Improvement of polyacrylonitrile ultrafiltration membranes’ properties using decane-functionalized reduced graphene oxide nanoparticles

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ABSTRACT

The effect of decane-functionalized reduced graphene oxide (decane-rGO) was studied on the performance of polyacrylonitrile (PAN) ultrafiltration membranes. The results showed that the decane-rGO/PAN membranes had greater salt rejections relative to their corresponding GO/PAN membranes, confirming superior performance of modified decane-rGO particles. Also, the membrane with 0.2 wt% decane-rGO exhibited maximum water flux and appropriate salt rejection. The field-emission scanning electron microscopy (FE-SEM) micrographs illustrated that the sponge-like pores in the pristine PAN membrane were changed to a finger-like structure in the membrane containing up to 0.2 wt% of decane-rGO and the vertical holes were converted to horizontal holes by further increasing the decane-rGO concentration in the polymer matrix.

Key words | FE-SEM, graphene oxide, polyacrylonitrile (PAN), surface modification, ultrafiltration (UF) membrane

INTRODUCTION

In recent years, graphene has attracted a large amount of scientists’ attention because of its unique properties. Graphene is an allotrope of carbon with a structure composed of a plane of sp² bonded atoms (Pumera et al. 2010; Huang et al. 2011; Liu et al. 2011; Yin et al. 2015). It is the thinnest compound known in the world and regarded as a theoretical building block used to portray graphite crystals (Cong et al. 2010; Kim et al. 2010; Terrones et al. 2010). Graphene sheets are held by van der Waals bonds and their electron mobility is faster than any known material in our universe (Stankovich et al. 2006a, 2006b, 2007; An et al. 2010). An important kind of graphene-based material is graphene oxide (GO), an oxygenated graphene molecule manufactured by the controlled oxidation of graphite that has amazing electrical, physical, and mechanical properties (Shen et al. 2009; Qiu et al. 2010; Sengupta et al. 2011). In 1859, Brodie synthesized GO by adding a portion of potassium chlorate to a slurry of graphite in fuming nitric acid (Brodie 1859). Staudenmaier added concentrated sulfuric and chloride in multiple aliquots over the course of the reaction (Staudenmaier 1898). Then, Hummers reported the most common method in which the graphite was oxidized using KMnO₄ and NaNO₃ in H₂SO₄ (Hummers & Offeman 1958). In 2010, Marcano et al. offered an improved method for synthesizing GO by increasing the amount of KMnO₄ and performing the reaction in a 9/1 mixture of H₂SO₄/H₃PO₄. This improved method yields a higher ratio of well-oxidized hydrophilic carbon material (Marcano et al. 2010). GO is a two-dimensional sheet which is formed from the covalently bonded carbon atoms and has two kinds of distributed areas, including aromatic areas with unoxidized benzene rings and areas with the presence of oxygen functional groups such as hydroxy, epoxide and carbonyl groups which cause GO sheets to be hydrophilic and highly dispersible in water (Figure 1) (Paredes et al. 2008; Xu et al. 2009; Lin et al. 2010). The GO nanosheet consists of sp³-hybridized carbons (hydroxyl and epoxide functional groups) on the top and bottom surfaces of each layer and
sp²-hybridized carbons (carboxyl and carbonyl groups) on their basal planes and edges (Stankovich et al. 2006b).

In general, two-dimensional carbon materials (graphene, GO, and reduced GO) attract a great deal of attention because of their unique properties, such as transparent conductors, composites, thermal interface materials, energy storage systems, and nano-bio hybrids (Tessonnier & Barteau 2012; Tian et al. 2014). GO can be dispersed in polar organic solvents such as N-methylpyrrolidone or N,N-dimethylformamide (DMF) without the assistance of chemical groups but, recently, the dispersion behavior of GO in different non-polar aprotic organic solvents has been investigated by introducing special chemical groups (Tessonnier & Barteau 2012). Today, significant efforts have been made to develop composite polymeric materials to improve both performance and antifouling properties of ultrafiltration (UF) membranes because it is essential to have a membrane lifetime as long as possible (Breuer & Sundararaj 2004; Ma 2010). Vatanpour et al. (2011) examined performance and antifouling properties of oxidized multiwalled carbon nanotubes (MWCNTs) in polyethersulfone (PES) matrix nanofiltration membranes. A mixture of MWCNTs and PES matrix caused improvements in the hydrophilicity and water flux of membranes. In addition, the MWCNTs affected pore size and porosity of membranes (Vatanpour et al. 2011). GO is much more attractive in the field of material research because of its high surface and mechanical properties. When GO is incorporated into polymer matrix, it can improve physical properties of the host polymer at extremely low doping concentration. Ganesh et al. (2013) enhanced the hydrophilicity, water flux, and salt rejection of membranes by dispersing GO in polysulfone (PS) matrix.

Zhang et al. (2013) investigated the effects of GO and oxidized carbon nanotubes on polyvinylidene fluoride (PVDF) composite membranes. A mixture of O-MWCNTs and GO increased the performance of membranes such as water flux. The GO and modified GO with polyacrylonitrile (PAN) and UF membranes are widely used for water treatment. Majeed et al. (2012) blended MWCNTs with PAN to prepare UF membranes. MWCNTs increased solution viscosity, reflecting their good dispersion in the polymer matrix. Moreover, MWCNTs increased the water flux and the transport properties of PAN membranes. The tensile strength was also improved by the addition of MWCNTs (Majeed et al. 2012).

In this work, the synthesis of the decane-functionalized rGO (decane-rGO) nanoparticles and their application in the preparation of UF PAN membranes were performed (for the first time) in order to improve membrane properties such as morphological properties, water flux, and salt rejection. The presence of decane groups on the surface of reduced GO was studied by Fourier transform-infrared (FT-IR) and X-ray diffraction (XRD) techniques. The field-emission scanning electron microscopy (FE-SEM) images of nanocomposite membranes’ surfaces and cross-sections were compared with those of the pure PAN membrane. Also, prepared membranes were examined for their surface roughness using atomic force microscopy (AFM) measurements.

**MATERIALS AND METHODS**

**Materials**

The materials including n-hexane, DMF, graphite powder, and hydrazine (N₂H₄) were extra pure and were purchased...
from Sigma-Aldrich and Merck companies and used without further purification. The PAN (average \( M_w = 150,000 \text{ g/mol} \), n-butyllithium (n-BuLi, 2.6 M in n-hexane) and 1-bromodecane were also provided from Sigma-Aldrich.

**Synthesis of decane-rGO**

GO was synthesized from natural graphite powder by the modified Hummers method (Hummers & Offeman 1958). 400 mg GO was put in a 500 mL round bottom flask, then 400 mL water was added and the dispersion was sonicated. The ultrasonic employed had a frequency of 37 kHz at a power of 80 W. After that, 4.0 mL \( N_2H_4 \) was added and the obtained mixture was heated in an oil bath at 100 °C for 48 h to yield the reduced GO (r-GO). The precipitated r-GO was washed with water and methanol, and dried at room temperature for 1 day. 300 mg of r-GO was placed in a 100 mL round-bottom flask and 40 mL of extra dry n-hexane was added. The suspension was sonicated for 1 h in order to disperse the sheets. The mixture was then transferred to a 250 mL three-neck flask under nitrogen atmosphere. Next, 100 mL of dry n-hexane and 60 mL of n-butyllithium (n-BuLi) were added. The mixture was stirred at room temperature under nitrogen atmosphere for 2 h in order for the n-BuLi to react with the r-GO sheets and to activate the surface. A total of 33 mL of 1-bromodecane was added and the mixture was kept at room temperature for another hour before starting heating to 70 °C. During the coagulation process, the temperature of the bath was adjusted at 10 °C.

**Characterization**

To investigate the presence of decane groups on the surface of rGO nanoparticles, the FT-IR spectra (FT-IR, Bomem Canada Mod SRG1100 g) were obtained. For measurement of interlayer distance and the characteristic peaks of nanoparticles, the XRD patterns were taken with an Inel Equinox 3000 X-ray diffractometer using Cu K\( _\alpha \) radiation (\( \lambda = 1.5406 \text{ Å} \)). Raman spectra were acquired in order to investigate the structural changes of nanoparticles with a laser source excited at 785 nm. The morphology of membrane surface and the role of decane-GO on porosity of UF membranes were studied by field-emission scanning electron microscopy (FE-SEM, VEGA3, TESCAN). AFM was used to analyze the surface morphology and roughness of the prepared membranes. The AFM device was Nanosurf Mobile S scanning probe-optical microscope (Digital Instrumental) equipped with Nanosurf MobileS software. Membrane hydrophobicity was quantified by measuring the contact angle which was formed between the membrane surface and a water drop. The contact angle was measured at three random locations for each sample and the average was calculated.

**Membrane performance test**

Pure PAN membranes consisted of 16 wt% PAN and 84 wt % DMF. The performances of PAN membranes containing decane-rGO were investigated by measuring the water flux and salt rejection tests. A cell with a 9 × 4 cm\(^2\) effective area was used for analyzing membranes at 25 °C temperature and operating pressure of 3 bars. The water flux (\( J \)) was calculated from the equation \( J = V/(S \times T) \), where \( V \) is the permeate volume, \( S \) is active membrane area and \( T \) is the permeation time. The salt rejection (\( R \)) was calculated from the equation \( R \text{ (\%)} = (C_f - C_p / C_f) \times 100 \), where \( C_f \) is the salt concentration of the feed and \( C_p \) is the salt concentration of permeate.
RESULTS AND DISCUSSION

Characterization of decane-rGO

The synthesis of decane-rGO particles is confirmed by FT-IR spectroscopy. The FT-IR spectra of GO, r-GO, and decane-rGO particles are shown in Figure 2. All samples exhibit one characteristic peak at about 3,391 cm\(^{-1}\) that is related to the OH groups, and the two bands at 1,638 and 1,712 cm\(^{-1}\) are attributed to stretching frequencies of C=\(C\) aromatic ring and carbonyl groups, respectively. Also, the bands at 1,231 cm\(^{-1}\) and 1,150 cm\(^{-1}\) are assigned to the C-OH and C-O stretching vibrations, respectively. After reduction of GO, the intensity of the oxygen functional groups such as the OH band at 3,391 cm\(^{-1}\) decreases and this change is indicative of the reduction of OH groups on the GO surface. In the case of decane-rGO, the presence of decane functionality on the reduced GO was confirmed by the peaks at 2,800 and 2,900 cm\(^{-1}\) indicating the CH stretching vibrations of decane groups. Practically, the GO particles are completely dispersed in water. In contrast, the decane-rGO particles cannot entirely be dispersed in water, thus decane groups are attached to the rGO surface.

Figure 3 displays the XRD patterns of GO, r-GO, and decane-rGO particles. The graphite shows a strong peak at 26.7° in the XRD pattern, corresponding to an interlayer spacing of 0.333 nm calculated via the Bragg equation (Wu et al. 2015). The XRD pattern of GO reveals a strong peak at 11.1°, which is related to an interlayer spacing of 0.800 nm. The results clearly confirm the presence of oxygen-containing functional groups within interlayer spaces of GO sheets which increase the interlayer spacing between the GO sheets. The r-GO particles demonstrate a broad peak at 23.9°, showing an interlayer spacing of 0.372 nm that is much smaller than that of GO which is due to removing a great number of oxygen-containing functional groups from GO particles (Wu et al. 2012). The results propose that the conjugated r-GO network, sp\(^2\) carbon, is re-established during the reduction (Fan et al. 2010; Pei et al. 2010; Wu et al. 2012). The maximum diffraction peak of decane-rGO powder appears at 7.8° in the XRD pattern corresponding to an interlayer of 1.130 nm. The presence of decane agents in rGO interlayer spaces enlarges the interlayer spacing between decane-rGO sheets which is remarkably greater than that of rGO.

The structural changes of GO, r-GO, and decane-rGO were characterized by Raman spectroscopy (Figure 4). Pristine graphite has a weak band at 1,352 cm\(^{-1}\) (D band) and a strong band at 1,580 cm\(^{-1}\) (G band), that are attributed to structure defects and the first-order scattering of the E\(_{2g}\) vibrational mode in graphite sheets, respectively, and I(D)/I(G) value is about 0.1 that indicates the intact graphitic domains (Guo et al. 2011; Wu et al. 2012). The Raman spectrum of GO reveals that the two D and G peaks shift to higher wave numbers compared with those of graphite which are accompanied by enhancing the I(D)/I(G) value to 1.28. This increased value shows the enhancement in the defect-like amorphous domains, which is related to the isolation of carbon double bonds. The I(D)/I(G) value for r-GO is increased compared to the value of GO. This can be related to the enhancement of the
number of polyaromatic domains with smaller overall size in r-GO. Also, it can be attributed to the highly defected carbon lattice in r-GO (Wu et al. 2015). The Raman spectrum of decane-rGO shows that the G band intensity is increased and the D band becomes wider. This may be due to a small increase in the size of the sp² domains (Tessonier & Barteau 2012).

Characteristics of UF membranes

The role of decane-rGO on the surface morphology of PAN UF membranes was investigated using FE-SEM micrographs. Figure 5 illustrates the cross-sectional FE-SEM micrographs of the pristine and nanocomposite PAN membranes including 0.1, 0.2, and 0.3 wt% of the decane-rGO particles. The pristine PAN membrane shows a characteristic asymmetric porous structure (Figure 5(a)). In this picture, a kind of sponge-like structure is observed. The results demonstrate that when the decane-rGO content in PAN membrane is less than 0.2 wt%, the presence of hydrophilic agents on the rGO surface, such as hydroxyl, carboxyl, and epoxide groups, enhances the rate of exchange process between solvent and non-solvent. Moreover, the porosity of membranes is increased because of the presence of decane-rGO. The size of pores and their amounts are enhanced with increasing the decane-rGO loading up to 0.2 wt%. Increasing the size and pore values are confirmed by enhancing the water flux of membranes. In addition, the morphologies of the membranes modified with decane-rGO particles are different from those of the pristine PAN
membrane. The sponge-like pores in the pristine PAN membrane changed to a finger-like structure in the membrane containing up to 0.2 wt% of decane-rGO and the vertical holes were converted to horizontal holes by further increasing the decane-rGO concentration in the polymer matrix. When the decane-rGO amount surpassed 0.2 wt%, the porosity of the PAN/decane-rGO membrane was decreased. This is probably due to the increased viscosity of PAN/decane-rGO blend and this can hamper the exchange between solvent and non-solvent during the coagulation. Furthermore, the results reflect that by increasing the decane-rGO content to 0.3 wt%, the presence of non-polar decane groups on the synthesized rGO particles leads to enhancement of the non-polar nature of rGO sheets, consequently the prepared PAN/decane-rGO membrane is non-polar and exhibits hydrophobic behavior. This phenomenon is obviously observed in the FE-SEM image of the PAN/0.3 wt% decane-rGO membrane. The important point is the formation of completely horizontal holes for the PAN membrane/0.3 wt% decane-rGO membrane. Therefore, by the appropriate selection of the decane-rGO percent in preparing the PAN/decane-rGO membranes, the pore morphological structure in the PAN support layer can be controlled. This issue was clearly observed in the FE-SEM micrographs.

The hydrophilicity of the prepared membranes’ surface can be investigated by water contact angle measurement. Water contact angle is one of the common ways to measure the wettability of a surface that was measured by the sessile drop method. As can be seen in Figure 6, the hydrophilicity is enhanced by increasing the decane-rGO amount up to 0.2 wt%. This is possibly due to the presence of hydrophilic agents on the rGO surface, such as hydroxyl, carboxyl, and epoxide groups, that can increase the rate of exchange process between solvent and non-solvent, whereas 0.3 wt% decane-rGO doped membrane possesses a water contact angle of 52.92°. Thus, by increasing the decane-rGO content to 0.3 wt%, the non-polar decane groups on the rGO particles result in the enhancement of the membrane hydrophobicity. The results demonstrate that pristine PAN membrane has the highest water contact angle of 54.68°, hence this leads to the conclusion that the membrane surface is the most hydrophobic in nature.

The membranes were also studied for their surface roughness by AFM measurements. The AFM images of the prepared membranes are as shown in Figure 7. In these images, the brightest area shows the highest point of the membrane surface and the dark areas illustrate valleys. The topographical images indicate that the roughness is increased by adding 0.1 wt% decane-rGO to PAN matrix. The average roughness was increased from 31.61 nm (in pure PAN membrane) to 55.12 nm for 0.1 wt% PAN/decane-GO membrane. The roughness was increased again by addition of 0.2 wt% decane-rGO to the membrane. Indeed, roughness of the membrane surface was increased by mixing the decane-rGO particles with polymer matrix up to 0.2 wt% modified nanoparticles due to increasing the pore size of decane-rGO/PAN membrane. When the decane-rGO amount was increased to 0.3 wt%, the porosity of the PAN/decane-rGO membrane was decreased, hence due to an increase in pore size and agglomeration of modified nanoparticles, roughness of membrane surface was decreased.

**Evaluation of UF membranes performances**

The water flux of membranes is controlled by several factors such as hydrophilicity, pore size, and morphology of the membranes. The presence of hydrophilic groups in the modified nanoparticles increase the rate of exchange process between solvent and non-solvent, thus the porosity of membranes are increased up to 0.2 wt% decane-rGO. Increasing the size and pore values are also confirmed by enhancing the water flux of membranes. As shown in Figure 8(a), the water fluxes of both membranes prepared using GO and decane-rGO are increased using up to 0.2 wt% of filler nanoparticles, which can be related to the improvement in the hydrophilicity of these membranes.
because of the hydrophilic groups that are present on the GO and decane-rGO nanoparticles. The results show that water permeation is decreased by further increase of GO/decane-rGO concentration in the PAN matrix to 0.3 wt%. This can be attributed to the decrease in the pore sizes of the prepared membranes using a higher filler amount (0.3 wt%). It may be stated that in the case of decane-rGO membranes, the existence of non-polar decane agents on the decane-rGO particles plays a main role in the enhancement of the non-polar nature of rGO sheets. In addition, decreasing water permeation can be a result of increased viscosity of synthesized decane-rGO particles on the surface of 0.3 wt% decane-rGO/PAN membrane.

Comparing water fluxes of membranes fabricated using GO and decane-rGO, in Figure 8(a), reveals that the water flux has been slightly decreased in the membranes containing decane-rGO nanosheets so that the highest water fluxes are 27.2 and 26.1 L/m².h for the membranes loaded by GO and decane-rGO, respectively. It is obvious that the water flux values are very close to each other in both membranes and the slight decrease in the water flux of the decane-rGO membrane may probably be attributed to the presence of nearly long decane chains within the PAN polymeric matrix, which can affect (decrease) the water flux.

Salt rejection measurements were carried out using NaCl solution at a pressure of three bars. Figure 8(b) exhibits the variation of NaCl rejection of GO/PAN and decane-rGO/PAN membranes. The rejection of NaCl for the pristine PAN membrane was near 20.2% but, as shown in Figure 8(b), this was changed to about 35.8, 37.9, and 40.1% for the GO/PAN membranes containing 0.1, 0.2, and 0.3 wt% GO particles, respectively. The salt rejection parameter is increased because of the presence of GO nanoparticles with nano-flake structure. This subject is indicated clearly in yield salt rejection results. Nano-flake structure of GO particles acts as a big barrier and can prevent NaCl particles from passing into the membrane.
The salt rejections for the decane-rGO/PAN membranes were greater compared with those of their related GO/PAN membranes. Therefore, the presence of decane agents between the interlayers of rGO particles can increase the salt barrier, hence salt rejection parameter is increased. As shown in Figure 3, the diffraction peak of decane-rGO powder appears at 7.8° in the XRD pattern, corresponding to the interlayer of 1.13 nm, whereas the XRD pattern of GO shows a strong peak at 11.10°, which corresponds to an interlayer spacing of 0.8 nm. Consequently, the presence of decane groups between the interlayers of rGO nanoparticles can increase the space between rGO sheets and the exfoliation of decane-rGO particles in PAN matrix can be an important reason for increasing the salt rejection parameter of decane-rGO/PAN membranes. This is an appropriate result obtained for these membranes that can aid convenient water desalination (separation of pure water from salt). The greater salt rejections for the decane-rGO/PAN membranes relative to their corresponding GO/PAN membranes confirm the superior performance of modified decane-rGO particles.

It must be mentioned that the optimization study for salt rejection was not performed by preparing membranes with filler contents higher than 0.3 wt%, because in order to select the optimum membrane, both of the water flux and salt rejection results must be considered. Herein, the water flux is the highest using 0.2 wt% decane-rGO/PAN membrane and its salt rejection is also a high value, thus this membrane is chosen as the optimum modified membrane. Similar results were reported in the literature using other membranes. For instance, exfoliated graphite nanoplatelets (xGnPs) decorated by Au nanoparticles (Au NPs) were used as model hierarchical nanofillers in PS membranes. It was shown that the pure water flux was increased by increasing the xGnPs wt% from 0 to 2 wt% but the dextran rejection was first increased and then decreased using 0 to 2 wt% of xGnPs particles (Crock et al. 2015). Considering these results, they selected the membrane containing 1 wt% xGnPs as the optimum membrane because it showed both appropriate water flux and dextran rejection.

**Comparison with other UF membranes reported in the literature**

Three PAN UF membranes were prepared containing 0.5, 1, and 2 wt% of hydroxyl functionalized MWCNTs (Majeed et al. 2012). For the flux measurements, the transmembrane pressure was kept at 2 bar for 40 min to calculate the water flux. It was found that the water flux of the membranes was increased by 63% (~70 L/m².h) using 0.5 wt% of MWCNTs compared to neat PAN membrane (~40 L/m².h), but it was decreased upon further increase in the concentration of MWCNTs to near 50 L/m².h. The contact angle measurements proved that the surface hydrophilicity of the membranes was enhanced by the addition of MWCNTs so that the contact angle was decreased from ~50° in neat PAN membrane to ~42–43° in nanocomposite membranes; thus, the increased hydrophilicity improved the water flux. The SEM images of the cross sections of the membranes demonstrated that by introduction of MWCNTs, fewer but enlarged macrovoids were observed, especially in the membrane loaded by 2 wt% MWCNTs. Also, the dextran retention was...
slightly reduced from ~90% in neat PAN membrane to almost 85% in MWCNT containing membranes.

In another study, three weight percents (0.5, 1, and 2 wt%) of 3-aminopropyltriethoxysilane-functionalized graphene oxide (fGO) were used for the fabrication of PVDF UF membranes with enhanced antifouling and mechanical properties (Xu et al. 2014). The membranes were compacted at 0.1 MPa to get a steady flux. The contact angle measurements demonstrated that the hydrophilicity of the membranes was increased by the addition of fGO so that the contact angle was decreased from ~65° in neat PVDF membrane to ~50–55° in nanocomposite membranes. The water flux values were higher in the fGO loaded membranes compared with that of neat membrane and the maximum flux values were approximately 400 and 350 L/m².h for the nanocomposite and neat PVDF membranes.

Meng et al. (2015) prepared three PS UF membranes using trace amounts of GO (GO, 5, 10, and 20 mg/mL) in a 15%wt polymer solution. The contact angles of the PS, PS/GO-5, PS/GO-10, and PS/GO-20 membranes were obtained equal to 74.08, 69.2, 66.5, and 63.75°, respectively, reflecting the trace GO nanosheets in coagulation had a minor impact on the hydrophilicity of the membranes. It was found that compared with PS membrane, the fluxes of the PS/GO-5, PS/GO-10, and PS/GO-20 membranes were decreased by 35.3%, 68.4%, and 75.1%, respectively. The PEG rejection of the PS membrane was the highest (86.15%) but those of the PS/GO membranes were decreased to ~74–76%, which were all lower than that of the PS membrane, confirming the trace amounts of GO affected the membranes' pore sizes and distributions in the range of 5–20 mg/L.

CONCLUSIONS

Reduced GO was functionalized by decane groups and the presence of decane agents was investigated using FT-IR spectroscopy. By attaching decane groups to the rGO surface, the interlayer distance was increased to 1.13 nm. The structural changes of GO, rGO, and decane-rGO were characterized by Raman spectroscopy. The FE-SEM micrographs exhibited the porous morphology of the PAN/decane-rGO UF membranes. In addition, increasing the weight percents of the decane-rGO particles into the membrane led to the formation of horizontal holes. Increasing the size and pore values were confirmed by enhancing water flux of the membranes. The salt rejection values were increased for both kinds of GO/PAN and decane-rGO/PAN membranes which were attributed to the presence of GO nano-flakes and decane-rGO particles between the GO and rGO interlayers, respectively, leading to easier water desalination applications. The membrane containing 0.2 wt% decane-rGO showed maximum water flux and appropriate salt rejection; thus, it was selected as the optimum membrane.

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