the angle (α) between the graphene layers and the fiber axis. In the case of a MWCNT, the angle is zero.[31]

MEMBRANES FOR OILY WASTEWATER TREATMENT

In microfiltration (MF) membranes, which are typically used for oily wastewater treatment, the water flux (J) is calculated based on the Hagen–Poiseuille equation:

$$J = \varepsilon \pi r_p^2 \Delta p / 8 \mu L \quad (1)$$

where ε is the surface porosity, r_p is the membrane's pores radius, Δp is the transmembrane pressure, μ is the viscosity of feed solution, and L is the thickness of the membrane. Oil rejection is calculated using the following equation:

$$R = \frac{C_f - C_p}{C_f} \times 100\% \quad (2)$$

where C_f and C_p are the concentration of oil in the feed and permeate solutions, respectively.[32,33]

Fouling is the most significant challenge that deteriorates the performance of the membranes in terms of flux and oil rejection. The accumulation of oil droplets on the surface of the membrane (surface fouling) or within the membrane's pores (internal fouling) increases the frequency of cleaning and membrane replacement, which enhances the operating cost of treatment significantly.[5,34–36] Given that, numerous research and development are currently underway to prepare fouling-resistant membranes.[19] As mentioned before, more hydrophilic membranes are less prone to fouling by oil droplets compared with hydrophobic membranes.[11,17,19,37,38] Antifouling performance of membranes is evaluated by calculating the flux recovery ratio (FRR), as follows:[39]

$$\mathrm{FRR} = \frac{F_{W2}}{F_{W1}} \quad (3)$$

where F_{W1} is the pure water flux of fresh membrane, and F_{W2} is the pure water flux after filtration and physical cleaning.

The main strategy toward reducing fouling has been the prevention of the undesired adhesion interactions between the foulants and the membrane[40] via membrane surface-modification techniques. These techniques primarily include: (i) chemical grafting of hydrophilic polymers or physical coating of a layer of hydrophilic polymers on the surface;[41] and (ii) applying functional nanomaterials to synthesize hybrid polymer/inorganic membranes.[42] The major challenge for the incorporation of nanomaterials, such as GO, CNT, and CNF, into the polymer matrix, is the creation of defects in the host polymer due to the aggregation of these nanomaterials. Nonuniform dispersion of nanomaterials within the polymer matrix forms nonselective voids at the interface of polymer and nanomaterials, which significantly decreases the rejection percentage.[43] These defects can increase water permeation flux, but they decrease the oil rejection owing to the typical trade-off relation between water flux and removal of contaminants. Therefore, the surface of nanomaterials must be functionalized to prevent their attachment by attractive intermolecular forces, such as hydrogen bonding, electrostatic attraction between oppositely charged ligands, London–van der Waals forces, and dipole–dipole interactions.[44,45]

INCORPORATION OF CARBON NANOMATERIALS INTO MEMBRANES FOR OILY WASTEWATER TREATMENT APPLICATION

Figure 2 shows the number of published papers on the application of graphene, GO, CNT, and CNF for the development of oil–water separation membranes over 18-years period, from 2000 to 2018. As can be observed, while CNT is used in membrane technology for a long time, the application of graphene and CNF received more attention over the past 10 years. In the following section, the

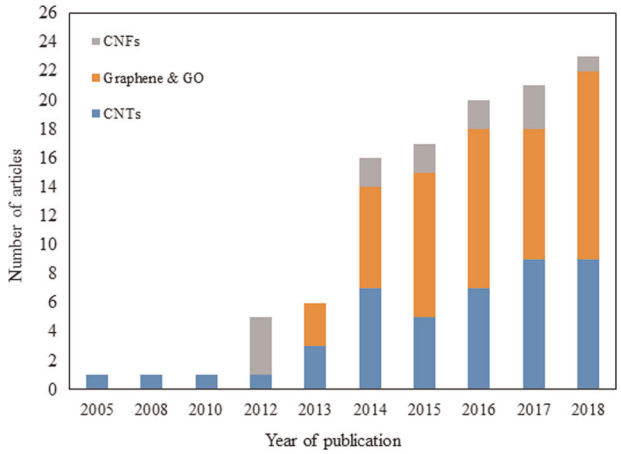

Fig. 2 Record of the number of publications in indexed journals on carbon-based nanocomposite membranes for oily wastewater treatment between 2005 and 2018. (Source: Scopus, searched on 3 October 2018)

impact of adding these nanomaterials on oil/water separation performance of synthesized nanocomposite membranes, in terms of flux, oil rejection, and FRR, is comprehensively reviewed.

GRAPHENE AND GO

Graphene has a two-dimensional planar structure with hydrophobic nature, that is used to enhance mechanical, thermal, electrical, and functional properties of membranes.[5,46,47] However, the inherent hydrophobicity of graphene and graphite makes them less attractive for the fabrication of hydrophilic membranes for oily wastewater treatment.[48] On the other hand, graphene oxide (GO), the oxidized state of graphene, is hydrophilic with strongly polarized functional groups. GO contains epoxide, hydroxyl, and carboxylic acid groups, which can potentially increase its compatibility with most polymers.[25,49–52] Given that, GO has been widely used for the fabrication of hydrophilic membranes.

Huang et al.[49] fabricated ultrafiltration (UF) membranes with antifouling property and high stability by coating GO nanosheets on a rough and porous substrate. To design surfaces with micro/nano hierarchical roughness a thin layer of nanoporous polyamide (200 nm) was used as a substrate for GO coating by the vacuum filtration method. Huang et al.[49] conducted cyclic oil–water separation experiments and a series of contact angle measurements to optimize micro/nanohierarchical roughness of the surface to achieve the best antifouling performance. Figure 3a shows the effect of GO-coating thickness on the roughness and simulated oil drag force. Increasing the thickness of the GO layer was found to decrease the surface roughness (Fig. 3a). PA support and PA with 5 nm GO coating demonstrated the highest oil-adhesive forces among all membranes. Finally, Huang et al.[49] concluded that applying a corrugated layer of GO with nanoscale roughness on a broad range of commercially available porous supports leads to the synthesis of low-oil-adhesion membranes.

Prince et al.[11] developed superhydrophilic UF membranes by grafting graphene attached poly acrylonitrile-co-maleimide (G-PANCMI) to polyethersulfone (PES) membranes by dry–wet spinning. Figure 3b shows the cross-sectional and outer surface SEM images for PES and PES-G-PANCMI membranes. They functionalized graphene by amine and carboxyl to increase its wettability (Fig. 3b). The water contact angle (WCA) decreased from 63.7 ± 3.8° for pristine PES membrane to 22.6 ± 2.5° for the modified membrane by G-PANCMI, whereas, oil contact angle (OCA) increased from 43.6 ± 3.5° to 112.5 ± 3.2°. It resulted in a 43% increase in water permeation and 99% oil rejection.

Liu et al.[53] developed a novel ultralightweight and antifouling carbon-based membrane by using polydopamine (PDA) and reduced graphene oxide (RGO). The graphene-based membrane exhibited high separation efficiency (99.6%) and excellent chemical stability under acidic and concentrated salt conditions. The reason for such a high separation performance was attributed to the high degree of oleophobicity (OCA = 156.10 ± 1.20) and superhydrophilicity (WCA about 00) of the synthesized membranes. However, the developed PDA-RGO membranes were not stable in alkaline conditions due to the dissolution of the PDA layer in an alkaline solution and thus removal of RGO coating layer.

Hu et al.[54] fabricated novel GO-modified MF membranes using commercially available alumina (Al_2O_3) as substrates via the vacuum filtration method. The permeate flux values of unmodified and GO-modified membranes were 522 $Lh^{-1}\,m^{-2}\,bar^{-1}$ and 677 $Lh^{-1}\,m^{-2}\,bar^{-1}$, respectively, which shows ~28% improvement after GO modification (Fig. 3c).

Ao et al.[7] fabricated the GO-coated electrospun cellulose nanofiberous membrane with enhanced hydrophilicity and antifouling properties. The advantages of the utilized cellulose in their study was reported to be their lightweight, cheap price, straightforward chemical modification, and high water-retaining capacity. Incorporating GO has improved resistance against oil penetration and also induced micro/nanoscale hierarchical roughness on the surface, which consequently endowed superhydrophilic properties to the synthesized electrospun nanofiberous membranes. These membranes showed >99% oil removal and water flux of 960 $Lh^{-1}\,m^{-2}$, which was three times more than the polysulfone nanofiberous membrane.[35]

An overview of recent research works on graphene/GO-based membranes for oily wastewater treatment is presented in Table 1.

In summary, due to high electrical and thermal conductivity, as well as excellent chemical stability and mechanical strength, graphene is an excellent candidate for developing water treatment membranes.[27] Using monolayer graphene as a membrane minimizes the transport resistance and consequently maximizes the permeation flux. This unique property is attributed to the one-atom thickness of graphene and its frictionless surface.[55] The fabrication of single-layer graphene is difficult at ambient temperature, and if the graphene layers are not separated well enough from each other, they tend to aggregate to form graphite through strong π–π stacking and van der Waals interactions. Since, most of the unique properties of graphene is only associated with individual sheets, it is important to reduce the attachment of graphene layers. To overcome this issue, covalent and noncovalent attachment of small molecules or polymers to the graphene sheets have been explored in the literature. Both hydrophilic and hydrophobic functional groups are added to the graphene layers to provide an effective dispersion in aqueous and organic solvents.[56–58]

GO has similar properties to graphene, but it is more hydrophilic due to a variety of oxygen functional groups, which allows it to disperse better in water and other organic solvents.[55,56,58] Using GO in membranes can also lead to higher permeate flux due to its hydrophilic nature.[55] In addition, GO sheets provide anti-biofouling properties, which is again associated with its hydrophilic functional groups and a large negative zeta potential.[55,56]

In addition, graphene/GO-based membranes have the potential to be commercialized due to their low cost and relatively straightforward integration with various polymers.

CARBON NANOTUBES (CNTS)

CNTs are a form of carbon structure with one-dimension cylindrical nanostructure and excellent thermal conductivity,

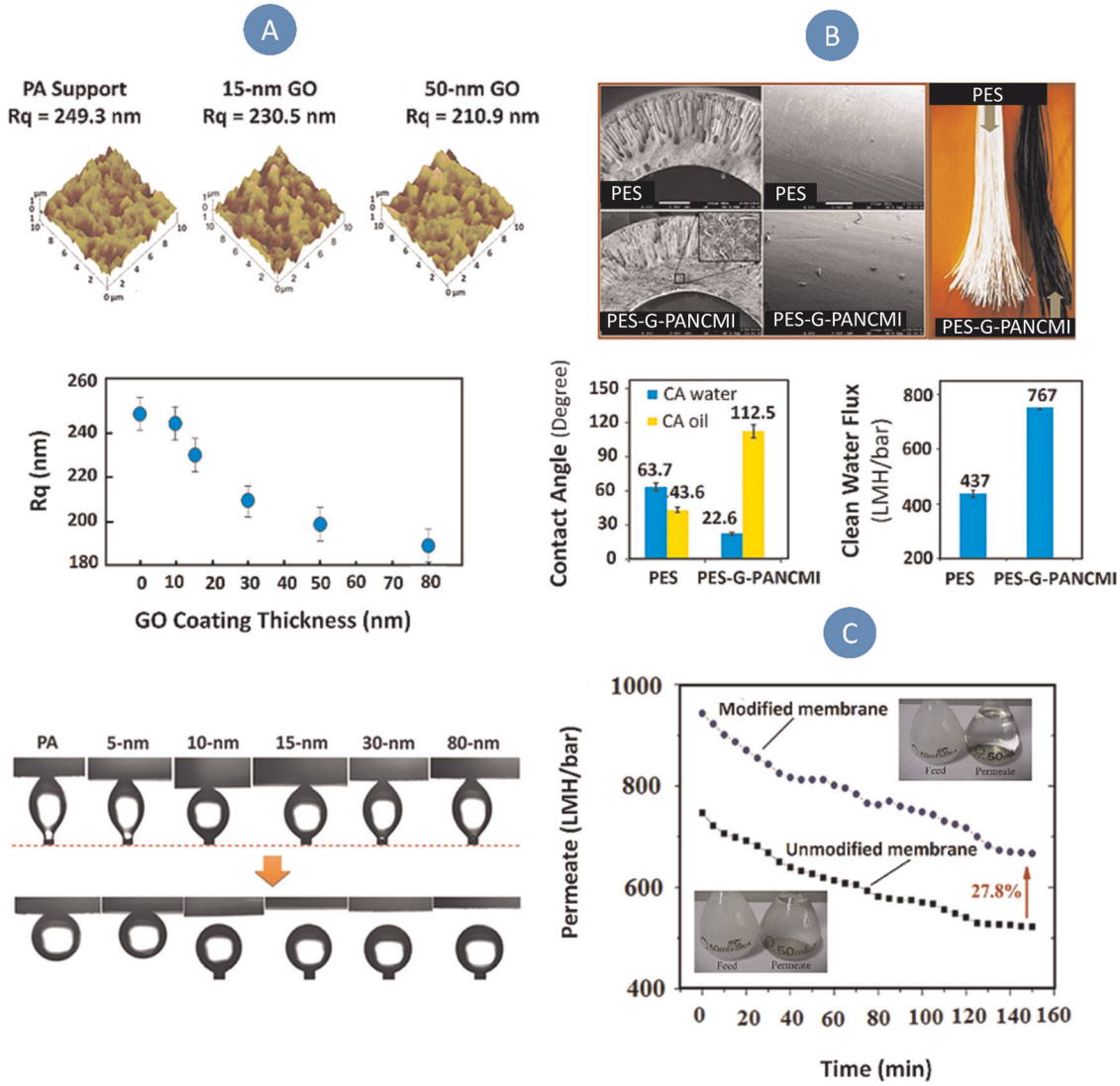

Fig. 3 **a** Top left: AFM images showing roughness of membranes, middle left: variation of root-mean-squared roughness (Rq) with the thickness of GO coating, and bottom left simulated oil drag force test for the PA support and the supports with different thicknesses of GO coating, adapted with permission from ref. [49] **b** Top right: cross-section and outer SEM images with actual picture of membranes and middle right: water and oil contact angle and pure water flux of the PES and PES-G-PANCMI membrane samples, adapted with permission from ref. [11] **c** Bottom right: permeate flux of unmodified and modified membrane with GO, adapted with permission from ref. [54]

tensile strength, and electrical properties.[20,59] A large specific surface area of CNTs and their oleophilic properties provide promising advantages for the production of "oil-removing" types of membranes with high permeation flux.[20] Therefore, a few studies in the literature explored the potential of these nanomaterials for fabrication of nanocomposite materials with "water-removing" property.

Gu et al.[60] have developed ultrathin and superhydrophilic membranes made of SWCNT and titania (TiO_2) nanoparticles (NPs). They coated TiO_2 on SWCNT films by the sol–gel method, followed by irradiation with UV light (Fig. 4a). Gu et al.[60] developed a unique structure with nanoscale pore size (20–60 nm) and ultrathin SWCNT film (60 nm), which showed superior performance to traditional mesh-based films in previous studies.[38,61] Due to the photocatalytic activity of TiO_2 NPs, the UV light irradiation has recovered the superhydrophilicity of oil-contaminated membranes. Therefore, the prepared nanocomposite membranes demonstrated self-cleaning and antifouling properties during multiple filtration tests. Figure 4a shows the water permeation flux through SWCNT/TiO_2 nanocomposite membranes during filtration of surfactant-free and surfactant-stabilized oil-in-water emulsions. As can be observed, the water flux values are as high as 30,000 $Lm^{-2}\,h^{-1}\,bar^{-1}$.[62,63] It was also proved that the synthesized SWCNT/TiO_2 nanocomposites were able to treat both surfactant-free and surfactant-stabilized oil-in-water emulsions with a wide range of droplet size between 100 nm to 3 µm. There were no droplets in the filtrate larger than 100 nm after filtration, indicating high separation efficiency of synthesized membranes.

Hsieh et al.[64] employed the spin-coating method to deposit fluorinated MWCNTs with 30–50 nm diameter on carbon fabrics substrates. The resulting membranes showed high water repellency as the WCA increased from 148° to 165°. This increment in water repellency was attributed to the nano/microscale heterogeneities created by MWCNTs on the carbon fabric substrate. The permeability and separation efficiency of the base membrane were compared with CNT-modified membranes in Fig. 4b. It is observed that both permeability and separation efficiency were improved for the modified membrane. The maximum permeation

Table 1. Summary of the recent publications using the graphene- and GO-based membranes in oily wastewater treatment at room temperature unless otherwise mentioned

Membrane materials	Fabrication method filtration process	Surface characteristics of membrane	Research highlights	Refs.
RGO-coated wire mesh RGO@mesh-300 (300 is mesh size)	Drop-coating method	WCA ~ 153° OCA = 0°	Separation efficiency > 98% Excellent recyclability antifouling properties High flux: 1752 $Lm^{-2} h^{-1}$ Durability in a wide range of humidity (RH: 10−90%) and temperature (−20 to 300 °C)	90
Fluorine-grafted reduced graphene oxide (f-rGO)-based coating	Dip-coating method Gravity-driven	under oil Superoleophilic WCA = 163.7°	High mechanical stability and recyclability Ability to tolerate harsh conditions, such as high temperature, and highly acidic and basic solutions High flux (1395 $Lm^{-2} h^{-1}$) only under gravity	91
PDA/RGO/halloysite nanotubes (HNTs)-cellulose acetate (CA) membrane	Vacuum filtration	WCA = 54.92° OCA = 150°	Antifouling property (FRR >82.27%) Oil rejection: 99.85%. Permeate flux ~60.3 $Lm^{-2} h^{-1}$	93
Polyvinylidene fluoride (PVDF)/RGO@SiO_2/PDA nanohybrid membranes	Surface deposition Vacuum filtration	Underwater Oleophobicity WCA = 39.8° OCA ~ 130°	FRR: 87.2% Flux ~125 $Lm^{-2} h^{-1}$ Oil rejection ~99%	94
GO-HNTs membrane	Vacuum-assisted filtration	Oleophobic WCA ~ 55°	High oil rejection at different pH (>99%) Excellent fouling resistance (FRR = 86.8%) Permeate flux: 716 $Lm^{-2} h^{-1}$	95
GO/graphitic carbon nitride ($g\text{-}C_3N_4$)@titania (TiO_2) 2D heterostructure membrane	Vacuum-assisted self-assembly process	OCA = 165° WCA = 43°	Permeate flux: 4536 $Lm^{-2} h^{-1} bar^{-1}$ Sunlight-driven self-cleaning property Excellent antifouling FRR>95% after 10 cycles Stable water permeation flux at pH range of 1–13 Oil rejection > 99.9%	96
GO/TiO_2 membrane	Vacuum filtration-assistant assembly process	WCA = 62° OCA = 162.8°	Water flux: 531 $Lm^{-2} h^{-1} bar^{-1}$ Oil rejection: 97.5% Good antifouling capability (FRR>80%)	97
RGO-silver (Ag)-TiO_2/CA photocatalytic membrane	Vacuum filtration	WCA = 42.78° OCA = 143.57°	Water flux: 191 $Lm^{-2} h^{-1}$ Oil rejection ~100% Excellent antifouling capacity and recyclability Stable oil rejection (~99%) after six cycles Higher flux/rejection under visible-light irradiation	98
TiO_2/GO/recycled cellulose triacetate nanofibrous membrane	Electrophoretic deposition method	WCA in air after UV irradiation <5°	Antifouling and self-cleaning ability Oil rejection >98%	99
Open-cell graphene network (OCGN)	Via self-assembly of graphene oxide and vapor rejection	Superhydrophobic (WCA = 153.6°) transformable to the superhydrophilicity (WCA = 0°)	The ultrafast transition from superhydrophobicity to superhydrophilicity in 1 s by plasma treatment, and then recovering superhydrophobicity in 1 min by self-induced Joule heating	100
TiO_2/sulfonated GO/Ag NPs membrane	Overlaying the SGO/Ag layer onto the TiO_2 mesh by vacuum deposition	Super-amphiphilicity underwater and in air, super-amphiphobicity under oil, OCA underwater: 155.3° WCA under oil = 150.2°	Excellent stability and durability High separation efficiency after ten cycles (99.6%) Flux: 53 $Lm^{-2} h^{-1}$ Photodegradation properties under UV irradiation	101
Poly(arylene ether nitrile) (PEN)/HNTs@GO-PDA nanofibrous composite membranes	Vacuum filtration and Electrospinning technique and hot-pressing process	WCA = 0° OCA ~ 145°	Thermally and chemically stable membranes at temperatures up to 90 °C and 1−14 pH range High rejection ratio >99.0% Remarkable antifouling performance for various oil/water emulsions High permeate flux = 1130.56 $Lm^{-2} h^{-1}$	102

flux for the modified membrane was 1800 $Lm^{-2} h^{-1} bar^{-1}$, which was 45% more than the base membrane. The highest separation efficiency was 99.7% and obtained for 0.35-mm thickness of the membrane.

Shi et al.[2] reported the use of free-standing SWCNT network films for separation of a wide range of water-in-oil emulsions, including the surfactant-free and surfactant-stabilized emulsions. They reported a very high permeate flux, up to 100,000 $Lm^{-2} h^{-1}$

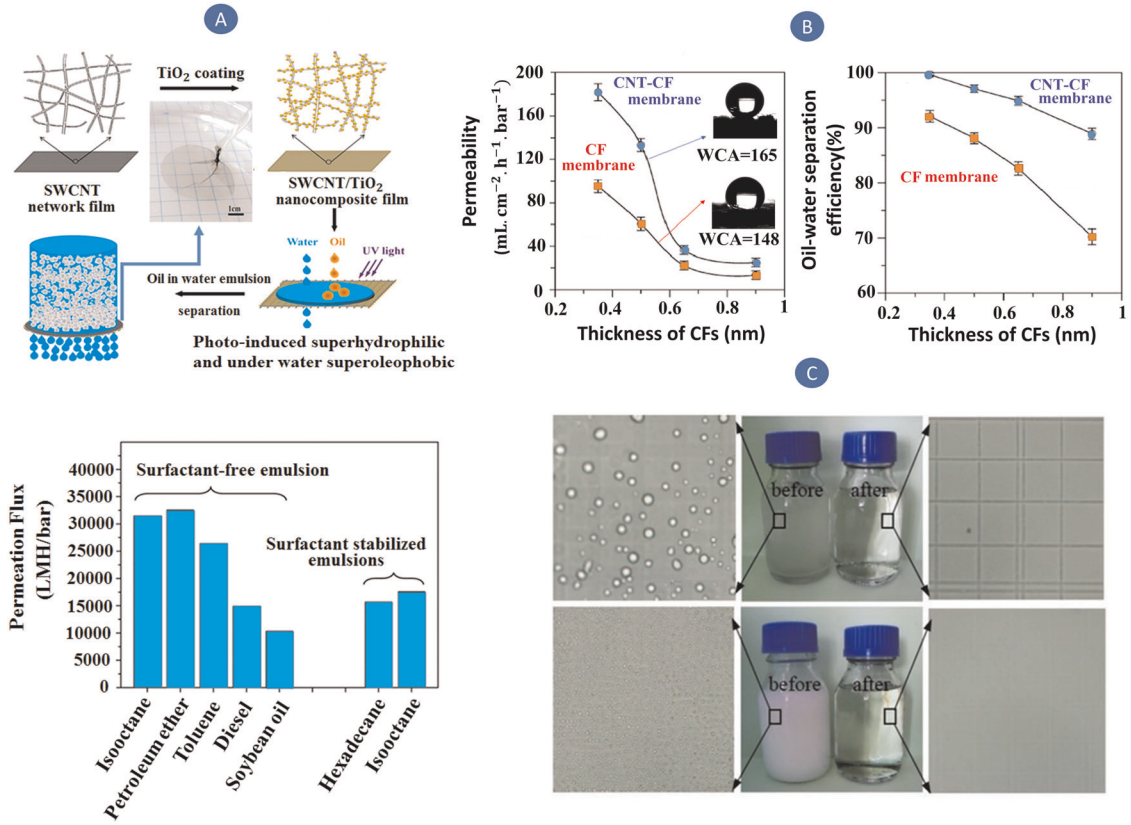

Fig. 4 **a** The fabrication process of a free-standing SWCNT/TiO_2 nanocomposite film and permeation fluxes of surfactant-free and stabilized oil-in-water emulsions separated by a SWCNT/TiO_2 nanocomposite film, adapted with permission from ref. [60] **b** Comparison between permeability and oil–water separation efficiency of CF membrane and CNT-CF membrane as a function of the CF thickness, adapted with permission from ref. [64] **c** Optical and microscopic images of water-in-petroleum ether and water-in-toluene (droplet size of ~270 nm) emulsions, respectively, before and after filtration tests though SWCNT film, the scale bar for top pictures are 20 μm and for bottom pictures are 2 μm, adapted with permission from ref. [2]

bar^{-1}, which is 2–3 orders of magnitude higher than conventional filtration membranes, and excellent separation efficiency of 99.95 %. They attributed such a high performance to the nanometere-scale thickness of the SWCNT films (30–90 nm) and their super-oleophilic property (OCA = 0°). Shi et al.[2] also tested the membrane antifouling property. After 20 cycles, the flux did not drop, and the oil purity in filtrate maintained >99.95 wt.%. Figure 4c shows optical and microscopic images of water-in-petroleum ether and water-in-toluene (droplet size of ~270 nm) emulsions before and after filtration by SWCNT film. As can be seen, the SWCNT film could successfully produce oil-free solutions using both emulsions containing different sizes of oil.

In another study, Hu et al.[65] showed that the incorporation of SWCNT films into a hydrophilic surface could enhance separation efficiency and flux for the treatment of oil-in-water nanoemulsions. The synthesized ultrathin Au nanorods/poly (N-isopropylacrylamide)-co-(acrylamide) (pNIPAm-co-AAm) cohybrid SWCNTs nanoporous membrane with photothermal-responsive properties. The synthesized membranes provided 99.99% oil removal with a water flux up to 35,890 $m^2 h^{-1} bar^{-1}$. The photothermal-responsive property of membranes was found to increase the water flux by light illumination. The developed membrane showed good antifouling and recyclability properties due to their hydrophilicity (WCA = 56°) and underwater oleophobicity (OCA = 134°). In addition, no reduction in the water flux was observed during filtration of n-hexadecane-in-water stabilized by sodium dodecyl sulfate (SDS) surfactant after almost ten cycles.

Saadati and Pakizeh[66] developed novel Polysulfone (PSf)/polyether block amide (Pebax)/Functionalized MWCNTs nanocomposite membranes for the nanofiltration (NF) of oil/water emulsions. They investigated the effect of 0.5, 1, 2 wt.% loading of functionalized MWCNTs on the permeate flux and rejection of the membranes. Increasing the MWCNTs content up to 2 wt.% enhanced membrane characteristics in terms of tensile strength (from 1.25 to 2.68 MPa), thermal stability (decomposition temprature increased ~100 °C), oil rejection (from 91.4% to 99.79%), hydrophilicity (WCA from 55.1° to 42.5°), and antifouling propertiy (FRR from 90.15% to 97.79%). Also, increasing MWCNTs loading up to 0.5 wt.% resulted in approximately three times increment in the permeation flux, while further increase, up to 2 wt.%, decreased the permeate flux ~30%.

Some recent publications about CNT-based nanocomposite membranes for oil–water mixtures separation are presented in Table 2.

In overall, low density, high porosity, antifouling properties, specific surface area, and hydrophobic nature of CNTs made them promising candidates for highly effective water and wastewater treatment.[60,66–68] However, the application of CNTs at full scale is limited mainly due to their high fabrication cost, and the release of CNTs into wastewater during filtration process, which may raise serious environmental concerns. The advantages and disadvantages of incorporation of CNTs in membrane fabrications are discussed in the following paragraphs.

CNTs can offer antifouling, self-cleaning, and reusable functions to membranes.[22] CNTs can also provide better performance than activated carbon in practical water treatment applications due to their unique physicochemical properties, desirable interactions with a diverse range of contaminants, and their capability of

Table 2. Summary of the recent publications using the CNTs membranes in oily wastewater treatment at room temperature

Membrane material	Fabrication method filtration process	Surface properties of membrane	Research highlights	Refs.
PSF-polyvinyl pyrrolidone (PVP)-acetyl-d-glucopyranoside UF membranes	Phase inversion	WCA = 69°	The deacetylated nanocomposite membranes exhibited higher flux = 112 $Lm^{-2} h^{-1}$ (LMH) at 2 bar Oil rejection: 100%	103
Asymmetric poly(vinyl alcohol)(PVA)-based aerogel membrane (self-cross-linking PVA & CNT)	one-pot hydrothermal reaction induced self-cross-linking of PVA	High porosity (>95%) Pore size <85 nm WCA ~ 40° OCA ~ 140°	High oil rejection (99.0%) Ultrahigh permeation flux = 135,000 $Lm^{-2} h^{-1} bar^{-1}$ Excellent antifouling properties for various oil in water emulsions FRR >93% after five cycles	84
CNT@MnO_2 on cellulose microfiber substrates membrane (nanorods wrapped on CNTs)	Vacuum filtration technique	OCA > 150° WCA = 0°	High oil-separation efficiency (>99.9%) High flux = 5500 $Lm^{-2} h^{-1} bar^{-1}$	104
CNTs modified with reductive (PAH)	Vacuum filtration	WCA < 14° OCA = 150°	Oil rejection: 98.6% Flux = 3500 $Lm^{-2} h^{-1} bar^{-1}$ Good stability and reproducibility	105
PVDF-CNT/ Polyurethane (PU)/PVDF-CNT) sandwich-structured microporous membranes	Sequential electrospinning	Waterproofness and breathability properties WCA = 136° OCA = 0°	Permeate flux ~2200 $Lm^{-2} h^{-1} bar^{-1}$ Separation efficiency ~70%	106
gCNTs blended with PSF and PVP	Phase inversion	WCA = 68°	Optimum flux: 112 LMH Oil rejection ~100% FRR: 88%	107

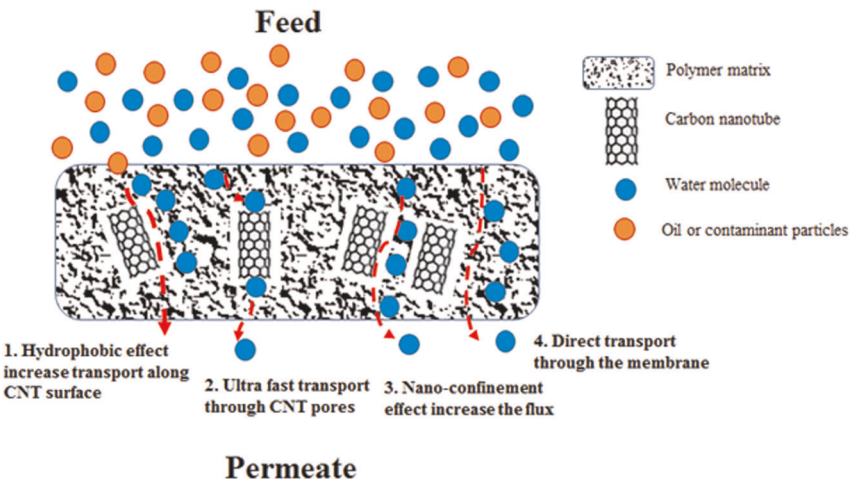

Fig. 5 The mechanism of flux enhancement by CNTs in nanocomposite membranes, adapted with permission from ref. [73]

self-assembling on supporting material by chemical vapor deposition.[68] The presence of functional groups at the open ends, sidewalls, and defect sites of CNTs potentially improves membrane performance in terms of water permeation and oil rejection.[69]

One solution to reduce membrane fouling is to apply electric field to the membrane. Electrical conductive CNT-based membranes act like a cathode in an external electric field and repel charged surfactant and oil molecules form the membrane surface.[70]

Another advantage that CNTs offer is the dramatic increase in the mass transfer rate of water through nanocomposite membranes. Although CNTs are hydrophobic in nature, they result in ultrahigh water flux as compared with other carbon-based materials (discussed later in Table 4). A possible explanation is that nanometer-sized hollow pores of CNTs and their smooth graphitic layers create a frictionless path for the ultrafast mass transportation.[22] The combined effect of the ultrafast transport through the CNT pores with other possible mechanisms, as indicated in Fig. 5, leads to a significant flux enhancement in CNT-based nanocomposite membranes.[22,44,45,71–74] To produce the most efficient CNT-blended membranes, in terms of water flux and oil rejection, well-dispersed CNTs must be oriented perpendicularly to the membrane plane.[73] However, controlling the agglomeration of CNTs and their vertical alignment are still major challenges.[44] Dielectrophoresis and special filtration techniques were used to align the CNTs. Vertical alignment of CNTs can be accomplished using high-quality CNTs (without any impurity which may block the tubes) and conducting complicated end-opening techniques (e.g., plasma etching or argon milling), which impedes further development of CNT-based nanocomposite membranes.[73]

As before mentioned, nanocomposite membranes made by CNTs benefit from many advantages including thermal stability,

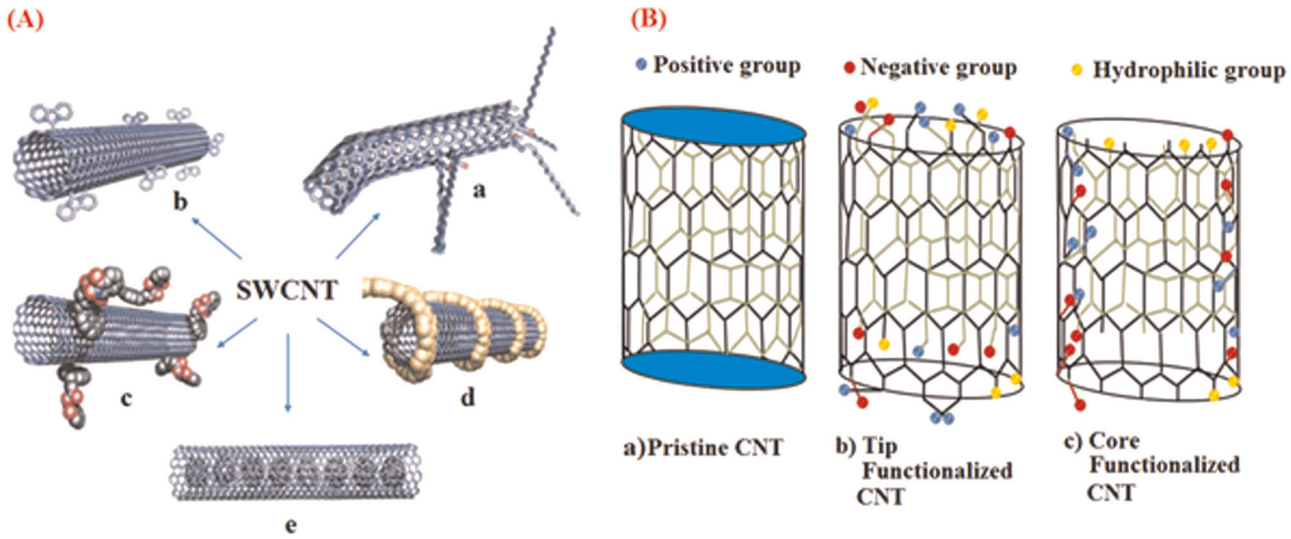

Fig. 6 **a** Functionalization possibilities for SWNTs: defect-group functionalization, covalent sidewall functionalization, noncovalent exohedral functionalization with surfactants, noncovalent exohedral functionalization with polymers, and endohedral functionalization, adapted with permission from ref. [76] **b** Functionalization of CNT membranes with positive, negative, and hydrophilic groups, adapted with permission from ref. [22]

mechanical strength, and electrical properties.[44,75] However, poor interfacial interaction of CNTs with polymer matrix restricts their application as reinforcement materials. To overcome dispersion problem of CNTs and their weak compatibility with polymers, surface-modification strategies must be developed. These strategies rely on chemical (covalent) and physical (non-covalent) functionalization of CNTs surface by positive negative, hydrophobic, or hydrophilic groups, such as, carboxyl, and hydroxyl groups (Fig. 6a, b).[22,44,45,75]

Chemical functionalization can be performed in different positions of CNT, such as the end caps of nanotubes or sidewalls. Due to the presence of many polar and nonpolar functional groups on CNTs, covalent functionalization is considered as a promising method to enhance solubility of CNTs in various organic solvents.[76] The main drawbacks, however, is formation of defects in sidewalls of CNTs, which may result in fragmentation of CNTs into smaller pieces.[45,76] Noncovalent functionalization of CNTs, on the other hand, does not affect their final structure as it does not destroy the conjugated system of CNTs sidewall. Noncovalent functionalization is performed by surfactant, aromatic compounds, and polymers by employing π–π stacking or hydrophobic interactions.[76]

There are still some challenges that need to be addressed for successful deployment of CNTs in water-purification membranes. CNTs are expensive and large-scale production of membranes may not be cost-efficient.[22,69] Moreover, toxicity of CNTs can cause serious health and environmental problems when they are released during water treatment processes.[44]

Compared with other carbon-based materials, Graphene and GO offer a low cost alternative to CNTs and have less negative impact on environment and human health.[58] Other advantages over CNTs include high processability and solubility, facile synthesis, moderate conductivity, and excellent biocompatibility.[56] However, since pore size and inter layer space of graphene layers affect the permeate flux, more efforts must be devoted to control these parameters during the fabrication process.[55]

CARBON NANOFIBERS (CNFS)

Fibrous carbon-based materials with cylindrical nanostructures have shown high oil sorption capacity for oil–water separation.[77] Generally, CNFs and CNTs have similar mechanical strength and electrical properties; however, CNFs possesses a much larger functionalized surface area compared with CNTs. CNFs can be produced by electrospinning, which creates nanofibrous films with chemical inertness, high porosity, uniform pass-through size, and interconnected open pore structure.[77]

Liu et al.[77] developed macroporous carbon nanofiber films with good flexibility and superhydrophobic (WCA = 155.3°) and superoleophilic (OCA~0°) properties. Purified terephthalic acid was used to generate micropores (89.2% porosity) inside electrospun carbon nanofibrous films, which reduced stresses and enhanced the flexibility. Figure 7a shows high flexibility of the synthesized membranes. Liu et al.[77] reported a high oil-absorption capacity ($k = (M_2 - M_1)/M_1$) for silicon oil with $k = 138.4\ g g^{-1}$, where M_2 and M_1 represent the weight of the sorbent before and after oil absorption. The absorbed oil could then be extracted by rinsing the saturated membrane with an organic solvent. Moreover, using electrospun nanofibrous CNFs provides a faster and easier separation of oil, which makes these membranes promising candidates for industrial applications (Fig. 7a).

Tai et al.[78] claimed that the main restriction of using CNFs for oil–water separation, i.e., low rigidity of macrostructure of CNFs, could be resolved by adding silica (SiO_2) into membrane structure. The loading of SiO_2 was maintained <2.7 wt. % to have a higher flexibility and toughness. They employed electrospinning to fabricate high rigidity carbon-based nanofibrous membranes, and tested them for oil–water separation at a broad range of temperature and pH (Fig. 7b).

Figure 7b depicts gravity-driven oil–water separation setup. A mixture of petroleum spirit and 0.2 M HCl aqueous solution, dyed with methyl violet, was used as oil/water mixture. A vial was first filled with 0.2 M $AgNO_3$ aqueous solution, which was dyed with methyl violet. The oil/water mixture was then poured into the vial through the mounted membrane in the opening of the vial. $AgNO_3$ in the vial easily reacts with Cl^- ions, which are penetrated through the membrane to form AgCl precipitates. The change in the pH of the $AgNO_3$ aqueous solution alters the methyl violet color and thus can serve as an indicator of water passage through the membrane. As can be seen in Fig. 7b, water was completely retained by the synthesized membrane. The nanofibers created a 3D microporous membrane, which has led to a high permeation flux across the membrane ($3032\ L m^{-2} h^{-1} bar^{-1}$) (Fig. 7b). The synthesized membranes showed high stability, as their wettability

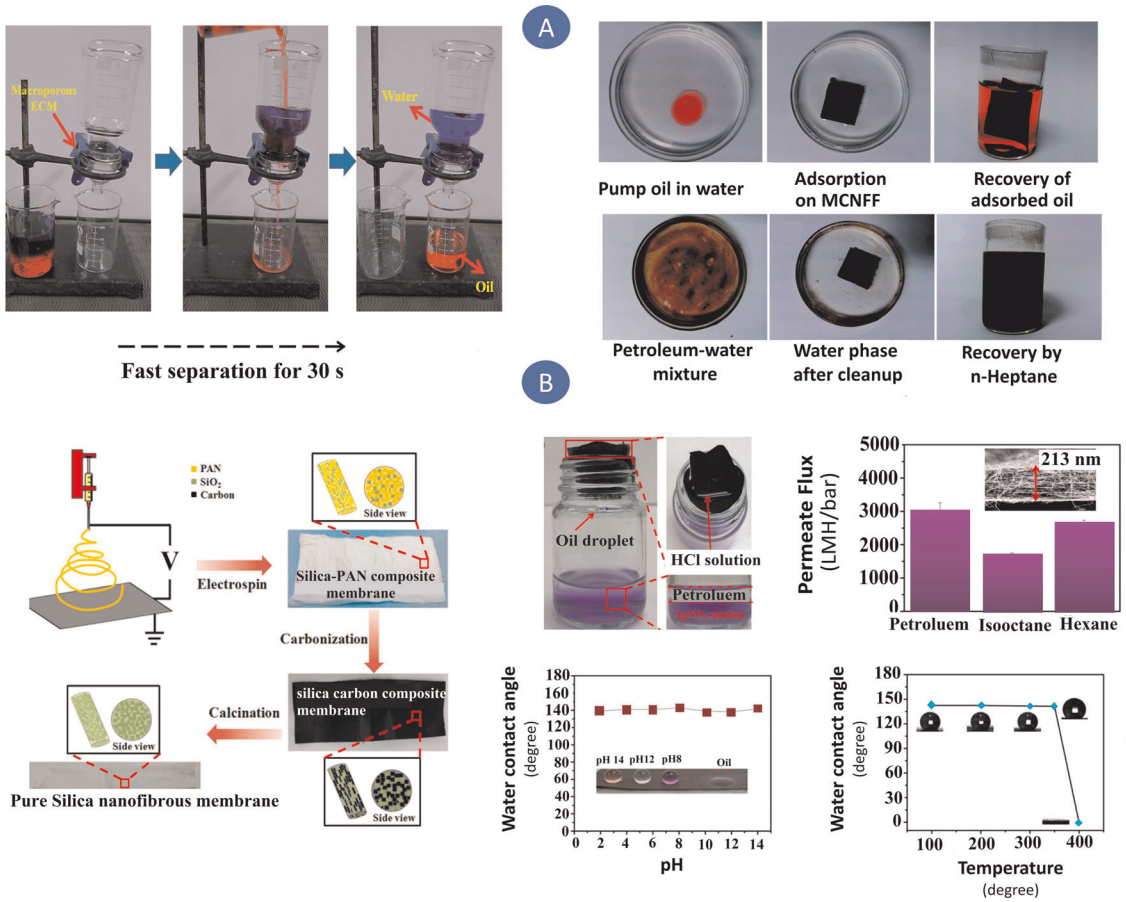

Fig. 7 **a** Left: facile oil–water separation process using macro-porous carbon nanofibers film (MCNFF), right: adsorption and recovery performance of MCNFF in removal of pump oil and petroleum from water, respectively, adapted with permission from ref. [77] **b** Left: schematic illustration of the fabrication method used for silica–PAN, silica–carbon and pure silica composite membrane, right: demonstration of gravity-driven oil–water separation, Permeate flux for different types of oils, WCAs of membrane at different pH values, and WCA variation after calcination at various temperatures for 2 h, adapted with permission from ref. [78]

was almost constant at high temperatures (up to 300 °C) and a wide range of pH (2–14) (Fig. 7b). Tai et al.[78] attributed the fast mass transport through the membrane to the superoleophilicity (OCA~0°) and porous structure of the membrane.

Some recent publications which have studied CNFs and nanofibrous membranes in oil–water mixtures separation are mentioned in Table 3.

Overall, CNFs are well known for their inherent hydrophobicity, as well as thermal stability and chemical inertness, which makes them excellent candidates for energy-efficient techniques for oil–water separation such as gravity-driven separation. In addition, CNFs have shown a high reinforcement capability, boosting the mechanical properties of the nanocomposite membrane. The final mechanical properties depend on the diameter and aspect ratio of CNFs, their dispersion quality and adhesion to the polymer matrix, as well as orientation of CNF fillers. For instance, the tensile strength increases by decreasing the diameter of CNFs and a good dispersion improves the mechanical properties.[79,80] In order to achieve a good dispersion and adhesion of CNFs fillers into the polymer matrix, chemical functionalization of CNFs is required.[81] Weak adhesion of nanofillers creates stress concentration at the interface of polymer/CNFs, which causes composite failure.[81]

However, they often suffer from low rigidity and flexibility, which restrict the practical usage of CNFs in the fabrication of membranes. In the literature, a few studies have shown that the combination of other material with CNFs could overcome the mentioned challenges.[5,75,77,78,82,83]

Compared with CNTs, CNFs have higher electron transport across their sidewalls and thus higher chemical reactivity, which are important for functionalization and electrochemical applications. In addition, CNFs have shown robustness as individual and free-standing structures.[31] Although CNTs provide better mechanical and permeation properties than CNFs, the much lower price of CNFs makes them more favorable materials for commercial production of nanocomposite membranes.[79,80]

DISCUSSION

In the previous sections, it is shown that the incorporation of carbon-based nanomaterials into polymeric membranes could tune up the properties of membranes, such as hydrophobicity/hydrophilicity, stability (mechanical, thermal and chemical), flux, rejection, antifouling, or antibacterial properties. Based on the hydrophobicity or hydrophilicity of the membrane, oil or water can be separated from the oil–water mixture. It has been found that superhydrophilic membranes are better in terms of antifouling properties;[19] while superhydrophobic membranes could result in self-cleaning properties. In superhydrophobic membranes, as the water droplets slide and roll over the membrane surface, they carry the dirt away with themselves. Most of the developed carbon-based membranes in the literature are hydrophilic membranes. As can be observed in Fig. 8, graphene, GO, and CNTs have been mostly utilized to fabricate hydrophilic membranes, whereas, CNFs are mostly used to prepare hydrophobic membranes. In this section, we first selected the highest flux

Table 3. Summary of the recent publications using the CNF-based membranes in oily wastewater treatment

Membrane materials	Fabrication method filtration process	Surface properties of membranes	Research highlights	Refs.
Macroporous CNF film using poly terephthalic acid (PTA) as a sublimation reagent	Electrospinning	WCA = 155.3° OCA ~ 0°	High oil absorption up to 138.4 g^{-1} for silicone oil and MCNFF4.4 (4.4% PTA ratio) High porosity, flexibility, and chemical stability	77
Flexible SiO_2–carbon composite nanofibers	Electrospinning	WCA = 144° OCA = 0°	Oil flux: 3032 ± 234.6 $Lm^{-2} h^{-1}$ (petroleum spirit) Oil flux: 2648.8 ± 89.7 $Lm^{-2} h^{-1}$ (hexane) Stable at a wide range of temperature (up to 350 °C) and pH (2–14)	78
Carbon–SiO_2 nanofibrous membrane	Electrospinning	A flexible, hydrophobic	High flux at low pressure Flux: 2481 $Lm^{-2} h^{-1}$ at $P = 0.07$ bar Flux: 35,961 $Lm^{-2} h^{-1}$ at P = 1 bar	92
Stainless-steel mesh (SSM)/CNFs-polydimethylsiloxane (PDMS)	Vacuum-based filtration	WCA = 163° OCA < 1°	Excellent resistance to harsh environmental conditions such as acid, salt, organic, biofouling, and mechanical abrasion (pH: 1–12) Flux: up to 2970 $Lm^{-2} h^{-1}$ Durable and high-flux molecular transport	75
Etched SSM/ CNFs–SWCNTs–PDMS	Simply assembled via vacuum filtration technique	WCA = 145°	High flux of 430 $Lm^{-2} h^{-1}$	108

No rejection or separation efficiency values were reported for the CNF-based nanocomposite membranes

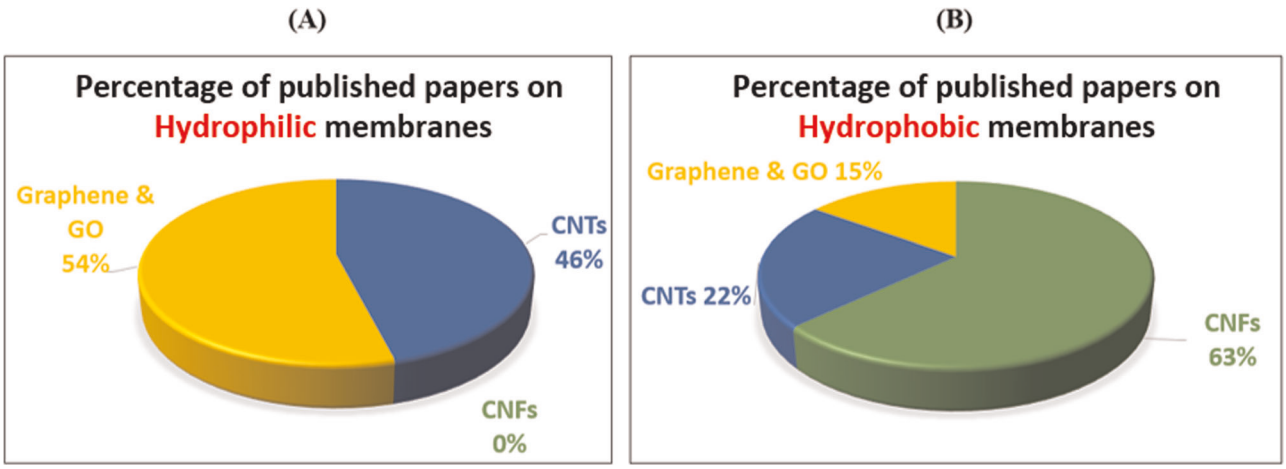

Fig. 8 The percentage of recent publications on (**a**) hydrophilic membranes and (**b**) hydrophobic membranes

hydrophilic and hydrophobic membranes ever reported for all carbon-based materials. The performance of selected membranes was then investigated and compared based on separation efficiency and antifouling property.

Hydrophilic membranes

The permeate flux and wettability of three best hydrophilic carbon-based membranes with the highest reported permeate flux in the recent literature are given in Table 4A. As can be seen, CNT-based membranes[84–86] resulted in higher fluxes as compared with the membranes prepared by graphene and GO.[49,81,87] CNF-based membranes, on the other hand, have not induced any hydrophilicity to nanocomposites. In terms of antifouling properties, Huang et al.[49] reported 58% FRR after three cycles of filtration for a thick GO coating (30 nm), and ~100% FRR for a very thin layer of GO coating (15 nm). The membranes developed by Zhang et al.[81] showed the highest permeate flux among all other graphene and GO membranes in the literature, while exhibited only 75% FRR. The CNT membrane introduced by Gao et al.[84] showed ~93% flux recovery after five cycles of filtration, while its permeate flux was extremely higher than other membranes. Jiang et al.[86] claimed no flux reduction after several cycles of filtration for their CNT-based membranes. Overall, Table 4A shows that CNTs resulted in higher permeability than other carbon-based materials.

Hydrophobic membranes

The hydrophobic carbon-based membranes with the highest permeate flux reported in the literature are presented in Table 4B. Again, the CNT-based membranes[85,88,89] demonstrated higher permeate flux compared with graphene, GO[90,91] and CNFs membranes.[75,78,92] In terms of FRR, Chen et al.,[90] Guo et al.,[91] and Abraham et al.[85] reported a nearly complete flux recovery for their graphene and CNT-based membranes, while flux recovery of the CNF-based membranes, synthesized by Lin et al.,[75] Tai et al.,[78] and Hang et al.[92] is not reported. In addition, CNT/CNF-based membranes are found to provide a promising separation efficiency >99%.

Table 4. (A) The highest permeate flux in each based material for hydrophilic membranes category in recent publications; (B) the highest permeate flux in each based material for hydrophobic membranes category in recent publications

Group name	Type of based materials	Wettability	Water and oil contact angle	The membranes and references	Permeation flux $Lm^{-2} h^{-1} bar^{-1}$
(A)	The graphene and GO membranes	Hydrophilic	Superhydrophilic OCA ~ 165°	GO/SiO_2[87]	4550
			WCA = 25.5° OCA = 164.5°	PA-GO[49]	5400
			Superhydrophilic	GO/aminated PAN[81]	10,000
	The CNTs membranes		WCA ~ 10°	CNT/poly (N-diethyl aminopropyl) methacrylate (PDEAEMA) with the introduction of (CO_2) to the surface[85]	58,000
			hydrophilic	J-CNTs@PAN (PAN side)[86]	80,000
			WCA ~ 40° OCA ~ 140°	PVA and CNT[84]	135,500
(B)	The graphene and GO membranes	Hydrophobic	Superhydrophobic in air and under oil. WCA = 164°	(f-rGO)-(γ-oxo-1-pyrenebutyric acid) (OPBA)-polypropylene(PP)/PU[91]	1395
			WCA ~ 153° OCA = 0°	RGO@mesh-300[90]	1752
	The CNTs membranes		WCA = 104° OCA ~ 0°	SWCNT-PDA[88,89]	48,300
			WCA ~ 113°	CNT/PDEAEMA with the introduction of (N_2) to the surface[85]	90,000
			WCA ~ 94° OCA ~ 0°	SWCNT-modified cellulose ester (MCE)[2,88]	100,000
	The CNFs membranes		WCA = 163° OCA < 1°	SSM/CNFs-PDMS[75]	2970
			WCA ~ 144° OCA = 0°	Flexible SiO_2-carbon composite nanofibers[78]	3032
			hydrophobic	Carbon-SiO_2 nanofibrous membrane[92]	35,961

Overall, Table 4 shows that CNTs results in a better performance regarding permeability and antifouling properties than other carbon-based materials. However, CNTs have not yet fulfilled their promise in water treatment application, most likely due to the high fabrication costs, as well as, serious challenges to make robust and defect-free nanocomposite membranes. The benefits, drawbacks, and the reason of higher permeation flux of CNTs over other carbon-based materials are discussed in above sections.

CONCLUSION AND OUTLOOK

Application of carbon-based nanomaterials in the fabrication of nanocomposite membranes for oil–water separation has been reviewed. Using CNTs, graphene, GO, and CNFs leads to a significant improvement in the membrane performance in terms of permeation, antifouling, and self-cleaning properties. Our literature survey showed that CNTs provide higher permeation flux and FRR compared with other materials. In addition, the hydrophilic membranes exhibit a higher permeation flux than hydrophobic membranes, which could be attributed to antifouling properties of hydrophilic membranes.

Each carbon-based nanomaterial has some advantages and disadvantages, and the selection of one material over another is primarily based on enhanced properties, cost-efficiency, and health and environmental issues. Although CNT-based membranes provide the highest permeate flux, their uniform distribution in the polymer matrix and vertical alignment are still major challenges. Moreover, CNTs are expensive and are associated with toxic effects when released into environment, which makes them less favorable for large-scale production. On the other hand, graphene and GO are cheaper alternatives and can induce mechanical flexibility, electrical/thermal conductivity, and antibiofouling properties to nanocomposite membranes. In addition, they do not have any negative impact on environment and human health. Compared with membranes prepared by graphene, GO, and CNTs, the CNF-based membranes provide lower flux, and thus the recent literature on utilizing these nanomaterials is sparse. The only advantage of CNFs over CNTs is found to be their lower price which makes them more suitable for cost-efficient production of commercial nanocomposite membranes. Although many challenges still remain, it is highly envisioned that carbon-based materials will significantly influence the next generation of nanocomposite membranes for oil–water separation.

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AUTHOR CONTRIBUTIONS

S.N. conducted a comprehensive literature survey and analyzed the date, S.N. and M.R. provided critical discussion on the literature data, M.S. played advisory role, and all authors contributed to the writing of the paper.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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