

GRAPHENE OXIDE/POLYMER COMPOSITE MEMBRANES AND METHODS OF FORMING THEREOF

Technical Field

[0001] The invention relates to composite membranes, and in particular, to graphene oxide/polymer composite membranes having graphene oxide embedded in the polymer matrix. Methods for forming the graphene oxide/polymer composite membranes are also provided.

Background

[0002] In recent years, many advances have been made in the field of wastewater treatment. Conventional methods of wastewater treatment are costly to operate and require a lot of space to build. As the world population continues to grow at a fast rate, water scarcity occurs.

[0003] There is considerable development in membrane technology in wastewater treatment. The use of membrane significantly improves the capacity of current wastewater treatment facilities. A membrane is a type of thin film-like material that acts as a selective barrier to allow only some molecules to pass through, but not others.

[0004] Currently the biggest problem with conventional membranes is fouling due to deposition of macromolecules on the hydrophobic region of membrane. It has been widely understood that by increasing the membrane hydrophilicity, fouling can be effectively minimized. It is reported that polysulfone membranes blended with multi-walled carbon nanotube (MWNT) have slightly higher water flux than polysulfone membranes alone due to the higher hydrophilicity of MWNT than pure polysulfone membranes.

Summary

[0005] Graphene oxide has been known to be able to disperse in water (therefore it is hydrophilic) due to the ionizable –COOH group on the edge and can be a possible candidate to be used in increasing the hydrophilicity of membrane surface. Accordingly, present inventors have investigated blending polymer membranes with graphene oxide to form graphene oxide/polymer composite membranes and the resultant water filtration properties.

[0006] To this end, present inventors have surprisingly found that by using graphite in a form of nanofiber as a precursor of graphene oxide by first oxidizing the graphite nanofiber to graphite oxide, and subsequently blending the graphite oxide and exfoliating the graphite oxide to form graphene oxide in a polymer dope solution, followed by casting the polymer dope solution to form the graphene oxide/polymer composite membrane, the thus-produced composite membrane is able to achieve about 2.9 times higher flux than conventional polysulfone membranes and improves chemical oxygen demand (COD) rejection rate from 20.60% to 24.05%.

[0007] Thus, in a first aspect of the disclosure, there is disclosed a method for forming a graphene oxide/polymer composite membrane. The graphene oxide is embedded in the polymer matrix and not on the surface of the composite membrane. The method may include:

- (a) providing a container containing concentrated sulfuric acid and placing the container in an ice bath;
- (b) adding graphite nanofibers to the container of (a);
- (c) adding potassium permanganate to the container of (b);
- (d) removing the container of (c) from the ice bath;
- (e) adding hydrogen peroxide to the container of (d);

- (f) filtering the mixture of (e) to obtain a filter cake;
- (g) dispersing the filter cake of (f) in water and drying the dispersion to obtain graphite oxide;
- (h) adding the graphite oxide of (g) to a solvent to obtain a hydrosol mixture and sonicating the hydrosol mixture;
- (i) adding the hydrosol mixture of (h) to a polymer dope solution; and
- (j) casting the polymer dope solution of (i) by wet phase inversion technique to form the graphene oxide/polymer composite membrane.

[0008] In a second aspect of the disclosure, a method for forming a graphene oxide/polymer composite membrane is provided. The graphene oxide is embedded in the polymer matrix and not on the surface of the composite membrane. The method may include:

- (a) providing a container containing a mixture of concentrated sulphuric acid and concentrated phosphoric acid;
- (b) adding graphite nanofibers to the container of (a);
- (c) adding potassium permanganate to the container of (b);
- (d) adding hydrogen peroxide to the container of (c);
- (e) filtering the mixture of (d) to obtain a filter cake;
- (f) dispersing the filter cake of (e) in water and drying the dispersion to obtain graphite oxide;
- (g) adding the graphite oxide of (f) to a solvent to obtain a hydrosol mixture and sonicating the hydrosol mixture;
- (h) adding the hydrosol mixture of (g) to a polymer dope solution; and
- (i) casting the polymer dope solution of (h) by wet phase inversion technique to form the graphene oxide/polymer composite membrane.

[0009] In a third aspect of the disclosure, there is disclosed a method for forming a graphene oxide/polymer composite membrane. The graphene oxide is embedded in the polymer matrix and not on the surface of the composite membrane. The method may include:

- (a) providing a container containing concentrated sulphuric acid and placing the container in an ice bath at about 0 °C;
- (b) adding graphite nanofibers to the container of (a);
- (c) adding a first amount of potassium permanganate to the container of (b) and keeping the temperature of the mixture in the container at about 10 °C or below;
- (d) adding a second amount of potassium permanganate to the container of (c);
- (e) removing the container of (d) from the ice bath;
- (f) adding hydrogen peroxide to the container of (e);
- (g) filtering the mixture of (f) to obtain a filter cake;
- (h) dispersing the filter cake of (g) in water and drying the dispersion to obtain graphite oxide;
- (i) adding the graphite oxide of (h) to a solvent to obtain a hydrosol mixture and sonicating the hydrosol mixture;
- (j) adding the hydrosol mixture of (i) to a polymer dope solution; and
- (k) casting the polymer dope solution of (j) by wet phase inversion technique to form the graphene oxide/polymer composite membrane.

[0010] In a fourth aspect of the disclosure, a graphene oxide/polymer composite membrane including graphene oxide embedded in the polymer matrix is provided. The graphene oxide is embedded in the polymer matrix and not on the surface of the composite membrane.

Brief Description of the Drawings

[0011] In the drawings, like reference characters generally refer to the same parts throughout the different views. The drawings are not necessarily drawn to scale, emphasis instead generally being placed upon illustrating the principles of various embodiments. In the following description, various embodiments of the invention are described with reference to the following drawings.

[0012] **Fig. 1** shows SEM image of 0 wt% GO/PSF composite membrane top surface. From (a) to (d): magnification of membrane surface at 350x, 10,000x, 30,000x, and 60,000x.

[0013] **Fig. 2** shows SEM image of 0.5 wt% GO/PSF composite membrane top surface. From (a) to (d): magnification of membrane surface at 350x, 10,000x, 30,000x, and 60,000x.

[0014] **Fig. 3** shows SEM image of 1.0 wt% GO/PSF composite membrane top surface. From (a) to (d): magnification of membrane surface at 350x, 10,000x, 30,000x, and 60,000x.

Description

[0015] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the invention may be practised. These embodiments are described in sufficient detail to enable those skilled in the art to practise the invention. Other embodiments may be utilized and structural, logical, and electrical changes may be made without departing from the scope of the invention. The various embodiments are not necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

[0016] A selectively permeable membrane (or semipermeable membrane) allows passage of water molecules, but rejects solute molecules or ions. The membrane filters the impurities from a water source which is suspected to contain impurities including ions, leaving purified

water on the other side of the membrane called permeate water. The impurities left on the membrane may then be washed away, for example, by water which is also called "reject".

[0017] In one aspect of the invention, a graphene oxide/polymer composite membrane including graphene oxide embedded in the polymer matrix is provided.

[0018] In present context, the term "composite" refers generally to a mixture of materials physically mixed or blended, whereby each material in the mixture generally retains the respective property. The term "composite membrane" therefore refers to a membrane formed of a mixture of materials, and in present case, the composite membrane is formed of a mixture of graphene oxide and a polymer. More specifically, the graphene oxide is embedded in the polymer matrix. Unless otherwise stated, the present composite membrane may also be simply termed as a membrane for brevity.

[0019] In present context, by "embedded" is meant that any graphene oxide present in the composite membrane is located or dispersed in the polymer matrix. The dispersion may be uniform or random. More specifically, no graphene oxide can be found on the surface of the composite membrane. This finding is confirmed by SEM images shown in **Figs. 1 to 3**.

[0020] Graphene can be treated as a 10-layered graphite. Thus, a monolayer of graphene consist of a mono-atom thick sheet of sp^2 bonded carbon atoms. Graphene has a chemical structure that closely resemble benzene and other polycyclic aromatic hydrocarbon. Thus, graphene is assumed to have the same chemical properties as aromatic hydrocarbon. In order to obtain graphene, graphite can be chemically modified by oxidation reaction to form graphite oxide which is then reduced to obtain graphene. In graphene oxide, the carbon atoms are bonded to oxygen functional groups through covalent bonds.

[0021] Graphite oxide is formed by many layers of graphene oxide. Graphene oxide may be prepared by the chemical exfoliation of graphite oxide which is oxidized in potassium permanganate dissolved in the concentrated sulfuric acid. The smaller the graphene oxide sheets, the higher the hydrophilicity of graphene oxide. Graphene oxide can be used as the fillers due to its hydrophilic and pH sensitive behaviour.

[0022] In present case, the graphene oxide is formed by the exfoliation of graphite oxide, which in turn is formed by oxidation of graphite nanofiber. Carbon nanofibers and graphite nanofibers are not the same. The atomic structure of carbon nanofibers is similar to that of graphite consisting of sheets of carbon atoms (graphene sheets) arranged in a regular hexagonal pattern. The difference lies in the way these sheets interlock. Graphite is a crystalline material in which the sheets are stacked parallel to one another in regular fashion. The inter-molecular forces between the sheets are relatively weak van der Waals forces, giving graphite its soft and brittle characteristics (like a pencil lead).

[0023] Graphite nanofiber material may be produced by the decomposition of carbon-containing gases over metal catalyst particles at temperatures ranging from 400 °C to 800 °C.

[0024] Present inventors have specifically selected graphite nanofibers as the raw materials for producing graphene oxide due to its larger pore size making it easier to process. Also, the interaction between the graphene sheets in both carbon nanofibers and graphite nanofibers are different. When carbon nanofibers are blended into a polymer matrix, particles of carbon nanofibers are separated from each other. On the other hand, when graphite nanofibers are blended into a polymer matrix, each individual sheet of the graphene oxide layer which forms the graphene oxide is separated. The separation of graphene oxide layer is possible because the interaction between the layers is the weak van der Waals forces.

[0025] Accordingly, in various embodiments, the graphene oxide exists in the polymer matrix in a form of sheets exfoliated from graphite oxide. The graphene oxide sheets may be exfoliated from graphite oxide nanofibers.

[0026] Thus, in another aspect of the invention, a method for forming a graphene oxide/polymer composite membrane is disclosed. The graphene oxide is embedded in the polymer matrix and not on the surface of the composite membrane.

[0027] The method may first include (a) providing a container containing concentrated sulfuric acid and placing the container in an ice bath. Concentrated sulfuric acid is used as a pre-oxidizer for subsequent steps. Concentrated sulfuric acid serves two main functions: i) increase the interlayer spacing between the graphene oxide sheets, and ii) oxidize graphite to graphite oxide with disrupting the honey comb structure of the carbon sheets. The container is placed in an ice bath so as to keep the temperature of concentrated sulfuric acid low, such as below 35 °C or room temperature.

[0028] The method may then include (b) adding graphite nanofibers to the container of (a). A predetermined amount of graphite nanofibers may be weighed and added to the concentrated sulfuric acid.

[0029] Optionally, sodium nitrate may also be added together with the graphite nanofibers. Sodium nitrate functions as a pre-oxidizer as well but it does not increase the interlayer spacing like concentrated sulfuric acid do.

[0030] The method may further include (c) adding potassium permanganate to the container of (b). In this step, potassium permanganate is the oxidizer, oxidizing graphite nanofibers to graphite oxide nanofibers.

[0031] To promote the rate of oxidation, step (d) of the method may include removing the container of (c) from the ice bath. The reaction mixture temperature automatically increases and rate of oxidation is accelerated.

[0032] To terminate the oxidation process, the method may include (e) adding hydrogen peroxide to the container of (d) after a period of time.

[0033] Next, in step (f), the mixture of (e) may be filtered to obtain a filter cake, which may then be dispersed in water and the dispersion dried to obtain graphite oxide (g).

[0034] In subsequent step (h), the graphite oxide of (g) is added to a solvent to obtain a hydrosol mixture and the hydrosol mixture is sonicated. After this, in step (i), the hydrosol mixture of (h) may be added to a polymer dope solution, and finally the polymer dope solution of (i) is casted by wet phase inversion technique to form the graphene oxide/polymer composite membrane (j).

[0035] In various embodiments, the method may be carried out by maintaining the temperature of the container in steps (a), (b), and (c) at 35 °C or below. For example, the temperature of the container may be kept at 0 °C.

[0036] In an alternative aspect of the disclosure, a second method for forming a graphene oxide/polymer composite membrane is provided. The graphene oxide is embedded in the polymer matrix and not on the surface of the composite membrane.

[0037] The method may include:

- (a) providing a container containing a mixture of concentrated sulphuric acid and concentrated phosphoric acid,
- (b) adding graphite nanofibers to the container of (a);
- (c) adding potassium permanganate to the container of (b);

- (d) adding hydrogen peroxide to the container of (c);
- (e) filtering the mixture of (d) to obtain a filter cake;
- (f) dispersing the filter cake of (e) in water and drying the dispersion to obtain graphite oxide;
- (g) adding the graphite oxide of (f) to a solvent to obtain a hydrosol mixture and sonicating the hydrosol mixture;
- (h) adding the hydrosol mixture of (g) to a polymer dope solution; and
- (i) casting the polymer dope solution of (h) by wet phase inversion technique to form the graphene oxide/polymer composite membrane.

[0038] In carrying out the second method, an ice bath may not be required.

[0039] In yet another alternative aspect of the disclosure, a third method for forming a graphene oxide/polymer composite membrane is provided. The graphene oxide is embedded in the polymer matrix and not on the surface of the composite membrane.

[0040] The method may include:

- (a) providing a container containing concentrated sulphuric acid and placing the container in an ice bath at about 0 °C;
- (b) adding graphite nanofibers to the container of (a);
- (c) adding a first amount of potassium permanganate to the container of (b) and keeping the temperature of the mixture in the container at about 10 °C or below;
- (d) adding a second amount of potassium permanganate to the container of (c);
- (e) removing the container of (d) from the ice bath;
- (f) adding hydrogen peroxide to the container of (e);
- (g) filtering the mixture of (f) to obtain a filter cake;
- (h) dispersing the filter cake of (g) in water and drying the dispersion to obtain graphite oxide;

- (i) adding the graphite oxide of (h) to a solvent to obtain a hydrosol mixture and sonicating the hydrosol mixture;
- (j) adding the hydrosol mixture of (i) to a polymer dope solution; and
- (k) casting the polymer dope solution of (j) by wet phase inversion technique to form the graphene oxide/polymer composite membrane.

[0041] In all three methods, the solvent used to obtain a hydrosol mixture prior to casting the polymer dope solution to form the respective composite membrane may be 1-methyl-2-pyrrolidone (NMP) or N,N-dimethylacetamide (DMAc). The solvent selection may also be based on solubility, safety, cost and availability, and such selection may be apparent to a person skilled in the art.

[0042] In addition to identifying graphite nanofibers as raw materials for the present study, present inventors have also investigated optimal amount of graphene oxide for use in the composite membrane for wastewater treatment applications. Present inventors have prepared and tested membranes up to 3 wt% of graphene oxide present in the polymer matrix (based on total amount of graphene oxide and polymer). The polymer tested is polysulfone. The water flux is found to have increased to 1415.6 l/m².h or about 4.7 times as compared to 0 wt%, i.e. pure polymer membrane but the rejection rate remains at about the same level as that of 0.5 wt% (actually a reduction when compared to that of 1 wt%). This might be due to agglomeration of graphene oxide, which means there is more imperfection in the membrane which can create more porosity during the membrane casting. Formation of more pores than the allowable optimum level will increase water flux and reduce rejection rate. It is likely that the optimum level of present methodology is below 3 wt%. The nanoparticles tend to agglomerate back rather than being exfoliated when the concentration is high. Such

agglomeration may cause defects on the membrane. Although the tested polymer is polysulfone, it is believed that the above trend (i.e. improved permeability and rejection) would be the same except for the degree of improvement might be different depending on the level of exfoliation of graphene. The level of exfoliation may be determined by the molecular weight of the polymer, functional groups of the polymer, and viscosity of the polymer solution. Suitable polymers for forming the composite membrane include, but are not limited to, polysulfone, polyethersulfone, polyethylene, polyvinylidene fluoride, and polytetrafluoroethylene.

[0043] Accordingly, in all three methods described above, the thus-formed composite membrane may include up to 3 wt% of graphene oxide embedded in the polymer matrix, such as about 0.5 wt% or 1.0 wt%.

[0044] In summary, present study involves the combination of graphene oxide and a polymer to form a graphene oxide/polymer composite membrane. Specifically, graphene oxide is produced from graphite nanofiber and blended with the polymer to form the composite membrane.

[0045] The graphite nanofiber used herein is obtained from expanded graphite, which is produced at relatively low costs. In certain cases, these expanded graphites are by-products.

[0046] Present study shows that present graphene oxide produced from graphite nanofibers remains dispersed in water without sedimentation even after three weeks while it has been reported elsewhere that graphene oxide produced from flakes forms sediment when left overnight. For dispersions in NMP, sedimentation is only observed after two weeks. The ability to keep graphene oxide in a stable dispersion state for longer period is very important. In the stable dispersion state, graphene oxide is exfoliated and remains so. Therefore, its full

potential as nanomaterial can be expected because the surface area is at its optimum and the interaction with any substances in contact with exfoliated graphene oxide is at nanometer scale. Other nanofillers cannot be exfoliated fully and normally it is very hard to keep the structure exfoliated for longer period of time.

[0047] Moreover, among the three different methods described herein, the method of the first aspect gives the best results in terms of oxidation percentage. The XRD peak also shows that the structure of graphite nanofiber is different from graphite flakes where the common peaks for graphite oxide flakes of between 9 to 10.5° is not observed for the graphite nanofiber. In present case, the peaks are observed at angle $2\theta = 2^\circ$ which is very much different from graphite flakes. This clearly indicates that the interlayer spacing between the graphene oxide sheets is very much larger compared to graphite flakes. In water flux tests, present study shows a higher water flux despite a low 2.2 pressure bar pressure compared to existing work, which in turns leads significant operation cost savings due to the use of the graphite oxide in the form of nanofiber.

[0048] In order that the invention may be readily understood and put into practical effect, particular embodiments will now be described by way of the following non-limiting examples.

Examples

[0049] Chemical Reagents for Producing Graphite Oxide

[0050] The chemical reagents used to convert graphite nanofibers to graphite oxide through oxidation are all of analytical grade. Three different synthesis methods are proposed in order to determine the best and safest chemical route to oxidize graphite nanofiber to graphite oxide. The first method is called the conventional Hummers method, the second method is called the improved Hummers method, and the third method is called the modified Hummers method.

[0051] In the conventional Hummers method, sodium nitrate (NaNO_3) and potassium permanganate (KMnO_4) are purchased from Bendosen Laboratory Chemicals. Concentrated sulfuric acid (H_2SO_4) is bought from R&M Chemicals in 2.5 litres bottles. 30 wt% hydrogen peroxide (H_2O_2) is obtained from R&M Chemicals. Distilled water (H_2O) is obtained from the lab.

[0052] In the improved Hummers method, concentrated H_2SO_4 and concentrated phosphoric acid (H_3PO_4) are obtained from R&M Chemicals and ACI Labscan, respectively. KMnO_4 is purchased from Bendosen Laboratory Chemicals. 30 wt% H_2O_2 is purchased from R&M Chemicals.

[0053] In the modified Hummers method, concentrated H_2SO_4 is purchased from R&M Chemicals while KMnO_4 is bought from Bendosen Laboratory Chemicals. 30 wt% H_2O_2 is bought from R&M Chemicals.

[0054] The chemical reagents used in membrane casting are all of analytical grade and can be sourced from local suppliers. 1-methyl-2-pyrrolidone (NMP) solvent is obtained from QreC lab chemicals. Polysulfone (PSF) pellets of lab grade are obtained from USM material chemistry department. Distilled water is obtained from chemical lab.

[0055] Industrial grade high purity graphite nanofibers are obtained from Platinum NanoChem. It has both high purity and has more than 99 % yield of the final product. The individual graphene sheets are oriented perpendicular to the fiber growth axis with a spacing of 0.34 nm apart in a stacked card configuration.

[0056] Example 1: Procedure for Producing Graphite Oxide via Conventional Hummers Method

[0057] 57.5 ml of concentrated H_2SO_4 is added to a beaker and cooled to below $35\text{ }^\circ\text{C}$ in an ice bath for 10 minutes and stirred at 400 rpm. Next, 2.5 g of graphite nanofiber is added into the beaker together with 0.25 g of NaNO_3 . The mixture is then stirred for 10 minutes keeping the temperature below $35\text{ }^\circ\text{C}$. Next, 3.5 g of KMnO_4 is then added slowly to the mixture. After 10 minutes, all the KMnO_4 has been added. The beaker is then taken out of the ice bath. The mixture heats up producing a purplish vapour. The mixture then turns greyish purple brown. 100 ml of H_2O is then added to the solution. The mixture is continuously stirred for 20 minutes at $98\text{ }^\circ\text{C}$. For the termination step, 50 ml of a 10 wt% H_2O_2 (diluted from 30 wt% H_2O_2 initial concentration) is added to the mixture.

[0058] After the mixture has cooled down, it is filtered using filter paper in a Buchner funnel. The filter cake collected is then dispersed in aliquots solution of 5 % hydrochloric acid (HCl). The solution is first filtered through the filter paper grade 3 to obtain the filter cake. The filter cake is then dispersed in 4 l of H_2O and then centrifuged at 4,000 rpm for 15 minutes. The gel collected is re-dispersed with some H_2O and then dried in an oven for 2 days at $50\text{ }^\circ\text{C}$.

[0059] Example 2: Procedure for Producing Graphite Oxide via Improved Hummers Method

[0060] A 9:1 mixture of 220 ml concentrated H_2SO_4 and 80 ml concentrated H_3PO_4 is prepared in a beaker. Next, 3.2 g of high purity graphite nanofiber is added into the mixture and stirred at 300 rpm until the mixture is homogenized. Next, 12 g of KMnO_4 is added slowly over the course of 10 minutes. The mixture then turns greenish purple. The mixture is left to stir for 3 days for oxidation to take place. Lastly, for the termination step, about 100 ml of 10 wt% H_2O_2 is added into the mixture together with 400 ml of H_2O . The mixture is stirred then continuously for another 15 minutes.

[0061] For the washing and filtering step, the mixture is filtered using filter paper grade 3 in a Buchner funnel. The filter cake collected is then dispersed in 2 l aliquots solution of 5 % HCl. The solution is first filtered through a polyester cloth filter and then the filter paper grade 3 to obtain the filter cake. The filter cake is then dispersed in 4l of H₂O and then centrifuged at 4,000 rpm for 15 minutes. The gel collected is re-dispersed with H₂O and then dried in an oven for 2 days at 50 °C.

[0062] Example 3: Procedure for Producing Graphite Oxide via Modified Hummers Method

[0063] The experimental setup and procedure are similar to the one used in conventional Hummers method. 10 g of graphite nanofiber is added into a beaker of 115 ml of concentrated H₂SO₄ and cooled to 0 °C in an ice bath. After mixing the suspension for 30 minutes, about 1.5g of KMNO₄ is added in small portion to keep the reactor temperature below 10 °C. A dark blue color is observed in the suspension. 10 minutes later, 10 g of KMNO₄ is added to the suspension slowly. At the end of the KMNO₄ addition, the suspension is taken out of the ice bath and the suspension heats up to 35 °C. The suspension becomes pasty and brown. At the end of this 30 minute period, 450 ml of H₂O is added into the paste causing the temperature to increase to 90 °C. The diluted solution is now brownish in colour. For the termination step, about 35 ml of 30 wt% H₂O₂ diluted with 265 ml of H₂O is added into the solution.

[0064] For the washing and filtering step, the mixture is filtered using filter paper grade 3 in a Buchner funnel. The filter cake collected is then dispersed in 2 l aliquots solution of 5% HCl. The solution is first filtered the filter paper grade 3 to obtain the filter cake. The filter cake is then dispersed in 4 l of H₂O and then centrifuged at 4,000 rpm for 15 minutes. The gel collected is re-dispersed with H₂O and then dried in an oven for 2 days at 50 °C.

[0065] Example 4: Procedure for Producing Polymer Dope with 0 wt% Graphite Oxide

[0066] The well-established phase inversion technique is used to produce a polymer dope required for membrane casting. The weight ratio of polymer:solvent is 14:86. The polymer used in this example is polysulfone (PSF) with MW 17,000 g/mol obtained from Solvay. 14 g of PSF is weighed in a small beaker. Next, 86 g of NMP solvent is weighed in a beaker. The NMP solvent is poured into a round bottomed flask and heated to 65 °C. The magnetic stirrer is switched on. PSF pellets are then gradually added one teaspoon at a time into the NMP solution. The PSF pellets are allowed to dissolve overnight. Once all the PSF pellets have fully dissolved, the thus-obtained polymer dope solution is poured into a bottle and sonicated for at least 1 hour using a sonicator bath for degassing and to ensure mixture is homogenous.

[0067] Example 5: Procedure for Producing Polymer Dope with 0.5 wt% Graphite Oxide

[0068] 13.93 g of PSF pellets are weighed in a beaker. Next, 76 g of NMP is poured into a round bottomed flask. The mixture is allowed to dissolve at 65 °C overnight to form a polymer dope solution. A stable hydrosol mixture of graphite oxide with the NMP solvent is prepared prior to the experiment. 0.07 g of graphite oxide powder from Example 1 is weighed and poured into 10 g of NMP solvent inside a Schott Duran bottle and then sonicated. The graphite oxide hydrosol is then poured into the polymer dope solution. The polymer dope containing graphite oxide is then sonicated for 1 hour in a sample bottle.

[0069] Example 6: Procedure for Producing Polymer Dope with 1.0 wt% Graphite Oxide

[0070] 13.86 g of PSF pellets are weighed in a beaker. Next, 76 g of NMP is poured into a round bottomed flask. The mixture is allowed to dissolve at 65 °C overnight to form a polymer dope solution. A stable hydrosol mixture of graphite oxide with NMP solvent is prepared prior to the experiment. 0.14 g of graphite oxide powder from Example 1 is weighed and poured

into 10 g of NMP solvent inside a Schott Duran bottle and then sonicated. The graphite oxide hydrosol is then poured into the polymer dope solution.

[0071] All three polymer dopes with different concentration of graphite oxide (i.e. Examples 4, 5, and 6) are kept in three separate sample bottles.

[0072] Example 7: Experimental Procedure for Membrane Casting

[0073] The as-produced polymer dope solutions from Examples 4, 5, and 6 are casted using well-established wet phase inversion technique. In each run, the respective polymer dope solution is deposited onto a glass plate evenly. The solution is then cast using a doctors knife on the membrane casting machine. On the membrane casting machine, the required parameter is input into the machine. The freshly cast membrane is then immersed in a water bath, thereby forming a graphene oxide/polysulfone composite membrane. The membranes having 0 wt%, 0.5 wt%, and 1.0 wt% graphene oxide, respectively, is then subjected to performance test like pure water flux permeation and rejection rate test.

[0074] Analysis of Samples

[0075] The as-produced graphite oxide and polymer membrane are subjected to several characterization tests such as Fourier Transform Infrared Spectroscopy (FTIR) , X-ray diffraction (XRD), Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy EDX (SEM/EDX).

[0076] Membrane Performance Test

[0077] Example 8: Pure Water Flux Permeation

[0078] The three membranes (Examples 4, 5, and 6) casted using phase inversion with varying amount of graphene oxide nanofiller prepared using conventional Hummers method are subjected to performance test for pure water flux permeation using distilled water in a dead-

end filtration setup. A fixed transmembrane pressure of around 2.2 bar is used for all three membrane samples. The pure water flux permeation test is run with 50 ml of distilled water. The water flux equation (Eq. (1)) is given by:

$$J_i = \frac{V}{a \times t \times p} \quad \text{Eq. (1)}$$

where

J_i = Water flux ($\frac{L}{m^2 h bar}$)

v = Volume of water

a = Membrane area

t = time

p = Transmembrane pressure (TMP)

[0079] Example 9: Rejection Rate of Membrane using Chemical Oxygen Demand (COD) Test

[0080] A synthetic wastewater solution is prepared using OECD peptone synthetic wastewater standard. About 10 ml of the synthetic wastewater solution is diluted to 300 ml with distilled water and then poured into a dead-end filtration cell and then capped tight with the respective membrane of Examples 4, 5, and 6 acting as a filtration medium. The filtrate is collected after passing through the membrane. Three membrane samples containing graphene oxide with concentration of 0 wt% , 0.5 wt% and 1 wt%, respectively, are tested at a transmembrane pressure of 2.2 bar.

[0081] The collected filtrate of the synthetic wastewater is subjected to COD test using the Hach method. A Hach high range plus COD reagent vial is used in conjunction with a colorimetry test to determine the COD value. The sample collected is diluted 100 times with

deionized water using serial dilution technique. About 0.2 ml of the diluted sample is pipetted into the reagent vial. A blank reagent vial is also prepared using deionized water. The reagent vial is then capped and placed into a COD block digester and heated to 150 °C for 2 hours. At the end of the 2 hours, the reagent vials are allowed to cool to room temperature. A DR-6000 UV-vis spectrophotometer is used to determine the COD value. A blank is first inserted into the machine to zero the value. Next, the reagent vial containing the respective sample is placed into the machine and the COD value is then read from the display.

[0082] Results

[0083] Example 10: Characterisation of as-produced Graphite Oxide (GO) - IR Spectrum of Graphite Oxide

[0084] 3 samples of graphite oxide labeled S01, S02 and S03 are prepared using the three different methods (conventional Hummers method, improved Hummers method and modified Hummers method per Examples 1, 2, and 3, respectively). The infrared (IR) spectrum of graphite oxide was recorded using a Nicolet 8700 spectrophotometer in KBr pellets. The spectra were recorded from 4,000 cm^{-1} to 400 cm^{-1} . **Table 1** shows the IR spectra of each individual graphite oxide sample.

Table 1: Infrared spectrum of graphite oxide sample from Fourier Transform Infrared**Spectroscopy (FTIR)**

Band (cm ⁻¹)	Samples (cm ⁻¹)			Vibration
	01	02	03	
3200 - 3550	3402	3400	3368	O-H stretch & COOH vibration
1710	1710	-	-	C=O stretch
1600 & 1500	1610	1587	1583	C=C ring stretching
1240 - 1040	1052	1054	1055	C-O-C stretching

[0085] Example 11: Characterisation of as-produced Graphite Oxide (GO) - X-ray Diffraction (XRD) of Graphite Oxide

[0086] The three graphite oxide samples are subjected to powder XRD test. The scanning speed is 1°/min with a degree range of 0 – 70°. Samples S01, S02 and S03 are produced using conventional Hummers method, improved Hummers method, and modified Hummers method, respectively. According to established literature, graphite oxide samples exhibit a characteristic peak at around 10.9°. However, such peak is not observed in all three present samples. **Table 2** shows the XRD results obtained from the three samples tested.

Table 2: XRD diffraction peak of graphite oxide sample

Samples	Strongest Peak (2θ)		
	01	02	03
S01	2.28	1.32	3.54
S02	0.5075	1.30	2.3555
S03	2.1	1.343	2.500

[0087] Example 12: Characterisation of as-produced Graphite Oxide (GO) - Scanning Electron Microscopy-EDX of Graphite Oxide

[0088] Scanning electron microscopy with energy dispersive x-ray (SEM-EDX) is used as a quantitative test. The EDX analysis of the three graphite oxide samples is obtained to determine their degree of oxidation. **Table 3** shows the concentration of carbon, oxygen and other element for the three graphite oxide sample. Samples 01, 02 and 03 refer to graphite oxide produced by conventional Hummers method, Improved Hummers method, and modified Hummers method, respectively.

Table 3: EDX concentration of element in graphite oxide sample

Elements	Samples (Atomic%)		
	01	02	03
C	73.95	74.87	73.91
O	25.64	24.73	25.58
S	0.16	0.11	0.07
Cl	0	0.02	0.03
K	0	0.04	0
Ca	0.03	0.04	0.25
Mn	0	0.03	0
Ni	0	0.02	0
Cu	0.11	0.07	0.10
Zn	0.10	0.06	0.07

[0089] Example 13: Characterisation of Membrane Samples with Varying GO Concentration - Fourier Transform Infrared Spectroscopy (FTIR) of Membrane

[0090] The three membrane samples labelled S1, S2 and S3 containing varying graphene oxide concentration of 0 wt%, 0.5 wt% and 1.0 wt%, respectively, are subjected to FTIR test. A square shaped membrane with a dimension of 2cm x 2cm is cut and then placed into the FTIR machine for analysis. The functional group corresponding to polysulfone is the S=O asymmetric stretch and the S=O sulfone symmetric stretch.

Table 4: Infrared spectrum of membrane sample from Fourier Transform Infrared

Spectroscopy (FTIR).

Band (cm ⁻¹)	Samples (cm ⁻¹)			Vibration
	1	2	3	
3200-3550	3542	3548	3537	O-H stretch & COOH vibration
1710-1780	-	1747	1744	Carbonyl C=O stretch
1630 - 1695	-	1636	1637	C=O (amide I) vibration
1240	1234	1241	1240	C-O-C stretching
2966	2963	2968	2966	S=O asymmetric stretch
1140 ± 20	1149	1151	1150	S=O sulfone symmetric stretch

[0091] Example 14: Characterisation of Membrane Samples with Varying GO Concentration - Scanning Electron Microscopy (SEM) of Membrane Surface

[0092] The membranes with varying concentration of graphene oxide samples labelled S1, S2 and S3 each with 0 wt%, 0.5 wt% and 1.0 wt%, respectively, are scanned in SEM at magnification from 350x up to 60,000x. The respective membrane is coated with platinum particles prior to the scan. The samples are placed on a disc and held in place with scotch tape.

Fig. 1, Fig. 2, and Fig. 3 show the SEM image of membrane sample S01, S02, and S03, respectively, with different magnification level.

[0093] Example 15: Graphene Oxide (GO)/PSF Composite Membrane Performance Test - Pure Water Flux Permeation Test

[0094] The effect of increase in GO loading in the membrane is studied using pure water flux permeation test. Three samples labeled S1, S2 and S3 with 0 wt%, 0.5 wt% and 1.0 wt% graphene oxide are prepared using the same polymer concentration of 14 wt% PSF dissolved in 86 wt% NMP solvent. The time taken to collect 50 ml of distilled water is recorded for each sample. **Table 5** shows the time taken to collect 50 ml of distilled water for each membrane.

Table 5: Time taken to collect 50 mL of distilled water at 2.2 bar pressure.

Samples	Time (s)	Water flux $\frac{L}{m^2 hr}$
S1	585	302.28
S2	446	396.45
S3	205	863.28

[0095] Example 16: Graphene Oxide (GO)/PSF Composite Membrane Performance Test - COD Rejection Rate Test

[0096] The three membrane samples are subjected to a rejection rate test using chemical oxygen demand (COD) as an indicator. The filtrate is collected in sample bottles for all three membrane S1, S2 and S3 with 0 wt%, 0.5 wt% and 1.0 wt% graphene oxide nanofiller. A Hach COD HR+ reagent vial is used together with a DR-6000 UV-vis spectrophotometer to determine the COD value of the samples. **Table 6** shows the COD result obtained.

Table 6: COD result for three samples collected from the membrane S1, S2 and S3

Samples	COD value (mg/l)	Rejection rate (%)
Blank (unfiltered)	9230	-
S1	7330	20.60
S2	7220	21.78
S3	7010	24.05

[0097] Example 17: Modulus Value (Tensile Modulus) Test

[0098] Three types of membranes, namely, i) polysulfone membrane; ii) polysulfone+graphene oxide (0.1wt%) membrane, and iii) polysulfone+graphene oxide (0.5 wt%) membrane, are compared in terms of their modulus value. The results are shown in Table 7.

Table 7: Modulus values of the different types of membranes.

No.	Type of membrane	Modulus value (MPa)
1.	Polysulfone membrane	0.41
2.	Polysulfone+graphene oxide (0.1wt%) membrane	0.46
3.	Polysulfone+graphene oxide (0.5wt%) membrane	0.51

[0099] It is found that the modulus values of the polysulfone membrane increased from 0.41 MPa to 0.46 MPa when the polysulfone membrane is incorporated with 0.1 wt% of graphene oxide. To increase the concentration of the graphene oxide from 0.1 wt% to 0.5 wt% in the polysulfone membrane would also increase the modulus value of the membrane from 0.46 MPa to 0.51 MPa. It shows that graphene oxide is able to enhance the stiffness of an elastic polymer such as polysulfone membrane.

[00100] By "comprising" it is meant including, but not limited to, whatever follows the word "comprising". Thus, use of the term "comprising" indicates that the listed elements are required or mandatory, but that other elements are optional and may or may not be present.

[00101] By "consisting of" is meant including, and limited to, whatever follows the phrase "consisting of". Thus, the phrase "consisting of" indicates that the listed elements are required or mandatory, and that no other elements may be present.

[00102] The inventions illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for example, the terms "comprising", "including", "containing", etc. shall be read expansively and without limitation. Additionally, the terms and expressions employed herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the inventions embodied therein herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention.

[00103] By "about" in relation to a given numerical value, such as for temperature and period of time, it is meant to include numerical values within 10% of the specified value.

[00104] The invention has been described broadly and generically herein. Each of the narrower species and sub-generic groupings falling within the generic disclosure also form part of the invention. This includes the generic description of the invention with a proviso or

negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

[00105] Other embodiments are within the following claims and non- limiting examples. In addition, where features or aspects of the invention are described in terms of Markush groups, those skilled in the art will recognize that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group.

Claims

1. A method for forming a graphene oxide/polymer composite membrane, wherein graphene oxide is embedded in the polymer matrix, the method comprising:
 - (a) providing a container containing concentrated sulfuric acid and placing the container in an ice bath;
 - (b) adding graphite nanofibers to the container of (a);
 - (c) adding potassium permanganate to the container of (b);
 - (d) removing the container of (c) from the ice bath;
 - (e) adding hydrogen peroxide to the container of (d);
 - (f) filtering the mixture of (e) to obtain a filter cake;
 - (g) dispersing the filter cake of (f) in water and drying the dispersion to obtain graphene oxide nanofibers;
 - (h) adding the graphene oxide nanofibers of (g) to a solvent to obtain a hydrosol mixture and sonicating the hydrosol mixture;
 - (i) adding the hydrosol mixture of (h) to a polymer dope solution; and
 - (j) casting the polymer dope solution of (i) by wet phase inversion technique to form the graphene oxide/polymer composite membrane.
2. The method of claim 1, wherein in steps (a), (b), and (c), the temperature of mixture in the container is maintained at 35 °C and below.
3. The method of claim 1 or 2, wherein the composite membrane comprises up to 3 wt% of graphene oxide embedded in the polymer matrix.
4. The method of claim 3, wherein the composite membrane comprises up to 1 wt% of graphene oxide embedded in the polymer matrix.

5. The method of claim 4, wherein the composite membrane comprises about 0.5 wt% of graphene oxide embedded in the polymer matrix.
6. The method of any one of claims 1 to 5, wherein the solvent of (h) is 1-methyl-2-pyrrolidone (NMP) or N,N-dimethylacetamide (DMAc).
7. The method of any one of claim 1 to 6, wherein in step (b) adding graphite nanofibers to the container of (a) comprises adding sodium nitrate simultaneously with the graphite nanofibers.
8. A method for forming a graphene oxide/polymer composite membrane, wherein graphene oxide is embedded in the polymer matrix, the method comprising:
 - (a) providing a container containing a mixture of concentrated sulphuric acid and concentrated phosphoric acid;
 - (b) adding graphite nanofibers to the container of (a);
 - (c) adding potassium permanganate to the container of (b);
 - (d) adding hydrogen peroxide to the container of (c);
 - (e) filtering the mixture of (d) to obtain a filter cake;
 - (f) dispersing the filter cake of (e) in water and drying the dispersion to obtain graphite oxide nanofibers;
 - (g) adding the graphite oxide nanofibers of (f) to a solvent to obtain a hydrosol mixture and sonicating the hydrosol mixture;
 - (h) adding the hydrosol mixture of (g) to a polymer dope solution; and
 - (i) casting the polymer dope solution of (h) by wet phase inversion technique to form the graphene oxide/polymer composite membrane.

9. The method of claim 8, wherein the composite membrane comprises up to 3 wt% of graphene oxide embedded in the polymer matrix.
10. The method of claim 9, wherein the composite membrane comprises up to 1 wt% of graphene oxide embedded in the polymer matrix.
11. The method of claim 10, wherein the composite membrane comprises about 0.5 wt% of graphene oxide embedded in the polymer matrix.
12. The method of any one of claims 8 to 11, wherein the solvent of (g) is 1-methyl-2-pyrrolidone (NMP) or N,N-dimethylacetamide (DMAc).
13. A method for forming a graphene oxide/polymer composite membrane, wherein graphene oxide is embedded in the polymer matrix, the method comprising:
 - (a) providing a container containing concentrated sulphuric acid and placing the container in an ice bath at about 0 °C;
 - (b) adding graphite nanofibers to the container of (a);
 - (c) adding a first amount of potassium permanganate to the container of (b) and keeping the temperature of the mixture in the container at about 10 °C or below;
 - (d) adding a second amount of potassium permanganate to the container of (c);
 - (e) removing the container of (d) from the ice bath;
 - (f) adding hydrogen peroxide to the container of (e);
 - (g) filtering the mixture of (f) to obtain a filter cake;
 - (h) dispersing the filter cake of (g) in water and drying the dispersion to obtain graphite oxide nanofibers;
 - (i) adding the graphite oxide nanofibers of (h) to a solvent to obtain a hydrosol mixture and sonicating the hydrosol mixture;

- (j) adding the hydrosol mixture of (i) to a polymer dope solution; and
- (k) casting the polymer dope solution of (j) by wet phase inversion technique to form the graphene oxide/polymer composite membrane.
14. The method of claim 13, wherein the composite membrane comprises up to 3 wt% of graphene oxide embedded in the polymer matrix.
 15. The method of claim 14, wherein the composite membrane comprises up to 1 wt% of graphene oxide embedded in the polymer matrix.
 16. The method of claim 15, wherein the composite membrane comprises about 0.5 wt% of graphene oxide embedded in the polymer matrix.
 17. The method of any one of claims 13 to 16, wherein the solvent of (i) is 1-methyl-2-pyrrolidone (NMP) or N,N-dimethylacetamide (DMAc).
 18. A graphene oxide/polymer composite membrane comprising graphene oxide embedded in the polymer matrix, wherein the graphene oxide exists in a form of sheets exfoliated from graphite oxide nanofibers.
 19. The composite membrane of claim 18, wherein the polymer is polysulfone or polyethersulfone.
 20. The composite membrane of claim 18 or 19, wherein the X-ray diffraction peak of the graphene oxide to be embedded in the polymer matrix at 2θ is 2° .