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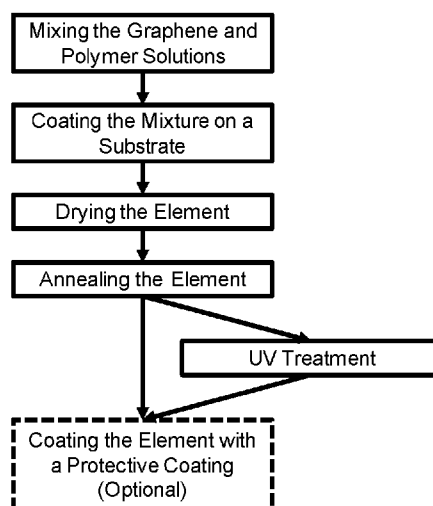
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(54) Title: CHLORINE RESISTANT MEMBRANE WITH SERICIN CROSS-LINKED GRAPHEN OXIDE COMPOUND AND METHOD FOR MAKING THE SAME

FIG. 2: Graphene Selectively Permeable Fabrication Methodology



(57) Abstract: In one form, a selectively permeable membrane is protected from degradation due to exposure to chlorine-based oxidants. Some embodiments include selectively permeable membrane elements having a protective coating comprising graphene oxide and sericin that are permeable to water but impermeable to solutes. In one form, the graphene oxide and sericin are crosslinked, and the protective coating may include one or more other crosslinking compounds.

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CHLORINE RESISTANT MEMBRANE WITH SERICIN CROSS-LINKED
GRAPHEN OXIDE COMPOUND AND METHOD FOR MAKING THE SAME

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CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Patent Application No. 62/864,366, filed June 20, 2019, the contents of which are incorporated herein by reference in their entirety.

BACKGROUND

As the human population increases, there has been a corresponding demand for safe drinking water. There has also been interest in new technologies for the desalination of sea water and purification of waste water streams. Reverse osmosis membranes have been used for the generation of potable water from saline water. However, these membranes suffer from various shortcomings. Many current reverse osmosis membranes have a thin-film composite (TFC) configuration with a thin aromatic polyamide selective layer on top of a microporous substrate, typically a polysulfone membrane on a non-woven polyester. Although these membranes can provide excellent salt rejection and high-water flux, the reverse osmosis processes in which they are used lack desired energy efficiency.

Reverse osmosis membranes can also be compromised by fouling resulting from algae growth, which may cause a decrease of water flux and higher energy consumption. One current response to fouling resulting from algae growth has been to incorporate chlorine or chloramine into the aqueous feed solution in order to suppress the growth of biological species on the reverse osmosis membrane surface. However, chlorine and chloramine, even if used at low levels, may be detrimental to the reverse osmosis membrane structure and cause a decrease in salt rejection and water flux. Thus, there remains a need for additional contributions in this technology.

The subject matter claimed herein is not limited to implementations that solve any disadvantages or that operate only in environments such as those described above. Rather, this background is only provided to illustrate one example technology area where some implementations described herein may be practiced.

SUMMARY

This Summary is provided to introduce a selection of concepts in a simplified form that are further described below in the Detailed Description. This Summary is not intended to identify key features or essential characteristics of the claimed subject matter, nor is it intended to be used as an aid in determining the scope of the claimed subject matter.

In one embodiment, a selectively permeable membrane element includes a membrane or porous support, and a protective coating including a crosslinked mixture of a graphene oxide compound and a crosslinker including sericin. The protective coating is disposed on a surface of the membrane or porous support and is effective for protecting the membrane or porous support from chlorine degradation.

In another embodiment, a desalination method includes applying to a selectively permeable membrane element a saline solution including at least one salt and water in a manner effective for providing a portion of the solution that passes through the selectively permeable membrane element with a lower salt content. The selectively permeable membrane element includes a membrane or porous support, and a protective coating including a crosslinked mixture of a graphene oxide compound and a crosslinker including sericin. The protective coating is disposed on a surface of the membrane or porous support and is effective for protecting the membrane or porous support from chlorine degradation.

In still another embodiment, a method of making a selectively permeable membrane element includes the steps of (1) mixing a graphene oxide compound and sericin; (2) applying the resulting mixture on a membrane or porous support to form a protective coating on said membrane or said porous support; and (3) curing the selectively permeable membrane element to facilitate crosslinking within the mixture.

Additional features and advantages of the invention will be set forth in the description which follows, and in part will be obvious from the description, or may be learned by the practice of the invention. The features and advantages of the invention may be realized and obtained by means of the instruments and combinations particularly pointed out in the appended claims. These and other features of the present invention will become more fully

apparent from the following description and appended claims, or may be learned by the practice of the invention as set forth hereinafter.

BRIEF DESCRIPTION OF THE DRAWINGS

To further clarify the above and other advantages and features of the present invention, a more particular description of the invention will be rendered by reference to specific embodiments thereof which are illustrated in the appended drawings. It is appreciated that these drawings depict only typical embodiments of the invention and are therefore not to be considered limiting of its scope. The invention will be described and explained with additional specificity and detail through the use of the accompanying drawings.

FIG. 1 is a schematic illustration of a protective coated selectively permeable membrane element.

FIG. 2 is a schematic illustration of one non-limiting process for making a selectively permeable membrane element.

FIG. 3 is a schematic illustration of a test cell in which a selectively permeable membrane element may be placed for mechanical strength and salt rejection testing.

DETAILED DESCRIPTION

Reference will now be made to the drawings to describe various aspects of example embodiments of the invention. It is to be understood that the drawings are diagrammatic and schematic representations of such example embodiments, and are not limiting of the present invention, nor are they necessarily drawn to scale.

The present disclosure generally relates to a selectively permeable membrane element. More particularly, but not exclusively, the present disclosure relates to a selectively permeable membrane element which includes a protective coating which is effective for protecting the membrane element from chlorine degradation. The protective coating may be disposed on a surface of a membrane or porous support, and it may include a crosslinked mixture of a graphene oxide compound and a sericin. It will be appreciated that embodiments disclosed herein may be employed in fields and/or operating environments where the

functionality disclosed herein may be useful in addition to or in lieu of those disclosed herein. Accordingly, the scope of the invention should not be construed to be limited to the exemplary implementations and operating environments disclosed herein.

Certain graphene materials have properties which may be desirable for various applications. Among these is a 2-dimensional sheet-like structure having nanometer scale thickness and high mechanical strength. Graphene oxide, which may be prepared from the exfoliative oxidation of graphite, can be mass produced at a low cost. Graphene oxide is unique in that it contains oxygen groups on its surface that can readily react with various nucleophiles to create a more functionalized surface. The oxygen groups of graphene oxide are generally hydroxyl groups, carboxyl groups, or epoxide groups which can react with a variety of molecules including but not limited to amines, amides, alcohols, carboxylic acids and sulfonic acids. Unlike traditional membranes, where water is transported through the pores of the material, in graphene oxide membranes the transportation of water can be between the interlayer spaces. The capillary effect of graphene oxide may result in long water slip lengths that offer fast water transportation rates. Additionally, the selectivity and water flux of a graphene oxide membrane may be tuned by manipulating the interlayer distance of the graphene sheets. In some cases, this manipulation may be accomplished by crosslinking. In addition, the surface of graphene oxide contains a large number of carbon-carbon double bonds, which can chemically react with and absorb chlorine and chloramine.

The present disclosure relates to a selectively permeable membrane element which includes a hydrophilic composite material with resistance to chlorine fouling, low organic compound permeability, and desired mechanical and chemical stability and which may be useful in a reverse osmosis membrane. In one aspect, the composite material is highly hydrophilic and provides high mechanical and chemical stability. The selectively permeable membrane elements disclosed herein may be suitable for purifying drinking water, or for waste water treatment, amongst other possibilities. Some selectively permeable membrane elements described herein are graphene oxide-based membrane elements having a high-water flux along with resistance to detrimental effects to the membrane structure caused by chlorine and chloramine (hereinafter referred to as “chlorine fouling”, which may result in

improved efficiency of the reverse osmosis membranes and improved water recovery/separation efficiency.

A graphene oxide-based membrane element may include one or more filtering layers, where at least one layer may include a composite protective coating which includes a graphene oxide compound crosslinked with a hydrophilic biopolymer. In some embodiments, the hydrophilic biopolymer may be the silk protein sericin. In some embodiments, the protective coating may be formed by reacting a graphene oxide compound with a crosslinker including sericin. It is believed that crosslinking a graphene oxide compound with sericin may protect the membrane elements from chlorine fouling. In addition, the membrane elements described herein may be prepared using water as a solvent, reducing environmental impact and increasing cost effectiveness of the related manufacturing process.

In some embodiments, a selectively permeable membrane element described herein may be suitable for the desalination of seawater or purification of unprocessed fluids. One or more of the selectively permeable membrane elements may be useful for solute removal from an unprocessed fluid, for example in waste water treatment. In some forms, one or more of the selectively permeable membrane elements may be suitable for fluid streams exposed to chlorinated solutions. In some embodiments, the selectively permeable membrane elements disclosed herein can be useful in preventing chlorine fouling. The selectively permeable membrane elements described herein may be useful in the removal of water/water vapor from an unprocessed fluid. In some forms, the selectively permeable membrane elements disclosed herein may have a high rate of water flux. In some forms, the selectively permeable membrane elements disclosed herein may have a high level of salt rejection. In some embodiments, one or more of the selectively permeable membrane elements described herein may include a protective coating, and the protective coating may chemically absorb chlorine and resist chlorine degradation.

In some embodiments, a selectively permeable membrane element may include a porous support and a protective coating, and the protective coating may include a crosslinked graphene oxide compound. The crosslinked graphene oxide compound may be formed by reacting a mixture of a graphene oxide compound and a sericin crosslinker. In some embodiments, the protective coating mixture may be disposed on a surface of the membrane

or porous support, and the protective coating may protect the membrane or porous support from chlorine fouling. For example, as illustrated in FIG. 1, a selectively permeable membrane element **100** includes a membrane or porous support **120** and a protective coating **110** is coated or disposed onto the membrane or porous support **120**.

In some embodiments, the membrane or porous support **120** may be a polymer. In some embodiments, the polymer may be polyethylene, polypropylene, polysulfone, polyether sulfone, polyvinylidene fluoride, polyamide, polyimide, and/or mixtures thereof, just to provide a few examples. In one particular but non-limiting forms, the polymer may be polysulfone. In some forms, the membrane or porous support may include a polyamide. In some embodiments, the polyamide may include a selective membrane. In one particular but non-limiting form, the polyamide may include ESPA. In some embodiments, the membrane or porous support may be a reverse osmosis membrane.

In some embodiments, the membrane or porous support may include hollow fibers. The hollow fibers may, for example, be cast or extruded. The hollow fibers may be made according to a variety of techniques, including for example those described in United States Patent Numbers 4,900,626 and 6,805,730 and United States Patent Application Publication No. 2015/0165389.

In some embodiments, the membrane or porous support may include a surface for fluid communication or contact with a chlorine solution (e.g., the protective coating). In some embodiments, a protective coating can be disposed upon the membrane or porous support's surface, which is in fluid communication with a chlorine solution. The protective coating may include a crosslinked graphene oxide compound in some forms. The crosslinked graphene oxide compound may be formed by reacting a mixture of a graphene oxide compound with a hydrophilic biopolymer crosslinker. In some embodiments, the hydrophilic biopolymer may include sericin. In some forms, the crosslinked graphene oxide compound can be formed by reacting a mixture of a graphene oxide compound with a crosslinker including sericin. In some embodiments, the protective coating may include an optionally substituted graphene oxide compound and a sericin crosslinker in fluid communication. In some forms, the protective coating including an optionally substituted graphene oxide material and a sericin crosslinker can be disposed on a surface of the membrane or porous support. In some embodiments,

the graphene oxide compound and the sericin crosslinker are crosslinked. In some embodiments, the fluid passing through the selectively permeable membrane element travels through all of the components regardless of whether they are in physical communication or order of arrangement.

In some embodiments, the protective coating includes a graphene oxide compound. In some embodiments, the graphene oxide compound may include graphene oxide, a reduced graphene oxide, a functionalized graphene oxide, or combinations thereof. In some embodiments, the graphene oxide compound may be an optionally substituted graphene oxide. In some forms, the optionally substituted graphene oxide may be arranged amongst the crosslinker material in such a manner as to create an exfoliated nanocomposite, an intercalated nanocomposite, or a phase-separated micro-composite. A phase-separated micro-composite phase may occur when, although mixed, the optionally substituted graphene oxide exists as a separate and distinct phase apart from the crosslinker. An intercalated nanocomposite may occur when the crosslinker compounds begin to intermingle amongst or between the graphene platelets, but the graphene material may not be distributed throughout the crosslinker. In an exfoliated nanocomposite phase, the individual graphene platelets may be distributed within or throughout the crosslinker. An exfoliated nanocomposite phase may be achieved by chemically exfoliating the graphene material by a modified Hummer's method, a process known to persons skill in the art. In some embodiments, the majority of the graphene material may be staggered to create an exfoliated nanocomposite as a dominant material phase.

As used herein, a graphene oxide may include any graphene having hydroxyl substituents and saturated carbon atoms. In some embodiments, a modified graphene may include a functionalized graphene base. In some embodiments, more than about 90%, about 80-90%, about 70-80%, about 60-70%, about 50-60%, about 40-50%, about 30-40%, about 20-30%, or about 10-20%, or any other percentage in a range bounded by these values, of the optionally substituted graphene oxide may be functionalized. In other embodiments, the majority of optionally substituted graphene oxide may be functionalized. In still other embodiments, substantially all the optionally substituted graphene oxide may be functionalized. In some embodiments, the functionalized graphene oxide may include a

graphene base and functional compound. In some embodiments, a graphene base may be “functionalized,” becoming functionalized graphene when there are one or more types of functional groups present. In some embodiments, the graphene oxide compound may be functionalized as a result of synthesis reactions, such as in graphene oxide where epoxide-based functional groups are formed. In some embodiments, the graphene oxide compound may be selected from reduced graphene oxide and/or graphene oxide. In some embodiments, the graphene oxide compound may be graphene oxide, reduced-graphene oxide, functionalized graphene oxide, functionalized reduced-graphene oxide or combinations thereof.

In some embodiments, the optionally substituted graphene oxide may be in the form of sheets, planes or flakes. In some embodiments, the graphene material may have a surface area of between about 100 m²/gm to about 5000 m²/gm. In some embodiments, the graphene material may have a surface area of about 100-200 m²/gm, about 200-300 m²/gm, about 300-400 m²/gm, about 400-500 m²/gm, about 500-600 m²/gm, about 600-700 m²/gm, about 700-800 m²/gm, about 800-900 m²/gm, about 900-1000 m²/gm, about 1000-2000 m²/gm, about 2000-3000 m²/gm, about 3000-4000 m²/gm, or about 4000-5000 m²/gm, or any surface area in a range bounded by these surface areas.

In some embodiments, the graphene oxide may be in the form of platelets having one or more dimensions in the nanometer to micron range. In some embodiments, the platelets may have dimensions in the x, y and/or z dimension. For example, the platelets may have: an average x dimension between about 0.05 μm to about 50 μm, about 0.05-0.1 μm, about 0.1-0.2 μm, about 0.2-0.3 μm, about 0.3-0.4 μm, about 0.4-0.5 μm, about 0.5-0.6 μm, about 0.6-0.7 μm, about 0.7-0.8 μm, about 0.8-0.9 μm, about 0.9-1 μm, about 1-2 μm, about 2-5 μm, about 5-10 μm, about 10-20 μm, about 20-30 μm, about 30-40 μm, about 40-50 μm, about 0.05-1 μm, or any value in a range bounded by any of these lengths; an average y dimension between about 0.05 μm to about 50 μm, about 0.05-0.1 μm, about 0.1-0.2 μm, about 0.2-0.3 μm, about 0.3-0.4 μm, about 0.4-0.5 μm, about 0.5-0.6 μm, about 0.6-0.7 μm, about 0.7-0.8 μm, about 0.8-0.9 μm, about 0.9-1 μm, about 1-2 μm, about 2-5 μm, about 5-10 μm, about 10-20 μm, about 20-30 μm, about 30-40 μm, about 40-50 μm, about 0.05-1 μm, or any value in a range bounded by any of these lengths; and an average z dimension between about 0.3

nm to about 50 μm , about 0.3-0.4 nm, about 0.4-0.5 nm, about 0.5-1 nm, about 1-10 nm, about 10-50 nm, about 0.05-0.1 μm , about 0.1-0.2 μm , about 0.2-0.3 μm , about 0.3-0.4 μm , about 0.4-0.5 μm , about 0.5-0.6 μm , about 0.6-0.7 μm , about 0.7-0.8 μm , about 0.8-0.9 μm , about 0.9-1 μm , about 1-2 μm , about 2-5 μm , about 5-10 μm , about 10-20 μm , about 20-30 μm , about 30-40 μm , about 40-50 μm , about 0.05-1 μm , or any value in a range bounded by any of these lengths. In some embodiments, the platelets include an average size of about 0.05 μm to about 50 μm , about 0.05-0.1 μm , about 0.1-0.2 μm , about 0.2-0.3 μm , about 0.3-0.4 μm , about 0.4-0.5 μm , about 0.5-0.6 μm , about 0.6-0.7 μm , about 0.7-0.8 μm , about 0.8-0.9 μm , about 0.9-1 μm , about 1-2 μm , about 2-5 μm , about 5-10 μm , about 10-20 μm , about 20-30 μm , about 30-40 μm , about 40-50 μm , about 0.05-1 μm , or any size in a range bounded by any of these values.

In some embodiments, the optionally substituted graphene oxide may be unsubstituted. In some embodiments, the optionally substituted graphene oxide may comprise a non-functionalized graphene base. In some embodiments, the graphene material may comprise a functionalized graphene base prepared by any suitable method.

In some embodiments, the mass percentage of the graphene oxide base relative to the total composition of the protective coating can be between about 1 wt% and about 95 wt%. In some embodiments, the mass percentage of the graphene oxide base relative to the total composition of the graphene material containing layer can be about 1-2 wt%, about 2-5 wt%, about 5-10 wt%, about 10-20 wt%, about 20-30 wt%, about 30-40 wt%, about 40-50 wt%, about 50-60 wt%, about 60-70 wt%, about 70-80 wt%, about 80-90 wt%, or about 90-95 wt%.

In some aspects, there may be a large number (~30%) of nucleophiles such as epoxy groups and carboxyl groups on the graphene oxide, which may be readily reactive with amino and/or hydroxyl groups at elevated temperatures. Typically, the sericin crosslinker contains a combination of polar side groups, such as hydroxyl groups and amine groups. Sericin comprises 18 different amino acids, and about 32% of the amino acids are serine. The sericin chain contains numerous free amino and free hydroxyl nucleophilic pendent groups which may covalently crosslink with graphene oxide. The crosslinked graphene oxide-sericin protective layer may have chlorine-reactive sites such as amide linkages (-CONH-), free

hydroxyl groups (-OH), and free amine groups (-NH₂). These reactive functional groups may act as chlorine-sensitive or chlorine-reactive sites on the graphene oxide-sericin protective layer and therefore operate as sacrificial sites for chlorine reactivity, allowing for the extended durability of the polyamide layer. Graphene oxide may also have a high aspect ratio which provides a large available gas/water diffusion surface over that of other materials and has the ability to decrease the effective pore diameter of any substrate supporting material to minimize contaminant infusion while retaining flux rates. The epoxy or hydroxyl groups of graphene oxide may increase the hydrophilicity of the materials, and thus contribute to the increase in water vapor permeability and selectivity of the membrane.

Unless otherwise indicated, when a compound or chemical structure, such as graphene oxide, is referred to as being “optionally substituted,” it includes a compound or chemical structure that has no substituents (i.e., unsubstituted), or has one or more substituents (i.e., substituted). The term “substituent” includes a moiety that replaces one or more hydrogen atoms attached to a parent compound or structure. In some embodiments, a substituent may be any type of group that may be present on a structure of an organic compound, which may have a molecular weight (e.g., the sum of the atomic masses of the atoms of the substituent) of about 15-50 g/mol, about 15-100 g/mol, about 15-150 g/mol, about 15-200 g/mol, about 15-300 g/mol, or about 15-500 g/mol. In some embodiments, a substituent comprises or consists of: about 0-30, about 0-20, about 0-10 or about 0-5 carbon atoms; and about 0-30, about 0-20, about 0-10 or about 0-5 heteroatoms, wherein each heteroatom may independently be: N, O, S, Si, F, Cl, Br, or I; provided that the substituent includes one C, N, O, S, Si, F, Cl, Br, or I atom. Examples of substituents include, but are not limited to, alkyl, alkenyl, alkynyl, heteroalkyl, heteroalkenyl, heteroalkynyl, aryl, heteroaryl, hydroxy, alkoxy, aryloxy, acyl, acyloxy, alkylcarboxylate, thiol, alkylthio, cyano, halo, thiocarbonyl, O-carbamyl, N-carbamyl, O-thiocarbamyl, N-thiocarbamyl, C-amido, N-amido, S-sulfonamido, N-sulfonamido, isocyanato, thiocyanato, isothiocyanato, nitro, silyl, sulfenyl, sulfinyl, sulfonyl, haloalkyl, haloalkoxyl, trihalomethanesulfonyl, trihalomethanesulfonamido, amino, etc.

For the sake of clarity, and as suggested above, the term “molecular weight” may be used with respect to a moiety or part of a molecule to indicate the sum of the atomic masses

of the atoms in the moiety or part of the molecule, even though it may not be a complete molecule.

As used herein the term “fluid” means any substance that continually deforms, or flows, under an applied shear stress, such as gases, liquids, and/or plasmas.

As used herein, the term “fluid communication” means that the individual components, membranes, or layers, referred to as being in fluid communication are arranged such that a fluid passing through the membrane travels through all the identified components regardless of whether they are in physical communication or order of arrangement.

As used herein the term “chlorine resistant” refers to the permeable membrane having a substantially similar or reduced membrane activity loss when exposed to chlorine, chloramine or hypochlorites in the fluid medium.

In some embodiments, the protective coating may further include at least one additional crosslinker. In some embodiments, the at least one additional crosslinker may be calcium chloride (CaCl_2), potassium tetraborate ($\text{K}_2\text{B}_4\text{O}_7$, or KBO), poly(ethylene glycol) diglycidyl ether (PEG-DE), and/or combinations thereof.

In some embodiments, the mass ratio of a graphene oxide compound to sericin in the protective coating may be from about 1:100 to about 15:1. In some embodiments, the weight ratio of optionally substituted graphene oxide to optionally substituted crosslinker may be from about 1:100 to about 15:1 (e.g. 15 mg graphene oxide and 1 mg sericin), about 1:90, about 1:80, about 1:70, about 1:60, about 1:50, about 1:40, about 1:30, about 1:20, about 1:10, about 1:1, about 2:1, about 3:1, about 4:1, about 5:1, about 10:1, about 15:1, or any ratio in a range bounded by any of these values. In some forms, the weight ratio of optionally substituted graphene oxide to optionally substituted crosslinker may be about 1:11, about 1:2.3, about 1:1.45, about 1:1, about 1.04:1; about 1.58:1, or about 2.5:1.

In some embodiments, the sericin can be about 15-95 wt%, about 20-30 wt%, about 30-40 wt%, about 40-50 wt%, about 50-60 wt%, about 60-70 wt%, about 70-80 wt%, about 80-90 wt%, about 90-95 wt%, or any weight percentage in a range bounded by any of these values, of the total weight percentage of the protective coating. In some more particular but

non-limiting forms, the ranges may encompass about 28 wt%, about 38 wt%, about 48 wt%, about 50 wt%, about 58 wt%, about 68 wt%, about 78 wt%, or about 88 wt%.

In some embodiments, the graphene oxide may be about 5-75 wt%, about 5-15 wt%, about 15-25 wt%, about 25-35 wt%, about 35-45 wt%, about 45-55 wt%, about 55-65 wt%, about 65-75 wt%, or any weight percentage in a range bounded by any of these values, of the total weight of the protective coating. In some more particular but non-limiting forms, the ranges may encompass about 8 wt%, about 30 wt%, about 40 wt%, about 50 wt%, about 60 wt%, or about 70 wt%.

In some embodiments, the additional crosslinker may include calcium chloride (CaCl_2). The calcium chloride may be about 0-10 wt%, about 0-1 wt%, about 1-8 wt%, about 1-10 wt%, about 1-2 wt%, about 2-3 wt%, about 3-4 wt%, about 4-5 wt%, about 5-6 wt%, about 6-7 wt%, about 7-8 wt%, about 8-9 wt%, about 9-10 wt%, about 1-3 wt%, about 3-5 wt%, or any weight percentage in a range bounded by any of these values, of the total weight of the protective coating. In some forms, the ranges may encompass one or more of the following weight percentages: about 2 wt% and about 4 wt%.

In some embodiments, the additional crosslinker may include potassium tetraborate ($\text{K}_2\text{B}_4\text{O}_7$). The potassium tetraborate can be about 0-10 wt%, about 0-1 wt%, about 1-8 wt%, about 1-10 wt%, about 1-2 wt%, about 2-3 wt%, about 3-4 wt%, about 4-5 wt%, about 5-6 wt%, about 6-7 wt%, about 7-8 wt%, about 8-9 wt%, about 9-10 wt%, about 1-3 wt%, about 3-5 wt%, or any weight percentage in a range bounded by any of these values, of the total weight percentage of the protective coating. In some forms, the ranges may encompass one or more of the following weight percentages: about 2 wt% and about 4 wt%.

In some embodiments, the additional crosslinker may include poly(ethylene glycol) diglycidyl ether (PEG-DE). The PEG-DE can be about 0-10 wt%, about 0-1 wt%, about 1-8 wt%, about 1-10 wt%, about 1-2 wt%, about 2-3 wt%, about 3-4 wt%, about 4-5 wt%, about 5-6 wt%, about 6-7 wt%, about 7-8 wt%, about 8-9 wt%, about 9-10 wt%, about 1-3 wt%, about 3-5 wt%, or any weight percentage in a range bounded by any of these values, of the total weight percentage of the protective coating. In some forms, the ranges may encompass one or more of the following weight percentages: about 2 wt% and about 4 wt%.

Some examples of a selectively permeable membrane element, e.g., selectively permeable membrane element **100** in FIG. 1, include a membrane or porous support and a protective coating. In some embodiments, the selectively permeable membrane element may include a membrane or porous support, e.g., membrane or porous support **120**, and a protective coating, e.g., protective coating **110**. In some embodiments, as shown in FIG. 1, the selectively permeable membrane may comprise a protective coating, and the protective coating can protect the components of the membrane or porous support from chlorinated environments and/or solutions. In some embodiments, the protective coating may include graphene oxide cross-linked with sericin. In some embodiments, the protective coating may be disposed on the surface of the membrane or porous support. The surface of the element can be exposed to, or in fluid communication with, a solution containing chlorine, hypochlorites, or other chlorine oxides. In some embodiments, the membrane or porous support may include any of the previously described copolymers. In some embodiments, the selectively permeable membrane element may include a separate salt rejection layer of a membrane construct. In some embodiments, the membrane or porous support may contain polyamide.

In some embodiments, a selectively permeable membrane element may be permeable to water while being impermeable to gas, solute, or liquid material from passing therethrough. In some embodiments, as a result of the layers, the selectively permeable membrane element may provide a durable desalination system that can be selectively permeable to water, and less permeable to salts. In some embodiments, as a result of the layers, the selectively permeable membrane element may provide a durable reverse osmosis system that may effectively filter or desalinate saline/polluted water or feed fluids. In some forms, the selectively permeable membrane element with a protective coating may provide any or all of the above-mentioned functions. In some examples, the selectively permeable membrane element with a protective coating can provide substantially similar flux and/or salt rejection during or after contact with a chlorinated solution.

In some embodiments, a protective coating including a graphene oxide/sericin mixture can also include at least one additional crosslinker. In some embodiments, the at least one additional crosslinker may be CaCl_2 , $\text{K}_2\text{B}_4\text{O}_7$, PEG-DE and/or a combination thereof.

In forms where the protective coating includes at least one additional crosslinker, the weight ratio of the additional crosslinker to graphene oxide can be from about 1:35 (e.g., 1 mg of additional crosslinker to 35 mg of graphene oxide) to about 1:2, about 1:35 to about 1:30, about 1:30 to about 1:25, about 1:25 to about 1:20, about 1:20 to about 1:15, about 1:15 to about 1:10, about 1:10 to about 1:5, about 1:5 to about 1:2, or about 1:2, about 1:15, about 1:20, about 1:25, about 1:30, about 1:35, or any weight ratio in a range bounded by any of these values.

In some embodiments where the protective coating includes the at least one additional crosslinker, the additional crosslinker may be about 0.5-6 wt%, about 1-5 wt%, about 2-4 wt%, about 0.5-1 wt%, about 1-2 wt%, about 2-3 wt%, about 3-4 wt%, about 4-5 wt%, or about 5-6 wt% of the total weight of the protective coating, or any wt% in a range bounded by any of these values. In some forms the ranges may encompass one or more of the following weight percentages: about 2 wt%, about 3 wt%, about 4 wt% and about 5 wt%.

The protective coating may have a thickness ranging from about 5-2500 nm, about 50-2500 nm, about 500-1000 nm, about 1000-1500 nm, about 1500-2000 nm, about 2000-2500 nm, about 10-1000 nm, about 50-900 nm, about 50-800 nm, about 50-700 nm, about 50-600 nm, about 50-500 nm, about 50-400 nm, about 50-300 nm, about 100-200 nm, about 200-300 nm, about 300-400 nm, about 400-500 nm, about 500-600 nm, about 600-700 nm, about 700-800 nm, about 800-900 nm, about 900-1000 nm, 1000-1100 nm, about 1100-1200 nm, about 1200-1300 nm, about 1300-1400 nm, about 1400-1500 nm, about 1500-1600 nm, about 1600-1700 nm, about 1700-1800 nm, about 1800-1900 nm, about 1900-2000 nm, about 2000-2100 nm, about 2100-2200 nm, about 2200-2300 nm, or about 600 nm, about 1300 nm, about 1400 nm, about 1500 nm, about 1600 nm, about 1700 nm, about 1800 nm, about 1900 nm, about 2000 nm, about 2100 nm, about 2200 nm, about 2300 nm, or any thickness in a range bounded by any of these values. In some forms, the ranges may encompass the following thicknesses: about 600 nm, about 1300-1400 nm, about 1500-1600 nm, about 1700-1800 nm, about 1800-1900 nm, about 2100-2200 nm and about 2200-2300 nm.

In some embodiments, the selectively permeable membrane element can provide a flux of about greater than at least 5 gallons per square feet per day (GFD), at least about 5-10

GFD, at least about 10-20 GFD, at least about 20-30 GFD, at least about 30-40 GFD, at least about 40-50 GFD, at least about 50-60 GFD, at least about 60-70 GFD, or at least about 5.0 GFD, or any flux in a range bounded by any of these values.

In some embodiments the selectively permeable membrane element can provide a resistance to chlorine deterioration. In some embodiments, the selectively permeable membrane may maintain at least 75%, 75-80%, 80-85%, 85-90%, 90-95% 95-100%, or at least 100% of the original flux rate over a period of time, e.g., of at least about 100 hours, about 100-200 hours, about 200-300 hours, about 300-400 hours, about 400-500 hours, about 500-600 hours, about 600-700 hours, about 700-800 hours, about 800-900 hours, about 900-1000 hours, about 1000-1200 hours, about 12-00-1400 hours, about 1400-1600 hours, about 1600-1800 hours, about 1800-2000 hours, about 2000-4000 hours, about 4000-6000 hours, about 6000-8000 hours, about 8000-10000 hours, or at least about 10,000 hours, or any time period in a range bounded by any of these time periods.

In some embodiments, the selectively permeable membrane may maintain at least about 75%, about 75-80%, about 80-85%, about 85-90%, about 90-95%, about 95-100%, or at least about 100% of the original flux rate after being in contact with an amount of chlorine exposure, e.g., of at least about 100 ppm·h, about 100-200 ppm·h, about 200-300 ppm·h, about 300-400 ppm·h, about 400-500 ppm·h, about 500-600 ppm·h, about 600-700 ppm·h, about 700-800 ppm·h, about 800-900 ppm·h, about 900-1000 ppm·h, about 1000-1200 ppm·h, about 1200-1400 ppm·h, about 1400-1600 ppm·h, about 1600-1800 ppm·h, about 1800-2000 ppm·h, about 2000-4000 ppm·h, about 4000-6000 ppm·h, about 6000-8000 ppm·h, 8 about 000-10000 ppm·h, about 10000-12000 ppm·h, about 12000-14000 ppm·h, about 14000-16000 ppm·h, about 16000-18000 ppm·h, about 18000-20000 ppm·h, about 20000-30000 ppm·h, about 30000-40000 ppm·h, or at least about 40000 ppm·h, or any amount of chlorine exposure in a range bounded by any of these values.

In some embodiments, the selectively permeable membrane may maintain at least about 75%, about 75-80%, about 80-85%, about 85-90%, about 90-95%, or about 95-100%, or at least about 80% of the original salt rejection rate after being in contact with an amount of chlorine exposure, e.g., of at least about 100 ppm·h, about 100-200 ppm·h, about 200-300 ppm·h, about 300-400 ppm·h, about 400-500 ppm·h, about 500-600 ppm·h, about 600-700

ppm·h, about 700-800 ppm·h, about 800-900 ppm·h, about 900-1000 ppm·h, about 1000-1200 ppm·h, about 1200-1400 ppm·h, about 1400-1600 ppm·h, about 1600-1800 ppm·h, about 1800-2000 ppm·h, about 2000-4000 ppm·h, about 4000-6000 ppm·h, about 6000-8000 ppm·h, about 8000-10000 ppm·h, about 10000-12000 ppm·h, about 12000-14000 ppm·h, about 14000-16000 ppm·h, about 16000-18000 ppm·h, about 18000-20000 ppm·h, about 20000-30000 ppm·h, about 30000-40000 ppm·h, or about 40000-43000 ppm·h, or any amount of chlorine exposure in a range bounded by any of these values.

In one embodiment, a method for preparation of the aforescribed selectively permeable membrane element includes applying a protective coating (which may include one material or a mixture of materials) to a membrane or porous support by any suitable coating method, and then exposing the resulting membrane to a temperature of about 70 °C to about 120 °C for about 30 seconds to about 15 minutes.

In some embodiments, a selectively permeable membrane element described herein may be used in an arrangement where it is disposed between or separates a fluidly communicated first fluid reservoir and a second fluid reservoir. In some forms, the first reservoir may contain an unprocessed fluid, e.g., a feed fluid or solution, upstream and/or at the membrane. In some embodiments, the feed fluid or solution may include chlorine, hypochlorites, or other chlorine oxides. In some forms, the second reservoir may contain a processed fluid downstream and/or at the membrane. In some embodiments, the selectively permeable membrane element can allow passing of water therethrough while retaining the solute or contaminant fluid material. In some embodiments, the selectively permeable membrane element may allow filtering to selectively remove solute and/or suspended contaminants from feed fluid. In some embodiments, the selectively permeable membrane element may provide a desired flow rate. In some embodiments, the selectively permeable membrane element may provide a desired flux rate. In some embodiments, the selectively permeable membrane element can provide the desired flow rate and/or flux rate over a desired period of time, e.g., as described elsewhere herein. In some embodiments, the selectively permeable membrane element can maintain the desired salt rejection rate over a desired period of time, e.g., as described elsewhere herein. In some embodiments, the selectively permeable membrane element may comprise ultrafiltration material. In some

embodiments, the selectively permeable membrane element may comprise additional crosslinkers described herein.

In one embodiment a method of desalinating water includes applying a saline water that includes one or more salts and water to a selectively permeable membrane element described herein. In one form, the saline water is applied to the selectively permeable membrane element so that some of the water passes through the element, while at least some of the salt does not pass through the element, to yield water with a lower salt content.

Other embodiments include a method of making a selectively permeable membrane element which includes the steps of: (1) mixing a graphene oxide compound and a sericin crosslinker to form a protective coating mixture; (2) applying the resulting mixture on a membrane or porous support to form a protective coating on the membrane or porous support; (3) repeating step (2) as necessary to achieve a protective layer in a desired thickness; and (4) curing the protective coated membrane or porous support to facilitate crosslinking within the mixture. In some embodiments, step (1) further includes the addition of an additional crosslinker comprising calcium chloride (CaCl_2), potassium tetraborate ($\text{K}_2\text{B}_4\text{O}_7$), poly(ethylene glycol) diglycidyl ether (PEG-DE), or a combination thereof. In one form, the desired thickness may be, for example, between about 100 nm and about 2500 nm. In this or another form, the curing may be performed at a temperature of 70 °C to 120 °C for 30 seconds to 15 minutes.

In some embodiments, the protective coating mixture may be blade coated on a permeable substrate to create a thin film between about 100 nm to about 2500 nm, e.g., and may then cast on a substrate to form a partial element. In some embodiments, the mixture may be disposed upon the substrate—which may be permeable, or porous—by spray coating, dip coating, spin coating and/or other methods for deposition of the mixture on a substrate known to those skilled in the art. In some embodiments, the casting may be done by co-extrusion, film deposition, blade coating or any other suitable method for deposition of a film on a substrate. In some embodiments, the mixture is cast onto a substrate by blade coating (or tape casting) by using a doctor blade and dried to form a partial element. The thickness of the resulting cast tape may be adjusted by changing the gap between the doctor blade and the moving substrate. In some embodiments, the gap between the doctor blade and the

moving substrate is in the range of about 0.002 mm to about 1.0 mm, although other variations are contemplated. In some embodiments, the gap between the doctor blade and the moving substrate is preferably between about 0.20 mm to about 0.50 mm. In some embodiments, the gap between the doctor blade and the moving substrate is about 10 mil. The speed of the moving substrate may have a rate in the range of about 30 cm/min to about 600 cm/min. By adjusting the moving substrate speed and the gap between the blade and moving substrate, the thickness of the resulting protective coating layer may be expected to be between about 400 nm and about 2500 nm although other variations are possible.

EXAMPLES

The following examples are intended to be illustrative, and are not intended to limit the scope or underlying principles disclosed herein in any way.

Example 1.1.1: Preparation of Protective Coating Mixture.

Graphene Oxide Solution Preparation: Graphene oxide (GO) was prepared from graphite using a modified Hummers method. Graphite flake (2.0 g MilliporeSigma, 100 mesh) was oxidized in a mixture of NaNO_3 (2.0 g), KMnO_4 (10 g) and concentrated 98% H_2SO_4 (96 mL) at 50 °C for 15 hrs. The resulting pasty mixture was poured into ice (400 g) followed by the addition of 30% hydrogen peroxide (20 mL). The solution was then stirred for two (2) hours to reduce manganese dioxide, then filtered through filter paper and washed with DI water. The solid was collected and dispersed in DI water by stirring followed by centrifugation at 6,300 rpm for 40 minutes. Following the centrifugation, the aqueous layer was decanted. The remaining solid was dispersed in DI water and the washing step was repeated four (4) more times. The purified GO was then dispersed in DI water under sonication (20 W) for 2.5 hours, resulting in a 0.4 % GO dispersion.

Example 1.1.2: GO-Sericin coating preparations:

Composition GO/Sericin = 50/50 (T1): In a vial, 7.62 mL of GO solution (0.4 % in water), 0.61 mL of sericin solution (5 % in water), and 0.04 mL water were added, and the resulting solution was stirred for 15 minutes. Once mixed, the solution was poured on to a ESPA2+ substrate (Hydranautics, Oceanside, CA, USA) which was mounted on a coating station under vacuum and coated onto the substrate with a 10 mil spacer. The coated sample was then allowed to dry under vacuum for at least 20 minutes and finally baked inside an oven at 110 °C for 8 minutes.

Composition GO/Sericin/KBO = 50/48/2 (T2): In a vial, 7.82 mL of GO solution (0.4 % in water), 0.6 mL of sericin solution (5 % in water), and 0.062 mL KBO solution (2 % in water) were added, and the resulting solution was stirred for 15 minutes. Once mixed, the solution was poured on to an ESPA2+ substrate (Hydranautics, Oceanside, CA, USA) which was mounted on a coating station under vacuum and coated onto the substrate with a 10 mil

spacer. The coated sample was then allowed to dry under vacuum for at least 20 minutes and finally baked inside an oven at 110 °C for 8 minutes.

Composition GO/Sericin/CaCl₂= 50/48/2 (T3-A): In a vial, 7.82 mL of GO solution (0.4 % in water), 0.6 mL of sericin solution (5 % in water), and 0.062 mL CaCl₂ solution (2 % in water) were added, and the resulting solution was stirred for 15 minutes. Once mixed, the solution was poured on to an ESPA2+ substrate (Hydranautics, Oceanside, CA, USA) which was mounted on a coating station under vacuum and coated onto the substrate with a 10 mil spacer. The coated sample was then allowed to dry under vacuum for at least 20 minutes and finally baked inside an oven at 110 °C for 8 minutes.

Composition GO/Sericin/PEG-DE= 50/48/2 (T4-C): In a vial, 7.82 mL of GO solution (0.4 % in water), 0.6 mL of sericin solution (5 % in water), and 0.062 mL PEG-DE solution (2 % in water) were added, and the resulting solution was stirred for 15 minutes. Once mixed, the solution was poured on to an ESPA2+ substrate (Hydranautics, Oceanside, CA, USA) which was mounted on a coating station under vacuum and coated onto the substrate with a 10 mil spacer. The coated sample was then allowed to dry under vacuum for at least 20 minutes and finally baked inside an oven at 110 °C for 8 minutes.

Additional coatings were prepared according to the above examples except the ratios of additives listed in Table 1, below, were adjusted accordingly.

Example 1.1.3: Measurement of Selectively Permeable Elements

Mechanical Strength Testing: The water flux of graphene oxide-sericin based protective coated porous/support substrates were found to be very high, which is comparable with porous polysulfone substrates which are widely used in current reverse osmosis membranes.

To test the mechanical strength capability, the membranes were tested by placing them into a laboratory apparatus similar to the one shown in FIG 3. Once secured in the test apparatus, the membrane was exposed to the unprocessed fluid at a gauge pressure of 50 PSI. The water flux through the membrane was recorded at different time intervals to see the flux over time. The initial water flux was recorded, shown in Table 1. From the data

collected, it was shown that the graphene oxide-sericin based membrane can withstand reverse osmosis pressures while providing sufficient flux.

Chlorine resistance of GO-Sericin Coated Membranes:

To test the chlorine resistance of the GO-sericin coated membranes, an aqueous chlorine solution was prepared using 200 ppm chlorine and 500 ppm CaCl_2 . Commercially available Clorox® chlorine bleach was employed as the chlorine source. For each film with a 3" diameter treatment area, the top surface of the film was placed in contact with one liter of the aqueous chlorine solution. The concentration of the aqueous chlorine solution was regularly checked and adjusted to 200 ppm of chlorine, if needed. The unit of measurement of the chlorine treatment unit is ppm-h (for example, treatment of the film for 10 hours with 200 ppm concentration solution (200 ppm * 10 hours = 2,000 ppm-h)). The water flux of the GO-sericin based membrane coated on a porous support was observed to be very high, which is comparable with porous polysulfone substrate widely used in current reverse osmosis membranes.

After treatment with the aqueous chlorine solution, the flux and the salt rejection capability of the chlorine-exposed reverse osmosis membranes were tested in a test cell similar to that shown in FIG. 3. To test the chlorine-exposed membranes' ability to reject salt and retain adequate water flux, the membranes were exposed to a 1500 ppm NaCl solution at 225 psi. After approximately 120 minutes when the membrane reached steady state, the salt rejection and the water flux was recorded. Results are shown in Table 2. The chlorine-exposed membranes coated with GO-sericin and GO-sericin plus an additional crosslinker demonstrated high NaCl salt rejection and good water flux as compared to the comparative membrane.

Table 1. Initial salt rejection and water flux of GO-Sericin coated Membranes

Example	Composition	Thickness	Chlorine Exposure	Flux	Rejection
	weight ratio	nm	ppm-h	(GFD)	(%)
T1	GO/Sericin= 50/50	1843	0	20.9	92.34

Example	Composition	Thickness	Chlorine Exposure	Flux	Rejection
	weight ratio	nm	ppm-h	(GFD)	(%)
T2	GO/Sericin/KBO= 50/48/2	1843	0	17.9	82.99
T3-A	GO/Sericin/CaCl ₂ = 8/88/4	600	0	32.4	99.47
T3-B	GO/Sericin/CaCl ₂ = 30/68/2	1800	0	20.7	98.52
T3-C	GO/Sericin/CaCl ₂ = 30/68/2	2249	0	25.1	99.29
T4-A	GO/Sericin/PEG-DE= 30/68/2	1800	0	22.2	99.38
T4-B	GO/Sericin/PEG-DE= 40/58/2	1775	0	23.6	99.52
T4-C	GO/Sericin/PEG-DE= 50/48/2	1843	0	23.6	99.48
T4-D	GO/Sericin/PEG-DE= 60/38/2	1576	0	19.6	98.82
T4-E	GO/Sericin/PEG-DE= 70/28/2	1376	0	8.7	98.81
Comparative 1	ESPA2+OCWD	0	0	38.3	99.48

Table 2. Chlorine resistance of GO-Sericin coated membranes

Example	Composition	Thickness	Chlorine Exposure	Flux	Rejection
	weight ratio	nm	ppm-h	(GFD)	(%)
T1	GO/Sericin= 50/50	1843	27,400	31.4	83.63
T2	GO/Sericin/KBO= 50/48/2	1843	27,400	27.2	80.25

Example	Composition	Thickness	Chlorine Exposure	Flux	Rejection
	weight ratio	nm	ppm-h	(GFD)	(%)
T3-A	GO/Sericin/CaCl ₂ = 8/88/4	600	13,550	54.0	97.29
T3-B	GO/Sericin/CaCl ₂ = 30/68/2	1800	32,983	55.4	83.12
T3-C	GO/Sericin/CaCl ₂ = 30/68/2	2249	42,200	64.6	81.65
T4-A	GO/Sericin/PEG-DE= 30/68/2	1800	27,400	57.9	84.04
T4-B	GO/Sericin/PEG-DE= 40/58/2	1775	27,400	61.6	86.90
T4-C	GO/Sericin/PEG-DE= 50/48/2	1843	27,400	33.2	90.48
T4-D	GO/Sericin/PEG-DE= 60/38/2	1576	27,400	34.5	83.74
T4-E	GO/Sericin/PEG-DE= 70/28/2	1376	27,400	15.4	89.39
Comparative 1	ESPA2+OCWD	0	27,400	160.7	63.0

Embodiments

The following specific embodiments are specifically contemplated:

Embodiment 1. A selectively permeable membrane element, comprising:

- a membrane or porous support; and
- a protective coating including a crosslinked mixture of a graphene oxide compound and a crosslinker including a sericin;

wherein the protective coating is disposed on a surface of the membrane or porous support and is effective for protecting the membrane or porous support from chlorine degradation.

Embodiment 2. The selectively permeable membrane element of embodiment 1, wherein the graphene oxide compound includes a graphene oxide, a reduced graphene oxide, a functionalized graphene oxide, or a combination thereof.

Embodiment 3. The selectively permeable membrane element of embodiment 1 or 2, wherein the graphene oxide compound is graphene oxide.

Embodiment 4. The selectively permeable membrane element of any one of embodiments 1-3, further comprising at least one additional crosslinker.

Embodiment 5. The selectively permeable membrane element of embodiment 4, wherein the additional crosslinker comprises calcium chloride, potassium tetraborate, poly(ethylene glycol) diglycidyl ether (PEG-DE), or a combination thereof.

Embodiment 6. The selectively permeable membrane element of embodiment 4 or 5, wherein the additional crosslinker comprises calcium chloride.

Embodiment 7. The selectively permeable membrane element of any one of embodiments 4-6 wherein the additional crosslinker comprises potassium tetraborate.

Embodiment 8. The selectively permeable membrane element of any one of embodiments 4-7, wherein the additional crosslinker comprises poly(ethylene glycol) diglycidyl ether (PEG-DE).

Embodiment 9. The selectively permeable membrane element of any one of embodiments 4-8, wherein the additional crosslinker is present in an amount of about 1-8 wt% of the total weight of the protective coating.

Embodiment 10. The selectively permeable membrane element of any one of embodiments 1-9, wherein the weight ratio of graphene oxide to the crosslinker is about 1:100 to about 15:1.

Embodiment 11. The selectively permeable membrane element of any one of embodiments 1-10, wherein the weight ratio of graphene oxide to the crosslinker is about 1:11 to about 2.5:1.

Embodiment 12. The selectively permeable membrane element of any one of embodiments 1-11, wherein the graphene oxide comprises platelets having a size between about 50 nm to about 1,000 nm.

Embodiment 13. The selectively permeable membrane element of any one of embodiments 1-12, wherein the protective coating comprises a thickness of about 400 nm to about 2,500 nm.

Embodiment 14. A desalination method, comprising applying to the selectively permeable membrane element of any one of embodiments 1-13 a saline solution including at least one salt and water in a manner effective for providing a portion of the solution that passes through the selectively permeable membrane element with a lower salt content.

Embodiment 15. A method of making a selectively permeable membrane element, comprising the steps of:

- (1) mixing a graphene oxide compound and sericin;
- (2) applying the resulting mixture on a membrane or porous support to form a protective coating on said membrane or said porous support; and
- (3) curing the selectively permeable membrane element to facilitate crosslinking within the mixture.

Embodiment 16. The method of embodiment 15, wherein the curing is performed at a temperature of 70 °C to 120 °C for 30 seconds to 15 minutes.

Embodiment 17. The method of embodiment 15, further comprising repeating step (2) as necessary to achieve a desired thickness of the protective coating.

Embodiment 18. The method of embodiment 17, wherein the desired thickness is between about 100 nm and about 2500 nm.

Embodiment 19. The method of embodiment 15, wherein step (1) further comprises mixing at least one of calcium chloride (CaCl_2), potassium tetraborate ($\text{K}_2\text{B}_4\text{O}_7$), poly(ethylene glycol)diglycidyl ether (PEG-DE), or a combination thereof with the graphene oxide compound and sericin.

Unless otherwise indicated, all numbers expressing quantities of ingredients, properties such as molecular weight, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth in the specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

The terms “a,” “an,” “the” and similar referents used in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. All methods described herein may be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., “such as”) provided herein is intended merely to better illuminate the invention and does not pose a limitation on the scope of any claim. No language in the specification should be construed as indicating any non-claimed element essential to the practice of the invention.

Groupings of alternative elements or embodiments disclosed herein are not to be construed as limitations. Each group member may be referred to and claimed individually or in any combination with other members of the group or other elements found herein. It is anticipated that one or more members of a group may be included in, or deleted from, a group for reasons of convenience and/or patentability.

Certain embodiments are described herein, including the best mode known to the inventors for carrying out the invention. Of course, variations on these described embodiments will become apparent to those of ordinary skill in the art upon reading the

foregoing description. The inventor expects skilled artisans to employ such variations as appropriate, and the inventors intend for the invention to be practiced otherwise than specifically described herein. Accordingly, the claims include all modifications and equivalents of the subject matter recited in the claims as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is contemplated unless otherwise indicated herein or otherwise clearly contradicted by context.

In closing, it is to be understood that the embodiments disclosed herein are illustrative of the principles of the claims. Other modifications that may be employed are within the scope of the claims. Thus, by way of example, but not of limitation, alternative embodiments may be utilized in accordance with the teachings herein. Accordingly, the claims are not limited to embodiments precisely as shown and described.

CLAIMS

What is claimed is:

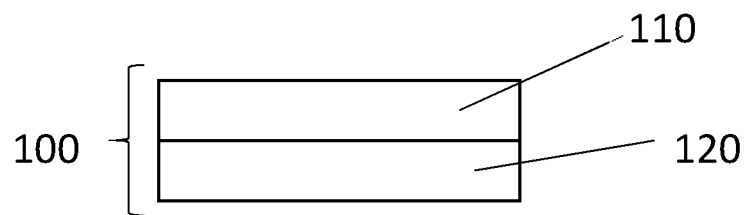
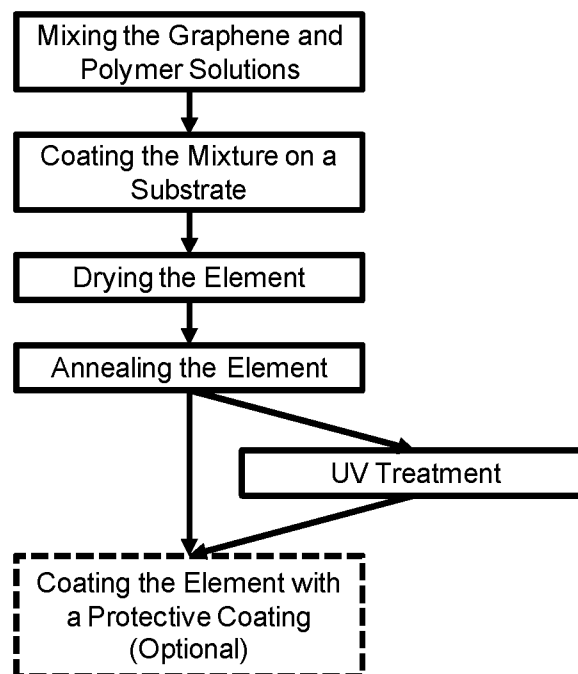
1. A selectively permeable membrane element, comprising:
a membrane or porous support; and
a protective coating including a crosslinked mixture of a graphene oxide compound and a crosslinker including sericin;
wherein the protective coating is disposed on a surface of the membrane or porous support and is effective for protecting the membrane or porous support from chlorine degradation.
2. The selectively permeable membrane element of claim 1, wherein the graphene oxide compound includes a graphene oxide, a reduced graphene oxide, a functionalized graphene oxide, or a combination thereof.
3. The selectively permeable membrane element of claim 1 or 2, wherein the graphene oxide compound is graphene oxide.
4. The selectively permeable membrane element of any one of claims 1-3, further comprising at least one additional crosslinker.
5. The selectively permeable membrane element of claim 4, wherein the additional crosslinker comprises calcium chloride, potassium tetraborate, poly(ethylene glycol) diglycidyl ether (PEG-DE), or a combination thereof.
6. The selectively permeable membrane element of claim 4 or 5, wherein the additional crosslinker comprises calcium chloride.
7. The selectively permeable membrane element of any one of claims 4-6 wherein the additional crosslinker comprises potassium tetraborate.
8. The selectively permeable membrane element of any one of claims 4-7, wherein the additional crosslinker comprises poly(ethylene glycol) diglycidyl ether (PEG-DE).

9. The selectively permeable membrane element of any one of claims 4-8, wherein the additional crosslinker is present in an amount of about 1-8 wt% of the total weight of the protective coating.
10. The selectively permeable membrane element of any one of claims 1-9, wherein the weight ratio of graphene oxide to the crosslinker is about 1:100 to about 15:1.
11. The selectively permeable membrane element of any one of claims 1-10, wherein the weight ratio of graphene oxide to the crosslinker is about 1:11 to about 2.5:1.
12. The selectively permeable membrane element of anyone claims 1-11, wherein the graphene oxide comprises platelets having a size between about 50 nm to about 1,000 nm.
13. The selectively permeable membrane element of any one of claims 1-12, wherein the protective coating comprises a thickness of about 400 nm to about 2,500 nm.
14. A desalination method, comprising applying to the selectively permeable membrane element of any one of claims 1-13, a saline solution including at least one salt and water in a manner effective for providing a portion of the solution that passes through the selectively permeable membrane element with a lower salt content.
15. A method of making a selectively permeable membrane element, comprising the steps of:
- (1) mixing a graphene oxide compound and sericin;
 - (2) applying the resulting mixture on a membrane or porous support to form a protective coating on said membrane or said porous support; and
 - (3) curing the selectively permeable membrane element to facilitate crosslinking within the mixture.
16. The method of claim 15, wherein the curing is performed at a temperature of 70 °C to 120 °C for 30 seconds to 15 minutes.
17. The method of claim 15, further comprising repeating step (2) as necessary to achieve a desired thickness of the protective coating.

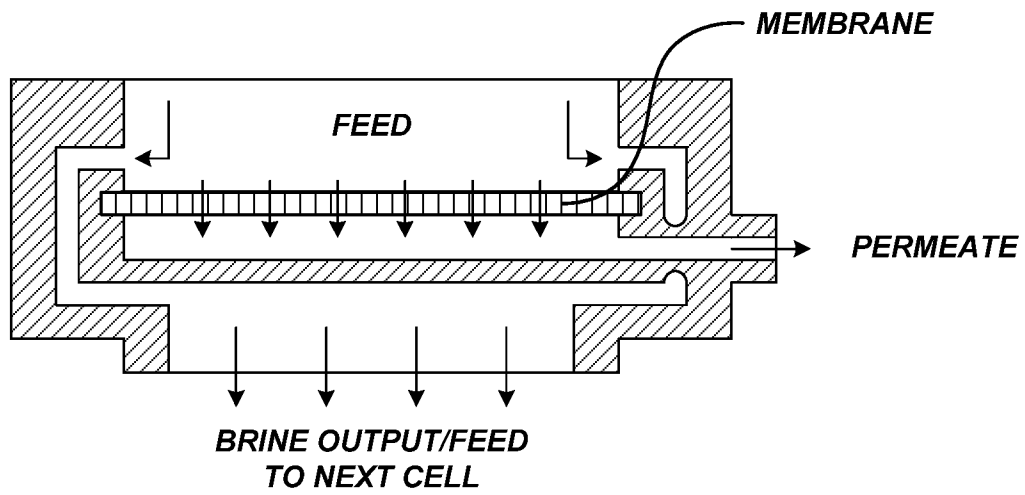
18. The method of claim 17, wherein the desired thickness is between about 100 nm and about 2500 nm.

19. The method of claim 15, wherein step (1) further comprises mixing at least one of calcium chloride (CaCl_2), potassium tetraborate ($\text{K}_2\text{B}_4\text{O}_7$), poly(ethylene glycol)diglycidyl ether (PEG-DE), or a combination thereof with the graphene oxide compound and sericin.

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FIG. 1: Example of Selectively Permeable Elements.**FIG. 2: Graphene Selectively Permeable Fabrication Methodology**

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FIG. 3: Illustrative Depiction of Mechanical Strength and Chlorine Resistant Test Cell

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2020/038232

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	B01D67/00	B01D69/02
	B01D69/10	B01D69/12
		B01D69/14
		B01D71/02
ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
B01D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	YANG ZHE ET AL: "Recent development of novel membranes for desalination", DESALINATION, ELSEVIER, AMSTERDAM, NL, vol. 434, 7 December 2017 (2017-12-07), pages 37-59, XP085356147, ISSN: 0011-9164, DOI: 10.1016/J.DESAL.2017.11.046 section 6.2.2; page 50	1-19
A	----- CN 104 306 325 B (UNIV JIANGSU SCIENCE & TECH) 15 February 2017 (2017-02-15) abstract	1-19
A	----- RO 133 145 A2 (INSTITUTUL NAT DE CERCETARE DEZVOLTARE PENTRU FIZICA LASERILOR PLASMEI) 29 March 2019 (2019-03-29) claim 1; figure 2	1-19
	----- -/-	
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
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Date of the actual completion of the international search		Date of mailing of the international search report
8 September 2020		17/09/2020
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Hennebrüder, K

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2020/038232

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	SEUNGJU KIM ET AL: "Highly crosslinked, chlorine tolerant polymer network entwined graphene oxide membrane for water desalination", JOURNAL OF MATERIALS CHEMISTRY A, vol. 5, no. 4, 1 January 2017 (2017-01-01) , pages 1533-1540, XP055728578, GB ISSN: 2050-7488, DOI: 10.1039/C6TA07350F abstract -----	1-19

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2020/038232

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
CN 104306325	B	15-02-2017	NONE	

RO 133145	A2	29-03-2019	NONE	
