compounds. In one example, biomimetic TFC membranes comprise protein-based, water-selective channels such as aquaporins (AQP). The presence of aquaporins was observed to lead to increased hydrophilicity of the membrane while maintaining a stable level of salt rejection. However, there are significant barriers to the upscaling or commercialization of such membranes. For instance, the production of biological proteins is a non-trivial endeavor involving protein expression by a host organism, which is a challenging process to control. Subsequently, a cascade of protein purification steps may be required in order to obtain the desired protein before incorporation into the membrane, leading to relatively higher costs of production compared to other types of RO/FO membranes

Nanocomposite membranes have also been extensively studied at the laboratory scale for use in the water treatment industry. Such membranes typically involve the incorporation of nanomaterials in the membrane in order to modify the physiochemical properties of the membrane, e.g., hydrophilicity, porosity, charge density, durability, etc. For example, carbon nanotubes have been embedded in polymeric membranes in the preparation of mixed matrix membranes for use in water purification processes. However, such nanocomposite membranes also require complicated fabrication processes and face difficulties when in operation, which may discourage the use of such membranes. Typical difficulties encountered in the fabrication or operation of such nanocomposite membranes include, for instance, poor dispersibility of the nanomaterials in the polymeric matrix, aggregation of nanoparticles causing defects on the membrane surface, and potential leakage of the nanomaterials causing toxicity and/or contamination of the treated water.

Accordingly, there is a need to provide an alternative method of preparing a membrane intended for use in water treatment or purification, which ameliorates or avoids the problems described above. Yet another objective of the present disclosure is to provide a novel membrane prepared from the method disclosed herein, and which is substantially free of biological proteins such as aquaporins.

Summary

In one aspect of the disclosure, there is provided a method of preparing a composite membrane, the method comprising: a) impregnating a surface of a porous membrane substrate with an aqueous suspension comprising a mixture of at least one polyamine and at least one phospholipid, wherein the aqueous suspension is substantially devoid of aquaporins; b) rinsing the impregnated surface of the porous membrane substrate with a non-polar organic solvent;

c) contacting the impregnated surface with an organic phase containing a monomer comprising at least one crosslinking group to thereby deposit a polyamide layer on the

impregnated surface, wherein the polyamide layer comprises the phospholipid dispersed therein, and wherein the polyamide layer is an interfacial polymerization product.

In another aspect of the present invention, there is provided a composite membrane comprising: at least one porous membrane substrate having nano-sized or micro-sized pores, and at least a polyamide layer disposed on a surface of the porous membrane substrate, the polyamide layer comprising phospholipids dispersed therein, and wherein the polyamide layer is an interfacial polymerization product, wherein the polyamide layer does not comprise aquaporins; wherein the polyamide layer is a fully aromatic polyamide layer comprising leaf-like structures, the leaf-like structures having an apparent height of between 500 nm to 4,000 nm and wherein the polyamide layer is formed via interfacial polymerization which comprises first impregnating the surface of the porous membrane substrate with an aqueous phase comprising at least one polyamine and the phospholipid, rinsing the surface of the impregnated porous membrane substrate with a non-polar organic solvent, optionally, gas purging or blowing the surface of the impregnated porous membrane substrate, and thereafter contacting the impregnated porous membrane substrate with an organic phase containing a monomer comprising at least one crosslinking group to thereby result in the formation of the polyamide layer.

Advantageously, it was observed that the incorporation of phospholipids into the polyamide layer resulted in unexpected and material improvements to the membrane selectivity, while not compromising its capability to reject solutes and impurities (e.g., salts) in the water being treated. In particular, it was found that a membrane prepared according to the present disclosure is able to substantially increase its permeability to water, while maintaining a salt (e.g. NaCl) rejection rate of at least 90% or greater, or preferably about 95% or greater at an applied pressure of about 2 bar.

The improvement in membrane permeability may be potentially attributed to the unique topography of the polyamide selective layer and the presence of lipids. In one embodiment, the formation of leaf-like structures or leaf-like features was observed on the polyamide layer formed from an aromatic polyamine and an aromatic crosslinker in the presence of a phospholipid. These leaf-like structures may be characterized as blade-like protrusions extending upward from the base of the polyamide layer. The base refers to the surface of the polyamide layer which is coupled to the underlying membrane substrate, which may be composed of a different polymer e.g., polyethersulfone. These protruding, leaf-like structures may typically be between 200 to

4,000 nm in height (calculated from the base of the polyamide layer). It is postulated that the presence of these surface structures on the fully aromatic polyamide layer provided increased surface area for contact with water molecules, thereby facilitating the transport of water through the membrane.

Furthermore, the polyamide layer formed in the presence of a phospholipid may also result in the formation of large interstitial spaces which help focus the transport of water molecules toward and across the underlying membrane substrate. Such effects may be observed for semi-aromatic

Claims

1. A method of preparing a composite membrane, the method comprising:
   a) impregnating a surface of a porous membrane substrate with an aqueous suspension comprising a mixture of at least one polyamine and at least one phospholipid, wherein the aqueous suspension is substantially devoid of aquaporins;
   b) rinsing the impregnated surface of the porous membrane substrate with a non-polar organic solvent;
   c) contacting the impregnated surface with an organic phase containing a monomer comprising at least one crosslinking group to thereby deposit a polyamide layer on the impregnated surface, wherein the polyamide layer comprises the at least one phospholipid dispersed therein, and wherein the polyamide layer is an interfacial polymerization product.

2. The method of claim 1, wherein the monomer comprises at least two acyl halide or sulfonyl halide groups; or

   wherein the monomer comprising at least one crosslinking group is selected from the group consisting of trimesoyl chloride (1,3,5–benzenetricarbonyl trichloride), terephthalic acid chloride, isophthalic acid chloride, biphenyl dicarboxylic acid chloride, naphthalene dicarboxylic acid dichloride, biphenyl-4,4′ -disulfonyl chloride , 1,3,6-naphthalenetrisulfonyl chloride and mixtures thereof; or

   wherein the polyamine is a monomer comprising at least two amine groups, wherein said amine groups are independently primary or secondary amine groups; or

   wherein the polyamine is selected from the group consisting of m-phenylenediamine (MPD), m-phenylenediamine-4-methyl, 1,3-cyclohexanebis(methylamine), o-phenylenediamine (OPD), piperazine, p-phenylenediamine (PPD), 1,1'-biphenyl-4,4'-diamine (benzidine), polyethyleneimine, and mixtures thereof.

3. The method of claim 1 or 2, further comprising a step of removing excess aqueous suspension by gas purging or blowing the impregnated surface of the porous membrane substrate prior to the contacting step c).

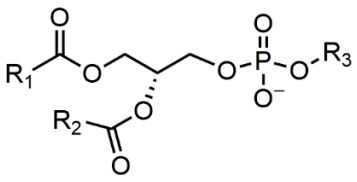
4. The method of any one of the preceding claims, wherein the aqueous suspension comprises the phospholipid in a molar concentration of from 10 μM to 10 mM; or from 50 μM to 4 mM.

5. The method of any one of the preceding claims, wherein the aqueous suspension comprises the polyamine in a concentration of from 0.001 wt. % to 10 wt. %; or

   from 0.5 wt. % to 3 wt. %.

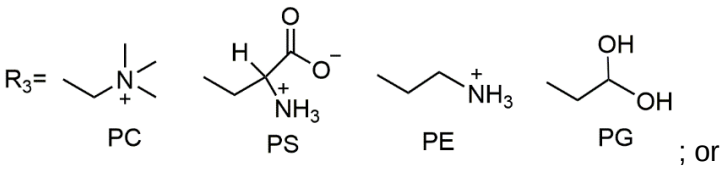
6. The method of any one of the preceding claims, wherein the aqueous suspension is substantially devoid of transmembrane proteins or analogues thereof.

7. The method of any one of the preceding claims, wherein the phospholipid has a formula (I):



(Formula I)

wherein R_1 represents a saturated or an unsaturated aliphatic group having 14 to 24 carbon atoms; and
wherein R_2 represents a saturated or an unsaturated aliphatic group having 14 to 24 carbon atoms; and
wherein R_3 is:



; or

wherein the phospholipid is selected from the group consisting of: 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC), 1,2-dioleoyl-sn-glycero-3-phosphoethanolamine (DOPE), 1,2-dioleoyl-sn-glycero-3-phospho-rac-(1-glycerol) (DOPG), L-α-phosphatidylcholine (egg PC), 1,2-ditetradecanoyl-sn-glycero-3-phosphocholine (DMPC), 2-oleoyl-1-palmitoyl-sn-glycero-3-phosphocholine (POPC), 1,2-dilauroyl-sn-glycero-3-phosphocholine (DLPC), 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC), 1,2-dipalmitoyl-sn-glycero-3-

phosphocholine (DPPC), 1,2-distearoyl-sn-glycero-3-phosphocholine (DSPC), 1,2-dilauroyl-sn-glycero-3-phospho-(1'-rac-glycerol) (sodium salt) (DLPG), 1,2-dimyristoyl-sn-glycero-3-phospho-(1'-rac-glycerol) (sodium salt) (DMPG), 1,2-dipalmitoyl-sn-glycero-3-phospho-(1'-rac-glycerol) (sodium salt) (DPPG), 1-palmitoyl-2-oleoyl-sn-glycero-3-phospho-(1'-rac-glycerol) (sodium salt) (POPG), 1,2-dimyristoyl-sn-glycero-3-phospho-L-serine (sodium salt) (DMPS), 1,2-dipalmitoyl-sn-glycero-3-phospho-L-serine (sodium salt) (DPPS), 1,2-distearoyl-sn-glycero-3-phospho-L-serine (sodium salt) (DSPS), 1,2-dioleoyl-sn-glycero-3-phospho-L-serine (sodium salt) (DOPS), 1-palmitoyl-2-oleoyl-sn-glycero-3-phospho-L-serine (sodium salt) (POPS), 1,2-dilauroyl-sn-glycero-3-phosphate (sodium salt) (DLPA), 1,2-dimyristoyl-sn-glycero-3-phosphate (sodium salt) (DMPA), 1,2-dipalmitoyl-sn-glycero-3-phosphate (sodium salt) (DPPA), 1,2-distearoyl-sn-glycero-3-phosphate (sodium salt) (DSPA), 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphate (sodium salt) (POPA), 1,2-dilauroyl-sn-glycero-3-phosphoethanolamine (DLPE), 1,2-dimyristoyl-sn-glycero-3-phosphoethanolamine (DMPE), 1,2-dipalmitoyl-sn-glycero-3-phosphoethanolamine (DPPE), 1,2-distearoyl-sn-glycero-3-phosphoethanolamine (DSPE), 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphoethanolamine (POPE), 1,2-di-O-octadecenyl-3-trimethylammonium propane (chloride salt) (DOTMA), *E.coli* lipid extract, soy lipid extract, yeast lipid extract, 1-palmitoyl-2-(dipyrromethene boron difluoride)undecanoyl-sn-glycero-3-phosphocholine, 1,2-dioleoyl-sn-glycero-3-phospho-(1'-myo-inositol) (ammonium salt) (DOPI), 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphoinositol (ammonium salt) (POPI), 1,2-dipalmitoyl-sn-glycero-3-phospho-(1'-myo-inositol) (ammonium salt) (DPPI), 1,1', 2,2'-tetraoleoyl cardiolipin (TOCL), 1,2-dioleoyl-sn-glycero-3-phosphoethanol (DOPEt), 1,2-dioleoyl-sn-glycero-3-phosphoethanol (DOPEt) (18:0 diethyl PC), or combinations thereof; or

wherein the phospholipid is selected from the group consisting of: 1,2-Dioleoyl-sn-glycero-3-phosphocholine (DOPC), 1,2-Dioleoyl-sn-glycero-3-phosphoethanolamine (DOPE), 1,2-Dioleoyl-snglycero-3-phospho-rac-(1-glycerol) (DOPG), L-α-phosphatidylcholine (egg PC), 1,2-ditetradecanoyl-sn-glycero-3-phosphocholine (DMPC), 2-Oleoyl-1-palmitoyl-sn-glycero-3-phosphocholine (POPC), and mixtures thereof.

8. The method of any one of the preceding claims, wherein the organic phase comprises the monomer comprising at least one crosslinking group in a concentration of from 0.00001 wt.% to 2 wt. %; or from 0.001 wt.% to 1 wt.%; or

wherein the organic phase further comprises an organic solvent which is unreactive with the monomer comprising at least one crosslinking group.

9. The method of any one of the preceding claims, wherein the contacting step (c) is undertaken for a duration sufficient to deposit the polyamide layer in a thickness of from 50 nm to 4,000 nm; or

wherein the contacting step c) is undertaken for a period of 10 s to 10 min; or

wherein the polyamide layer is a fully-aromatic polyamide layer comprising leaf-like structures, the leaf-like structures having an apparent height of 500 - 4000 nm, or wherein the polyamide layer is a semi-aromatic polyamide layer with an apparent height of less than 100 nm.

10. A composite membrane comprising:
    a) at least one porous membrane substrate having nano-sized or micro-sized pores, and
    b) at least a polyamide layer disposed on a surface of the porous membrane substrate, the polyamide layer comprising at least one phospholipid dispersed therein, and wherein the polyamide layer is an interfacial polymerization product;

    wherein the polyamide layer does not comprise aquaporins;

    wherein the polyamide layer is a fully-aromatic polyamide layer comprising leaf-like structures, the leaf-like structures having an apparent height of 500 – 4000 nm; and

    wherein the polyamide layer is formed via interfacial polymerization which comprises first impregnating the surface of the porous membrane substrate with an aqueous phase comprising at least one polyamine and the phospholipid,

    rinsing the surface of the impregnated porous membrane substrate with a non-polar organic solvent,

    optionally, gas purging or blowing the surface of the impregnated porous membrane substrate,

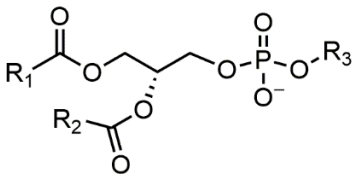
    and thereafter contacting the impregnated porous membrane substrate with an organic phase containing a monomer comprising at least one crosslinking group to thereby result in the formation of the polyamide layer.

11. The composite membrane of claim 10, wherein the monomer comprises at least two acyl halide or sulfonyl halide groups.

12. The composite membrane of claim 10 or 11, wherein the phospholipid is provided in a molar concentration of from 10 μM to 10 mM in the aqueous phase; or from 50 μM to 4 mM.

13. The composite membrane of any one of claims 10 to 12, wherein the interfacial polymerization occurs on the surface of the porous membrane substrate to thereby deposit the polyamide layer thereon.

14. The composite membrane of any one of claims 10 to 13, wherein the phospholipid has a formula (I):

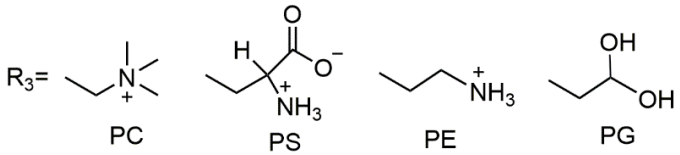


(Formula I)

wherein R_1 represents a saturated or an unsaturated aliphatic group having 14 to 24 carbon atoms; and

wherein R_2 represents a saturated or an unsaturated aliphatic group having 14 to 24 carbon atoms; and

wherein R_3 is:



wherein the phospholipid is selected from the group consisting of: 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC), 1,2-dioleoyl-sn-glycero-3-phosphoethanolamine (DOPE), 1,2-dioleoyl-sn-glycero-3-phospho-rac-(1-glycerol) (DOPG), L-α-phosphatidylcholine (egg PC), 1,2-ditetradecanoyl-sn-glycero-3-phosphocholine (DMPC), 2-oleoyl-1-palmitoyl-sn-glycero-3-phosphocholine (POPC), 1,2-dilauroyl-sn-glycero-3-phosphocholine (DLPC), 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC), 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC), 1,2-distearoyl-sn-glycero-3-phosphocholine (DSPC), 1,2-dilauroyl-sn-glycero-3-phospho-(1'-rac-glycerol) (sodium salt) (DLPG), 1,2-dimyristoyl-sn-glycero-3-

phospho-(1'-rac-glycerol) (sodium salt) (DMPG), 1,2-dipalmitoyl-sn-glycero-3-phospho-(1'-rac-glycerol) (sodium salt) (DPPG), 1-palmitoyl-2-oleoyl-sn-glycero-3-phospho-(1'-rac-glycerol) (sodium salt) (POPG), 1,2-dimyristoyl-sn-glycero-3-phospho-L-serine (sodium salt) (DMPS), 1,2-dipalmitoyl-sn-glycero-3-phospho-L-serine (sodium salt) (DPPS), 1,2-distearoyl-sn-glycero-3-phospho-L-serine (sodium salt) (DSPS), 1,2-dioleoyl-sn-glycero-3-phospho-L-serine (sodium salt) (DOPS), 1-palmitoyl-2-oleoyl-sn-glycero-3-phospho-L-serine (sodium salt) (POPS), 1,2-dilauroyl-sn-glycero-3-phosphate (sodium salt) (DLPA), 1,2-dimyristoyl-sn-glycero-3-phosphate (sodium salt) (DMPA), 1,2-dipalmitoyl-sn-glycero-3-phosphate (sodium salt) (DPPA), 1,2-distearoyl-sn-glycero-3-phosphate (sodium salt) (DSPA), 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphate (sodium salt) (POPA), 1,2-dilauroyl-sn-glycero-3-phosphoethanolamine (DLPE), 1,2-dimyristoyl-sn-glycero-3-phosphoethanolamine (DMPE), 1,2-dipalmitoyl-sn-glycero-3-phosphoethanolamine (DPPE), 1,2-distearoyl-sn-glycero-3-phosphoethanolamine (DSPE), 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphoethanolamine (POPE), *E.coli* lipid extract, soy lipid extract, yeast lipid extract, 1-palmitoyl-2-(dipyrrometheneboron difluoride)undecanoyl-sn-glycero-3-phosphocholine, 1,2-dioleoyl-sn-glycero-3-phospho-(1'-myo-inositol) (ammonium salt) (DOPI), 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphoinositol (ammonium salt) (POPI), 1,2-dipalmitoyl-sn-glycero-3-phospho-(1'-myo-inositol) (ammonium salt) (DPPI), 1,1', 2,2'-tetraoleoyl cardiolipin (TOCL), 1,2-dioleoyl-sn-glycero-3-phosphoethanol (DOPEt), 1,2-dioleoyl-sn-glycero-3-phosphoethanol (DOPEt) (18:0 diethyl PC), or combinations thereof; or .

wherein the phospholipid is selected from the group consisting of: 1,2-Dioleoyl-sn-glycero-3-phosphocholine (DOPC), 1,2-Dioleoyl-sn-glycero-3-phosphoethanolamine (DOPE), 1,2-Dioleoyl-snglycero-3-phospho-rac-(1-glycerol) (DOPG), L-α-phosphatidylcholine (egg PC), 1,2-ditetradecanoyl-sn-glycero-3-phosphocholine (DMPC), 2-Oleoyl-1-palmitoyl-sn-glycero-3-phosphocholine (POPC), and mixtures thereof.

15. The composite membrane of any one of claims 10 to 14, wherein the polyamine comprises at least two amine groups, wherein said amine groups are independently primary amine or secondary amine groups; or

wherein the polyamine is selected from the group consisting of m-phenylenediamine (MPD), m-phenylenediamine-4-methyl, 1,3-cyclohexanebis(methylamine), o-phenylenediamine

(OPD), piperazine, p-phenylenediamine (PPD), 1,1'-biphenyl-4,4'-diamine (benzidine), polyethyleneimine, and mixtures thereof; or

wherein the monomer comprising at least one crosslinking group is selected from the group consisting of trimesoyl chloride (1,3,5–benzenetricarbonyl trichloride), terephthalic acid chloride, isophthalic acid chloride, biphenyl dicarboxylic acid chloride, naphthalene dicarboxylic acid dichloride, biphenyl-4,4′-disulfonyl chloride, 1,3,6-naphthalenetrisulfonyl chloride, and mixtures thereof.

16. The composite membrane of any one of claims 10 to 15, wherein the organic phase comprises the monomer comprising at least one crosslinking group in a concentration of from 0.00001 wt.% to 2 wt.%; or from 0.001 wt.% to 1 wt.%; or

wherein the organic phase further comprises an organic solvent which is unreactive with the monomer comprising at least one crosslinking group.

17. The composite membrane of any one of claims 10 to 16, wherein the porous membrane substrate comprises polyethersulfone, polyetherimide, polysulfone, polyacrylonitrile, polyimide, polyvinylidene fluoride, polypropylene, poly(tetrafluoroethylene), or co-polymers thereof.

18. The composite membrane of any one of claims 10 to 17, wherein the polyamide layer does not comprise a transmembrane protein or analogues thereof.

19. A hollow fiber membrane or a flat-sheet membrane comprising the composite membrane of any one of claims 10 to 18.