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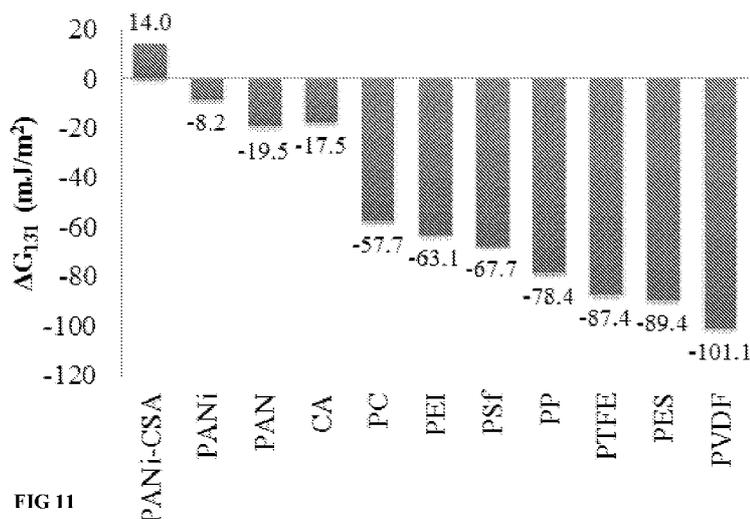


FIG 11

(57) Abstract: Disclosed herein are methods of increasing the hydrophilicity of a membrane. Membranes comprising polyaniline or co-polymer thereof and one or more gel inhibiting agents are treated with one or more hydrophilicity restoration agents, thereby increasing the hydrophilicity of a membrane. Also disclosed are membranes produced by the disclosed methods. This abstract is intended as a scanning tool for purposes of searching in the particular art and is not intended to be limiting of the present invention.

WO 2014/059339 A1

POLYANILINE MEMBRANES, USES, AND METHODS THERETO

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This Application claims the benefit of U.S. Provisional Application No. 61/713,439, filed on October 12, 2012, which is incorporated herein by reference in its entirety.

BACKGROUND

[0002] The conducting polymer, polyaniline, has historically been used to make sensors [1-3], battery electrodes [4], electromagnetic shielding devices [5, 6], and anticorrosion coatings [7-9]. Polyaniline has recently attracted attention as a membrane material [10-12]. The processability of polyaniline is somewhat limited to specific solvents. Gel-inhibitor agents have been used in solvent systems to increase the processability of polyaniline. However, the resulting membrane have a higher hydrophobicity when a gel-inhibitor agent is used which can negatively impact the performance and maintenance of the membrane.

[0003] Accordingly, described herein are membranes, methods of making membranes, and uses of membranes, wherein membranes produced with a gel-inhibiting agent have been treated to increase the hydrophilicity of membrane.

SUMMARY OF THE INVENTION

[0004] In accordance with the purpose(s) of the invention, as embodied and broadly described herein, the invention, in one aspect, relates to methods that increases the hydrophilicity of a membrane comprising polyaniline or co-polymer thereof and one or more gel inhibiting agents.

[0005] Disclosed herein is a method of increasing membrane hydrophilicity comprising steps of: (a) providing a membrane comprising polyaniline, a polyaniline derivative, or co-polymer thereof and one or more gel inhibiting agents; and (b) treating the membrane with one or more hydrophilicity restoration agents, thereby increasing the hydrophilicity of the membrane.

[0006] Also disclosed herein are membranes subjected to the methods disclosed herein.

[0007] Also disclosed herein are articles of manufacture comprising one or more membranes disclosed herein.

[0008] While aspects of the present invention can be described and claimed in a particular statutory class, such as the system statutory class, this is for convenience only and one of skill in the art will understand that each aspect of the present invention can be described and claimed in any statutory class. Unless otherwise expressly stated, it is in no way intended that any method or aspect set forth herein be construed as requiring that its steps be performed in a specific order. Accordingly, where a method claim does not specifically state in the claims or descriptions that the steps are to be limited to a specific order, it is no way intended that an order be inferred, in any respect. This holds for any possible non-express basis for interpretation, including matters of logic with respect to arrangement of steps or operational flow, plain meaning derived from grammatical organization or punctuation, or the number or type of aspects described in the specification.

BRIEF DESCRIPTION OF THE FIGURES

[0009] The accompanying figures, which are incorporated in and constitute a part of this specification, illustrate several aspects and together with the description serve to explain the principles of the invention.

[0010] Figure 1 shows the potential hydrogen bonding interactions between the emeraldine base form of polyaniline (PANi), the solvent 1-methyl-2-pyrrolidinone (NMP), and the gel inhibitor 4-methylpiperidine (4MP).

[0011] Figure 2 shows the water contact angle for PANi-NMP-4MP membranes after 100 mM CSA post-treatments at 50 °C using differing time intervals.

[0012] Figure 3 shows the thermal decomposition of nonwoven support and PANi membranes.

[0013] Figure 4 shows the FTIR spectra for PANi membranes and CSA.

[0014] Figure 5 shows the ^1H NMR spectra for a) NMP, b) 4MP, c) a PANi-NMP membrane, d) a PANi-NMP-4MP membrane, e) a CSA-treated PANi-NMP-4MP membrane, and f) a NH_4OH -CSA-treated PANi-NMP-4MP membrane.

[0015] Figure 6 shows the Zeta potentials of PANi membranes determined by streaming current measurements.

[0016] Figure 7 shows PANi membrane cross-sections and surface SEM images.

[0017] Figure 8 shows a schematic diagram illustrating the reduction and ring substitution of 4MP onto PANi emeraldine base.

[0018] Figure 9 shows an SEM image of a membrane made from PANi-NMP without a gel-inhibitor.

[0019] Figure 10 shows an SEM image of a membrane made from PANi-NMP with 4-MP as a gel-inhibitor.

[0020] Figure 11 shows a plot of free energy of cohesion for various membrane materials.

[0021] Figure 12 shows a plot of free energy of adhesion for various membrane and fouling materials. Each of the membranes (e.g. PANi-CAS) was tested against nine fouling materials. In the plot for each membrane, from the left, the order of the fouling material is PEG, *E. coli*, *S. cerevisiae*, HSA, *P. putida*, silica, alumina, carboxyl modified latex, and hexadecane.

[0022] Additional advantages of the invention will be set forth in part in the description which follows, and in part will be obvious from the description, or can be learned by practice of the invention. The advantages of the invention will be realized and attained by means of the elements and combinations particularly pointed out in the appended claims. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as claimed.

DESCRIPTION

A. DEFINITIONS

[0023] As used in the specification and the appended claims, the singular forms “a,” “an” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a functional group,” “an alkyl,” or “a residue” includes mixtures of two or more such functional groups, alkyls, or residues, and the like.

[0024] Ranges can be expressed herein as from “about” one particular value, and/or to “about” another particular value. When such a range is expressed, a further aspect includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent “about,” it will be understood that the particular value forms a further aspect. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of

the other endpoint. It is also understood that there are a number of values disclosed herein, and that each value is also herein disclosed as “about” that particular value in addition to the value itself. For example, if the value “10” is disclosed, then “about 10” is also disclosed. It is also understood that each unit between two particular units are also disclosed. For example, if 10 and 15 are disclosed, then 11, 12, 13, and 14 are also disclosed.

[0025] References in the specification and concluding claims to parts by weight of a particular element or component in a composition denotes the weight relationship between the element or component and any other elements or components in the composition or article for which a part by weight is expressed. Thus, in a compound containing 2 parts by weight of component X and 5 parts by weight component Y, X and Y are present at a weight ratio of 2:5, and are present in such ratio regardless of whether additional components are contained in the compound.

[0026] A weight percent (wt. %) of a component, unless specifically stated to the contrary, is based on the total weight of the formulation or composition in which the component is included.

[0027] As used herein, the term “derivative” refers to a compound (e.g. a polymer) having a structure derived from the structure of a parent compound (e.g., polyaniline) and whose structure is sufficiently similar to those disclosed herein and based upon that similarity, would be expected by one skilled in the art to exhibit the same or similar properties and utilities as the parent compound. Exemplary derivatives include esters, amides, alkyl substitutions, and other suitable substitutions of a parent compound.

[0028] As used herein, the terms “optional” or “optionally” means that the subsequently described event or circumstance can or cannot occur, and that the description includes instances where said event or circumstance occurs and instances where it does not.

[0029] The term “contacting” as used herein refers to bringing a substance, for example a hydrophilicity restoration agent, and membrane together in such a manner that the substance can interact with the membrane.

[0030] As used herein, the terms “effective amount” and “amount effective” refer to an amount that is sufficient to achieve the desired result or to have an effect on an undesired condition. For example, an “effective amount of a hydrophilicity restoration agent” refers to an amount that is sufficient to achieve the desired increase in hydrophilicity of a membrane.

B. HYDROPHILICITY

[0031] Wettability of Solid Surfaces. The classical definition of “lyophilic” or “wetting” is a liquid contact angle less than 90 degrees, whereas “lyophobic” or “non-wetting” is a liquid contact angle greater than 90 degrees. According to the Dupre equation, the solid-liquid interfacial free energy derives from the difference between the solid (1), liquid (3), and solid-liquid (13) interfacial tensions. (A. Dupre, *Theorie Mecanique de la Chaleur*; Gauthier-Villars: Paris, 1869) The solid-liquid interfacial free energy is calculated directly from the liquid contact angle using the Young-Dupre equation,

$$-\Delta G_{13} = \gamma_3 \left(1 + \frac{\cos \theta_3}{r} \right), \quad (1)$$

which is derived by combining the Dupre equation with the Young equation. (T. Young, “An Essay on the Cohesion of Fluids,” *Philosophical Transactions of the Royal Society of London* **1805**, 95, 65-87). In fact, eq (1) is a modified form of the Young-Dupre equation that accounts for the excess interfacial area created by surface roughness as suggested by Wenzel. In eq (2), r is the actual surface area of a roughened solid surface, which can be derived from Atomic Force Microscopy (AFM) surface area difference (a.k.a., Wenzel’s “roughness factor” or the ratio of actual surface area to geometric surface area). (R. N. Wenzel, *Industrial and Engineering Chemistry* **1936**, 28, 988-994).

[0032] Components of Solid Surface Tension and their Determination. According to van Oss, the total surface tension of any media is the sum of apolar (Lifshitz-van der Waals) and polar (Lewis acid-base) components, or

$$\gamma^{TOT} = \gamma^{LW} + \gamma^{AB}, \quad (2)$$

where $\gamma^{AB} (= 2\sqrt{\gamma^+ \gamma^-})$ is the acid-base component, γ^+ and γ^- are electron-acceptor and electron-donor components, and γ^{LW} is the Lifshitz-van der Waals component. (C. J. van Oss, *Interfacial Forces in Aqueous Media*; Marcel Dekker, Inc.: New York, NY, 1994). Individual surface tension components are determined from contact angles measured using three probe liquids of known surface tension and calculated by the extended Young equation,

$$\left(1 + \frac{\cos \theta}{r} \right) \gamma_l^{TOT} = 2 \left(\sqrt{\gamma_s^{LW} \gamma_l^{LW}} + \sqrt{\gamma_s^+ \gamma_l^-} + \sqrt{\gamma_s^- \gamma_l^+} \right) \quad (3)$$

where θ is the equilibrium contact angle of a probe liquid on the surface, γ_l^{TOT} is the total liquid surface tension. The subscripts s and l represent the solid surface and the probe liquid, respectively.

[0033] Interfacial Free Energy, Hydrophilicity and Fouling Resistance. The interfacial free energy at contact, ΔG_{132}^{IF} , offers additional insight into the inherent stability of a solid material (1) interacting through a liquid media (3) with another solid material (2). It accounts for interactions between the two solid surfaces, between water molecules and each of the solid surfaces, and among water molecules themselves. The interfacial free energy gives an indication of the thermodynamic tendency of the surfaces to be attracted or repelled by one another and is determined from, (D. Myers, *Surfaces, Interfaces, and Colloids: Principles and Applications*; 2nd ed.; John Wiley & Sons: New York, NY, 1999)

$$\Delta G_{132}^{IF} = \Delta G_{132}^{LW} + \Delta G_{132}^{AB}, \quad (4a)$$

$$\Delta G_{132}^{LW} = 2\left(\sqrt{\gamma_3^{LW}} - \sqrt{\gamma_1^{LW}}\right)\left(\sqrt{\gamma_2^{LW}} - \sqrt{\gamma_3^{LW}}\right), \quad (b)$$

$$\Delta G_{132}^{AB} = 2\sqrt{\gamma_3^+}\left(\sqrt{\gamma_1^-} + \sqrt{\gamma_2^-} - \sqrt{\gamma_3^-}\right) + 2\sqrt{\gamma_3^-}\left(\sqrt{\gamma_1^+} + \sqrt{\gamma_2^+} - \sqrt{\gamma_3^+}\right) - 2\sqrt{\gamma_1^+\gamma_2^-} - 2\sqrt{\gamma_1^-\gamma_2^+}. \quad (c)$$

[0034] If surface 1 and 2 are the same material (i.e., $2 = 1$), ΔG_{131}^{IF} indicates the interfacial free energy of cohesion at contact. This is the most fundamental thermodynamic definition of “hydrophilicity” and “hydrophobicity”. The term “hydrophilicity” and the like terms, as used herein, refer to is the interfacial free energy of cohesion at contact as determined by the value of ΔG_{131}^{IF} . ΔG_{131}^{IF} is measured in mJ/m^2 . If ΔG_{131}^{IF} is a positive value (i.e. above 0), then a material is considered “hydrophilic” because there is an energy barrier preventing the surfaces from spontaneously contacting (i.e., hydrophilic repulsion or hydration energy). In contrast, if cohesive free energy is negative the two surfaces would spontaneously come together expelling water from between them; this is known as hydrophobic attraction or the hydrophobic effect. Also, a material is “more hydrophilic” or “less hydrophobic” as compared to another material if the material has a larger positive or less negative value of ΔG_{131}^{IF} as compared to the other material.

[0035] The terms “increasing the hydrophilicity” or “increases hydrophilicity” or the like terms, as used herein, refer to an increase in the value of ΔG_{131}^{IF} . For example, the value can be increased from a negative number (i.e. -20) to a less negative number (i.e. -5). In another example, the value can be increased from a negative number (i.e. -20) to a positive number (i.e. 5). In yet another example, the value can be increased from a positive value (i.e. 5) to a more positive value (i.e. 20). All these examples fall within the definition of “increasing the hydrophilicity” or “increases hydrophilicity.” A non-limiting example for a method that increases the value of ΔG_{131}^{IF} of a membrane with 5 mJ/m² can, for example, increase the value of ΔG_{131}^{IF} from -10 mJ/m² to -5 mJ/m², or from -3 mJ/m² to 2 mJ/m², or from 5 mJ/m² to 10 mJ/m² of the membrane.

[0036] If surfaces 1 and 2 are different materials (e.g., a bacteria cell and a membrane), ΔG_{132}^{IF} indicates the interfacial free energy of adhesion at contact. The term “adhesion propensity” and the like terms, as used herein, refer to the interfacial free energy of adhesion at contact as determined by the value of ΔG_{132}^{IF} . ΔG_{132}^{IF} is measured in mJ/m². The adhesion propensity describes the thermodynamic favorability of two surfaces comprised of different materials coming into contact when separated by water. Thus, a positive adhesive free energy indicates that energy must be input to expel water from between the two material surfaces and force them together, while a negative free energy indicates adhesion is a spontaneous process. The adhesion propensity of a material is determinative of the fouling resistance of the material (i.e. a polyaniline membrane). A larger negative value of ΔG_{132}^{IF} is associated with a material (e.g., a membrane) and a foulant (e.g., a bacteria cell) that would be highly fouling prone and difficult to clean because it is energetically favorable for the foulant to remain adhered to the material. A positive and value of ΔG_{132}^{IF} is associated with a material that would be less fouling prone and easy to clean.

[0037] The terms “increasing the adhesion propensity” or “increases adhesion propensity” or the like terms, as used herein, refer to increasing the value of ΔG_{132}^{IF} . For

example, the value can be increased from a negative number (i.e. -20) to a less negative number (i.e. -5). In another example, the value can be increased from a negative number (i.e. -20) to a positive number (i.e. 5). In yet another example, the value can be increased from a positive value (i.e. 5) to a more positive value (i.e. 20). All these examples fall within the definition of “increasing the adhesion propensity” or “increases adhesion propensity.” An increase in adhesion propensity of a material is indicative of an increase of the “fouling resistance” of the material (i.e. a polyaniline membrane). A non-limiting example for a

method that increases the value of ΔG_{132}^{IF} of a membrane with 5 mJ/m² can, for example, increase the value of ΔG_{132}^{IF} from -10 mJ/m² to -5 mJ/m², or from -3 mJ/m² to 2 mJ/m², or from 5 mJ/m² to 10 mJ/m² of the membrane.

[0038] Polymers containing polar functional groups (most often O, N, S, and P containing moieties) are sometimes described and thought of as hydrophilic. In the case of membranes, the term “hydrophilic” is often used synonymously with “fouling resistant” but there has been some confusion in the literature about apparently hydrophilic polymers (according to classical definitions of wettability and hydrophilicity) being somewhat fouling prone (e.g., PSf, PES, PC, and PEI). Perhaps for water treatment membranes, a special case should be considered. van Oss points out that when two materials with significant mixed polar functionality (i.e., seemingly “hydrophilic” but containing both electron donor and electron acceptor) that they can be thermodynamically attracted to one another through Lewis acid-base attraction (see eq. 4c). (C. J. van Oss, *The Properties of Water and their Role in Colloidal and Biological Systems*; Academic Press/Elsevier Ltd.: New York, NY, 2008) Through the third and fourth terms of eq. 4c, such materials can introduce negative AB interfacial free energy, and in particular, when the electron donor or acceptor surface tension components of either of the solid materials are less than those of water. This phenomenon affects both the free energy of cohesion and adhesion; hence, seemingly “hydrophilic” materials may actually produce negative “hydrophobic” free energies of cohesion or adhesion.

C. METHODS OF INCREASING HYDROPHILICITY OF A MEMBRANE

[0039] Polyaniline’s processability has been a concern with the choice of solvent generally limited to NMP and *N,N*’-dimethylpropyleneurea (DMPU) [13, 14]. Interchain and

intrachain hydrogen bonding between the imine and amine nitrogens in the emeraldine base form of PANi causes aggregation and the eventual formation of a gel. As many as 3 to 4 hydrogen bonds may form between the tetrameric repeat unit in PANi emeraldine base in an NMP solution [15]. Gelation can occur at PANi concentrations of less than 1 wt% [16-18] and often takes place in a very short time interval [19-21]; hence, the high concentrations desirable for membrane formation (*ca.* 15-25%) are with few exceptions generally not possible.

[0040] Gel-inhibiting agents, typically secondary and tertiary amine additives, help alleviate some of these PANi processability problems [22, 23]. Gel-inhibiting agents hydrogen bond to the imine nitrogens and thereby prevent gelation by inter-chain hydrogen bonding [24-28]. Fig. 1 illustrates the interaction and hydrogen bonding expected to occur between the emeraldine base form of PANi and the gel inhibitor 4MP in NMP. While these additives provide a means to produce concentrated PANi solutions from which robust membranes can be formed, gel-inhibiting agents may alter the polymer structure and chemistry. This can negatively alter film mechanical strength, conductivity, hydrophilicity, etc. [14, 27-31]. More hydrophobic membranes are more prone to fouling and, ultimately, need to be cleaned more frequently and require higher operating pressures, which requires more energy and is more costly, over time to maintain productivity [32-44].

[0041] Disclosed herein is a method of increasing membrane hydrophilicity comprising steps of: (a) providing a membrane comprising polyaniline, a polyaniline derivative, or co-polymer thereof and one or more gel inhibiting agents; and (b) treating the membrane with one or more hydrophilicity restoration agents, thereby increasing the hydrophilicity of the membrane. The disclosed method increases and/or restores the hydrophilicity of the membrane comprising polyaniline or co-polymer thereof and one or more gel inhibiting agents. Thus, in one aspect, the method makes the membrane less prone to fouling and can also increase the mechanical strength, conductivity and/or hydrophilicity of the membrane.

[0042] The preparation of solutions comprising polyaniline or co-polymer thereof and the one or more gel inhibiting agent which can be used to form membranes are described in U.S. Patents 5,981,695; 6,123,883; 6,429,282; 6,797,325; and 7,563,484 which are all herein incorporated by in their entirety by reference.

[0043] In one aspect, the solution comprising polyaniline or co-polymer thereof and the one or more gel inhibiting agent which can be used to form membranes can comprise a

solvent comprising N-methyl-2-pyrrolidinone, N-ethyl-2-pyrrolidinone, 1-cyclohexyl-2-pyrrolidinone, 1-methyl-2-piperidone, N-methylcaprolactam, 1,5-dimethyl-2-pyrrolidinone 2pyrrolidinone, 1,3-dimethyl-2-imidazolidinone, 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone, 1-methyl-2-pyridone, 1-acetylpyrrolidine, 1-acetylpiperidine, 4-acetylmorpholine, 1-acetyl-3-methylpiperidine, N,N-dimethylpropionamide, N,N,N',N'-tetramethyurea, N,N-dimethylacetamide, dimethylsulfoxide, tetramethylene sulfoxide, hexamethylphosphoramide, Δ -valerolactam, or N,N-2-trimethylpropionamide, or a combination thereof. For example, the solution comprising polyaniline or co-polymer thereof and the one or more gel inhibiting agent which can be used to form membranes can comprise a solvent comprising 1-methyl-2-pyrrolidinone.

[0044] In one aspect, the membrane comprises polyaniline, a polyaniline derivative, and a co-polymer thereof. For example, the membrane can comprise polyaniline and/or the membrane can comprise a polyaniline derivative and/or the membrane can comprise a polyaniline co-polymer. In another example, the membrane comprises polyaniline. In yet another example, the membrane comprises a polyaniline derivative. In yet another example, the membrane comprises a polyaniline co-polymer. In yet another example, the membrane comprises a polyaniline derivative co-polymer. A polyaniline co-polymer can be a polymer which comprises aniline repeat units, such as a PANi emeraldine base tetramer. Thus, a polyaniline co-polymer can be a random or block co-polymer.

[0045] In one aspect, the one or more gel inhibiting agents comprises a primary amine, secondary amine, or a tertiary amine, or a combination thereof. For example, the one or more gel inhibiting agents comprises a primary amine or secondary amine, or combination thereof. In another example, the one or more gel inhibiting agents comprises a secondary amine.

[0046] In one aspect, the secondary amine comprises 4-methylpiperidine, 2-methylaziridine, azetidine, pyrrolidine, piperidine, hexamethyleneimine, heptamethyleneimine, 3-pyrroline, 3-pyrrolidinol, (R)-(-)-pyrrolidine-2-methanol, (S)-(+)-pyrrolidine-2-methanol, 4-ethyl-2-methyl-(3-methylbutyl)oxazolidine, (S)-(+)-(anilinomethyl)pyrrolidine, 1,3,3-trimethyl-6-azabicyclo[3,2,1]octane, (S)-(+)-(methoxymethyl)pyrrolidine, indoline, thiomorpholine, decahydroquinoline, 2,6-dimethylmorpholine, diethylamine, dicyclohexylamine, dipropylamine, dibutylamine, N-methylhexylamine, 1-aza-15-crown-5, 1,2,3,6-tetrahydropyridine, 1,4,5,6-

tetrahydropyrimidine, 1,4-dioxo-8-azaspiro[4.5]-decane, 3,3-dimethylpiperidine, morpholine, or 3,5-dimethylpiperidine, or a combination thereof.

[0047] In one aspect, the primary amine comprises cyclopropylamine, n-butylamine, cyclobutylamine, cyclohexylamine, amylamine, t-amylamine, 2-amino-1-methoxypropane, 4-aminomorpholine, (+/-)-exo-2-aminonorbornane, 1,2-diaminopropane, 1,2-diaminocyclohexane, cyclooctylamine, 1,4-diaminobutane, 1-aminopiperidine, 1-aminohomopiperidine, tetrahydrofurfurylamine, furfurylamine, 1,2-diamino-2-methylpropane, 1-methyl-4-(methylamino)piperidine, or 4-(2-aminoethyl)morpholine, or a combination thereof.

[0048] In one aspect, the tertiary amine comprises N-Methylpiperidine, N,N'-Dimethylpiperazine, or triethylamine, or a combination thereof.

[0049] In one aspect, the one or more gel inhibiting agents comprises 4-methylpiperidine, n-Butylamine, 2,5-dimethyl-3-pyrroline, 3,3-dimethylpiperidine, heptamethyleneimine, diisopropylamine, hexamethyleneimine, N-ethylbenzylamine, piperazine, 2,6-dimethylmorpholine, piperidine, dibutylamine, N-methylpiperidine, N,N'-dimethylpiperazine, or diethylnipecotinamide, triethylamine or a combination thereof. For example, the one or more gel inhibiting agents can comprise 4-methylpiperidine.

[0050] In one aspect, the membrane comprising polyaniline or co-polymer thereof and one or more gel inhibiting agents can be made from a solution comprising a mole ratio of polyaniline or co-polymer thereof to one or more gel inhibiting agents of 0.1 to 5:0.1 to 10, such as, for example, a mole ratio of 1:2. In one aspect, the ratio of polyaniline or co-polymer thereof to one or more gel inhibiting agents can be a ratio capable to form a membrane, wherein prevent gelation by inter-chain hydrogen bonding between the emeraldine base form of PANi. Such ration can for example be a 1:2 mole ratio of polyaniline or co-polymer thereof to one or more gel inhibiting agents.

[0051] In one aspect, the membrane comprising the polyaniline or co-polymer thereof and the one or more gel inhibiting agents comprises at least 0.1% by weight of the one or more gel inhibiting agents. For example ,the membrane comprising the polyaniline or co-polymer thereof and the one or more gel inhibiting agents comprises at least 0.1%, 0.5%, 1%, 3%, 5%, 7.5%, 10%, 15%, 20%, or 30%, by weight of the one or more gel inhibiting agents.

[0052] In one aspect, the membrane comprising the polyaniline or co-polymer thereof and the one or more gel inhibiting agents is cast on a substrate, such as a fabric.

[0053] In one aspect, the membrane comprising the polyaniline or co-polymer thereof and the one or more gel inhibiting agents has a surface porosity of less than 5%, 4%, 3%, 2%, 1%, 0.8%, 0.6%, 0.4%, 0.2%, 0.1%, or 0.05%. For example, the membrane comprising the polyaniline or co-polymer thereof and the one or more gel inhibiting agents has a surface porosity of less than 1%, 0.8%, 0.6%, 0.4%, 0.2%, 0.1%, or 0.05%, such as for example, less than 0.4% or 0.2%.

[0054] In one aspect, the membrane comprising the polyaniline or co-polymer thereof and the one or more gel inhibiting agents has an average pore size diameter of less than 20 nm, 15 nm, 10 nm, 7.5 nm, 5 nm, or 2.5 nm. For example, the membrane comprising the polyaniline or co-polymer thereof and the one or more gel inhibiting agents has an average pore size diameter of less than 10 nm, 7.5 nm, 5 nm, or 2.5 nm., such as for example, less than 7.5 nm or 5 nm.

[0055] In one aspect, the treating comprises contacting the membrane with the hydrophilicity restoration agent for at least 15 min, 30 min, 45 min, 60 min, 90 min, 120 min or 180 min. For example, the treating comprises contacting the membrane with the hydrophilicity restoration agent for at least 15 min. In another example, the treating comprises contacting the membrane with the hydrophilicity restoration agent for at least 60 min.

[0056] In one aspect, treating the membrane comprising the polyaniline or co-polymer thereof and the one or more gel inhibiting agents with one or more hydrophilicity restoration agents comprises treating the membrane with an effective amount of the one or more hydrophilicity restoration agents to increase the hydrophilicity of the membrane.

[0057] In one aspect, the treating comprises filtering the membrane with one or more hydrophilicity restoration agents. In one aspect, the filtering comprises filtering the membrane with the hydrophilicity restoration agent for at least 15 min, 30 min, 45 min, 60 min, 90 min, 120 min or 180 min. For example, the filtering comprises filtering the membrane with the hydrophilicity restoration agent for at least 15 min. In another example, the filtering comprises filtering the membrane with the hydrophilicity restoration agent for at least 60 min.

[0058] In one aspect, the one or more hydrophilicity restoration agents comprises an organic sulfonic acid. The organic sulfonic acid can be a mono- or di-sulfonic acid. In one aspect, the organic sulfonic acid comprises C1-C12 substituted or unsubstituted alkyl, C1-C12 substituted or unsubstituted alkenyl, C1-C12 substituted or unsubstituted alkyl, C1-C12 substituted or unsubstituted cycloalkyl, C1-C12 substituted or unsubstituted heteroaryl, C1-C12 substituted or unsubstituted heterocyclyl. For example, the organic sulfonic acid comprises C3-C12 substituted or unsubstituted alkyl, C3-C12 substituted or unsubstituted alkenyl, C3-C12 substituted or unsubstituted alkyl, C3-C12 substituted or unsubstituted cycloalkyl, C3-C12 substituted or unsubstituted heteroaryl, C3-C12 substituted or unsubstituted heterocyclyl. In another example, the organic sulfonic acid comprises C6-C12 substituted or unsubstituted alkyl, C6-C12 substituted or unsubstituted alkenyl, C6-C12 substituted or unsubstituted alkyl, C6-C12 substituted or unsubstituted cycloalkyl, C6-C12 substituted or unsubstituted heteroaryl, C6-C12 substituted or unsubstituted heterocyclyl.

[0059] In one aspect, the one or more hydrophilicity restoration agents comprises (+/-) camphor-10-sulfonic acid, sulfuric acid, methane sulfonic acid, ethane sulfonic acid, propanesulfonic acid, perfluoropropanesulfonic acid, butane sulfonic acid, perfluorobutane sulfonic acid, hexane sulfonic acid, perfluorohexane sulfonic acid, perfluorooctanesulfonic acid, benzene sulfonic acid, toluene sulfonic acid, dodecyl benzene, sulfonic acid, taurine (2-aminoethanesulfonic acid), homotaurine (3-aminopropanesulfonic acid), naphthalene sulfonic acid, 2,5 naphthalene disulfonic acid, dinonylnaphthalene sulfonic acid, dinonlynaphthalene disulfonic acid, polyvinylsulfonate, or polystyrenesulfonate, or a combination thereof. For example, the one or more hydrophilicity restoration agents comprises (+/-) camphor-10-sulfonic acid, methane sulfonic acid, ethane sulfonic acid, propanesulfonic acid, perfluoropropanesulfonic acid, butane sulfonic acid, perfluorobutane sulfonic acid, hexane sulfonic acid, perfluorohexane sulfonic acid, perfluorooctanesulfonic acid, benzene sulfonic acid, toluene sulfonic acid, dodecyl benzene, sulfonic acid, taurine (2-aminoethanesulfonic acid), homotaurine (3-aminopropanesulfonic acid), naphthalene sulfonic acid, 2,5 naphthalene disulfonic acid, dinonylnaphthalene sulfonic acid, dinonlynaphthalene disulfonic acid, polyvinylsulfonate, or polystyrenesulfonate, or a combination thereof. In another example, the one or more hydrophilicity restoration agents can comprise (+/-) camphor-10-sulfonic acid, such as (-) camphor-10-sulfonic acid or (+) camphor-10-sulfonic acid, or a combination thereof.

[0060] In one aspect, the membrane has a negative ΔG_{131}^{IF} value before treatment. For example, the membrane can have a negative ΔG_{131}^{IF} value of less than -2, -4, -6, -8, -10, -15, or -20 mJ/m² before treatment. For example, the membrane can have a negative ΔG_{131}^{IF} value of less than -8 mJ/m² before treatment. In one aspect, the membrane can have a negative ΔG_{131}^{IF} value from -2 to -20 mJ/m² before treatment.

[0061] In one aspect, the membrane has a positive value of ΔG_{131}^{IF} after treatment. In one aspect, the membrane has a positive value of ΔG_{131}^{IF} of at least 1, 5, 10, 15, 20, 25, 30, or 50 mJ/m² after treatment. For example, the membrane can have a positive value of ΔG_{131}^{IF} of at least 10 mJ/m² after treatment. In another aspect, the membrane can have a positive value of ΔG_{131}^{IF} from 1 to 50 mJ/m² after treatment. For example, the membrane can have a positive value of ΔG_{131}^{IF} from 5 to 25 mJ/m² after treatment.

[0062] In one aspect, the membrane has an increased value of ΔG_{131}^{IF} of at least 5, 10, 15, 20, 25, 30, 50, 75, or 100 mJ/m² after treatment. For example, the membrane can have an increased value of ΔG_{131}^{IF} of at least 5, 10, 15, 20, 25, 30, or 50 J/m² after treatment, such as at least 20, 25, or 30 J/m² after treatment. In another aspect, the membrane can have an increased value of ΔG_{131}^{IF} from 5 to 100 mJ/m² after treatment. For example, the membrane can have an increased value of ΔG_{131}^{IF} from 5 to 50 mJ/m² after treatment, such as from 20 to 50 mJ/m² after treatment.

[0063] In one aspect, the membrane has a decreased adhesion propensity after treatment.

[0064] In another aspect, the membrane has an increased fouling resistance after treatment.

[0065] In one aspect, the membrane has a positive value of ΔG_{132}^{IF} after treatment.

In one aspect, the membrane has a positive value of ΔG_{132}^{IF} of at least 1, 5, 10, 15, 20, 25, 30, or 50 mJ/m² after treatment. For example, the membrane can have a positive value of

ΔG_{132}^{IF} of at least 10 mJ/m² after treatment. In another aspect, the membrane can have a

positive value of ΔG_{132}^{IF} from 1 to 50 mJ/m² after treatment. For example, the membrane

can have a positive value of ΔG_{132}^{IF} from 5 to 35 mJ/m² after treatment.

[0066] In one aspect, the membrane has an increased value of ΔG_{132}^{IF} of at least 5, 10, 15, 20, 25, 30, 50, 75, or 100 mJ/m² after treatment. For example, the membrane can have an

increased value of ΔG_{132}^{IF} of at least 5, 10, 15, 20, 25, 30, or 50 J/m² after treatment, such as at least 20, 25, or 30 J/m² after treatment. In another aspect, the membrane can have an

increased value of ΔG_{132}^{IF} from 5 to 100 mJ/m² after treatment. For example, the

membrane can have an increased value of ΔG_{132}^{IF} from 5 to 50 mJ/m² after treatment, such as from 20 to 50 mJ/m² after treatment.

[0067] In one aspect, the membrane has a positive value of ΔG_{132}^{IF} of at least 1, 5, 10, 15, 20, 25, 30, or 50 mJ/m² after treatment as measured against silica, polyethylene glycol (PEG), human serum albumin (HSA), hexadecane, *E. coli*, *S. cerevisiae*, and *P. putida*. For

example, the membrane can have a positive value of ΔG_{132}^{IF} of at least 10 mJ/m² after treatment as measured against silica, PEG, HSA, hexadecane, *E. coli*, *S. cerevisiae*, and *P.*

putida. In another aspect, the membrane can have a positive value of ΔG_{132}^{IF} from 1 to 50 mJ/m² after treatment as measured against silica, PEG, HSA, hexadecane, *E. Coli*, *S. cerevisiae*, and *P. putida*. For example, the membrane can have a positive value of

ΔG_{132}^{IF} from 5 to 35 mJ/m² after treatment as measured against silica, PEG, HSA, hexadecane, *E. coli*, *S. cerevisiae*, and *P. putida*.

[0068] In one aspect, the membrane has an increased value of ΔG_{132}^{IF} of at least 5, 10, 15, 20, 25, 30, 50, 75, or 100 mJ/m² after treatment as measured against silica, PEG, HSA, hexadecane, *E. coli*, *S. cerevisiae*, and *P. putida*. For example, the membrane can have an increased value of ΔG_{132}^{IF} of at least 5, 10, 15, 20, 25, 30, or 50 J/m² after treatment, such as at least 20, 25, or 30 J/m² after treatment as measured against silica, PEG, HSA, hexadecane, *E. coli*, *S. cerevisiae*, and *P. putida*. In another aspect, the membrane can have an increased value of ΔG_{132}^{IF} from 5 to 100 mJ/m² after treatment as measured against silica, PEG, HSA, hexadecane, *E. coli*, *S. cerevisiae*, and *P. putida*. For example, the membrane can have an increased value of ΔG_{132}^{IF} from 5 to 50 mJ/m² after treatment, such as from 20 to 50 mJ/m² after treatment as measured against PEG, HSA, hexadecane, *E. coli*, *S. cerevisiae*, and *P. putida*.

[0069] In one aspect, the membrane has a positive value of ΔG_{132}^{IF} of at least 1, 5, 10, 15, 20, 25, 30, or 50 mJ/m² after treatment as measured against silica, PEG, HSA, hexadecane, *E. coli*, *S. cerevisiae*, or *P. putida*, or a combination thereof. For example, the membrane can have a positive value of ΔG_{132}^{IF} of at least 10 mJ/m² after treatment as measured against silica, PEG, HSA, hexadecane, *E. coli*, *S. cerevisiae*, or *P. putida*, or a combination thereof. In another aspect, the membrane can have a positive value of ΔG_{132}^{IF} from 1 to 50 mJ/m² after treatment as measured against silica, PEG, HSA, hexadecane, *E. coli*, *S. cerevisiae*, or *P. putida*, or a combination thereof. For example, the membrane can have a positive value of ΔG_{132}^{IF} from 5 to 35 mJ/m² after treatment as measured against silica, PEG, HSA, hexadecane, *E. coli*, *S. cerevisiae*, or *P. putida*, or a combination thereof.

[0070] In one aspect, the membrane has an increased value of ΔG_{132}^{IF} of at least 5, 10, 15, 20, 25, 30, 50, 75, or 100 mJ/m² after treatment as measured against silica, PEG, HSA, hexadecane, *E. coli*, *S. cerevisiae*, or *P. putida*, or a combination thereof. For example, the membrane can have an increased value of ΔG_{132}^{IF} of at least 5, 10, 15, 20, 25, 30, or 50 mJ/m² after treatment, such as at least 20, 25, or 30 J/m² after treatment as measured against silica, PEG, HSA, hexadecane, *E. coli*, *S. cerevisiae*, or *P. putida*, or a combination thereof.

In another aspect, the membrane can have an increased value of ΔG_{132}^{IF} from 5 to 100 mJ/m² after treatment as measured against silica, PEG, HSA, hexadecane, *E. coli*, *S. cerevisiae*, or *P. putida*, or a combination thereof. For example, the membrane can have an increased value of ΔG_{132}^{IF} from 5 to 50 mJ/m² after treatment, such as from 20 to 50 mJ/m² after treatment as measured against silica, PEG, HSA, hexadecane, *E. coli*, *S. cerevisiae*, or *P. putida*, or a combination thereof.

D. MEMBRANES

[0071] Also disclosed herein are membranes comprising polyaniline, a polyaniline derivative, or a co-polymer thereof, wherein the membrane has been subjected to one or more of the methods disclosed herein. For example, the membranes comprising polyaniline or a co-polymer thereof can have been subjected to a method disclosed herein.

[0072] In one aspect, the membrane has a positive value of ΔG_{131}^{IF} . In one aspect, the membrane can have a positive value of ΔG_{131}^{IF} of at least 1, 5, 10, 15, 20, 25, 30, or 50 mJ/m². For example, the membrane can have a positive value of ΔG_{131}^{IF} of at least 10 mJ/m². In another aspect, the membrane can have a positive value of ΔG_{131}^{IF} from 1 to 50 mJ/m². For example, the membrane can have a positive value of ΔG_{131}^{IF} from 5 to 25 mJ/m².

[0073] In one aspect, the membrane has a positive value of ΔG_{132}^{IF} . In one aspect, the membrane has a positive value of ΔG_{132}^{IF} of at least 1, 5, 10, 15, 20, 25, 30, or 50 mJ/m². For example, the membrane can have a positive value of ΔG_{132}^{IF} of at least 10 mJ/m². In another aspect, the membrane can have a positive value of ΔG_{132}^{IF} from 1 to 50 mJ/m². For example, the membrane can have a positive value of ΔG_{132}^{IF} from 5 to 35 mJ/m².

[0074] In one aspect, the membrane has a positive value of ΔG_{132}^{IF} as measured against silica, PEG, HSA, hexadecane, *E. coli*, *S. cerevisiae*, and *P. putida*. In one aspect, the membrane has a positive value of ΔG_{132}^{IF} of at least 1, 5, 10, 15, 20, 25, 30, or 50 mJ/m² as measured against silica, PEG, HSA, hexadecane, *E. coli*, *S. cerevisiae*, and *P. putida*. For example, the membrane can have a positive value of ΔG_{132}^{IF} of at least 10 mJ/m² as measured against PEG, HSA, hexadecane, *E. coli*, *S. cerevisiae*, and *P. putida*. In another aspect, the membrane can have a positive value of ΔG_{132}^{IF} from 1 to 50 mJ/m² as measured against silica, PEG, HSA, hexadecane, *E. coli*, *S. cerevisiae*, and *P. putida*. For example, the membrane can have a positive value of ΔG_{132}^{IF} from 5 to 35 mJ/m² as measured against silica, PEG, HSA, hexadecane, *E. coli*, *S. cerevisiae*, and *P. putida*.

[0075] In one aspect, the membrane has a positive value of ΔG_{132}^{IF} as measured against silica, PEG, HSA, hexadecane, *E. coli*, *S. cerevisiae*, or *P. putida*, or a combination thereof. In one aspect, the membrane has a positive value of ΔG_{132}^{IF} of at least 1, 5, 10, 15, 20, 25, 30, or 50 mJ/m² after treatment as measured against silica, PEG, HSA, hexadecane, *E. coli*, *S. cerevisiae*, or *P. putida*, or a combination thereof. For example, the membrane can

have a positive value of ΔG_{132}^{IF} of at least 10 mJ/m² after treatment as measured against silica, PEG, HSA, hexadecane, *E. coli*, *S. cerevisiae*, or *P. putida*, or a combination thereof.

In another aspect, the membrane can have a positive value of ΔG_{132}^{IF} from 1 to 50 mJ/m² as measured against silica, PEG, HSA, hexadecane, *E. coli*, *S. cerevisiae*, or *P. putida*, or a combination thereof. For example, the membrane can have a positive value of ΔG_{132}^{IF} from 5 to 25 mJ/m² as measured against silica, PEG, HSA, hexadecane, *E. coli*, *S. cerevisiae*, or *P. putida*, or a combination thereof.

E. ARTICLE OF MANUFACTURE

[0076] Also disclosed herein is an article of manufacture comprising one or more of the membranes disclosed herein. For example, the article of manufacture can comprise a membrane disclosed herein.

[0077] In one aspect, the article of manufacture is a device for purifying. For example, the article of manufacture can be a device for purifying water fresh surface water, seawater ahead of desalination by reverse osmosis membranes, oily wastewater, municipal sewage or other industrial wastewaters. For example, the article of manufacture can be a device for separating proteins, purifying liquid food and beverage products, performing kidney dialysis.

F. METHODS OF USE

[0078] Also disclosed herein is a method for purifying water comprising the steps of: (a) providing a membrane disclosed herein, wherein the membrane has a first face and a second face; (b) contacting the first face of the membrane with a first solution of a first volume having a first salt concentration at a first pressure; and (c) contacting the second face of the membrane with a second solution of a second volume having a second salt concentration at a second pressure; wherein the first solution is in fluid communication with the second solution through the membrane, wherein the first salt concentration is higher than the second salt concentration, thereby creating an osmotic pressure across the membrane, and wherein the first pressure is sufficiently higher than the second pressure to overcome the osmotic pressure, thereby increasing the second volume and decreasing the first volume.

[0079] Also disclosed herein is a method for concentrating an impurity comprising the steps of: (a) providing a membrane disclosed herein, wherein the membrane has a first face and a second face; (b) contacting the first face of the membrane with a first mixture of a first volume having a first impurity concentration at a first pressure; (c) contacting the second face of the membrane with a second mixture of a second volume having a second impurity concentration at a second pressure; and (d) collecting the impurity, wherein the first mixture is in fluid communication with the second solution through the membrane, wherein the first impurity concentration is higher than the second impurity concentration, thereby creating an osmotic pressure across the membrane, and wherein the first pressure is sufficiently higher than the second pressure to overcome the osmotic pressure, thereby increasing the second volume and decreasing the first volume.

EXAMPLES

[0080] The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how the compounds, compositions, articles, devices and/or methods claimed herein are made and evaluated, and are intended to be purely exemplary of the invention and are not intended to limit the scope of what the inventors regard as their invention. Efforts have been made to ensure accuracy with respect to numbers (*e.g.*, amounts, temperature, etc.), but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight, temperature is in °C or is at ambient temperature, and pressure is at or near atmospheric.

[0081] Several methods for preparing the compounds of this invention are illustrated in the following Examples. Starting materials and the requisite intermediates are in some cases commercially available, or can be prepared according to literature procedures or as illustrated herein.

a. EXAMPLE 1

[0082] The addition of the gel-inhibiting agent, 4-methylpiperidine (4MP), to polyaniline (PANi)/1-methyl-2-pyrrolidinone (NMP) mixtures produced stable polymer solutions at high polymer concentrations. Membranes cast from 18 polymer wt% PANi in NMP-4MP solutions were 98% less water permeable, but exhibited 91% greater protein rejection than those cast from 18 polymer wt% PANi in NMP. After phase inversion using deionized water, PANi-NMP membranes had water contact angles of 24° while PANi-NMP-4MP membranes

had contact angles of 42°. This decrease in membrane hydrophilicity arose from a combination of hydrogen-bonded and ring-substituted 4MP/polyaniline associations. Chemical post-treatment with different acid and base solvents produced a range of water fluxes, protein rejections, interfacial hydrophilicities and mechanical properties. Post-treatment with camphorsulfonic acid completely removed the hydrogen-bonded fraction of 4MP from the polymer matrix and was most effective at recovering membrane hydrophilicity. The implications are that pure polyaniline ultrafiltration membranes can be made with excellent mechanical, interfacial and separation properties through use of gel-inhibitors and chemical post-treatments.

(a) *MATERIALS AND METHODS*

(i) **MATERIALS**

[0083] Ultra-pure 18 MΩ deionized (DI) water was produced by a reverse osmosis system (RODI-C-12BL, Aqua Solutions, Inc.). Sulfuric acid (Sigma-Aldrich, No. 320501), ammonium peroxydisulfate (Fisher, No. A682), sodium hydroxide (Fisher, No. S612), methanol (Sigma-Aldrich, No. 322415), NMP (Sigma-Aldrich, No. 443778), 4MP (Sigma-Aldrich, No. M73206), hydrochloric acid (Sigma-Aldrich, No. 258148), *p*-toluenesulfonic acid monohydrate (PTSA) (Fisher, No. AC17178), (+/-) camphor-10-sulfonic acid (CSA) (AlfaAesar, No. A12620), 4-dodecylbenzenesulfonic acid (DBSA) (Sigma-Aldrich, No. 44198), ammonium hydroxide (Sigma-Aldrich, No. 320145), bovine serum albumin (BSA) (Sigma-Aldrich, No. A9647), sodium chloride (Fisher, No. S271), dimethyl sulfoxide- d_6 (Cambridge Isotope Laboratories, No. DLM-10), and potassium chloride (Fisher, No. P217) were all used as received.

(ii) **POLYMER SOLUTION PREPARATION AND MEMBRANE FORMATION**

[0084] Polyaniline was synthesized in our laboratory as previously reported in detail [12]. Polyaniline was dried in a vacuum oven (~25 in. Hg) at 50 °C overnight prior to addition to the solvents. Polymer solutions were prepared by adding 18 wt% crushed PANi powder to 82 wt% NMP (PANi-NMP) or a mixture of 72 wt% NMP and 10 wt% 4MP (PANi-NMP-4MP), i.e., 2 moles 4MP:mole PANi emeraldine base tetramer; 0.547 g 4MP/g PANi emeraldine base [15, 22, 26-28]. PANi was added to the solvent(s) over the course of 1 h while vigorously stirring. Polymer solutions were allowed to stir for 3 d in a tightly sealed glass vial.

[0085] PANi ultrafiltration membranes were formed by immersion precipitation [45]. Polymer solutions were allowed to stand sealed for 1 h before film casting. Films were spread using a casting knife (Gardco Adjustable Micrometer Film Applicator, Microm II, AP-99500701) with a blade height of 152 μm set using a feeler gauge. Films were hand-cast on a nonwoven polyester fabric (NanoH₂O, Inc., Los Angeles, CA) and immediately placed in a coagulation bath containing 3 liters of DI water at 20 °C. The relative humidity during film casting was 50-55%. Membranes remained in the coagulation bath for 30 min before being transferred to plastic storage bags where they were soaked in DI water. Water in the storage bags was replaced with fresh DI water every 30 min for 2 h. Membranes were then stored at 4 °C in DI water prior to post-treatment and further characterization.

(iii) MEMBRANE POST-TREATMENT

[0086] PANi UF membranes were post-treated by placing membrane coupons in beakers containing 150 ml aqueous solutions of 100 mM HCl, H₂SO₄, PTSA, CSA, DBSA, or NH₄OH. A similar post-treatment was carried out using DI water at 50 °C. Gentle stirring was maintained at 125 rpm. A special post-treatment intended to remove CSA from the membrane was carried out in 100 mM NH₄OH at 50 °C for 3 h with gentle stirring. CSA post-treatment was conducted using 100 mM CSA at 50 °C for 1 h unless otherwise noted.

(iv) MEMBRANE CHARACTERIZATION

[0087] Membrane samples were cut for performance testing using a 25 mm punch (Osborne arch punch, OS-149-m25, Campbell Bosworth Machinery Co.). Samples were kept wet and placed in a dead-end stirred cell (UHP-25, Advantec MFS, Inc.) with a membrane area (A_m) of 3.5 cm². Permeate volumetric flow rates were measured using a digital HPLC liquid flow meter (FlowCal 5000, Tovatech, LLC). Membranes were compacted with DI water under 20 psi transmembrane pressure at 20 °C until a decrease in permeability of < 5% over 30 min was achieved. Permeate volumetric flowrate (Q_p) was then recorded at transmembrane pressures (Δp) of 20, 10, and 5 psi. Membrane pure water permeabilities (L_p) were calculated from [46]:

$$L_p = \frac{Q_p}{A_m \cdot \Delta p} \quad (5)$$

[0088] Membrane protein rejection was measured immediately after the pure water permeability test. Residual water from the permeability test was removed from the stirred cell and replaced with a 10 ml solution of 1000 mg l⁻¹ BSA in 50 mM NaCl. BSA has a hydrodynamic diameter of 6 nm in this solution [12]. The stir rate was maintained at 350 rpm (Re_{SC} = 2963). The stirred cell Reynolds number was calculated from

$$\text{Re}_{SC} = \frac{\rho \cdot \omega \cdot r_{SC}^2}{\mu} \quad (6)$$

[0089] where ρ is the fluid density (kg m⁻³), ω is the angular velocity (rad s⁻¹), r_{SC} is the stirred cell radius (9×10⁻³ m), and μ is the fluid dynamic viscosity (kg m⁻¹ s⁻¹) [47]. The stirred cell mass transfer coefficient (k_{SC}) of 4.1×10⁻⁶ m s⁻¹ was calculated using [47]:

$$\frac{k_{SC} \cdot r_{SC}}{D} = \text{Sh}_{SC} = 0.27 \text{Re}_{SC}^{0.567} \text{Sc}^{0.33} \quad (7)$$

[0090] where D is the diffusion coefficient of BSA (5.9×10⁻¹¹ m² s⁻¹), Sh_{SC} is the stirred cell Sherwood number, and Sc is the Schmidt number ($\text{Sc} = \mu \cdot \rho^{-1} \cdot D^{-1}$). A constant transmembrane pressure was set to give an initial permeate flux ($J_v = Q_p/A_m$) of 40 gallons ft⁻² d⁻¹ (19 μm s⁻¹), and 5 ml of permeate was collected (50% recovery). Protein concentrations in the feed (c_f) and permeate (c_p) were determined by UV-vis absorption at $\lambda = 278$ nm (DU[®] 730 Life Science UV/Vis Spectrophotometer, Beckman Coulter). Solute rejection (R_s) was calculated based on

$$R_s = 1 - \frac{c_p}{c_f} \quad (8)$$

[0091] Deionized water contact angles were measured using a goniometer (DSA10, KRÜSS GmbH). The captive bubble measurement technique was employed here due to the hydrophilicity of the PANi films. Ten drops were measured and the highest and lowest values were discarded. Fourier transform infrared (FTIR) (JASCO FT/IR-6300 with ATR PRO450-S ZnSe crystal) spectra were measured for each membrane. Films were dried in a desiccator overnight at 20 °C prior to measurement.

[0092] ¹H-Nuclear Magnetic Resonance (¹H-NMR) studies were carried out in a Bruker Avance AV300 (300.1 MHz) instrument at room temperature. The membranes were not dried in vacuo or thermally to prevent NMP and/or 4MP from evaporating from the membranes.

Saturated membrane solutions were prepared in DMSO-d₆ and the NMP/4MP standards were measured as neat solutions. The ¹H-NMR chemical shifts were reported relative to the deuterated DMSO solvent signal.

[0093] Streaming current was measured using an adjustable gap electrokinetic analyzer (SurPASS Electrokinetic Analyzer, Anton-Paar GmbH). The flow channel gap was set at 100 μm, and a 1 mM KCl solution at 20 °C was used as the background electrolyte. Streaming current was determined in a pH range of 2-10, adjusted using HCl and NaOH. Membrane zeta potential (ζ) was calculated using the Helmholtz-Smoluchowski equation,

$$\zeta = \frac{dI}{dp} \cdot \frac{\mu}{\varepsilon \cdot \varepsilon_0} \cdot \frac{L}{A}, \quad (9)$$

[0094] where dI/dp is the slope of the streaming current versus pressure, μ is the solution dynamic viscosity, ε is the dielectric constant of the solution, ε_0 is the vacuum permittivity, L is the streaming channel length and A is the cross-section of the streaming channel.

[0095] Membrane samples were prepared for SEM (Nova 600 NanoLab DualBeamTM-SEM/FIB, FEI Company) by soaking in H₂SO₄ at pH 1 for 1 h to make PANi fully doped and electrically conducting. Samples were dried in a desiccator overnight at 20 °C. Cross-sections were prepared from unsupported films by freeze fracturing using liquid nitrogen. Membrane surface SEM images were analyzed for porosity and pore size by a previously described procedure [12, 48].

[0096] Membrane tensile strength analyses were conducted on 5 mm x 100 mm membrane samples. The thickness of the samples was measured using a micrometer before the analysis, and the average value of the thickness was used to calculate the result. All samples were placed in a United Testing Systems tensile test apparatus at 25 °C, with a gauge length of 80 mm, and pulled at a rate of 2 mm min⁻¹. Two sets of sample conditions were used. One set of samples was measured under wet conditions, in which the samples were directly tested after removal from the water storage bags and dabbed dry using napkins. Another set of samples was tested under dried conditions, in which the samples were dried first in air for 1 h and then placed in a desiccator for 24 h.

[0097] Thermal gravimetric analyses (TGA) were conducted on a Seiko ExStar TG/DTA 6200 from Haake Instruments. The samples were measure under protection of N₂ flow (90 ml

min⁻¹), with the heating rate at 2 °C min⁻¹, and temperature tested from 20 – 550 °C. Samples were dried in a desiccator for 24 h prior to TGA measurements.

(b) RESULTS

(i) EFFECT OF 4MP ON PANi PROCESSABILITY

[0098] Adding 4MP in a 2:1 molar 4MP: PANi emeraldine base tetramer ratio improves the polymer solution quality. An 18 wt% PANi mixture containing 72 wt% NMP and 10 wt% 4MP produces a viable polymer solution within 1 d. A viable polymer solution is defined here as a mixture of polymer and solvent from which a membrane can be cast; non-viable polymer solutions form a gel within seconds that cannot be cast into a membrane. Polymer solutions containing our synthesized PANi with a 2:1 molar ratio of 4MP: PANi emeraldine base do not gel for several months. However, a PANi-NMP mixture without 4MP takes 2 d to form a viable polymer solution, and this polymer solution remains viable for 2 – 5 d before a gel forms. The addition of 4MP allows for the complete dissolution of PANi and greatly expands the window of polymer solution viability.

(ii) EFFECT OF CHEMICAL POST-TREATMENTS ON PANi MEMBRANE HYDROPHILICITY

[0099] Captive bubble water contact angles for PANi-NMP membranes and untreated and post-treated PANi-NMP-4MP membranes are summarized in Table 1 along with molecular weight, anion dimensions, and pK_a of the acids and bases used for post-treatment.

TABLE 1

Membrane/Post-treatment	MW (Da)	Anion Dimensions (Å)	pK _a	Contact Angle (°)
PANi-NMP	-	-	-	24.2 ± 2.1
PANi-NMP-4MP	-	-	-	41.9 ± 1.6
H ₂ O	18.0	-	15.7	40.5 ± 2.9
HCl	36.5	3.3	-6.1	53.0 ± 4.1
H ₂ SO ₄	98.1	3.4, 2.5, 2.4	-3.0, 2.0	43.7 ± 3.2
PTSA	190.2	7.0, 4.3, 2.5	0.7	44.5 ± 3.6
CSA	232.3	7.0, 5.4, 5.6	2.0	18.4 ± 1.0
DBSA	326.5	22.2, 5.0, 2.4	2.6	43.9 ± 2.9
NH ₄ OH	35.0	-	9.2	47.1 ± 1.9
CSA-NH ₄ OH	-	-	-	17.2 ± 1.1
CSA-filter-acid-base-filter	-	-	-	17.1 ± 0.5

[00100] Table 1 shows the molecular weight, anion dimensions, pK_a of post-treatment molecules, and water contact angles for PANi-NMP-4MP membranes after 1 h post-treatments at 50 °C.

[00101] Anion dimensions were approximated using Chem3D software (CambridgeSoft) via the protocol outlined by Yang et al. [28]. The dimension for the chloride ion is an ionic diameter [49]. The addition of 4MP to the polymer solution increases the membrane water contact angle from 22° to 42° (untreated) [12]. Post-treatment of this PANi-NMP-4MP membrane in H₂O at 50 °C for 1 h does not alter the membrane water contact angle. Post-treatments for 1 h with 100 mM H₂SO₄, PTSA, and DBSA at 50 °C have little effect on membrane hydrophilicity. Post-treatments for 1 h with 100 mM HCl and NH₄OH at 50 °C appear to increase membrane hydrophobicity. Post-treatment of the PANi-NMP-4MP membrane in 100 mM CSA for 1 h at 50 °C, however, reduces membrane water contact angle to 18.4°. In an attempt to remove excess CSA from the membrane surface, CSA-post-treated PANi-NMP-4MP membranes were further treated for 3 h in 100 mM NH₄OH at 50 °C (CSA-NH₄OH). This treatment does not further affect membrane hydrophilicity (contact angle = 17.2°). A PANi-NMP-4MP membrane was extensively post-treated by the following process: 1 h treatment in 100 mM CSA at 50 °C → 60 min filtration of DI H₂O under 20 psi at 20 °C → 10 min with 0.5 M H₂SO₄ treatment at 45 °C → 10 min with 1 M NaOH treatment at 45 °C → 30 min filtration with DI H₂O under 20 psi at 20 °C. This treatment is labeled “CSA-

filter-acid-base-filter” in Table 1. CSA-treated membrane hydrophilicity was unaffected by the additional water filtration and acid and base treatments (contact angle = 17.1°).

[00102] The effect of CSA treatment time on membrane hydrophilicity is shown in Fig. 2. PANi-NMP-4MP membranes were treated with 100 mM CSA at 50 °C. Membrane hydrophilicity began to increase after treatment for 10 min. There was a transitional time between 10 and 60 min where areas of the treated membrane remained relatively hydrophobic (contact angle = 42°) while areas a few millimeters away had recovered hydrophilicity (contact angle < 20°). This is the reason for the larger error bars for contact angle values at 15 and 30 min CSA treatment times. The maximum membrane hydrophilicity was achieved after 1 h of CSA treatment. The effect of CSA treatment temperature on membrane hydrophilicity is shown in Table 2. PANi-NMP-4MP membranes were treated with 100 mM CSA for 1 h. The membrane hydrophilicity was recovered at all temperatures tested.

Table 2

Treatment temp. (°C)	Contact angle (°)
10	18.8 ± 1.2
20	17.6 ± 1.0
50	18.4 ± 1.0

[00103] Table 2 shows the water contact angles for PANi-NMP-4MP membranes after 1 h 100 mM CSA post-treatment at different temperatures.

(iii) EFFECT OF CSA POST-TREATMENT ON PANI MEMBRANE PERFORMANCE

[00104] Pure water permeability was measured for untreated and CSA-treated PANi-NMP-4MP membranes and is summarized in Table 3. It was previously reported a membrane pure water permeability of 1050 $\mu\text{m s}^{-1} \text{bar}^{-1}$ with 0% BSA rejection for an 18 wt% PANi-82 wt% NMP membrane containing no 4MP [12]. Membrane permeability decreases by 98% upon addition of 10 wt% 4MP to the polymer solution. BSA protein rejection of the PANi-NMP-4MP membrane increases from 0% to 91%. Post-treatment of the PANi-NMP-4MP membrane with 100 mM CSA for 1 h at 50 °C decreases BSA rejection by ~15% with a slight decrease in permeability.

Table 3

Membrane	Permeability ($\mu\text{m s}^{-1} \text{bar}^{-1}$)	BSA rejection
PANi-NMP-4MP	24.5 ± 3.0	0.91 ± 0.01
PANi-NMP-4MP CSA-treated	20.3 ± 4.4	0.74 ± 0.03

[00105] Table 3 shows the membrane pure water permeability and BSA rejection for untreated and CSA-post-treated membrane.

(iv) PANI MEMBRANE MECHANICAL AND THERMAL PROPERTIES

[00106] Nonwoven support fabric and membrane thicknesses and tensile moduli are given in Table 4. The dried support fabric is about 13% thinner than the wet sample. Of the PANi membranes, only the untreated PANi-NMP membrane showed a minor decrease in thickness (7%). Post-treatment using 100 mM CSA at 50 °C had no effect on membrane thickness. Both CSA-treated and untreated PANi-NMP-4MP membranes showed no difference in wet/dry thickness. Tensile strength increases by adding a PANi layer to the support fabric. The PANi-NMP membrane has about double the breaking strength of the nonwoven fabric support. Tensile modulus decreases in the PANi-NMP-4MP membrane but is still greater than the support fabric. The PANi-NMP-4MP CSA-treated membrane has the greatest tensile modulus. This trend is the same for wet and dry membranes, with the dried membranes having a greater breaking strength.

Table 4

Sample	Wet		Dry	
	Thickness (μm)	Modulus (MPa)	Thickness (μm)	Modulus (MPa)
Nonwoven support	170 ± 1	243 ± 26	148 ± 5	294 ± 21
PANi-NMP	230 ± 9	434 ± 66	214 ± 17	723 ± 61
PANi-NMP-4MP	224 ± 9	360 ± 65	223 ± 1	561 ± 90
PANi-NMP-4MP CSA-treated	222 ± 13	453 ± 98	220 ± 1	796 ± 28

[00107] Table 4 shows a nonwoven support and membrane thicknesses and tensile moduli for wet and dry testing conditions.

[00108] TGA results are given in Fig. 3. All samples are thermally stable up to 300 – 330 °C before decomposition. The nonwoven support and the PANi-NMP membrane left ~15

wt% residues after decomposition, while the PANi-NMP-4MP and PANi-NMP-4MP CSA-treated membranes left ~35 wt% residues. Water loss was observed in all samples before 300 °C, and the dried samples have < 0.3 wt% water.

(v) PANI MEMBRANE CHEMICAL PROPERTIES

[00109] Fourier transform infrared (FTIR) spectroscopic analysis was carried out on an 18 wt% PANi-82 wt% NMP membrane (PANi-NMP), an 18 wt% PANi-72 wt% NMP-10 wt% 4MP membrane (PANi-NMP-4MP), an 18 wt% PANi-72 wt% NMP-10 wt% 4MP membrane treated for 1 h in 100 mM CSA at 50 °C (PANi-NMP-4MP CSA-treated), a CSA-treated 18 wt% PANi-72 wt% NMP-10 wt% 4MP membrane that was further treated with 100 mM NH₄OH for 3 h at 50 °C (PANi-NMP-4MP CSA+NH₄OH-treated), and neat CSA. These spectra are shown in Fig. 4. The locations of carbonyls (C=O), quinoid rings (Q), and benzenoid rings (B) peaks are outlined. This spectrum matches very closely to those reported in previous studies [27, 50-53]. The spectrum for the CSA-treated PANi-NMP-4MP membrane exhibits a peak around 1740 cm⁻¹, which may correspond to the presence of the C=O bond of CSA. This peak is prominent in the neat CSA spectrum and is greatly diminished after NH₄OH treatment. The locations and ratios of quinoid to benzenoid peaks for each membrane are shown in Table 5. The ratio of quinoid (1587 cm⁻¹) to benzenoid (1495 cm⁻¹) peaks (Q/B) for the PANi-NMP membrane is 0.87, which matches values of the Q/B ratio found by others [27, 28]. The Q/B ratio of the PANi-NMP-4MP membrane decreases to 0.52. There is no shift in Q peak between PANi-NMP and PANi-NMP-4MP membranes.

Table 5

Membrane	Wave No. (cm ⁻¹)		Q/B ratio
	Q	B	
PANi-NMP	1587	1495	0.87
PANi-NMP-4MP	1588	1502	0.52
PANi-NMP-4MP CSA-treated	1576	1496	0.43
PANi-NMP-4MP CSA+NH ₄ OH-treated	1591	1496	0.64

[00110] Table 5 shows the locations of quinoid and benzenoid FTIR peaks and Q/B ratios for PANi membranes.

[00111] ^1H NMR experiments were performed to further investigate the composition of the PANi membranes before and after 1 h of 100 mM CSA at 50 °C treatment. ^1H NMR spectra are shown in Fig. 5. Spectra of NMP (a) and 4MP (b) have been included for reference. The NMR spectrum of the PANi-NMP membrane made without 4MP (c) indicates that NMP is completely removed from the membrane during the phase inversion process. When 4MP is used as a gel-inhibitor in the polymer solution, some 4MP and NMP remain in the membrane after the phase inversion process (d). This is shown by the singlet at $\delta = 2.66$ ppm, which is indicative of the N-CH₃ protons in NMP and the multiplet at $\delta = 0.91\text{-}0.81$ ppm that can be attributed to the proton attached to the methyl group and the proton attached to the ring at the 4-position of the 6-membered ring in 4MP. Upon treatment with 100 mM CSA, a fraction of the NMP and 4MP is removed from the membrane (e). Quantitatively the amount of NMP and 4MP removed by CSA treatment cannot be interpreted due to the increased number of signals in the aromatic region when PANi is doped with a strong acid. However, it is observed that more NMP than 4MP is removed by CSA post-treatment. Additionally, CSA remains in the membrane after treatment and washing with DI water, as shown by two peaks at $\delta = 1.01$ and 0.70 ppm that can be attributed to the two primary methyl groups on CSA. Treatment with 100 mM NH₄OH (f) reduces the peaks at $\delta = 1.01$ and 0.70 ppm, but they are still observed. Since the samples could not be dried using heat or vacuum, there is still some residual water in each membrane.

(vi) PANI MEMBRANE SURFACE CHARGE CHARACTERISTICS

[00112] The membrane surface charge for PANi-NMP, PANi-NMP-4MP, and PANi-NMP-4MP CSA-treated membranes are shown in Fig. 6. Streaming current measurements show that the addition of 4MP produces a more positively charged membrane as indicated by a shift in the isoelectric point from 4.5 to 5.8. The PANi-NMP membrane has a zeta potential of -50 mV at pH 7, while both untreated and CSA-treated PANi-NMP-4MP membranes have zeta potentials of -20 to -25 mV at pH 7. CSA post-treatment decreases the magnitude of the membrane zeta potential.

(vii) PANI MEMBRANE SURFACE AND CROSS-SECTIONAL MORPHOLOGY

[00113] Surface and cross-sectional SEM images for PANi-NMP, PANi-NMP-4MP, and CSA-treated PANi-NMP-4MP membranes are shown in Fig. 6. SEM cross-sections show

that these membranes have an asymmetric structure with finger-like macrovoids. The addition of 4MP produces a membrane with less void space when compared to the PANi-NMP membrane. CSA post-treatment does not appear to affect the membrane void structure. The membrane surface porosity and average pore diameter are presented in Table 6. Surface porosity and average pore diameter are reduced upon addition of 4MP. CSA post-treatment increases both surface porosity and average pore diameter.

Table 6

Membrane	ε	d_p (nm)
PANi-NMP	$2.8\% \pm 1.3\%$	8.8 ± 0.6
PANi-NMP-4MP	$0.2\% \pm 0.1\%$	5.0 ± 0.6
PANi-NMP-4MP CSA-treated	$0.4\% \pm 0.3\%$	5.5 ± 0.1

[00114] Table 6 shows the surface porosity (ε) and average pore diameter (d_p) of PANi membranes determined by SEM image analysis.

(c) DISCUSSION

[00115] The addition of 4MP to a PANi-NMP polymer solution affects PANi beyond disrupting interchain and intrachain PANi hydrogen bonding. The strong basicity ($pK_a = 11.3$) and size (7.29 \AA) of 4MP are very similar to heptamethyleneimine (HPMI), which has a $pK_a = 11.2$ and size of 7.16 \AA , respectively [28]. HPMI is a PANi gel-inhibitor that has been shown to reduce the quinoid structure in PANi EB to the benzenoid via ring substitution [27]. The decrease in the FTIR Q/B ratio from 0.87 to 0.52 for membranes cast using 4MP indicates that there may be some ring substitution, however, the lack of Q peak shift may show there is no covalent bonding.

[00116] PANi-4MP hydrogen bonding and ring substitution reduce the interaction between water and the relatively hydrophilic PANi imine nitrogens. The presence of the relatively hydrophobic ring and methyl group on 4MP, as shown in Fig. 8, leads to an increase in PANi UF membrane hydrophobicity.

[00117] The membrane hydrophilicity is recovered by 1 h post-treatment using 100 mM CSA and maintained after an additional 3 h 100 mM NH_4OH treatment at $50 \text{ }^\circ\text{C}$. The reduction in the FTIR peak at 1740 cm^{-1} after NH_4OH treatment (Fig. 4) along with the reduction in ^1H NMR peaks at $\delta = 1.01$ and 0.70 ppm in Fig. 5 f) show that the excess CSA

has been removed. There may be some residual CSA dissolved in the water remaining in the NH_4OH -treated membrane. Membrane hydrophilicity is not recovered after a 1 h post-treatment using 100 mM NH_4OH at 50 °C, so this NH_4OH treatment does not contribute to membrane hydrophilicity when used to remove excess CSA. Although the mechanism for hydrophilicity is uncertain, we believe there may be some strong interaction between the hydrogen-bonded 4MP and CSA that produces a more hydrophilic membrane. CSA treatment may remove the hydrogen-bonded 4MP, but only at the membrane surface. If CSA were to remove 4MP only at the exposed surfaces of a PANi-NMP-4MP membrane due to physical and/or mass transfer limitations, then ^1H NMR would not detect a noticeable decrease in 4MP because treated films are dissolved in a solvent for analysis and the bulk of the membrane may still contain 4MP. FTIR is a surface technique and is more sensitive to chemical changes at the membrane surface. We are unable to detect the presence or removal of 4MP from a PANi membrane perhaps due to the similar chemical structure of 4MP and PANi. Treating PANi with an acid protonates the PANi backbone and saturates the imine nitrogens with which 4MP forms hydrogen bonds. Likewise, the acid protonates 4MP and eliminates its ability to hydrogen bond with PANi. One might expect that any acid would liberate hydrogen bonded 4MP. Acids other than CSA are unable to restore membrane hydrophilicity. It is known that CSA induces an expanded coil conformation in PANi, increasing the separation between neighboring chains [54, 55]. However, PANi is normally in a tightly coiled conformation and we suspect that HCl and H_2SO_4 are too small to expand PANi chains sufficiently to create the free volume necessary for the outward diffusion of 4MP. The relatively 2-dimensional geometry of *p*-toluenesulfonic acid does not promote chain expansion and dodecylbenzenesulfonic acid is likely too large to fit between PANi chains.

[00118] Introduction of 4MP produces a less porous membrane with smaller pores. The resulting membrane is much less permeable, but has much higher protein rejection. The higher porosity and larger pores observed in CSA-post-treated membranes potentially arise due to structural re-arrangement of PANi caused by the post-treatment process such as polymer disentanglement or the like. The resulting membrane has a lower BSA rejection. These defects can be minimized by designing a more gentle post-treatment process. Although PANi membrane hydrophilicity is recovered, membrane surface charge is still shifted after CSA post-treatment. This again indicates that there can be strongly-associated 4MP remaining on the membrane surface even after CSA post-treatment.

[00119] Pure polyaniline ultrafiltration membranes with improved protein rejection have been formed with the aid of a gel-inhibiting agent, 4-methylpiperidine. These membranes, however, show decreased water permeability and increased hydrophobicity when compared to PANi membranes made from NMP only. 4MP was found to reduce the quinoid ring structure of PANi emeraldine base to the benzenoid form by ring substitution. Hydrogen-bonded and ring-substituted 4MP increased PANi membrane hydrophobicity by occupying a relatively hydrophilic imine nitrogen site and replacing it with a relatively hydrophobic ring and methyl group. Post-treatments using acid solutions indicate that the camphorsulfonate ion causes PANi to take on a more expanded coil conformation which allows the hydrogen-bonded 4MP to diffuse out of the membrane. Removal of this fraction of 4MP enabled polyaniline ultrafiltration membranes to recover their hydrophilicity. Tailoring membrane properties by a simple post-treatment step has implications for extending the range of separation performance for PANi based membranes.

[00120] Figure 9 shows an SEM image of a PANi-NMP membrane that was made without a gel-inhibiting agent. This membrane has several defects (cracks). Figure 10 an SEM image of a PANi-NMP membrane that was made with a gel-inhibiting agent (4-MP). This membrane has no defects.

b. EXAMPLE 2

(a) MEASURING CONTACT ANGLES OF POLAR AND APOLAR LIQUIDS ON POLYMERIC MEMBRANES

[00121] Surface tensions of microbial cells were determined from sessile drop contact angles (VCA-1000, AST Products Inc., Billerica, MA) of deionized water, ethylene glycol, glycerol, and diiodomethane on microbial lawns filtered onto 0.1 μm Whatman filter papers as described elsewhere. (G. A. Burks, et al., *Langmuir* **2003**, *19*, 2366-2371) Colloidal particles (silica, alumina and carboxyl modified latex) were from a previously published source. (J. A. Brant, et al., *Journal of Membrane Science* **2004**, *241*, 235-248) Surface tensions of polyaniline and post-treated polyaniline membranes were determined by measuring sessile drop contact angles of deionized water, ethylene glycol, glycerol, and diiodomethane on membrane samples mounted on glass slides with double-sided tape. At least twelve equilibrium contact angles were measured for each sample obtained directly for this study, where the equilibrium angle was determined from the average of right and left

angles. The highest and lowest values were discarded before taking the average and standard deviation. Contact angles and corresponding surface tensions of other membrane materials were obtained from a previously published study. (E.R. Cornelissen, et al., *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **1998**, 138, 283–289)

[00122] Measured contact angles of PANi and CSA post-treated PANi (“PANi-CSA”) are shown in Table 7 along with the most popular commercial polymeric membrane materials including: cellulose acetate (CA), polyacrylonitrile (PAN), polycarbonate (PC), polyetherimide (PEI), polyethersulfone (PES), polypropylene (PP), polysulfone (PSf), polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF). The measured contact angles are all measured via the sessile drop method, and hence, directly comparable. In the case of water contact angles, the PANi membranes exhibit contact angles similar to the CA and PAN membranes, while the PANi-CSA membranes produce a distinctly lower contact angle which generally correlates with more hydrophilic and fouling resistant membrane materials.

TABLE 7 - Measured contact angles (degrees) of probe liquids on membranes

Polymers	θ_{water}	θ_{polar}^*	θ_{apolar}^{**}
CA	59 ± 3	54 ± 3	26 ± 2
PAN	57 ± 3	49 ± 4	6 ± 1
PC	78 ± 1	66 ± 2	12 ± 1
PEI	79 ± 2	63 ± 2	8 ± 1
PES	92 ± 2	68 ± 5	13 ± 2
PP	94 ± 2	83 ± 3	42 ± 1
PSf	82 ± 2	67 ± 4	14 ± 7
PTFE	117 ± 2	112 ± 2	93 ± 2
PVDF	92 ± 2	104 ± 3	29 ± 2
PANi	57 ± 5	36 ± 3	35 ± 3
PANi-CSA	41 ± 2	19 ± 2	36 ± 1

* ethylene glycol used here; glycerol used by Cornelissen et al.

** diiodomethane used here; a-bromonaphthalene used by Cornelissen et al.

[00123] Contact angle probe liquid surface tension components (Table 8) are used to extract surface tension components of fouling materials (Table 9) and membrane materials (Table 10). What can be deduced is that PP, PVDF and PTFE are practically apolar and decidedly lower energy than all the other materials. The PANi materials exhibit similar total surface tensions as CA and PAN materials, but decidedly lower electron acceptor and higher

electron donor functionality. In general, it has been observed that as materials approach monopolar electron donor or acceptor functionality they appear more hydrophilic and fouling resistant; this is well accepted for polyethylene glycol (PEG) functionalized surfaces.

Table 8 - Surface tension components of probe liquids

Liquids	γ^{LW} (mJ/m ²)	γ^+ (mJ/m ²)	γ^- (mJ/m ²)	γ^{TOT} (mJ/m ²)
Water	21.8	25.5	25.5	72.8
Glycerol	34.0	3.9	57.4	64.0
Ethylene Glycol	29.0	1.9	47.0	48.0
Diiodomethane	50.8	0.0	0.0	50.8
α-Bromonaphthalene	44.4	0.0	0.0	44.4

Table 9 - Surface tension components of model foulants

Foulants	γ^{LW} (mJ/m ²)	γ^+ (mJ/m ²)	γ^- (mJ/m ²)	γ^{TOT} (mJ/m ²)
HSA	26.8	6.3	50.6	62.5
PEG	43.0	0.0	64.0	43.0
Hexadecane	27.5	0.0	0.0	27.5
Silica particles (100 nm)	34.3	1.0	31.7	45.8
Alumina (300 nm)	42.9	3.7	19.6	59.9
Carboxyl modified latex	37.5	0.6	5.3	41.0
<i>E. coli</i>	39.1	0.6	59.0	50.9
<i>S. cerevisiae</i>	14.2	0.5	44.4	23.8
<i>P. putida</i>	25.4	0.0	39.5	26.3

Table 10 - Calculated interfacial tension components of the different polymers

Membrane Polymers	γ^{LW} (mJ/m ²)	γ^+ (mJ/m ²)	γ^- (mJ/m ²)	γ^{TOT} (mJ/m ²)
CA	40.0	0.5	19.0	46.2
PAN	44.0	0.6	19.0	50.8
PC	44.0	0.1	5.8	45.5
PEI	44.0	0.3	3.9	46.2
PES	43.0	0.5	0.1	43.4
PP	34.0	0.0	1.7	34.0
PSf	43.0	0.2	3.1	44.6
PTFE	10.0	0.0	0.9	10.0

PVDF	40.0	0.0	0.1	40.0
PANi-untreated	41.9	0.1	24.6	44.2
PANi-CSA-treated	41.6	0.3	38.1	47.8

[00124] What is clear from the free energy of cohesion data (Figure 11) is that virtually all the polymeric membranes appear “hydrophobic” according to their negative free energy of cohesion; one exception is the CSA treated PANi membrane which exhibits a significantly positive free energy of cohesion. Hence, a PANi-CSA membrane can be considered to be truly “hydrophilic.” Similarly, the free energy of adhesion data (Figure 12) indicates that the PANi membrane is along with the PAN and CA membranes among the most fouling resistant materials available, but the PANi-CSA membrane is even more fouling resistant.

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CLAIMS

What is claimed is:

1. A method of increasing membrane hydrophilicity comprising steps of:
 - a) providing a membrane comprising polyaniline, a polyaniline derivative, or copolymer thereof and one or more gel inhibiting agents; and
 - b) treating the membrane with one or more hydrophilicity restoration agents, thereby increasing the hydrophilicity of the membrane.
2. The method of claim 1, wherein the treating comprises contacting the membrane with the hydrophilicity restoration agent for at least 60 min.
3. The method of claim 1, wherein the treating comprises filtering the membrane with one or more hydrophilicity restoration agents.
4. The method of claim 3, wherein the filtering comprises filtering the one or more hydrophilicity restoration agents for at least 60 min.
5. The method of any one of claims 1-4, wherein the one or more gel inhibiting agents comprises a primary amine, secondary amine, or a tertiary amine, or a combination thereof.
6. The method of any one of claims 1-4, wherein the one or more gel inhibiting agents comprises 4-methylpiperidine, n-Butylamine, 2,5-dimethyl-3-pyrroline, 3,3-dimethylpiperidine, heptamethyleneimine, diisopropylamine, hexamethyleneimine, N-ethylbenzylamine, piperazine, 2,6-dimethylmorpholine, piperidine, dibutylamine, N-methylpiperidine, N,N'-dimethylpiperazine, triethylamine, or diethylnipecotinamide, or a combination thereof.
7. The method of any one of claims 1-6, wherein the one or more hydrophilicity restoration agents comprises (+/-) camphor-10-sulfonic acid, sulfuric acid, methane sulfonic acid, ethane sulfonic acid, propanesulfonic acid, perfluoropropanesulfonic acid, butane sulfonic acid, perfluorobutane sulfonic acid, hexane sulfonic acid, perfluorohexane sulfonic acid, perfluorooctanesulfonic acid, benzene sulfonic acid, toluene sulfonic acid, dodecyl benzene, sulfonic acid, taurine (2-aminoethanesulfonic

- acid), homotaurine (3-aminopropanesulfonic acid), naphthalene sulfonic acid, 2,5 naphthalene disulfonic acid, dinonylnaphthalene sulfonic acid, dinonylnaphthalene disulfonic acid, polyvinylsulfonate, or polystyrenesulfonate, or a combination thereof.
8. The method of any one of claims 1-6, wherein the one or more hydrophilicity restoration agents comprises (+/-) camphor-10-sulfonic acid.
 9. The method of any one of claims 1-8, wherein the membrane has an increased value of ΔG_{131}^{IF} of at least 5, 10, 15, 20, 25, 30, 50, 75, or 100 mJ/m² after treatment.
 10. The method of any one of claims 1-9, wherein the membrane has a positive ΔG_{131}^{IF} value after treatment.
 11. The method of any one of claims 1-9, wherein the membrane has a positive value of ΔG_{131}^{IF} of at least 5, 10, 15, 20, 25, 30, or 50 mJ/m² after treatment.
 12. The method of any one of claims 1-11, wherein the membrane has an increase value of ΔG_{132}^{IF} of at least 5, 10, 15, 20, 25, 30, 50, 75, or 100 mJ/m² after treatment.
 13. The method of any one of claims 1-12, wherein the membrane has a positive value of ΔG_{132}^{IF} after treatment.
 14. The method of any one of claims 1-13, wherein the membrane has a positive value of ΔG_{132}^{IF} as measured against silica, polyethylene glycol (PEG), human serum albumin (HSA), hexadecane, *E. coli*, *S. cerevisiae*, and *P. putida* after treatment.
 15. A membrane comprising polyaniline, a polyaniline derivative, or a co-polymer thereof, wherein the membrane has been subjected to the method of any one of claims 1-14.
 16. The membrane of claim 15, wherein the membrane has a positive value of ΔG_{131}^{IF} .

17. The membrane of claims 15 or 16, wherein the membrane has a positive value of ΔG_{131}^{IF} of at least 5, 10, 15, 20, 25, 30, or 50 mJ/m².
18. The membrane of any one of claims 15-17, wherein the membrane has a positive value of ΔG_{132}^{IF} as measured against silica, PEG, HSA, hexadecane, *E. coli*, *S. cerevisiae*, and *P. putida*.
19. The membrane of any one of claims 15-18, wherein the membrane has a positive value of ΔG_{132}^{IF} as measured against silica, PEG, HSA, hexadecane, *E. coli*, *S. cerevisiae*, or *P. putida*, or a combination thereof.
20. An article of manufacture comprising the membrane of any one of claims 15-19.

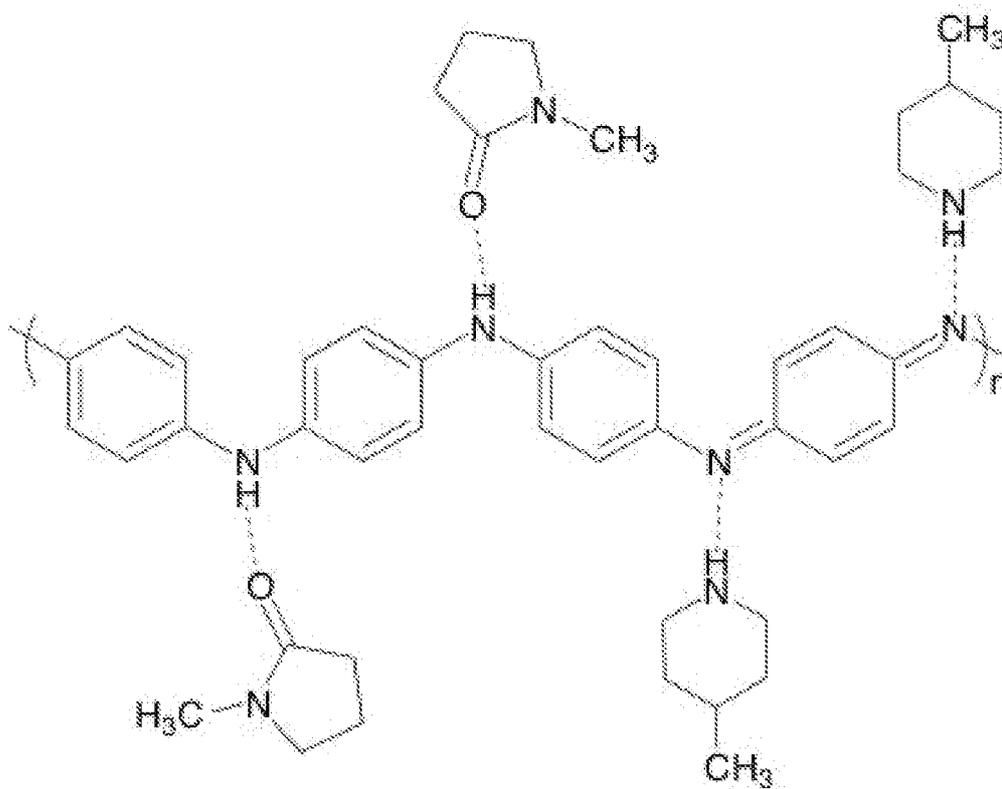


FIG 1

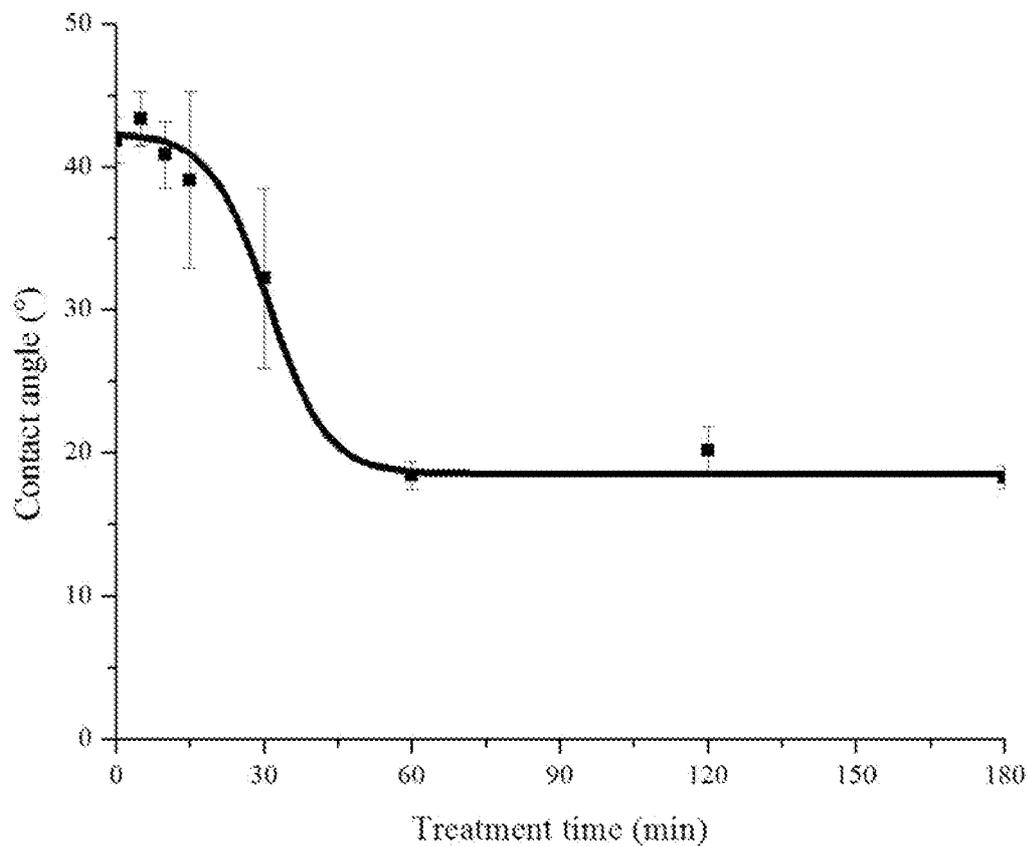


FIG 2

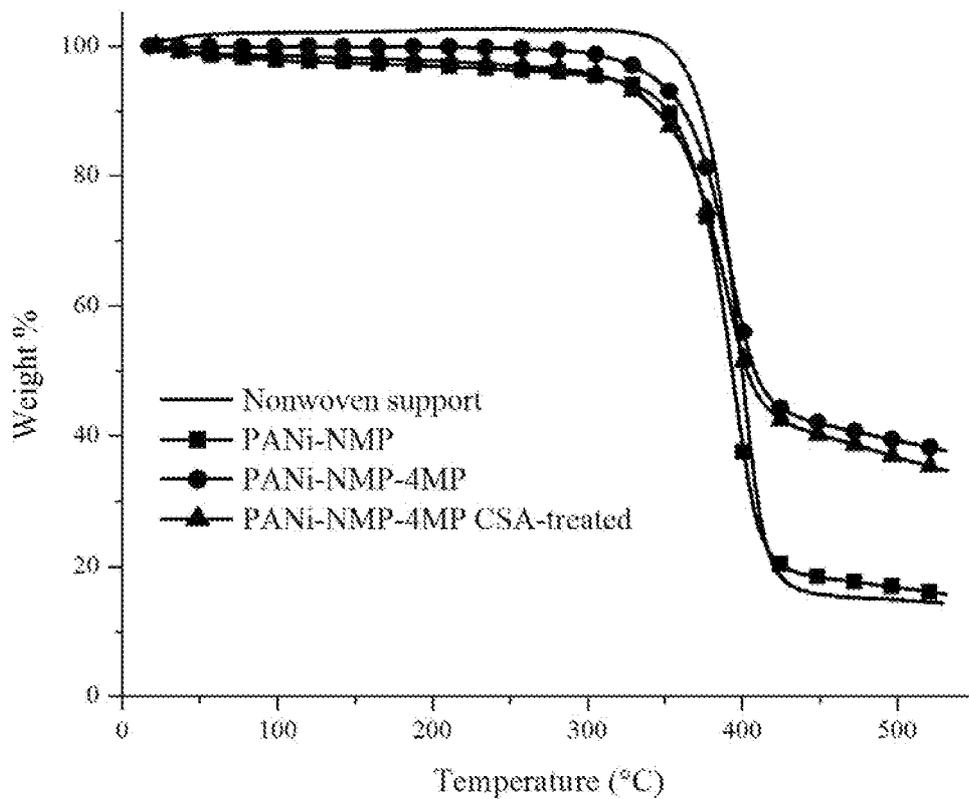


FIG 3

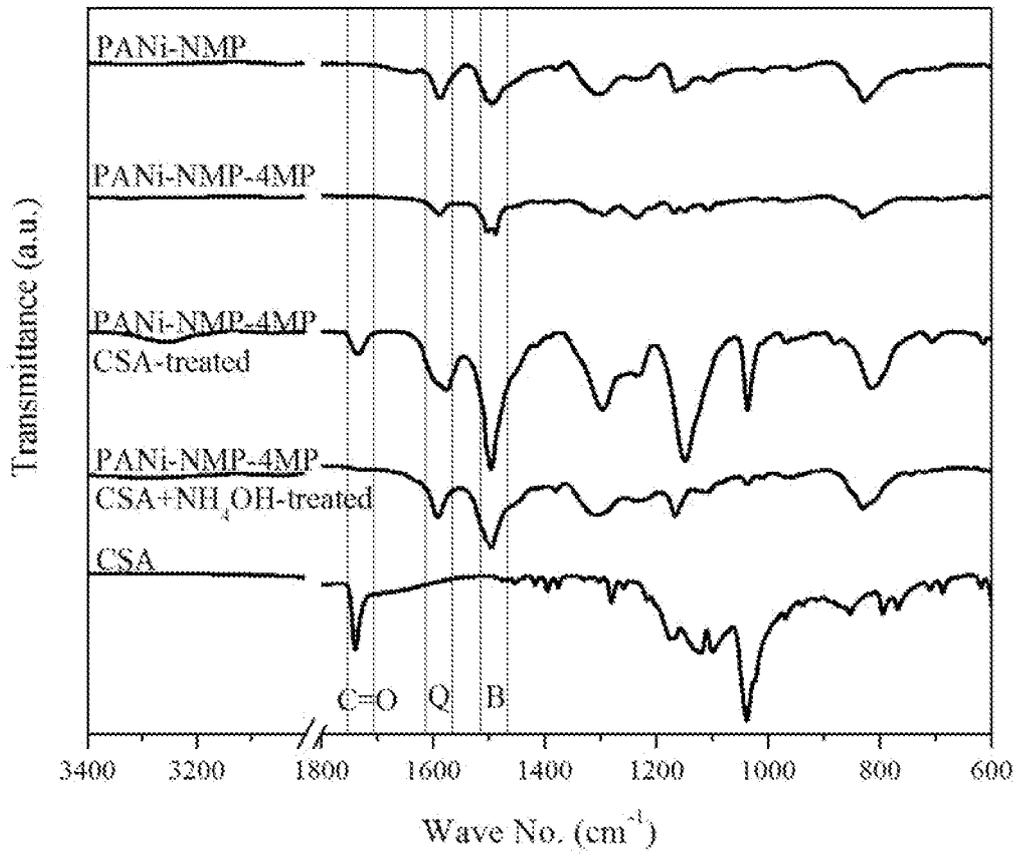


FIG 4

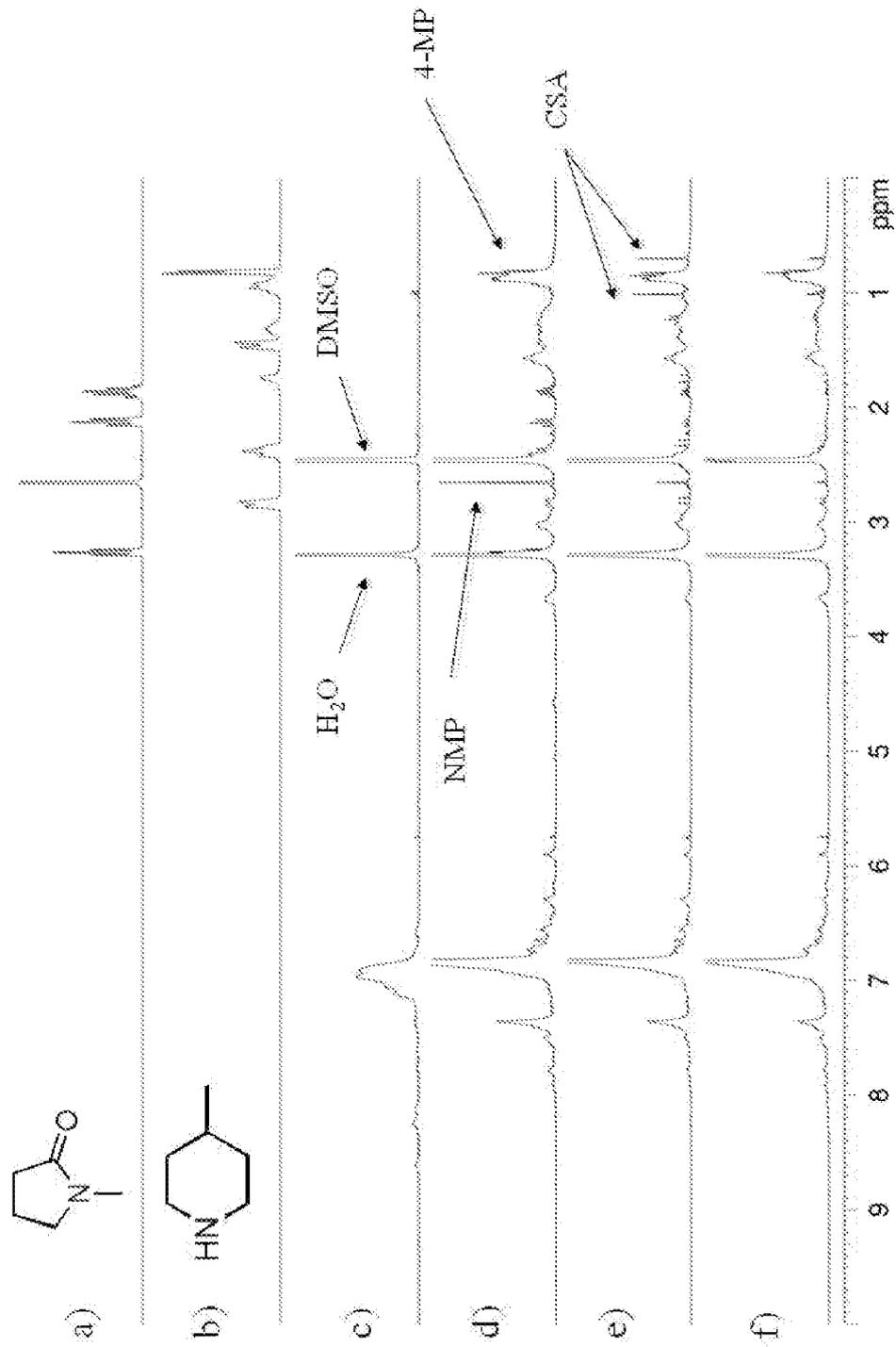


FIG.5

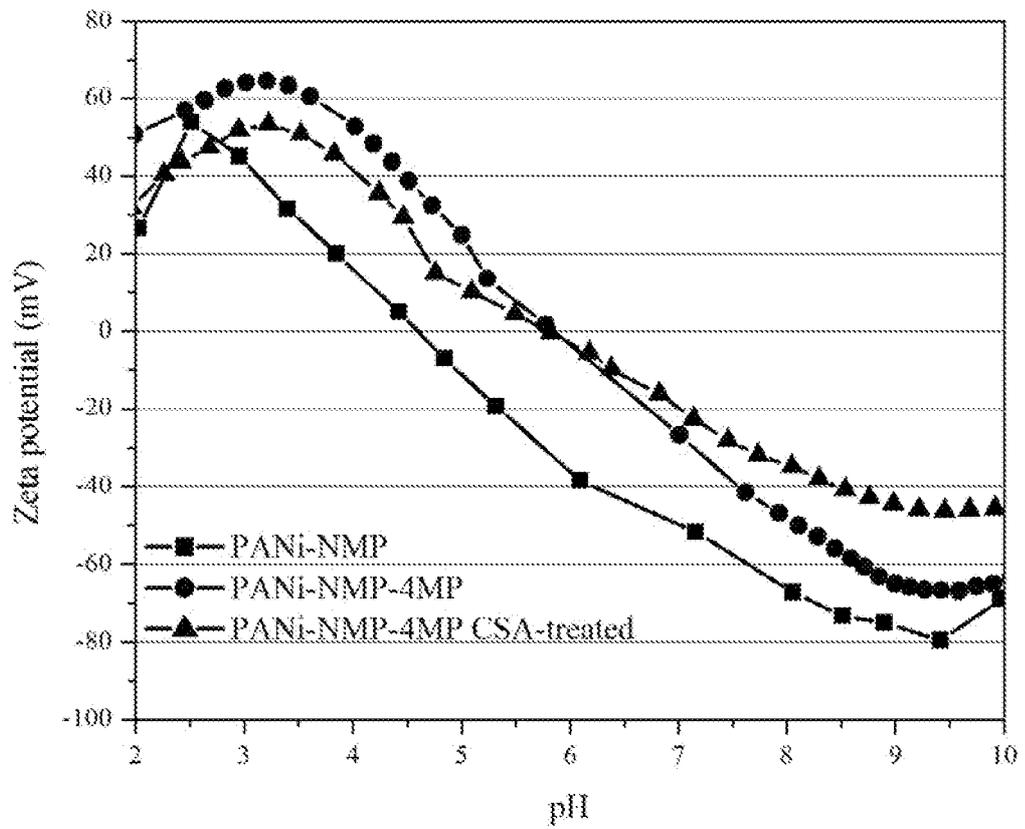


FIG 6

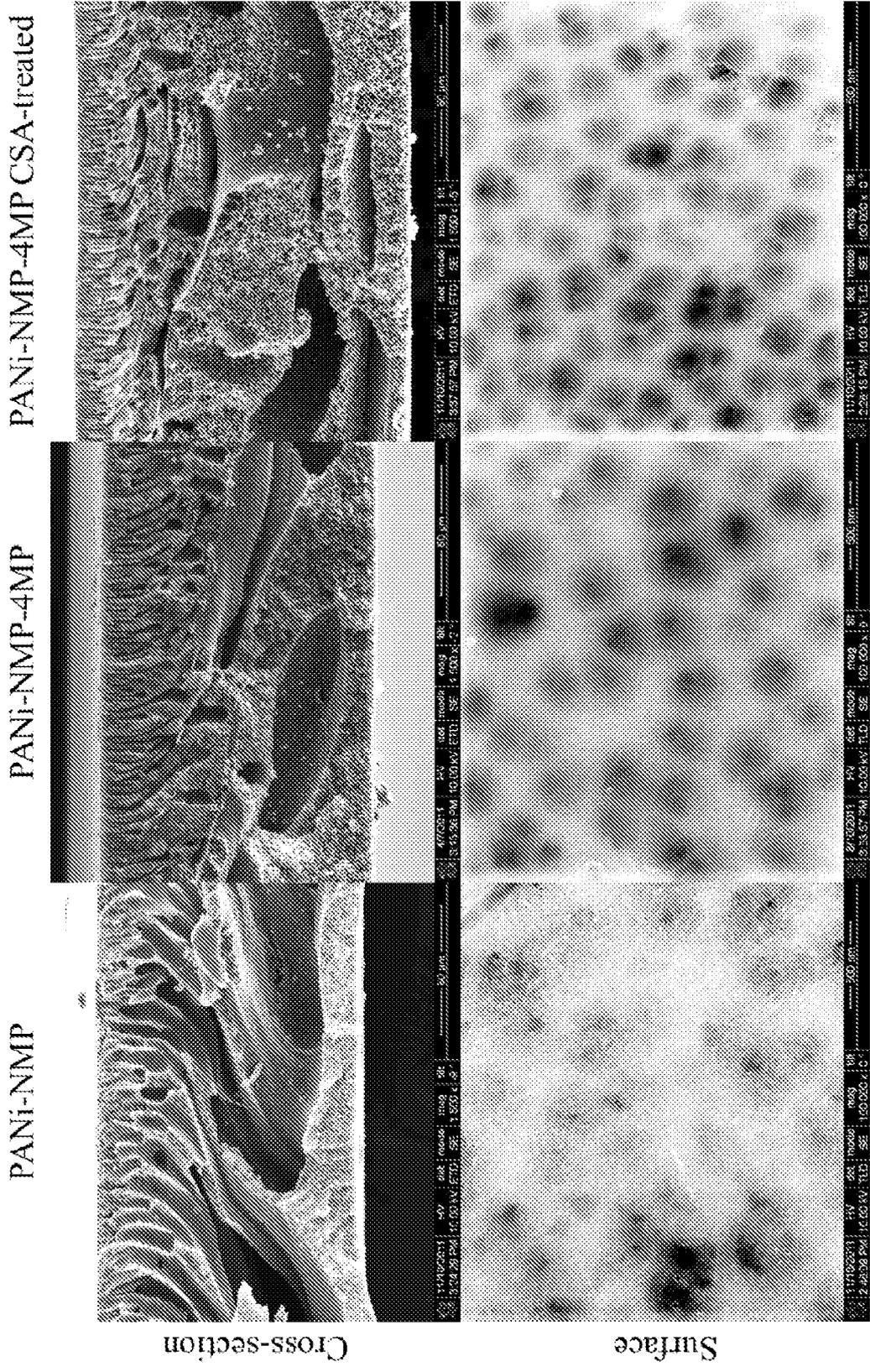


FIG.7

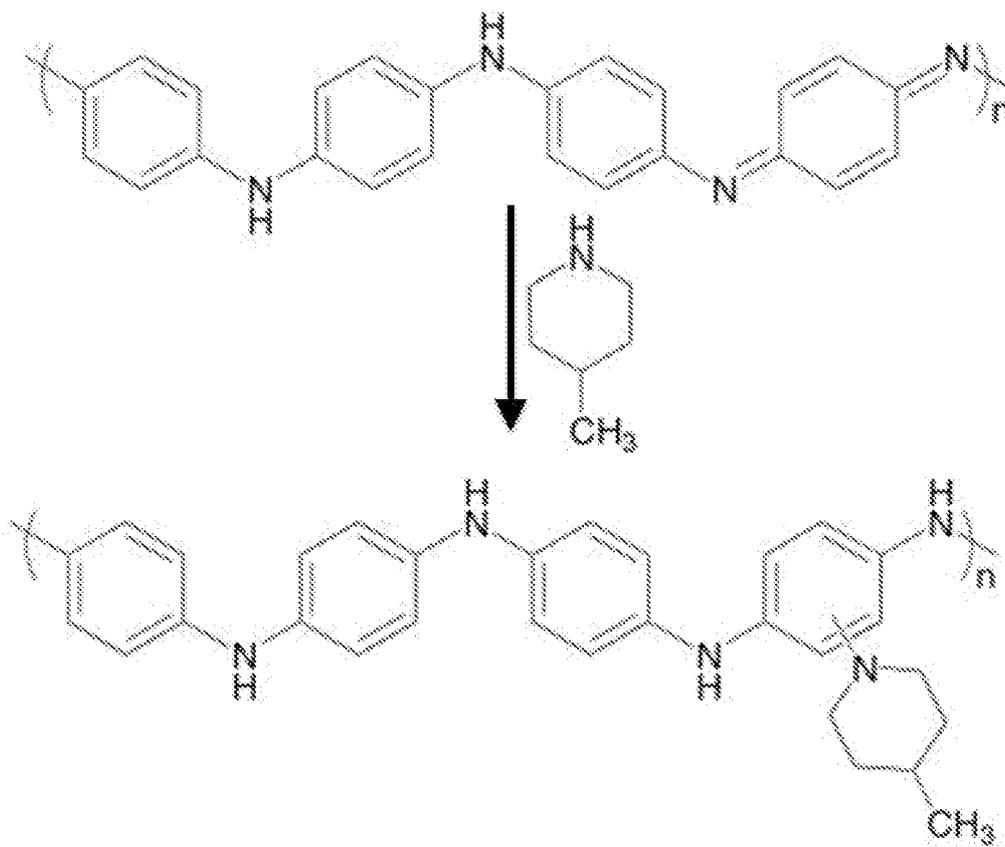


FIG 8

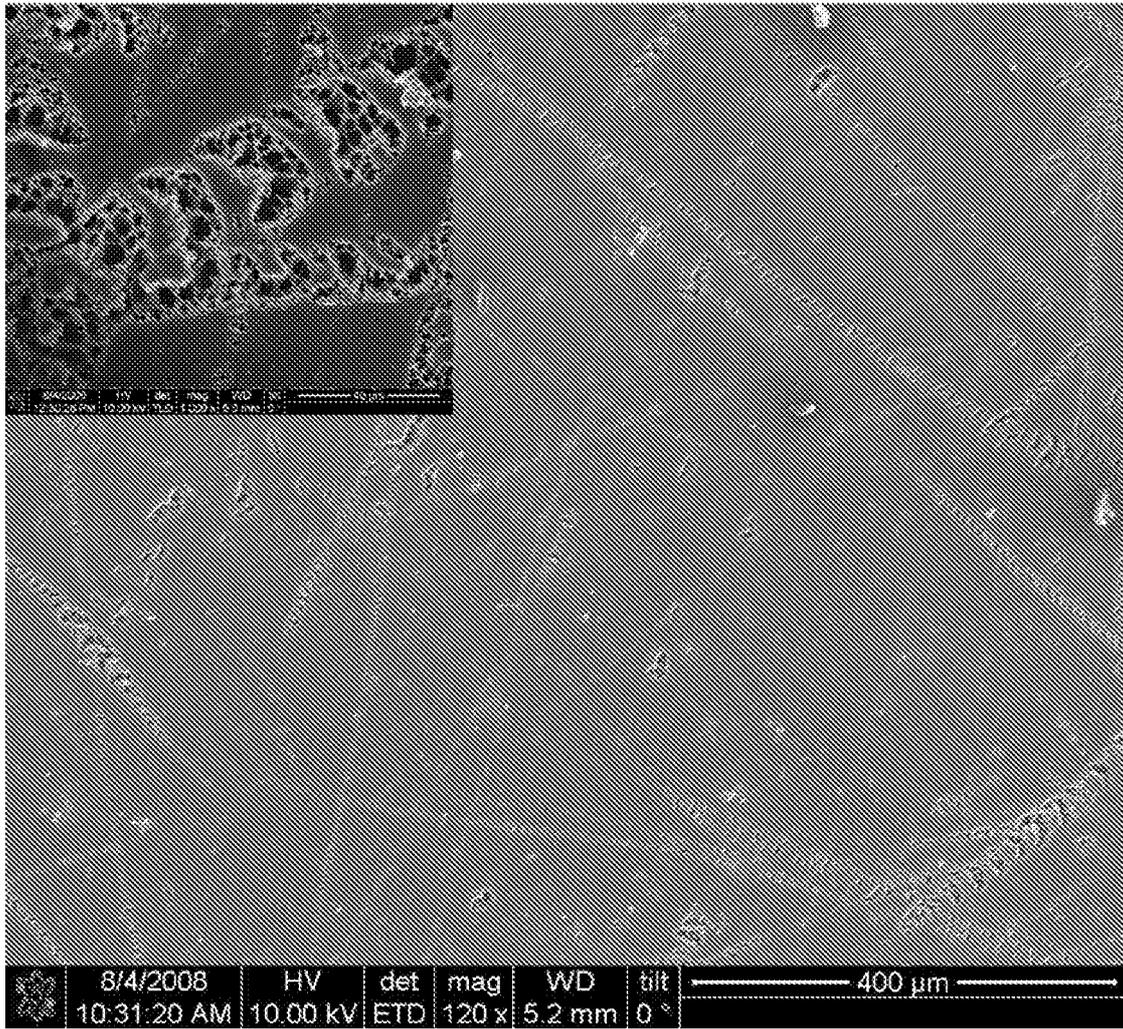


FIG. 9

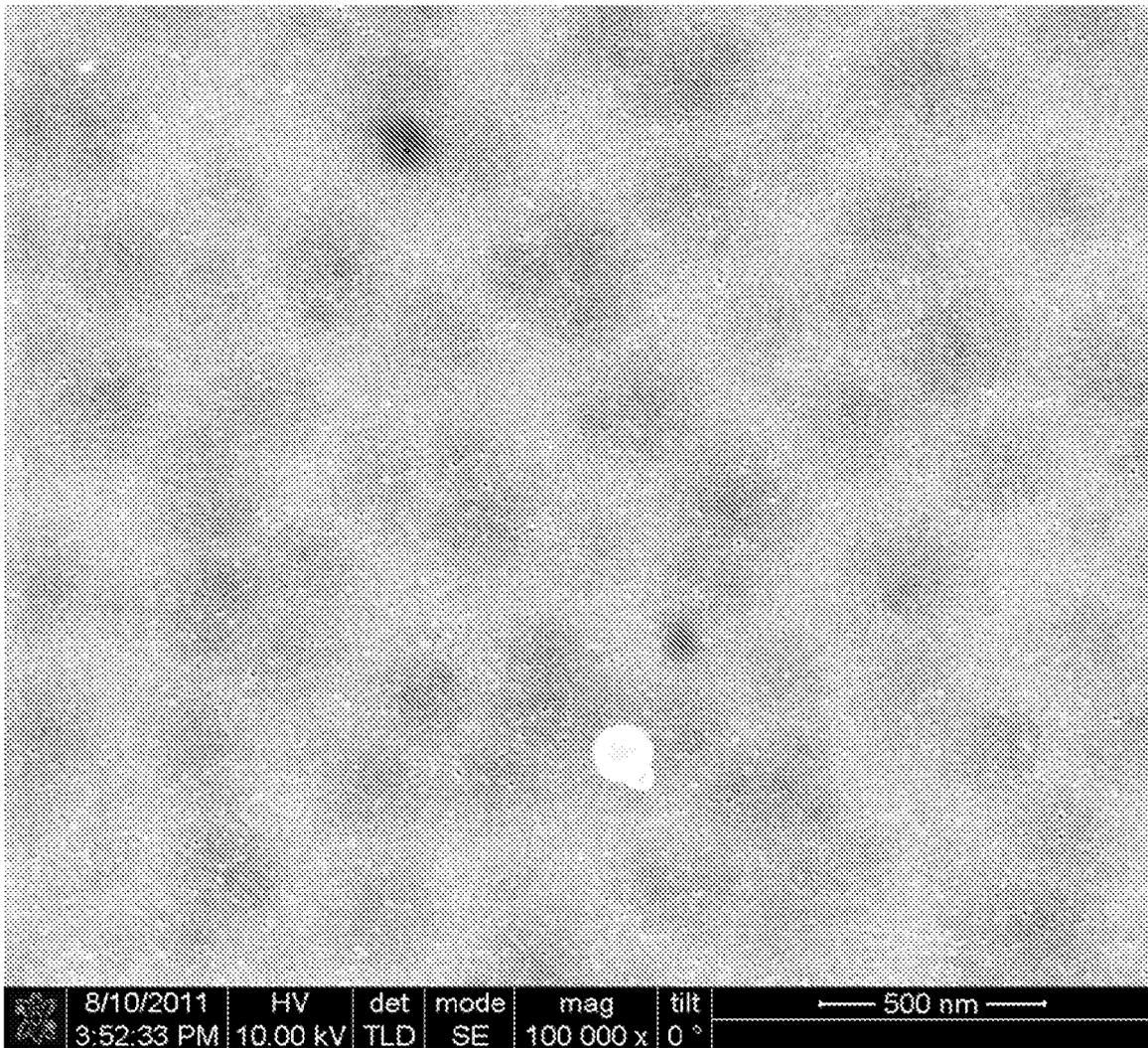


FIG. 10

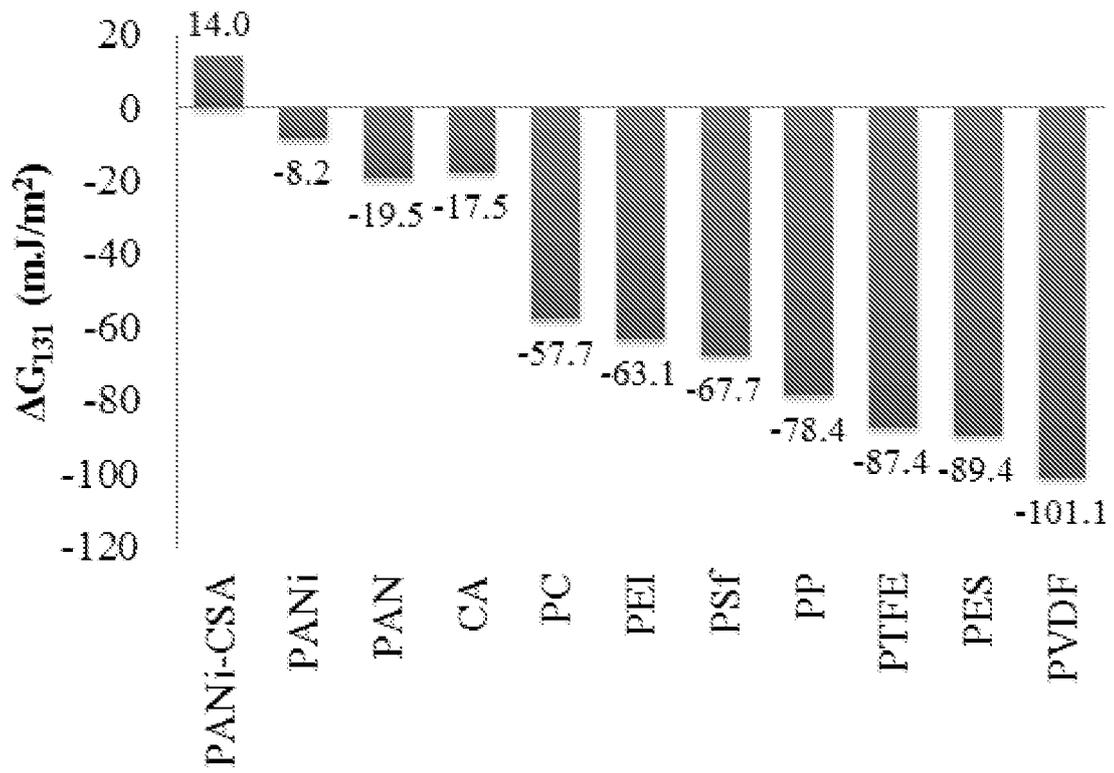


FIG 11

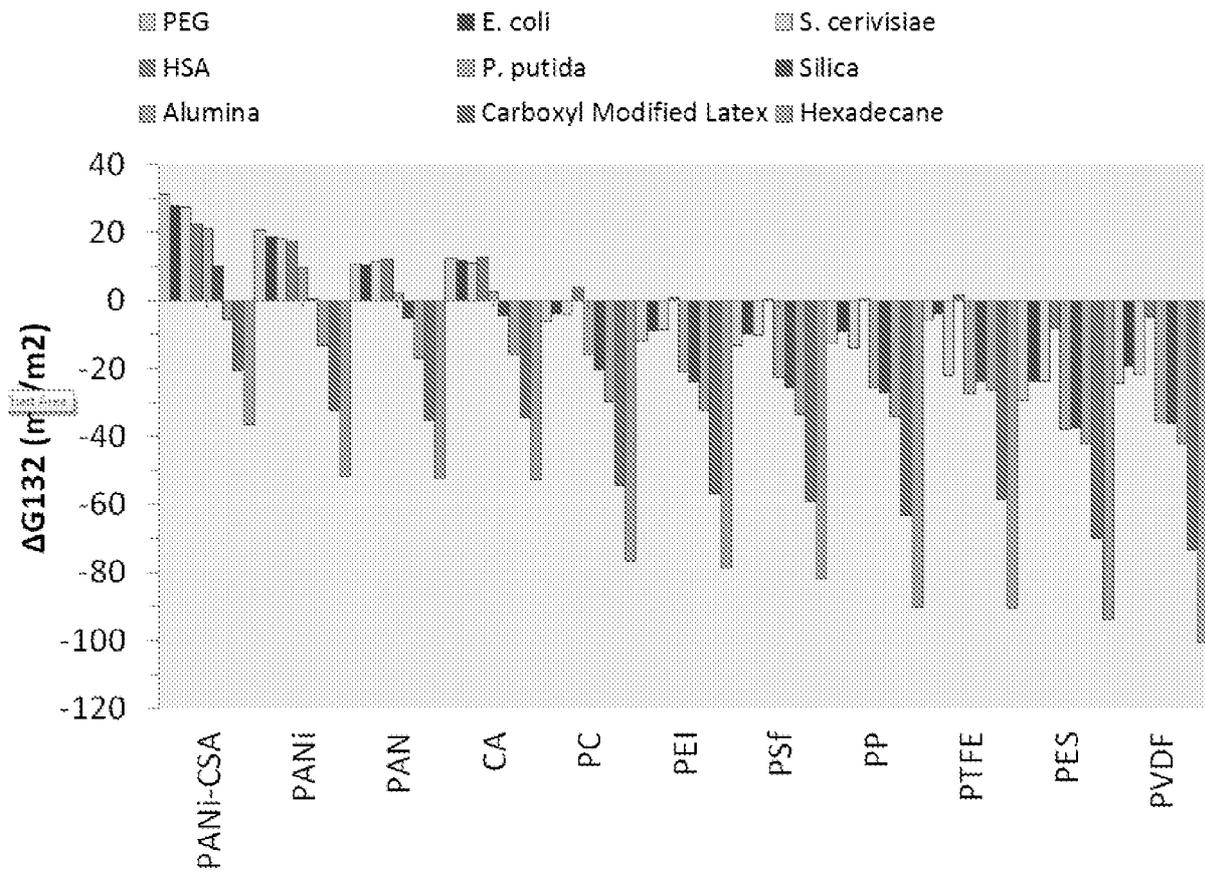


FIG 12

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 13/64641

A. CLASSIFICATION OF SUBJECT MATTER IPC(8) - C08G 12/00; C08K 5/00 (2013.01) USPC - 528/229,422; 524/236 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) IPC(8): C08G 12/00; C08K 5/00 (2013.01) USPC: 528/229,422; 524/236		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched USPC: 210/500.21,520.36; 528/373,398,423,425 (keywords limited; search terms below)		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) PubWEST(PGPB, USPT, EPAB, JPAB); PatBase; Google Scholar; Google Patents Search terms: membrane\$2 hydrophilicity polyaniline gel inhibit\$6 restor\$6 filtering contacting amine\$2 butylamine piperidine methylpiperidine		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2008/0203012 A1 (Yeager et al.) 28 August 2008 (28.08.2008), especially, claim 12 and para [0006], [0059] and [0066].	1-6
Y	US 2010/0300488 A1 (Watanabe et al.) 2 December 2010 (02.12.2010), especially, para [0003], [0012] and [0040].	1-6
Y	US 2012/0111791 A1 (Freeman et al.) 10 May 2012 (10.05.2012), especially, para [0025] and [0029].	3-4, 5/(3-4), 6/(3-4)
Y	US 2003/0162939 A1 (Wang et al.) 28 August 2003 (28.08.2003), especially, para [0003] and [0035].	5, 6
A	US 2003/0138619 A1 (David et al.) 24 July 2003 (24.07.2003), especially, para [0001]-[0009].	1
A	US 2010/0051538 A1 (Freeman et al.) 4 March 2010 (04.03.2010), especially, para [0006]-[0011].	1, 3, 4
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/>		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 30 January 2014 (30.01.2014)		Date of mailing of the international search report 20 FEB 2014
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201		Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 13/64641

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.: 7-20
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.



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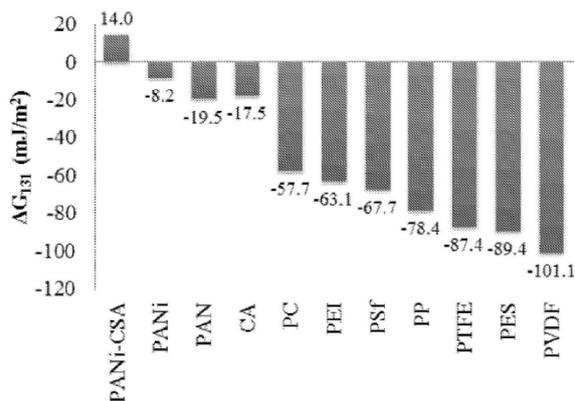
权利要求书2页 说明书25页 附图11页

(54) 发明名称

聚苯胺膜、其用途及其方法

(57) 摘要

本文公开了增加膜的亲水性的方法。用一种或多种亲水性恢复剂处理包含聚苯胺或其共聚物和一种或多种凝胶抑制剂的膜,从而增加所述膜的亲水性。还公开了由所公开的方法产生的膜。本摘要旨在作为用于在具体领域中搜索目的的浏览工具,而非意图限制本发明。



1. 一种增加膜亲水性的方法,所述方法包括以下步骤:
 - a) 提供包含聚苯胺、聚苯胺衍生物或其共聚物和一种或多种凝胶抑制剂的膜;和
 - b) 用一种或多种亲水性恢复剂处理所述膜,从而增加所述膜的亲水性。
2. 如权利要求 1 所述的方法,其中所述处理包括将所述膜与所述亲水性恢复剂接触至少 60 分钟。
3. 如权利要求 1 所述的方法,其中所述处理包括用一种或多种亲水性恢复剂过滤所述膜。
4. 如权利要求 3 所述的方法,其中所述过滤包括用所述一种或多种亲水性恢复剂将所述膜过滤至少 60 分钟。
5. 如权利要求 1-4 中任一项所述的方法,其中所述一种或多种凝胶抑制剂包括伯胺、仲胺或叔胺或其组合。
6. 如权利要求 1-4 中任一项所述的方法,其中所述一种或多种凝胶抑制剂包括 4-甲基哌啶、正丁胺、2,5-二甲基-3-吡咯啉、3,3-二甲基哌啶、七亚甲基亚胺、二异丙胺、六亚甲基亚胺、N-乙基苄胺、哌嗪、2,6-二甲基吗啉、哌啶、二丁胺、N-甲基哌啶、N,N'-二甲基哌嗪、三乙胺或二乙基-3-哌啶甲酰胺或其组合。
7. 如权利要求 1-6 中任一项所述的方法,其中所述一种或多种亲水性恢复剂包括(+/-)樟脑-10-磺酸、硫酸、甲磺酸、乙磺酸、丙磺酸、全氟代丙磺酸、丁磺酸、全氟代丁磺酸、己磺酸、全氟代己磺酸、全氟代辛磺酸、苯磺酸、甲苯磺酸、十二烷基苯磺酸、牛磺酸(2-氨基乙磺酸)、高牛磺酸(3-氨基丙磺酸)、萘磺酸、2,5-萘二磺酸、二壬基萘磺酸、二壬基萘二磺酸、聚乙烯磺酸盐或聚苯乙烯磺酸盐或其组合。
8. 如权利要求 1-6 中任一项所述的方法,其中所述一种或多种亲水性恢复剂包括(+/-)樟脑-10-磺酸。
9. 如权利要求 1-8 中任一项所述的方法,其中所述膜在处理后的具有至少 5、10、15、20、25、30、50、75 或 100mJ/m²的 ΔG_{131}^{IF} 的增加值。
10. 如权利要求 1-9 中任一项所述的方法,其中所述膜在处理后的具有正的 ΔG_{131}^{IF} 值。
11. 如权利要求 1-9 中任一项所述的方法,其中所述膜在处理后的具有至少 5、10、15、20、25、30 或 50mJ/m²的正的 ΔG_{131}^{IF} 值。
12. 如权利要求 1-11 中任一项所述的方法,其中所述膜在处理后的具有至少 5、10、15、20、25、30、50、75 或 100mJ/m²的 ΔG_{132}^{IF} 的增加值。
13. 如权利要求 1-12 中任一项所述的方法,其中所述膜在处理后的具有正的 ΔG_{132}^{IF} 值。
14. 如权利要求 1-13 中任一项所述的方法,其中当针对二氧化硅、聚乙二醇(PEG)、人血清白蛋白(HSA)、十六烷、大肠杆菌、酿酒酵母和恶臭假单胞菌测定时,所述膜在处理后的具有正的 ΔG_{132}^{IF} 值。
15. 一种包含聚苯胺、聚苯胺衍生物或其共聚物的膜,其中所述膜已被实施了权利要求 1-14 中任一项所述的方法。

16. 如权利要求 15 所述的膜,其中所述膜具有正的 ΔG_{131}^{IF} 值。
17. 如权利要求 15 或 16 所述的膜,其中所述膜具有至少 5、10、15、20、25、30 或 50mJ/m²的正的 ΔG_{131}^{IF} 值。
18. 如权利要求 15-17 中任一项所述的膜,其中当针对二氧化硅、PEG、HSA、十六烷、大肠杆菌、酿酒酵母和恶臭假单胞菌测定时,所述膜具有正的 ΔG_{132}^{IF} 值。
19. 如权利要求 15-18 中任一项所述的膜,其中当针对二氧化硅、PEG、HSA、十六烷、大肠杆菌、酿酒酵母或恶臭假单胞菌或其组合测定时,所述膜具有正的 ΔG_{132}^{IF} 值。
20. 包括权利要求 15-19 中任一项所述的膜的制品。

聚苯胺膜、其用途及其方法

[0001] 相关申请的交叉引用

[0002] 本申请要求 2012 年 10 月 12 日提交的第 61/713, 439 号美国临时申请的权益, 该临时申请通过引用全部并入本文中。

[0003] 发明背景

[0004] 导电性聚合物 (聚苯胺) 历来用于制造传感器 [1-3]、电池电极 [4]、电磁屏蔽装置 [5, 6] 和抗腐蚀涂料 [7-9]。聚苯胺最近作为膜材料引起了关注 [10-12]。聚苯胺的可加工性在某种程度上受限于特定的溶剂。凝胶抑制剂已被用于溶剂系统中, 以增加聚苯胺的可加工性。然而, 当使用凝胶抑制剂时所得到的膜具有较高的疏水性, 这可能会对膜的性能和维护产生负面影响。

[0005] 因此, 本文描述了膜、制造膜的方法以及膜的用途, 其中采用凝胶抑制剂产生的膜已被处理以增加膜的亲水性。

[0006] 概述

[0007] 根据本发明的目的, 如本文中所体现和广泛描述的, 本发明在一个方面涉及增加包含聚苯胺或其共聚物和一种或多种凝胶抑制剂的膜的亲水性的方法。

[0008] 本文公开了增加膜亲水性的方法, 所述方法包括以下步骤: (a) 提供包含聚苯胺、聚苯胺衍生物或其共聚物和一种或多种凝胶抑制剂的膜; 和 (b) 用一种或多种亲水性恢复剂处理所述膜, 从而增加所述膜的亲水性。

[0009] 本文还公开了被实施了本文所公开的方法的膜。

[0010] 本文还公开了包含一个或多个本文所公开的膜的制品。

[0011] 虽然可以用特定的法定类别 (如系统法定类别) 对本发明的方面进行描述和要求保护, 但这仅是为了方便, 并且本领域技术人员将理解到可以用任何的法定类别对本发明的各方面进行描述和要求保护。除非另有明确说明, 否则决非意图将本文所列出的任何方法或方面解释为要求以特定顺序来进行其步骤。因此, 在权利要求书或说明书中, 当方法权利要求没有确切地说明步骤是限于特定顺序时, 在任何方面决非意图推断顺序。这适用于任何可能的非表达解释基础, 包括相对于步骤排列或操作流程的逻辑事项、从语法组织或标点中得到的明显含义或者在说明书中所描述的方面的数字或类型。

附图说明

[0012] 被包括在本说明书中并构成本说明书的一部分的附图示出了几个方面, 并与说明书一起用于解释本发明的原理。

[0013] 图 1 示出了聚苯胺 (PANi) 的翠绿亚胺碱形式、溶剂 1-甲基-2-吡咯烷酮 (NMP) 和凝胶抑制剂 4-甲基吡啶 (4MP) 之间的潜在的氢键合相互作用。

[0014] 图 2 示出了针对在使用不同的时间间隔在 50°C 下的 100mM CSA 后处理之后的 PANi-NMP-4MP 膜的水接触角。

[0015] 图 3 示出了非织造载体和 PANi 膜的热分解。

[0016] 图 4 示出了针对 PANi 膜和 CSA 的 FTIR 谱图。

[0017] 图 5 示出了针对 a) NMP、b) 4MP、c) PANi-NMP 膜、d) PANi-NMP-4MP 膜、e) CSA 处理的 PANi-NMP-4MP 膜和 f) NH_4OH -CSA 处理的 PANi-NMP-4MP 膜的 ^1H NMR 谱图。

[0018] 图 6 示出了通过流动电流测定确定的 PANi 膜的 Zeta 电势。

[0019] 图 7 示出了 PANi 膜横截面和表面 SEM 图像。

[0020] 图 8 示出了说明 PANi 翠绿亚胺碱上的 4MP 的还原和环取代的示意图。

[0021] 图 9 示出了无凝胶抑制剂下由 PANi-NMP 制成的膜的 SEM 图像。

[0022] 图 10 示出了采用 4-MP 作为凝胶抑制剂由 PANi-NMP 制成的膜的 SEM 图像。

[0023] 图 11 示出了针对不同膜材料的粘聚 (cohesion) 的自由能的曲线图。

[0024] 图 12 示出了针对不同膜材料和积垢材料的粘聚的自由能的曲线图。针对 9 种积垢材料对每种膜 (如 PANi-CAS) 进行了测试。在针对每种膜的曲线图中, 从左开始积垢材料的顺序是 PEG、大肠杆菌, 酿酒酵母、HSA、恶臭假单胞菌、二氧化硅、氧化铝、羧基改性胶乳和十六烷。

[0025] 本发明的其它优点将在下面的说明中部分列出, 并且部分将是说明中显而易见的, 或可以通过本发明的实践而得知。本发明的优点将借助在所附权利要求书中特别指出的要素和组合来实现和达到。应当理解, 以上概述和以下详述都仅是示例性和解释性的, 并且不限制要求保护的本发明。

[0026] 说明

[0027] A. 定义

[0028] 如本说明书和所附的权利要求书所用, 除非上下文清楚地指出, 单数形式“一 (a)”、“一 (an)”、“所述 (the)”包括复数的指代物。因此, 例如, 提及的“官能团”、“烷基”或“残基”包括两个或更多个这样的官能团、烷基或残基等的混合物。

[0029] 在本文中范围可被表示成从“约”一个具体值和 / 或到“约”另一个具体值。当表示这样的范围时, 另一个方面包括从所述一个特定值和 / 或到所述另一个特定值。类似地, 当数值通过使用先行词“约”被表示为近似值时, 将被理解的是, 所述特定值形成另一个方面。应当进一步理解, 每个范围的端点相对于另一个端点都是显著的并独立于另一个端点。也可以理解, 存在许多本文中所公开的值, 并且每个值在本文中也公开成除了该值本身之外的“约”的该特定值。例如, 如果公开了值“10”, 则“约 10”也被公开。也可以理解, 还公开了两个具体单元之间的每个单元。例如, 如果 10 和 15 被公开, 那么 11、12、13 和 14 也被公开。

[0030] 在本说明书和结论性权利要求书中提及的组合物中的特定元素或组分的重量份数表示所述元素或组分和所述组合物或制品中的被表示成重量份数的任何其他元素或组分之间的重量关系。因此, 在含 2 重量份组分 X 和 5 重量份的组分 Y 的化合物中, X 和 Y 以 2 : 5 的重量比存在, 并且无论所述化合物是否包含另外的组分都以这样的比存在。

[0031] 除非有特别的相反说明, 组分的重量百分比 (wt. %) 是基于包含所述组分的制剂或组合物的总重量。

[0032] 如本文所用, 术语“衍生物”是指一种化合物 (例如聚合物), 其具有从母体化合物 (例如聚苯胺) 的结构中衍生的结构, 并且其结构充分地类似于本文公开的那些结构, 并基于该相似性, 本领域的技术人员可以预期其表现出与母体化合物相同的或类似的性质和功用。示例性的衍生物包括母体化合物的酯、酰胺、烷基取代物和其他合适的取代物。

[0033] 如本文所用,术语“任选的”或“任选地”是指随后描述的事件或情形会发生或不会发生,而且该描述包括其中所述事件或情形发生的情况和其中所述事件或情形不发生的情况。

[0034] 如本文所用,术语“接触”是指以使得一种物质能与膜相互作用的方式将所述物质(例如亲水性恢复剂)和膜合在一起。

[0035] 如本文所用,术语“有效量(effective amount)”和“有效量(amount effective)”是指一种足以达到所期望的结果或者足以对不希望的情形产生影响的量。例如,“有效量的亲水性恢复剂”是指足以实现膜的亲水性的期望的增加的量。

[0036] B. 亲水性

[0037] 固体表面的可润湿性。“亲液的”或“润湿的”的典型定义为小于 90 度的液体接触角,而“疏液的”或“非润湿的”是大于 90 度的液体接触角。根据 Dupre 方程,固液界面自由能产生自固体(1)、液体(3)和固-液(13)界面张力之间的差。(A. Dupre, *Theorie Mecanique de la Chaleur*; Gauthier-Villars: Paris, 1869) 所述固-液界面自由能通过 Young-Dupre 方程直接由液体接触角计算,

$$[0038] \quad -\Delta G_{13} = \gamma_3 \left(1 + \frac{\cos\theta_3}{r} \right), \quad (1)$$

[0039] 其通过将 Dupre 方程与 Young 方程结合获得。(T. Young, “An Essay on the Cohesion of Fluids,” *Philosophical Transactions of the Royal Society of London* 1805, 95, 65-87)。事实上,方程(1)是 Young-Dupre 方程的修饰形式,其说明了如 Wenzel 所建议的由表面粗糙度产生的过大的界面面积的原因。在方程(2)中, r 是粗糙的固体表面的实际表面积,这可以由原子力显微镜(AFM)表面面积差(亦称 Wenzel 的“粗糙度因子”或实际表面积对几何表面积之比)获得。(R. N. Wenzel, *Industrial and Engineering Chemistry* 1936, 28, 988-994)。

[0040] 固体表面张力的分量和它们的确定。根据 van Oss, 任何介质的总表面张力是非极性(Lifshitz-van der Waals)分量和极性(Lewis 酸-碱)分量的和,或

$$[0041] \quad \gamma^{TOT} = \gamma^{LW} + \gamma^{AB}, \quad (2)$$

[0042] 其中, $\gamma^{AB} (= 2\sqrt{\gamma^+ \gamma^-})$ 是酸-碱分量, γ^+ 和 γ^- 是电子受体分量和电子给体分量,并且 γ^{LW} 是 Lifshitz-van der Waals 分量。(C. J. van Oss, *Interfacial Forces in Aqueous Media*; Marcel Dekker, Inc.: New York, NY, 1994)。各表面张力分量通过使用三种具有已知表面张力的探针液体测定的接触角来确定并通过扩展的 Young 方程计算,

$$[0043] \quad \left(1 + \frac{\cos\theta}{r} \right) \gamma_l^{TOT} = 2 \left(\sqrt{\gamma_s^{LW} \gamma_l^{LW}} + \sqrt{\gamma_s^+ \gamma_l^-} + \sqrt{\gamma_s^- \gamma_l^+} \right), \quad (3)$$

[0044] 其中 θ 是表面上的探针液体的平衡接触角, γ_l^{TOT} 是总的液体表面张力。下标 s 和 l 分别代表所述固体表面和所述探针液体。

[0045] 界面自由能、亲水性和抗积垢性。接触时的界面自由能 ΔG_{132}^{IF} 提供了通过液体介质(3)与另一固体材料(2)相互作用的固体材料(1)的固有稳定性的另外的见解。它说明了两个固体表面之间、水分子和每一个固体表面之间以及在水分子本身中的相互作用的

原因。界面自由能表示所述待彼此被吸引或被排斥的表面的热力学趋势,并由 (D. Myers, Surfaces, Interfaces, and Colloids :Principles and Applications ; 第二版 ;John Wiley&Sons :New York, NY,1999) 确定

$$[0046] \quad \Delta G_{132}^{IF} = \Delta G_{132}^{LW} + \Delta G_{132}^{AB}, \quad (4a)$$

$$[0047] \quad \Delta G_{132}^{LW} = 2 \left(\sqrt{\gamma_3^{LW}} - \sqrt{\gamma_1^{LW}} \right) \left(\sqrt{\gamma_2^{LW}} - \sqrt{\gamma_3^{LW}} \right), \quad (b)$$

$$[0048] \quad \Delta G_{132}^{AB} = 2\sqrt{\gamma_3^A} \left(\sqrt{\gamma_1^A} + \sqrt{\gamma_2^A} - \sqrt{\gamma_3^A} \right) + 2\sqrt{\gamma_3^B} \left(\sqrt{\gamma_1^B} + \sqrt{\gamma_2^B} - \sqrt{\gamma_3^B} \right) - 2\sqrt{\gamma_1^A \gamma_2^A} - 2\sqrt{\gamma_1^B \gamma_2^B}. \quad (c)$$

[0049] 如果表面 1 和表面 2 是相同的材料 (即, $2 = 1$), 则 ΔG_{131}^{IF} 表示接触时粘聚的界面自由能。这是“亲水性”和“疏水性”的最基本的热力学定义。如本文所用, 术语“亲水性”和类似术语是指接触时通过 ΔG_{131}^{IF} 的值确定的粘聚的界面自由能。 ΔG_{131}^{IF} 按 mJ/m^2 测定。如果 ΔG_{131}^{IF} 是正值 (即, 大于 0), 那么材料被认为是“亲水性的”, 因为存在阻止表面自发性接触的能量势垒 (即, 亲水性的斥力或水合能量)。相反, 如果粘聚自由能为负的, 则两个表面会自发地聚集在一起, 从它们之间驱逐水 ; 这被称为疏水性的吸引力或疏水作用。此外, 如果一种材料相比于另一种材料具有较大的 ΔG_{131}^{IF} 的正值或较大的 ΔG_{131}^{IF} 的负值, 则所述一种材料相比于所述另一种材料是“更亲水性的”或“较不疏水性的”。

[0050] 如本文所用, 术语“增加 (increasing) 亲水性”或“增加 (increases) 亲水性”和类似术语是指 ΔG_{131}^{IF} 值的增加。例如, 该值可以从负数 (即 -20) 增加至较大的负数 (即 -5)。在另一个实例中, 该值可以从负数 (即 -20) 增加至正数 (即 5)。在又一实例中, 该值可以从正值 (即 5) 增加至更大的正值 (即 20)。所有这些实施例落入“增加 (increasing) 亲水性”或“增加 (increases) 亲水性”的定义中。针对将膜的 ΔG_{131}^{IF} 值增加 $5\text{mJ}/\text{m}^2$ 的方法的非限制性实例可以例如将所述膜的 ΔG_{131}^{IF} 值从 $-10\text{mJ}/\text{m}^2$ 增加至 $-5\text{mJ}/\text{m}^2$, 或从 $-3\text{mJ}/\text{m}^2$ 增加至 $2\text{mJ}/\text{m}^2$, 或从 $5\text{mJ}/\text{m}^2$ 增加至 $10\text{mJ}/\text{m}^2$ 。

[0051] 如果表面 1 和表面 2 是不同的材料 (例如, 细菌细胞和膜), 则 ΔG_{132}^{IF} 表示接触时粘附 (adhesion) 的界面自由能。如本文所用, 术语“粘附倾向”和类似术语是指接触时通过 ΔG_{132}^{IF} 的值确定的粘附的界面自由能。 ΔG_{132}^{IF} 按 mJ/m^2 测定。粘附倾向描述了当通过水分离时的由不同的材料组成的两个表面发生接触的热力学支持。因此, 正的粘附自由能表示必须输入能量以从两个材料表面之间驱逐出水, 并迫使它们在一起, 而负的自由能表示粘附是自发过程。材料的粘附倾向决定了材料 (即聚苯胺膜) 的抗积垢性。较小的 ΔG_{132}^{IF} 的负值与材料 (例如, 膜) 和具有高度积垢倾向并难以清洁的污物 (例如, 细菌细胞) 相关, 因为它对于污物保持粘附至所述材料而言是能量上有利的。 ΔG_{132}^{IF} 的正值与具有较小的积垢倾向并易于清洁的材料相关。

[0052] 如本文所用, 术语“增加 (increasing) 粘附倾向”或“增加 (increases) 粘附倾向”或类似术语是指增加 ΔG_{132}^{IF} 的值。例如, 该值可以从负数 (即 -20) 增加至较大的负数

(即 -5)。在另一个实例中,该值可以从负数(即 -20)增加至正数(即 5)。在又一实例中,该值可以从正值(即 5)增加至更大的正值(即 20)。所有这些实施例落入“增加(increasing)粘附倾向”或“增加(increases)粘附倾向”的定义中。材料的粘附倾向的增加表示所述材料(即聚苯胺膜)的“抗积垢性”的增加。针对将膜的 ΔG_{132}^{IF} 值增加 $5\text{mJ}/\text{m}^2$ 的方法的非限制性实例可以例如将所述膜的 ΔG_{132}^{IF} 值从 $-10\text{mJ}/\text{m}^2$ 增加至 $-5\text{mJ}/\text{m}^2$,或从 $-3\text{mJ}/\text{m}^2$ 增加至 $2\text{mJ}/\text{m}^2$,或从 $5\text{mJ}/\text{m}^2$ 增加至 $10\text{mJ}/\text{m}^2$ 。

[0053] 含有极性官能团(最常见的是含有 O、N、S 和 P 的部分)的聚合物有时被描述成并被认为是亲水性的。在膜的情况下,术语“亲水性的”经常与“抗积垢性”同义使用,但在关于明显亲水性的聚合物(根据可润湿性和亲水性的经典定义)一定程度上易发生积垢(例如,PSf、PES、PC 和 PEI)的文献中存在一些困惑。也许对于水处理膜而言,应被认为是特殊情况。van Oss 指出当是两种具有显著混合极性官能度的材料(即,看似“亲水性的”,但含有电子给体和电子受体两者)时,它们可以通过 Lewis 酸-碱吸引力彼此热力学吸引(参见方程 4c)。(C. J. van Oss, *The Properties of Water and their Role in Colloidal and Biological Systems*; Academic Press/Elsevier Ltd. :New York, NY, 2008) 通过方程 4c 的第三和第四项,这样的材料可以引入负的 AB 界面自由能,特别是当固体材料中的任一种的电子给体或受体表面张力分量小于水的表面张力分量时。这种现象影响了粘聚自由能和粘附自由能两者;因此,看似“亲水性的”材料实际上可能会产生负的“疏水性”的粘聚自由能或粘附自由能。

[0054] C. 增加膜的亲水性的方法

[0055] 聚苯胺的可加工性已经与通常受限于 NMP 和 N, N' - 二甲基亚丙基脲 (DMPU) 的溶剂的选择有关 [13, 14]。在 PANi 的翠绿亚胺碱形式中的亚胺氮和胺氮之间的链间氢键合和链内氢键合引起聚集并最终形成凝胶。可在 NMP 溶液中的 PANi 翠绿亚胺碱的四聚体重复单元之间形成多达 3 至 4 个氢键合 [15]。凝胶化可以在小于 1wt% 的 PANi 浓度下发生 [16-18] 并经常以非常短的时间间隔发生 [19-21]; 因此,除了少数例外,对于成膜而言理想的高浓度(约 15-25%)通常是不可能。

[0056] 凝胶抑制剂,典型地仲胺和叔胺添加剂,有助于减轻这些 PANi 的可加工性问题中的一部分 [22, 23]。凝胶抑制剂氢连接至亚胺氮,从而防止通过链间氢键合而凝胶化 [24-28]。图 1 示出了被预期在 PANi 的翠绿亚胺碱形式和 NMP 中的凝胶抑制剂 4MP 之间发生的相互作用和氢键合。尽管这些添加剂提供了产生浓缩的 PANi 溶液(通过该溶液可以形成强健的膜)的手段,但是凝胶抑制剂可能改变聚合物结构和化学。这可能使膜的机械强度、导电性、亲水性产生负面的变化 [14, 27-31]。更疏水性的膜更容易积垢,并最终需要更频繁地被清洁,并需要更高的操作压力,这需要更多的能量并且随时间的推移需付出更大的代价以维持产率 [32-44]。

[0057] 本文公开了增加膜的亲水性的方法,所述方法包括以下步骤:(a) 提供包含聚苯胺、聚苯胺衍生物或其共聚物和一种或多种凝胶抑制剂的膜;和 (b) 用一种或多种亲水性恢复剂处理所述膜,从而增加所述膜的亲水性。所公开的方法增加和/或恢复包含聚苯胺或其共聚物和一种或多种凝胶抑制剂的膜的亲水性。因此,在一个方面,所述方法使得所述膜较不容易积垢并且还可以增加膜的机械强度、导电性和/或亲水性。

[0058] 可用于形成膜的包含聚苯胺或其共聚物和一种或多种凝胶抑制剂的溶液的制备被描述在美国专利 5,981,695 ;6,123,883 ;6,429,282 ;6,797,325 ;和 7,563,484 中,所有这些通过引用全部并入本文。

[0059] 在一个方面,可用于形成膜的包含聚苯胺或其共聚物和一种或多种凝胶抑制剂的溶液可以包含包括 N-甲基-2-吡咯烷酮、N-乙基-2-吡咯烷酮、1-环己基-2-吡咯烷酮、1-甲基-2-哌啶酮、N-甲基己内酰胺、1,5-二甲基-2-吡咯烷酮 2 吡咯烷酮、1,3-二甲基-2-咪唑啉酮、1,3-二甲基-3,4,5,6-四氢-2(1H)-嘧啶酮、1-甲基-2-吡啶酮、1-乙酰基吡咯烷、1-乙酰基哌啶、4-乙酰基吗啉、1-乙酰基-3-甲基哌啶、N,N-二甲基丙酰胺、N,N,N',N'-四甲基脒、N,N-二甲基乙酰胺、二甲基亚砷、四亚甲基亚砷、六甲基磷酰胺、 Δ -戊内酰胺或 N,N-2-三甲基丙酰胺或其组合在内的溶剂。例如,可用于形成膜的包含聚苯胺或其共聚物和一种或多种凝胶抑制剂的溶液可以包含包括 1-甲基-2-吡咯烷酮的溶剂。

[0060] 在一个方面,所述膜包含聚苯胺、聚苯胺衍生物和其共聚物。例如,所述膜可以包含聚苯胺和 / 或所述膜可以包含聚苯胺衍生物和 / 或所述膜可以包含聚苯胺共聚物。在另一实例中,所述膜包含聚苯胺。在又一实例中,所述膜包含聚苯胺衍生物。在又一实例中,所述膜包含聚苯胺共聚物。在又一实例中,所述膜包含聚苯胺衍生物共聚物。聚苯胺共聚物可以是包含苯胺重复单元的聚合物,例如 PANi 翠绿亚胺碱四聚体。因此,聚苯胺共聚物可以是无规或嵌段共聚物。

[0061] 在一个方面,所述一种或多种凝胶抑制剂包括伯胺、仲胺或叔胺或其组合。例如,所述一种或多种凝胶抑制剂包括伯胺或仲胺或其组合。在另一实例中,所述一种或多种凝胶抑制剂包括仲胺。

[0062] 在一个方面,所述仲胺包括 4-甲基哌啶、2-甲基氮杂环丙烷、氮杂环丁烷、吡咯烷、哌啶、六亚甲基亚胺、七亚甲基亚胺、3-吡咯啉、3-吡咯烷醇、(R)-(-)-吡咯烷-2-甲醇、(S)-(+)-吡咯烷-2-甲醇、4-乙基-2-甲基-(3-甲基丁基)噁唑烷、(S)-(+)-(苯胺基甲基)吡咯烷、1,3,3-三甲基-6-氮杂双环[3,2,1]辛烷、(S)-(+)-(甲氧基甲基)吡咯烷、二氢吲哚、硫吗啉、十氢喹啉、2,6-二甲基吗啉、二乙胺、二环己胺、二丙胺、二丁胺、N-甲基己胺、1-氮杂-15-冠-5,1,2,3,6-四氢吡啶、1,4,5,6-四氢嘧啶、1,4-二氧杂-8-氮杂螺[4.5]癸烷、3,3-二甲基哌啶、吗啉或 3,5-二甲基哌啶或其组合。

[0063] 在一个方面,所述伯胺包括环丙胺、正丁胺、环丁胺、环己胺、戊胺、叔戊胺、2-氨基-1-甲氧基丙烷、4-氨基吗啉、(+/-)-外-2-氨基降冰片烷、1,2-二氨基丙烷、1,2-二氨基环己烷、环辛胺、1,4-二氨基丁烷、1-氨基哌啶、1-氨基高哌啶、四氢糠胺、糠胺、1,2-二氨基-2-甲基丙烷、1-甲基-4-(甲基氨基)哌啶或 4-(2-氨基乙基)吗啉或其组合。

[0064] 在一个方面,所述叔胺包括 N-甲基哌啶、N,N'-二甲基哌啶或三乙胺或其组合。

[0065] 在一个方面,所述一种或多种凝胶抑制剂包括 4-甲基哌啶、正丁胺、2,5-二甲基-3-吡咯啉、3,3-二甲基哌啶、七亚甲基亚胺、二异丙基胺、六亚甲基亚胺、N-乙基苄胺、哌啶、2,6-二甲基吗啉、哌啶、二丁胺、N-甲基哌啶、N,N'-二甲基哌啶或二乙基-3-哌啶甲酰胺(diethylnipecotinamide)、三乙胺或其组合。例如,所述一种或多种凝胶抑制剂可以包括 4-甲基哌啶。

[0066] 在一个方面,包含聚苯胺或其共聚物和一种或多种凝胶抑制剂的膜可由包含聚苯

胺或其共聚物和一种或多种凝胶抑制剂的溶液制成,所述聚苯胺或其共聚物对所述一种或多种凝胶抑制剂的摩尔比为 0.1-5 : 0.1-10,例如 1 : 2 的摩尔比。在一个方面,聚苯胺或其共聚物对一种或多种凝胶抑制剂的比可以是一比能够形成膜的比,其中通过 PANi 的翠绿亚胺碱形式之间的链间氢键合防止凝胶化。这样定量可以例如是聚苯胺或其共聚物对一种或多种凝胶抑制剂的 1 : 2 的摩尔比。

[0067] 在一个方面,包含所述聚苯胺或其共聚物和所述一种或多种凝胶抑制剂的膜包含按重量计至少 0.1% 的一种或多种凝胶抑制剂。例如,包含所述聚苯胺或其共聚物和所述一种或多种凝胶抑制剂的膜包含按重量计至少 0.1%、0.5%、1%、3%、5%、7.5%、10%、15%、20% 或 30% 的一种或多种凝胶抑制剂。

[0068] 在一个方面,将包含所述聚苯胺或其共聚物和一种或多种凝胶抑制剂的膜浇注在基板上,如织物。

[0069] 在一个方面,包含所述聚苯胺或其共聚物和所述一种或多种凝胶抑制剂的膜具有小于 5%、4%、3%、2%、1%、0.8%、0.6%、0.4%、0.2%、0.1% 或 0.05% 的表面孔隙率。例如,包含所述聚苯胺或其共聚物和所述一种或多种凝胶抑制剂的膜具有小于 1%、0.8%、0.6%、0.4%、0.2%、0.1% 或 0.05% 的表面孔隙率,例如小于 0.4% 或 0.2%。

[0070] 在一个方面,包含所述聚苯胺或其共聚物和所述一种或多种凝胶抑制剂的膜具有小于 20nm、15nm、10nm、7.5nm、5nm 或 2.5nm 的平均孔隙直径。例如,包含所述聚苯胺或其共聚物和所述一种或多种凝胶抑制剂的膜具有小于 10nm、7.5nm、5nm 或 2.5nm 的平均孔隙直径,例如小于 7.5nm 或 5nm。

[0071] 在一个方面,所述处理包括将所述膜与亲水性恢复剂接触至少 15 分钟、30 分钟、45 分钟、60 分钟、90 分钟、120 分钟或 180 分钟。例如,所述处理包括将所述膜与亲水性恢复剂接触至少 15 分钟。在另一实例中,所述处理包括将所述膜与亲水性恢复剂接触至少 60 分钟。

[0072] 在一个方面,用一种或多种亲水性恢复剂处理包含所述聚苯胺或其共聚物和所述一种或多种凝胶抑制剂的膜包括用有效量的所述一种或多种亲水性恢复剂处理所述膜,以增加所述膜的亲水性。

[0073] 在一个方面,所述处理包括用一种或多种亲水性恢复剂过滤所述膜。在一个方面,所述过滤包括用所述亲水性恢复剂将所述膜过滤至少 15 分钟、30 分钟、45 分钟、60 分钟、90 分钟、120 分钟或 180 分钟。例如,所述过滤包括用所述亲水性恢复剂将所述膜过滤至少 15 分钟。在另一实例中,所述过滤包括用所述亲水性恢复剂将所述膜过滤至少 60 分钟。

[0074] 在一个方面,所述一种或多种亲水性恢复剂包括有机磺酸。所述有机磺酸可以是单磺酸或二磺酸。在一个方面,所述有机磺酸包含 C1-C12 取代的或未取代的烷基、C1-C12 取代的或未取代的烯基、C1-C12 取代的或未取代的烷基、C1-C12 取代的或未取代的环烷基、C1-C12 取代的或未取代的杂芳基、C1-C12 取代的或未取代的杂环基。例如,所述有机磺酸包含 C3-C12 取代的或未取代的烷基、C3-C12 取代的或未取代的烯基、C3-C12 取代的或未取代的烷基、C3-C12 取代的或未取代的环烷基、C3-C12 取代的或未取代的杂芳基、C3-C12 取代的或未取代的杂环基。在另一实例中,所述有机磺酸包含 C6-C12 取代的或未取代的烷基、C6-C12 取代的或未取代的烯基、C6-C12 取代的或未取代的烷基、C6-C12 取代的或未取代的环烷基、C6-C12 取代的或未取代的杂芳基、C6-C12 取代的或未取代的杂环基。

[0075] 在一个方面,所述一种或多种亲水性恢复剂包括 (+/-) 樟脑-10-磺酸、硫酸、甲磺酸、乙磺酸、丙磺酸、全氟代丙磺酸、丁磺酸、全氟代丁磺酸、己磺酸、全氟代己磺酸、全氟代辛磺酸、苯磺酸、甲苯磺酸、十二烷基苯、磺酸、牛磺酸(2-氨基乙磺酸)、高牛磺酸(3-氨基丙磺酸)、萘磺酸、2,5-萘二磺酸、二壬基萘磺酸、二壬基萘二磺酸、聚乙烯磺酸盐或聚苯乙烯磺酸盐或其组合。例如,所述一种或多种亲水性恢复剂包括 (+/-) 樟脑-10-磺酸、甲磺酸、乙磺酸、丙磺酸、全氟代丙磺酸、丁磺酸、全氟代丁磺酸、己磺酸、全氟代己磺酸、全氟代辛磺酸、苯磺酸、甲苯磺酸、十二烷基苯、磺酸、牛磺酸(2-氨基乙磺酸)、高牛磺酸(3-氨基丙磺酸)、萘磺酸、2,5-萘二磺酸、二壬基萘磺酸、二壬基萘二磺酸、聚乙烯磺酸盐或聚苯乙烯磺酸盐或其组合。在另一实例中,所述一种或多种亲水性恢复剂可包括 (+/-) 樟脑-10-磺酸,如 (-) 樟脑-10-磺酸或 (+) 樟脑-10-磺酸或其组合。

[0076] 在一个方面,所述膜在处理前具有负的 ΔG_{131}^{IF} 值。例如,所述膜在处理前可以具有小于 -2、-4、-6、-8、-10、-15 或 -20mJ/m² 的负的 ΔG_{131}^{IF} 值。例如,所述膜在处理前可以具有小于 -8mJ/m² 的负的 ΔG_{131}^{IF} 值。在一个方面,所述膜在处理前可以具有 -2 至 -20mJ/m² 的负的 ΔG_{131}^{IF} 值。

[0077] 在一个方面,所述膜在处理前具有正的 ΔG_{131}^{IF} 值。在一个方面,膜在处理前具有至少 1、5、10、15、20、25、30 或 50mJ/m² 的正的 ΔG_{131}^{IF} 值。例如,所述膜在处理前可具有至少 10mJ/m² 的正的 ΔG_{131}^{IF} 值。在另一个方面,所述膜在处理前可具有 1 至 50mJ/m² 的正的 ΔG_{131}^{IF} 值。例如,所述膜在处理前可具有 5 至 25mJ/m² 的正的 ΔG_{131}^{IF} 值。

[0078] 在一个方面,所述膜在处理前具有至少 5、10、15、20、25、30、50、75 或 100mJ/m² 的 ΔG_{131}^{IF} 的增加值。例如,所述膜在处理前可以具有至少 5、10、15、20、25、30 或 50J/m² 的 ΔG_{131}^{IF} 的增加值,例如在处理前至少 20、25 或 30J/m² 的 ΔG_{131}^{IF} 的增加值。在另一个方面,所述膜在处理前可以具有 5 至 100mJ/m² 的 ΔG_{131}^{IF} 增加值。例如,所述膜在处理前可以具有 5 至 50mJ/m²、例如在处理前 20 至 50mJ/m² 的 ΔG_{131}^{IF} 的增加值。

[0079] 在一个方面,所述膜在处理前具有降低的粘附倾向。

[0080] 在另一个方面,所述膜在处理前具有增加的抗积垢性。

[0081] 在一个方面,所述膜在处理前具有正的 ΔG_{132}^{IF} 值。在一个方面,所述膜在处理前具有至少 1、5、10、15、20、25、30 或 50mJ/m² 的正的 ΔG_{132}^{IF} 值。例如,所述膜在处理前可具有至少 10mJ/m² 的正的 ΔG_{132}^{IF} 值。在另一个方面,所述膜在处理前可以具有 1 至 50mJ/m² 的正的 ΔG_{132}^{IF} 值。例如,所述膜在处理前可以具有 5 至 35mJ/m² 的正的 ΔG_{132}^{IF} 值。

[0082] 在一个方面,所述膜在处理前具有至少 5、10、15、20、25、30、50、75 或 100mJ/m² 的 ΔG_{132}^{IF} 的增加值。例如,所述膜在处理前可以具有至少 5、10、15、20、25、30 或 50J/m²、例如在处理前至少 20、25 或 30J/m² 的 ΔG_{132}^{IF} 的增加值。在另一个方面,所述膜在处理前可以具有 5 至 100mJ/m² 的 ΔG_{132}^{IF} 的增加值。例如,所述膜在处理前可以具有 5 至 50mJ/m²、例如在

处理后 20 至 50mJ/m²的 ΔG_{132}^{IF} 的增加值。

[0083] 在一个方面,当针对二氧化硅、聚乙二醇 (PEG)、人血清白蛋白 (HSA)、十六烷、大肠杆菌 (E. coli)、酿酒酵母 (S. cerevisiae) 和恶臭假单胞菌 (P. putida) 测定时,所述膜在处理后可具有至少 1、5、10、15、20、25、30 或 50mJ/m²的正的 ΔG_{132}^{IF} 值。例如,当针对二氧化硅、PEG、HSA、十六烷、大肠杆菌、酿酒酵母和恶臭假单胞菌测定时,所述膜在处理后可具有至少 10mJ/m²的正的 ΔG_{132}^{IF} 值。在另一个方面,当针对二氧化硅、PEG、HSA、十六烷、大肠杆菌、酿酒酵母和恶臭假单胞菌测定时,所述膜在处理后可具有 1 至 50mJ/m²的正的 ΔG_{132}^{IF} 值。例如,当针对二氧化硅、PEG、HSA、十六烷、大肠杆菌、酿酒酵母和恶臭假单胞菌测定时,所述膜在处理后可具有 5 至 35mJ/m²的正的 ΔG_{132}^{IF} 值。

[0084] 在一个方面,当针对二氧化硅、PEG、HSA、十六烷、大肠杆菌、酿酒酵母和恶臭假单胞菌测定时,所述膜在处理后可具有至少 5、10、15、20、25、30、50、75 或 100mJ/m²的 ΔG_{132}^{IF} 的增加值。例如,当针对二氧化硅、PEG、HSA、十六烷、大肠杆菌、酿酒酵母和恶臭假单胞菌测定时,所述膜在处理后可具有至少 5、10、15、20、25、30 或 50J/m²、例如至少 20、25 或 30J/m²的 ΔG_{132}^{IF} 的增加值。在另一个方面,当针对二氧化硅、PEG、HSA、十六烷、大肠杆菌、酿酒酵母和恶臭假单胞菌测定时,所述膜在处理后可具有 5 至 100mJ/m²的 ΔG_{132}^{IF} 的增加值。例如,当针对二氧化硅、PEG、HSA、十六烷、大肠杆菌、酿酒酵母和恶臭假单胞菌测定时,所述膜在处理后可具有 5 至 50mJ/m²、例如在处理后可具有 20 至 50mJ/m²的 ΔG_{132}^{IF} 的增加值。

[0085] 在一个方面,当针对二氧化硅、PEG、HSA、十六烷、大肠杆菌、酿酒酵母或恶臭假单胞菌或其组合测定时,所述膜在处理后可具有至少 1、5、10、15、20、25、30 或 50mJ/m²的正的 ΔG_{132}^{IF} 值。例如,当针对二氧化硅、PEG、HSA、十六烷、大肠杆菌、酿酒酵母或恶臭假单胞菌或其组合测定时,所述膜在处理后可具有至少 10mJ/m²的正的 ΔG_{132}^{IF} 值。在另一个方面,当针对二氧化硅、PEG、HSA、十六烷、大肠杆菌、酿酒酵母或恶臭假单胞菌或其组合测定时,所述膜在处理后可具有 1 至 50mJ/m²的正的 ΔG_{132}^{IF} 值。例如,当针对二氧化硅、PEG、HSA、十六烷、大肠杆菌、酿酒酵母或恶臭假单胞菌或其组合测定时,所述膜在处理后可具有 5 至 35mJ/m²的正的 ΔG_{132}^{IF} 值。

[0086] 在一个方面,当针对二氧化硅、PEG、HSA、十六烷、大肠杆菌、酿酒酵母或恶臭假单胞菌或其组合测定时,所述膜在处理后可具有至少 5、10、15、20、25、30、50、75 或 100mJ/m²的 ΔG_{132}^{IF} 的增加值。例如,当针对二氧化硅、PEG、HSA、十六烷、大肠杆菌、酿酒酵母或恶臭假单胞菌或其组合测定时,所述膜在处理后可具有至少 5、10、15、20、25、30 或 50mJ/m²、例如在处理后可具有至少 20、25 或 30J/m²的 ΔG_{132}^{IF} 的增加值。在另一个方面,当针对二氧化硅、PEG、HSA、十六烷、大肠杆菌、酿酒酵母或恶臭假单胞菌或其组合测定时,所述膜在处理后可具有 5 至 100mJ/m²的 ΔG_{132}^{IF} 的增加值。例如,当针对二氧化硅、PEG、HSA、十六烷、大肠杆菌、酿酒酵母或恶臭假单胞菌或其组合测定时,所述膜在处理后可具有 5 至 50mJ/m²、例如在处理后可具有 20 至 50mJ/m²的 ΔG_{132}^{IF} 的增加值。

[0087] D. 膜

[0088] 本文还公开了包含聚苯胺、聚苯胺衍生物或其共聚物的膜，其中所述膜已经被实施一个或多个本文所公开的方法。例如，包含聚苯胺或其共聚物的膜可以已经被实施本文所公开的方法。

[0089] 在一个方面，所述膜具有正的 ΔG_{131}^{IF} 值。在一个方面，所述膜可以具有至少 1、5、10、15、20、25、30 或 50mJ/m²的正的 ΔG_{131}^{IF} 值。例如，所述膜可具有至少 10mJ/m²的正的 ΔG_{131}^{IF} 值。在另一个方面，所述膜可以具有 1 至 50mJ/m²的正的 ΔG_{131}^{IF} 值。例如，所述膜可以具有 5 至 25mJ/m²的正的 ΔG_{131}^{IF} 值。

[0090] 在一个方面，所述膜具有正的 ΔG_{132}^{IF} 值。在一个方面，所述膜具有至少 1、5、10、15、20、25、30 或 50mJ/m²的正的 ΔG_{132}^{IF} 值。例如，所述膜可具有至少 10mJ/m²的正的 ΔG_{132}^{IF} 值。在另一个方面，所述膜可具有 1 至 50mJ/m²的正的 ΔG_{132}^{IF} 值。例如，所述膜可具有 5 至 35mJ/m²的正的 ΔG_{132}^{IF} 值。

[0091] 在一个方面，当针对二氧化硅、PEG、HSA、十六烷、大肠杆菌、酿酒酵母和恶臭假单胞菌测定时，所述膜具有正的 ΔG_{132}^{IF} 值。在一个方面，当针对二氧化硅、PEG、HSA、十六烷、大肠杆菌、酿酒酵母和恶臭假单胞菌测定时，所述膜具有至少 1、5、10、15、20、25、30 或 50mJ/m²的正的 ΔG_{132}^{IF} 值。例如，当针对二氧化硅、PEG、HSA、十六烷、大肠杆菌、酿酒酵母和恶臭假单胞菌测定时，所述膜可具有至少 10mJ/m²的正的 ΔG_{132}^{IF} 值。在另一个方面，当针对二氧化硅、PEG、HSA、十六烷、大肠杆菌、酿酒酵母和恶臭假单胞菌测定时，所述膜可具有 1 至 50mJ/m²的正的 ΔG_{132}^{IF} 值。例如，当针对二氧化硅、PEG、HSA、十六烷、大肠杆菌、酿酒酵母和恶臭假单胞菌测定时，所述膜可具有 5 至 35mJ/m²的正的 ΔG_{132}^{IF} 值。

[0092] 在一个方面，当针对二氧化硅、PEG、HSA、十六烷、大肠杆菌、酿酒酵母或恶臭假单胞菌或其组合测定时，所述膜具有正的 ΔG_{132}^{IF} 值。在一个方面，当针对二氧化硅、PEG、HSA、十六烷、大肠杆菌、酿酒酵母或恶臭假单胞菌或其组合测定时，所述膜在处理后可具有至少 1、5、10、15、20、25、30 或 50mJ/m²的正的 ΔG_{132}^{IF} 值。例如，当针对二氧化硅、PEG、HSA、十六烷、大肠杆菌、酿酒酵母或恶臭假单胞菌或其组合测定时，所述膜在处理后可具有至少 10mJ/m²的正的 ΔG_{132}^{IF} 值。在另一个方面，当针对二氧化硅、PEG、HSA、十六烷、大肠杆菌、酿酒酵母或恶臭假单胞菌或其组合测定时，所述膜可具有 1 至 50mJ/m²的正的 ΔG_{132}^{IF} 值。例如，当针对二氧化硅、PEG、HSA、十六烷、大肠杆菌、酿酒酵母或恶臭假单胞菌或其组合测定时，所述膜可具有 5 至 25mJ/m²的正的 ΔG_{132}^{IF} 值。

[0093] E. 制品

[0094] 本文还公开了包含一个或多个本文所公开的膜的制品。例如，所述制品可以包括本文所公开的膜。

[0095] 在一个方面，所述制品是用于净化的装置。例如，所述制品可以是装置，用于净化新鲜的地表水、通过反渗透膜进行脱盐前的海水、含油废水、市政污水或其它工业废水。

例如,所述制品可以是用于分离蛋白质、纯化液体食品和饮料产品、进行肾透析的装置。

[0096] F. 使用方法

[0097] 本文还公开了用于净化水的方法,所述方法包括以下步骤:(a) 提供本文所公开的膜,其中所述膜具有第一面和第二面;(b) 在第一压力下将所述膜的第一面与具有第一盐浓度的第一体积的第一溶液接触;和(c) 在第二压力下将所述膜的第二面与具有第二盐浓度的第二体积的第二溶液接触;其中所述第一溶液通过所述膜与所述第二溶液流体连通,其中,所述第一盐浓度高于所述第二盐浓度,从而产生穿过所述膜的渗透压,并且其中第一压力足够高于第二压力,以克服所述渗透压,从而增加所述第二体积和减小所述第一体积。

[0098] 本文还公开了用于浓缩杂质的方法,所述方法包括以下步骤:(a) 提供本文所公开的膜,其中所述膜具有第一面和第二面;(b) 在第一压力下将所述膜的第一面与具有第一杂质浓度的第一体积的第一混合物接触;(c) 在第二压力下将所述膜的第二面与具有第二杂质浓度的第二体积的第二混合物接触;和(d) 收集所述杂质,其中所述第一混合物通过所述膜与所述第二溶液流体连通,其中所述第一杂质浓度高于所述第二杂质浓度,从而产生穿过所述膜的渗透压,并且其中第一压力足够高于第二压力,以克服所述渗透压,从而增加所述第二体积和减小所述第一体积。

实施例

[0099] 提出下列实施例以便为本领域普通技术人员提供完整的公开内容和本文所要求的化合物、组合物、制品、装置和/或方法如何制得和评价的说明,并且旨在是纯粹示例性的,并且不旨在限制本公开内容。虽然就使用的数字(例如,量、温度等)而言已努力确保准确,但仍应该对某些实验误差和差异进行说明。除非另外指出,否则份数是重量份数,温度以℃表示或处于环境温度,并且压力处于或接近大气压。

[0100] 几种方法制备本发明的化合物示于以下实施例。原料和所需的中间体在某些情况下可商购,或可以按照文献方法或如本文所示来制备。

[0101] a. 实施例 1

[0102] 将凝胶抑制剂 4-甲基哌啶(4MP)添加至聚苯胺(PANi)/1-甲基-2-吡咯烷酮(NMP)混合物产生在高聚合物浓度下的稳定的聚合物溶液。相比于由在 NMP 中的 18 聚合物 wt% PANi 浇注成的那些膜,由 NMP-4MP 中的 18 聚合物 wt% 的 PANi 溶液浇注成的膜的水渗透率低 98%,但表现出高出 91% 的蛋白质截留率(rejection)。使用去离子水相转化后, PANi-NMP 膜具有 24° 的水接触角,而 PANi-NMP-4MP 膜具有 42° 的接触角。这种膜的亲水性的减少源于氢键合的和环取代的 4MP/聚苯胺缔合的组合。采用不同酸和碱溶剂的化学后处理产生了一系列的水通量、蛋白质截留率、界面亲水性和机械性能。采用樟脑磺酸的后处理完全从聚合物基质中除去 4MP 的氢键合成分,并且在恢复膜的亲水性方面是最有效的。影响是纯聚苯胺超滤膜可以通过使用凝胶抑制剂和化学后处理被赋予优异的机械、界面和分离特性。

[0103] (a) 材料与方法

[0104] (i) 材料

[0105] 超纯的 18M Ω 去离子(DI)水通过反渗透系统(RODI-C-12BL, Aqua Solutions,

Inc.) 产生。硫酸 (Sigma-Aldrich, No. 320501)、过氧二硫酸铵 (Fisher, No. A682)、氢氧化钠 (Fisher, No. S612)、甲醇 (Sigma-Aldrich, No. 322415)、NMP (Sigma-Aldrich, No. 443778)、4MP (Sigma-Aldrich, No. M73206)、盐酸 (Sigma-Aldrich, No. 258148)、对甲苯磺酸一水合物 (PTSA) (Fisher, No. AC17178)、(+/-) 樟脑-10-磺酸 (CSA) (AlfaAesar, No. A12620)、4-十二烷基苯磺酸 (DBSA) (Sigma-Aldrich, No. 44198)、氢氧化铵 (Sigma-Aldrich, No. 320145)、牛血清白蛋白 (BSA) (Sigma-Aldrich, No. A9647)、氯化钠 (Fisher, No. S271)、二甲基亚砜-d₆ (Cambridge Isotope Laboratories, No. DLM-10) 和氯化钾 (Fisher, No. P217) 均原样使用。

[0106] (ii) 聚合物溶液的制备及成膜

[0107] 如前面详细报道的那样在我们的实验室合成聚苯胺 [12]。在被添加至溶剂前在真空烘箱 (~ 25 英寸汞柱) 中于 50°C 下将聚苯胺干燥过夜。通过将 18wt% 的粉碎的 PANi 粉末添加至 82wt% 的 NMP (PANi-NMP) 或 72wt% 的 NMP 和 10wt% 的 4MP 的混合物 (PANi-NMP-4MP) 中 (即, 2 摩尔 4MP : 摩尔 PANi 翠绿亚胺碱四聚体 ; 0.547g 4MP/g 的 PANi 翠绿亚胺碱) 来制备聚合物溶液 [15, 22, 26-28]。经 1 小时将 PANi 加入到溶剂中, 同时剧烈搅拌。可以在密封的玻璃小瓶中将聚合物溶液搅拌 3 天。

[0108] 通过浸入沉淀法形成 PANi 超滤膜 [45]。在膜浇注之前可以将聚合物溶液静置密封 1 小时。采用具有使用测隙规设定的 152 μm 的刀锋高度的浇注刀 (Gardco Adjustable Micrometer Film Applicator, Microm II, AP-99500701) 分割膜。膜被手工浇注在非织造聚酯织物 (NanoH₂O, Inc., Los Angeles, CA) 上, 并立即置于含有 3 升的 DI 水的 20°C 的凝固浴中。在膜浇注过程中, 相对湿度为 50-55%。在被转移到塑料储存袋 (在那里它们被浸泡在 DI 水中) 之前使膜在凝固浴中保持 30 分钟。每 30 分钟使用新鲜的 DI 水替换储存袋中的水, 持续 2 小时。然后在后处理以及进一步表征之前于 4°C 下将膜储存在 DI 水中。

[0109] (iii) 膜后处理

[0110] 对 PANi UF 膜进行后处理, 通过将膜取样片置于含有 100mM HCl、H₂SO₄、PTSA、CSA、DBSA 或 NH₄OH 的 150ml 水溶液的烧杯中。使用 DI 水在 50°C 下进行类似的后处理。在 125rpm 下保持轻轻搅拌。旨在从所述膜除去 CSA 的特殊的后处理于 50°C 下在 100mM NH₄OH 中进行 3 小时, 并轻轻搅拌。除非另有说明, 否则使用 100mM CSA 在 50°C 下进行 CSA 后处理 1 小时。

[0111] (iv) 膜表征

[0112] 使用 25mm 冲头 (Osborne arch punch, OS-149-m25, Campbell Bosworth Machinery Co.) 切割膜样品用于性能测试。将样品保持湿润并放置在具有 3.5cm² 的膜面积 (A_m) 的一端闭塞的搅拌槽 (UHP-25, Advantec MFS, Inc.) 中。使用数字型 HPLC 液体流量计 (FlowCal 5000, Tovatech, LLC) 测定渗透体积流速。在 20psi 的跨膜压力、20°C 下用 DI 水压紧膜, 直到经过 30 分钟获得 < 5% 的渗透率的降低。然后在 20、10 和 5psi. 的跨膜压力 (Δp) 下记录渗透体积流速 (Q_p)。通过下式计算膜的纯水渗透率 (L_p) [46]:

$$[0113] \quad L_p = \frac{Q_p}{A_m \cdot \Delta p} \quad (5)$$

[0114] 在纯水渗透率试验之后立即测定膜蛋白截留率。从搅拌槽中除去来自渗透率试验的残留的水, 并用 10ml 的 1000mg l⁻¹ 的 BSA 在 50mM NaCl 中的溶液代替。在该溶液中 BSA

具有 6nm 的流体动力学直径 [12]。使搅拌速率保持在 350rpm ($Re_{SC} = 2963$)。通过下式计算搅拌槽的雷诺数：

$$[0115] \quad Re_{SC} = \frac{\rho \cdot \omega \cdot r_{SC}^2}{\mu}, \quad (6)$$

[0116] 其中 ρ 是流体密度 ($kg \cdot m^{-3}$)， ω 为角速度 ($rad \cdot s^{-1}$)， r_{SC} 是搅拌槽半径 ($9 \times 10^{-3}m$)，而且 μ 是流体的动态粘度 ($kg \cdot m^{-1} \cdot s^{-1}$) [47]。使用下式计算 $4.1 \times 10^{-6} m \cdot s^{-1}$ 的搅拌槽质量传递系数 (k_{SC}) [47]：

$$[0117] \quad \frac{k_{SC} \cdot r_{SC}}{D} = Sh_{SC} = 0.27 Re_{SC}^{0.567} Sc^{0.33} \quad (7)$$

[0118] 其中 D 是 BSA 的扩散系数 ($5.9 \times 10^{-11} m^2 \cdot s^{-1}$)， Sh_{SC} 是搅拌槽的舍伍德数，而且 Sc 是施密特数 ($Sc = u \cdot \rho^{-1} \cdot D^{-1}$)。恒定的跨膜压被设定成提供 40 加仑英尺⁻²天⁻¹ ($19 \mu m \cdot s^{-1}$) 的初始渗透通量 ($J_v = Q_p / A_m$)，并且 5ml 的渗透物被收集 (50% 的回收率)。通过在 $\lambda = 278nm$ 的 UV- 可见光吸收率 ($DU^{\text{®}} 730$ Life Science UV/ 可见光分光光度计, Beckman Coulter) 确定蛋白质浓度进料中的蛋白质浓度 (c_f) 和渗透物中的蛋白质浓度 (c_p)。基于下式计算溶质截留率 (R_s)：

$$[0119] \quad R_s = 1 - \frac{c_p}{c_f} \quad (8)$$

[0120] 使用测角仪 (DSA10, KRÜSS GmbH) 测定去离子水接触角。由于 PANi 膜的亲水性，所以在本文采用了捕泡测定技术。测定十滴并弃除最高值和最低值。针对每个膜测定傅里叶变换红外 (FTIR) (具有 ATR PRO 450-S ZnSe 晶体的 JASCO FT/IR-6300) 谱图。在测定前在干燥器中于 20°C 下将膜干燥过夜。

[0121] 在 Bruker Avance AV300 (300.1MHz) 仪器中于室温下进行了 ¹H- 核磁共振 (¹H-NMR) 研究。未在真空中干燥膜或加热干燥膜，以防止从所述膜挥发出 NMP 和 / 或 4MP。在 DMSO-d₆ 中制备饱和的膜溶液，并且将 NMP/4MP 标准物作为纯溶液测定。出现了相对于氘代 DMSO 溶剂信号的 ¹H-NMR 化学位移。

[0122] 采用可调间隙电动分析仪 (SurPASS Electrokinetic Analyzer, Anton-Paar GmbH) 测定流动电流。将流动通道间隙设定为 100 μm ，并将 20°C 的 1mM KCl 溶液用作背景电解质。在使用 HCl 和 NaOH 调节的 2-10 的 pH 范围内确定流动电流。使用 Helmholtz-Smoluchowski 方程计算膜 zeta 电势 (ζ)，

$$[0123] \quad \zeta = \frac{dI}{dp} \cdot \frac{\mu}{\varepsilon \cdot \varepsilon_0} \cdot \frac{L}{A}, \quad (9)$$

[0124] 其中 dI/dp 是流动电流对压力的斜率， μ 是所述溶液的动态粘度， ε 为溶液的介电常数， ε_0 为真空介电常数， L 为流动通道长度，而且 A 是流动通道的横截面积。

[0125] 通过在 pH 为 1 的 H₂SO₄ 中浸泡 1 小时以使 PANi 被充分地掺杂且导电来制备膜样品用于 SEM (Nova 600 NanoLab DualBeamTM-SEM/FIB, FEI Company)。在干燥器中于 20°C 下将样品干燥过夜。通过冷冻破裂使用液氮由不被支撑的膜制备横截面。通过先前描述的程

序针对孔隙率和孔尺寸对膜表面的 SEM 图像进行了分析 [12, 48]。

[0126] 在 5mm×100mm 的膜样品上进行膜的拉伸强度分析。在分析之前使用千分尺测定样品的厚度,且厚度的平均值用于计算结果。所有样品被放置在 25℃ 下的 United Testing Systems 拉伸试验装置中,采用 80mm 的标距长度,并以 2mm min⁻¹ 的速率拉伸。使用两组样品条件。在湿条件下测定一组样品,其中从水储存袋移除之后并用纸巾擦干直接对所述样品进行测试。在干燥条件下测试另一组样品,其中首先将所述样品在空气中干燥 1 小时,然后被放置在干燥器中 24 小时。

[0127] 在来自 Haake Instruments 的 Seiko ExStar TG/DTA 6200 上进行热重分析 (TGA)。在 N₂ 流 (90ml min⁻¹) 的保护下测定所述样品,其中加热速率为 2℃ min⁻¹,并且测试温度为 20–550℃。在 TGA 测定之前在干燥器中将样品干燥 24 小时。

[0128] (b) 结果

[0129] (i) 4MP 对 PANi 可加工性的影响

[0130] 以 2 : 1 的 4MP : PANi 翠绿亚胺碱四聚体的摩尔比添加 4MP 提高了聚合物溶液质量。含有 72wt% NMP 和 10wt% 的 4MP 的 18wt% PANi 混合物产生了在 1 天内为活性的聚合物溶液。活性的聚合物溶液在本文被定义为聚合物和溶剂的混合物,可以由所述混合物浇注成膜;非活性的聚合物溶液在几秒内形成不能被浇注成膜的凝胶。具有 2 : 1 的 4MP : PANi 翠绿亚胺碱的摩尔比的含有我们的合成 PANi 的聚合物溶液数月都不会形成凝胶。然而,不含 4MP 的 PANi–NMP 混合物花了 2 天形成活性的聚合物溶液,并且该聚合物溶液在形成凝胶前的 2–5 天保持为活性的。4MP 的加入可以使 PANi 完全溶解,并极大地扩大了聚合物溶液活性的窗口。

[0131] (ii) 化学后处理对 PANi 膜亲水性的影响

[0132] 针对 PANi–NMP 膜和未处理的和后处理的 PANi–NMP–4MP 膜的捕泡水接触角连同用于后处理的酸和碱的分子量、阴离子尺寸和 pK_a 一起被总结在表 1 中。

[0133] 表 1

[0134]

膜/后处理	MW (Da)	阴离子 尺寸(Å)	pK _a	接触角(°)
PANi–NMP	-	-	-	24.2 ± 2.1
PANi–NMP–4MP	-	-	-	41.9 ± 1.6
H ₂ O	18.0	-	15.7	40.5 ± 2.9
HCl	36.5	3.3	-6.1	53.0 ± 4.1
H ₂ SO ₄	98.1	3.4, 2.5, 2.4	-3.0, 2.0	43.7 ± 3.2
PTSA	190.2	7.0, 4.3, 2.5	0.7	44.5 ± 3.6
CSA	232.3	7.0, 5.4, 5.6	2.0	18.4 ± 1.0
DBSA	326.5	22.2, 5.0, 2.4	2.6	43.9 ± 2.9
NH ₄ OH	35.0	-	9.2	47.1 ± 1.9
CSA–NH ₄ OH	-	-	-	17.2 ± 1.1
CSA–过滤–酸–碱–过滤	-	-	-	17.1 ± 0.5

[0135] 表 1 示出了后处理分子的分子量、阴离子尺寸、pK_a 以及经过在 50℃ 下 1 小时后处理后的 PANi–NMP–4MP 膜的水接触角。

[0136] 通过由 Yang 等人概括的程序使用 Chem3D 软件 (CambridgeSoft) 近似出阴离子尺寸 [28]。氯离子的尺寸为离子直径 [49]。将 4MP 加入到聚合物溶液使膜的水接触角从 22° 增加至 42° (未处理的) [12]。在 H₂O 中将此 PANi-NMP-4MP 膜于 50°C 下后处理 1 小时不会改变所述膜的水接触角。在 50°C 下采用 100mM H₂SO₄、PTSA 和 DBSA 后处理 1 小时对膜亲水性的影响很小。在 50°C 下采用 100mM HCl 和 NH₄OH 后处理 1 小时似乎增加膜疏水性。然而, 在 100mM CSA 中于 50°C 下对 PANi-NMP-4MP 膜后处理 1 小时使膜的水接触角降至 18.4°。在从膜表面除去过量的 CSA 的尝试中, 在 100mM NH₄OH 中于 50°C 下对 CSA 后处理的 PANi-NMP-4MP 膜进一步处理 3 小时 (CSA-NH₄OH)。这种处理不会进一步影响膜亲水性 (接触角 = 17.2°)。通过以下过程对 PANi-NMP-4MP 膜进行了广泛的后处理: 在 100mM CSA 中于 50°C 下处理 1 小时 → 在 20psi、20°C 下 DI H₂O 的 60 分钟过滤 → 在 45°C 下采用 0.5M H₂SO₄ 处理 10 分钟 → 在 45°C 下采用 1M NaOH 处理 10 分钟 → 在 20psi、20°C 下用 DI H₂O 过滤 30 分钟。此处理在表 1 中被标记为“CSA-过滤-酸-碱-过滤”。CSA 处理的膜的亲水性不受另外的水过滤以及酸和碱处理的影响 (接触角 = 17.1°)。

[0137] CSA 处理时间对膜的亲水性的影响示于图 2 中。在 50°C 下采用 100mM CSA 处理 PANi-NMP-4MP 膜。在处理 10 分钟后膜的亲水性开始增加。有 10 至 60 分钟的过渡时间, 其中处理过的膜的区域保持相对疏水性 (接触角 = 42°), 而数毫米远的区域已恢复亲水性 (接触角 < 20°)。这是由于在 15 至 30 分钟的 CSA 处理时间时接触角值的较大误差条的原因。在 1 小时的 CSA 处理后达到最大的膜亲水性。CSA 处理温度对膜亲水性的影响示于表 2 中。采用 100mM CSA 对 PANi-NMP-4MP 膜处理 1 小时。在所有测试温度下恢复了膜亲水性。

[0138] 表 2

[0139]

[0140]

处理温度(°C)	接触角(°)
10	18.8±1.2
20	17.6±1.0
50	18.4±1.0

[0141] 表 2 示出了在不同温度下经过 1 小时的 100mM CSA 后处理后的 PANi-NMP-4MP 膜的水接触角。

[0142] (iii) CSA 后处理对 PANI 膜性能的影响

[0143] 针对未处理的和 CSA 处理的 PANi-NMP-4MP 膜测定纯水渗透率并总结于表 3 中。以前报道了对于不含 4MP 的 18wt% PANi-82wt% 的 NMP 膜的膜的纯水渗透率为 1050 μm s⁻¹bar⁻¹, 其中 BSA 截留率为 0% [12]。当 10wt% 4MP 加入到聚合物溶液时膜渗透率降低了 98%。PANi-NMP-4MP 膜的 BSA 蛋白质截留率从 0% 增加至 91%。在 50°C 下采用 100mM CSA 对 PANi-NMP-4MP 膜后处理 1 小时使 BSA 截留率降低了 ~ 15%, 其中渗透率略有下降。

[0144] 表 3

[0145]

膜	渗透率 ($\mu\text{m s}^{-1} \text{bar}^{-1}$)	BSA 截留率
PANi-NMP-4MP	24.5±3.0	0.91±0.01
CSA 处理的 PANi-NMP-4MP	20.3±4.4	0.74±0.03

[0146] 表 3 示出了针对未处理的和 CSA 后处理的膜的膜纯水渗透率和 BSA 截留率。

[0147] (iv) PANI 膜机械性能和热性能

[0148] 非织造载体织物和膜厚度和拉伸模量列于表 4 中。干燥的载体织物比湿样品薄约 13%。PANi 膜, 只有未处理的 PANi-NMP 膜表现出厚度的轻微下降 (7%)。在 50°C 下使用 100mM CSA 的后处理对膜厚度没有影响。CSA 处理的和未处理的 PANi-NMP-4MP 膜两者在湿 / 干厚度方面并未表现出差别。通过将 PANi 层添加到所述载体织物增加了拉伸强度。PANi-NMP 膜具有约两倍于非织造载体织物的断裂强度。PANi-NMP-4MP 膜中的拉伸弹性模量下降, 但仍大于载体织物。CSA 处理的 PANi-NMP-4MP 膜具有最大的拉伸模量。这种趋势对于湿膜和干膜而言是相同的, 其中干膜具有更大的断裂强度。

[0149] 表 4

[0150]

样品	湿		干	
	厚度 (μm)	模量 (MPa)	厚度(μm)	模量 (MPa)
非织造载体	170±1	243±26	148±5	294±21
PANi-NMP	230±9	434±66	214±17	723±61
PANi-NMP-4MP	224±9	360±65	223±1	561±90
CSA 处理的 PANi-NMP-4MP	222±13	453±98	220±1	796±28

[0151] 表 4 示出了针对湿和干的测试条件的非织造载体和膜的厚度和拉伸模量。

[0152] TGA 结果列于图 3 中。在分解前所有的样品是热稳定的直至 300-330°C。在分解后非织造载体和 PANi-NMP 膜留下 ~ 15wt% 的残余物, 而 PANi-NMP-4MP 膜和 CSA 处理的 PANi-NMP-4MP 膜留下 ~ 35wt% 的残余物。在 300°C 之前在所有样品中观察到水的损失, 干燥后的样品含有 < 0.3wt% 的水。

[0153] (v) PANI 膜化学特性

[0154] 在 18wt% PANi-82wt% NMP 膜 (PANi-NMP)、18wt% PANi-72wt% NMP-10wt% 4MP 膜 (PANi-NMP-4MP)、在 100mM CSA 中于 50°C 下处理 1 小时的 18wt% PANi-72wt% NMP-10wt% 4MP 膜 (CSA 处理的 PANi-NMP-4MP)、在 50°C 下用 100mM NH_4OH 对 CSA 处理的 18wt% PANi-72wt% NMP-10wt% 4MP 膜进一步处理 3 小时 (CSA+ NH_4OH 处理的 PANi-NMP-4MP) 以及纯的 CSA 上进行傅里叶变换红外 (FTIR) 分光光度法分析。这些谱图示于图 4 中。对羰基峰 (C=O)、醌型环峰 (Q) 和苯型环峰 (B) 的位置进行了概述。此谱图非常接近在以往的研究 [27, 50-53] 中报道的那些。针对 CSA 处理的 PANi-NMP-4MP 膜的谱图展示出约 1740cm^{-1} 的峰, 其可对应于 CSA 的 C=O 键的存在。此峰在纯的 CSA 谱图中是突出的并且在 NH_4OH 处理后显著地减弱。针对每个膜的醌型峰和苯型峰的位置以及醌型峰对苯型峰的比示于表 5

中。针对 PANi-NMP 膜的醌型峰 (1587cm^{-1}) 对苯型峰 (1495cm^{-1}) 的比 (Q/B) 是 0.87, 这与别人发现的 Q/B 比的值 [27,28] 相匹配。PANi-NMP-4MP 膜的 Q/B 比下降至 0.52。Q 峰在 PANi-NMP 膜和 PANi-NMP-4MP 膜之间无偏移。

[0155] 表 5

[0156]

膜	波数(cm^{-1})		
	Q	B	Q/B 比
PANi-NMP	1587	1495	0.87
PANi-NMP-4MP	1588	1502	0.52
CSA 处理的 PANi-NMP-4MP	1576	1496	0.43
CSA+ NH_4OH 处理的 PANi-NMP-4MP	1591	1496	0.64

[0157] 表 5 示出了 PANi 膜的醌型和苯型 FTIR 峰的位置和 Q/B 比。

[0158] 在 100mM CSA 中于 50°C 下处理 1 小时之前和之后进行 ^1H NMR 实验, 以进一步研究 PANi 膜的组成。 ^1H NMR 谱图示于图 5 中。NMP(a) 和 4MP(b) 的谱图已包括在内以供参考。无 4MP 下制成的 PANi-NMP 膜 (c) 的 NMR 谱图表明在相转化过程中从所述膜完全除去了 NMP。当 4MP 在聚合物溶液中用作凝胶抑制剂时, 在相转化方法之后一些 4MP 和 NMP 留在膜中 (d)。这通过 $\delta = 2.66\text{ppm}$ 时的单峰以及 $\delta = 0.91\text{--}0.81\text{ppm}$ 时的多重峰示出, 所述单峰表示 NMP 中的 N-CH₃ 质子, 所述多重峰可以归因于 4MP 中的附着到甲基的质子和在 6 元环的 4- 位处附着到所述环的质子。当采用 100mM CSA 处理时, 从膜 (e) 中除去一部分的 NMP 和 4MP。当 PANi 掺杂有强酸时, 通过 CSA 处理除去的 NMP 和 4MP 的数量上的量不能被解释成芳族区域中信号数目的增加的原因。然而, 可以观察到相比于 4MP, 更多的 NMP 通过 CSA 后处理被除去。此外, 在处理 and 用 DI 水洗涤后 CSA 留在了膜中, 如 $\delta = 1.01$ 和 0.70ppm 时的两个峰所示, 其可以归因于 CSA 上两个主要甲基。采用 100mM NH_4OH 进行处理 (f) 降低了 $\delta = 1.01$ 和 0.70ppm 处的峰, 但它们仍然被观察到。由于样品不能使用热或真空干燥, 因此在每个膜中仍有部分残留的水。

[0159] (vi) PANI 膜表面电荷特性

[0160] 针对 PANi-NMP 膜、PANi-NMP-4MP 膜和 CSA 处理的 PANi-NMP-4MP 膜的膜表面电荷示于图 6 中。流动电流测定结果表明 4MP 的加入产生了带更多正电荷的膜, 如等电点中从 4.5 移至 5.8 的偏移所示。PANi-NMP 膜在 pH 7 具有 -50mV 的 zeta 电势, 而未处理的和 CSA 处理的 PANi-NMP-4MP 膜两者在 pH 7 具有 -20 至 -25mV 的 zeta 电势。CSA 后处理降低了膜 zeta 电势的幅度。

[0161] (vii) PANI 膜表面和横截面形态

[0162] 针对 PANi-NMP 膜、PANi-NMP-4MP 膜和 CSA 处理的 PANi-NMP-4MP 膜的表面和横截面 SEM 图像示于图 6 中。SEM 横截面表明, 这些膜具有含指状微孔的非对称结构。当相比于 PANi-NMP 膜时, 加入 4MP 产生了具有更小的空隙空间的膜。CSA 后处理似乎不影响膜空隙结构。膜表面孔隙率和平均孔径示于表 6 中。当加入 4MP 时, 表面孔隙率和平均孔径减小。CSA 后处理增加了表面孔隙率和平均孔径两者。

[0163] 表 6

[0164]

膜	ε	$d_p(\text{nm})$
PANi-NMP	2.8%±1.3%	8.8±0.6
PANi-NMP-4MP	0.2%±0.1%	5.0±0.6
CSA 处理的 PANi-NMP-4MP	0.4%±0.3%	5.5±0.1

[0165] 表 6 示出了通过 SEM 图像分析确定的 PANi 膜的表面孔隙率 (ε) 和平均孔径 (d_p)。

[0166] (c) 讨论

[0167] 将 4MP 添加到 PANi-NMP 聚合物溶液影响 PANi 超出了破坏链间和链内 PANi 氢键合。4MP 的强碱性 ($\text{pK}_a = 11.3$) 和尺寸 (7.29\AA) 非常类似于七亚甲基亚胺 (HPMI), 七亚甲基亚胺分别具有 $\text{pK}_a = 11.2$ 和 7.16\AA 的尺寸 [28]。HPMI 是 PANi 凝胶抑制剂, 其已被证明经由环取代将 PANi EB 中的醌型结构还原至苯型 [27]。对于使用 4MP 浇注的膜而言, FTIR Q/B 比从 0.87 降低至 0.52 表明尽管可能存在一些环取代, 但是 Q 峰偏移的缺乏可能显示不存在共价键合。

[0168] PANi-4MP 氢键合和环取代减少了水和相对亲水性的 PANi 亚胺氮原子之间的相互作用。如图 8 所示, 4MP 上的相对疏水性的环和甲基的存在导致 PANi UF 膜的疏水性增加。

[0169] 通过在 50°C 下使用 100mM CSA 的 1 小时后处理来恢复所述膜的亲水性和并在另外的 3 小时的 100mM NH_4OH 处理后保持。在 NH_4OH 处理后在 1740cm^{-1} 处的 FTIR 峰的减少 (图 4) 以及图 5f) 中在 $\delta = 1.01$ 和 0.70ppm 处的 ^1H NMR 峰的减少表示过量的 CSA 已被除去。部分溶解在水中的残余 CSA 可能存在于 NH_4OH 处理过的膜中。在 50°C 下使用 100mM NH_4OH 后处理 1 小时后, 膜的亲水性并未得到恢复, 因此当用于除去过量的 CSA 时此 NH_4OH 处理对膜的亲水性并无帮助。虽然亲水性机制尚不确定, 但我们认为在氢键合的 4MP 和 CSA 之间可能存在一些能产生更加亲水性的膜的较强相互作用。CSA 处理可以除去氢键合的 4MP, 但仅在膜表面上。如果 CSA 因受物理和 / 或质量传递限制仅用于在 PANi-NMP-4MP 膜的暴露表面除去 4MP, 那么 ^1H NMR 不会检测到 4MP 的明显减少, 因为处理过的膜被溶解于用于分析的溶剂并且大部分的膜可能仍包含 4MP。FTIR 是一种表面技术, 并且对膜表面的化学变化更敏感。我们无法检测到 PANi 膜上的 4MP 的存在或去除, 可能是由于 4MP 和 PANi 的化学结构类似所导致。用酸处理 PANi 使 PANi 骨干质子化并使亚胺氮饱和, 所述亚胺氮与 4MP 形成氢键。类似地, 酸使 4MP 质子化并消除它能够与 PANi 氢键合的能力。人们可以预料任何的酸会释放氢键合的 4MP。除了 CSA 以外的酸无法恢复膜亲水性。已知 CSA 诱导 PANi 中的扩展卷曲构象, 增大相邻的链之间的距离 [54, 55]。然而, PANi 通常处于紧密盘绕的构象中, 我们怀疑 HCl 和 H_2SO_4 太小以至于不能使 PANi 链足以扩展至产生为 4MP 的向外扩散所需的自由体积。对甲苯磺酸的相对 2 维几何构造不会促进链的扩展并且十二烷基苯磺酸可能太大以至于不适合 PANi 链之间。

[0170] 4MP 的引入产生了具有较小孔隙的较不多孔的膜。所得膜是少得多的可渗透的, 但具有高得多的蛋白截留率。在 CSA 后处理的膜中观察到较高的孔隙率和较大的孔可能起因于由后处理过程造成的 PANi 的结构重排, 例如聚合物解绕等。所得膜具有较低的 BSA 截留率。可以通过设计较为缓和的后处理过程将这些缺陷最小化。虽然 PANi 膜亲水性得到了恢复, 但是 CSA 后处理后的膜表面电荷仍有偏移。这再次表明即使在 CSA 后处理之后, 强关联的 4MP 仍可以留在膜表面上。

[0171] 具有改进的蛋白质截留率的纯聚苯胺超滤膜已在凝胶抑制剂 4- 甲基哌啶的帮助

下形成。但是当相比于仅由 NMP 制成的 PANi 膜时这些膜显示出降低的水渗透率和增加的疏水性。发现 4MP 通过环取代苯环使聚 PANi 翠绿亚胺碱的醌型环结构还原至苯型形式。氢键合的和环取代的 4MP 通过占据相对亲水性的亚胺氮位点并将其替换为相对疏水性的环和甲基增加了 PANi 膜的疏水性。使用酸溶液的后处理表明樟脑磺酸盐离子使 PANi 采取了更加扩展的卷曲构象,这允许氢键合的 4MP 扩散出所述膜。除去这部分的 4MP 可以使得聚苯胺超滤膜恢复其亲水性。通过简单的后处理步骤定制膜性能对于延长基于 PANi 的膜的分离性能范围是有意义的。

[0172] 图 9 示出了无凝胶抑制剂下制得的 PANi-NMP 膜的 SEM 图像。这种膜有几处缺陷(裂缝)。图 10 是采用凝胶抑制剂(4-MP)制得的 PANi-NMP 膜的 SEM 图像。这种膜没有缺陷。

[0173] b. 实施例 2

[0174] (a) 测定聚合物膜上的极性液体和非极性液体的接触角

[0175] 由在如其他地方所述的 $0.1\ \mu\text{m}$ 的 Whatman 滤纸上过滤的微生物菌苔上的去离子水、乙二醇、甘油和二碘甲烷的座滴接触角(VCA-1000,AST Products Inc.,Billerica,MA)测定微生物细胞的表面张力。(G. A. Burks 等人, Langmuir 2003,19,2366-2371) 胶体粒子(二氧化硅、氧化铝和羧基改性胶乳)来自以前公开的来源。(J. A. Brant 等人, Journal of Membrane Science 2004,241,235-248) 通过测定用双面胶带固定在载玻片上的膜样品上的去离子水、乙二醇、甘油和二碘甲烷的座滴接触角来确定聚苯胺和后处理的聚苯胺膜的表面张力。针对每个直接用于本研究的所得样品测定至少 12 个平衡接触角,其中所述平衡角度由右角度和左角度的平均值来确定。在取平均值和标准偏差之前弃除最高值和最低值。其他膜材料的接触角和对应的表面张力获自先前公开的研究。(E. R. Cornelissen 等人, Colloids and Surfaces A:Physicochemical and Engineering Aspects 1998,138,283-289)

[0176] PANi 和 CSA 后处理的 PANi (“PANi-CSA”) 的测定的接触角连同最流行的商业聚合物膜材料一起示于表 7 中,所述商业聚合物膜材料包括:醋酸纤维素(CA)、聚丙烯腈(PAN)、聚碳酸酯(PC)、聚醚酰亚胺(PEI)、聚醚砜(PES)、聚丙烯(PP)、聚砜(PSf)、聚四氟乙烯(PTFE)和聚偏二氟乙烯(PVDF)。测定的接触角全部通过座滴法测定,因此是直接可比的。在水接触角的情况下,PANi 膜显示出于 CA 膜和 PAN 膜类似的接触角,而 PANi-CSA 膜产生通常与更亲水性的和抗积垢的膜材料相关的明显较低的接触角。

[0177] 表 7- 膜上的探针液体的测定的接触角(度)

[0178]

聚合物	θ ,水	θ ,极性*	θ ,非极性**
CA	59 ± 3	54 ± 3	26 ± 2
PAN	57 ± 3	49 ± 4	6 ± 1
PC	78 ± 1	66 ± 2	12 ± 1
PEI	79 ± 2	63 ± 2	8 ± 1
PES	92 ± 2	68 ± 5	13 ± 2
PP	94 ± 2	83 ± 3	42 ± 1
PSf	82 ± 2	67 ± 4	14 ± 7
PTFE	117 ± 2	112 ± 2	93 ± 2
PVDF	92 ± 2	104 ± 3	29 ± 2
PANi	57 ± 5	36 ± 3	35 ± 3
PANi-CSA	41 ± 2	19 ± 2	36 ± 1

[0179] * 本文使用乙二醇 ;Cornelissen 等人使用甘油。

[0180] ** 本文使用二碘甲烷 ;Cornelissen 等人使用 α - 溴萘。

[0181] 接触角探针液体表面张力分量 (表 8) 被用来提取积垢材料 (表 9) 和膜材料 (表 10) 的表面张力分量。可以推断 PP、PVDF 和 PTFE 实际上是非极性的并且能量明显低于所有其他材料。PANi 材料表现出与 CA 和 PAN 材料类似的总表面张力,但电子受体功能明显更低且电子供体功能明显更高。在一般情况下,已经观察到作为接近于单极性的电子给体或受体功能的材料,它们显得更加亲水性的和抗积垢的 ;这对于聚乙二醇 (PEG) 官能化表面而言是广泛接受的。

[0182] 表 8- 探针液体的表面张力分量

[0183]

液体	γ^{LW} (mJ/m ²)	γ^+ (mJ/m ²)	γ^- (mJ/m ²)	γ^{TOT} (mJ/m ²)
水	21.8	25.5	25.5	72.8
甘油	34.0	3.9	57.4	64.0
乙二醇	29.0	1.9	47.0	48.0
二碘甲烷	50.8	0.0	0.0	50.8
α -溴萘	44.4	0.0	0.0	44.4

[0184] 表 9- 典型污物的表面张力分量

[0185]

污物	γ^{LW} (mJ/m ²)	γ^+ (mJ/m ²)	γ^- (mJ/m ²)	γ^{TOT} (mJ/m ²)
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[0186]

HSA	26.8	6.3	50.6	62.5
PEG	43.0	0.0	64.0	43.0
十六烷	27.5	0.0	0.0	27.5
二氧化硅颗粒(100 nm)	34.3	1.0	31.7	45.8
氧化铝(300 nm)	42.9	3.7	19.6	59.9
羧基改性胶乳	37.5	0.6	5.3	41.0
大肠杆菌	39.1	0.6	59.0	50.9
酿酒酵母	14.2	0.5	44.4	23.8
恶臭假单胞菌	25.4	0.0	39.5	26.3

[0187] 表 10- 计算的不同聚合物的界面张力分量

[0188]

膜聚合物	γ^{LW} (mJ/m ²)	γ^+ (mJ/m ²)	γ^- (mJ/m ²)	γ^{TOT} (mJ/m ²)
CA	40.0	0.5	19.0	46.2
PAN	44.0	0.6	19.0	50.8
PC	44.0	0.1	5.8	45.5
PEI	44.0	0.3	3.9	46.2
PES	43.0	0.5	0.1	43.4
PP	34.0	0.0	1.7	34.0
PSf	43.0	0.2	3.1	44.6
PTFE	10.0	0.0	0.9	10.0
PVDF	40.0	0.0	0.1	40.0
未处理的 PANi	41.9	0.1	24.6	44.2
CSA 处理的 PANi	41.6	0.3	38.1	47.8

[0189] 从粘聚自由能数据 (图 11) 清楚地可知几乎所有的聚合物膜根据其负的粘聚自由能显示为“疏水性的”;一个例外是表现出显著为正的粘聚自由能的 CSA 处理的 PANi 膜。因此, PANi-CSA 膜可以被认为是真正的“亲水性的”。类似地, 粘附自由能数据 (图 12) 表明在可获得的最耐积垢的材料中 PANi 膜陪伴 PAN 膜和 CA 膜, 但 PANi-CSA 膜是更加抗积垢的。

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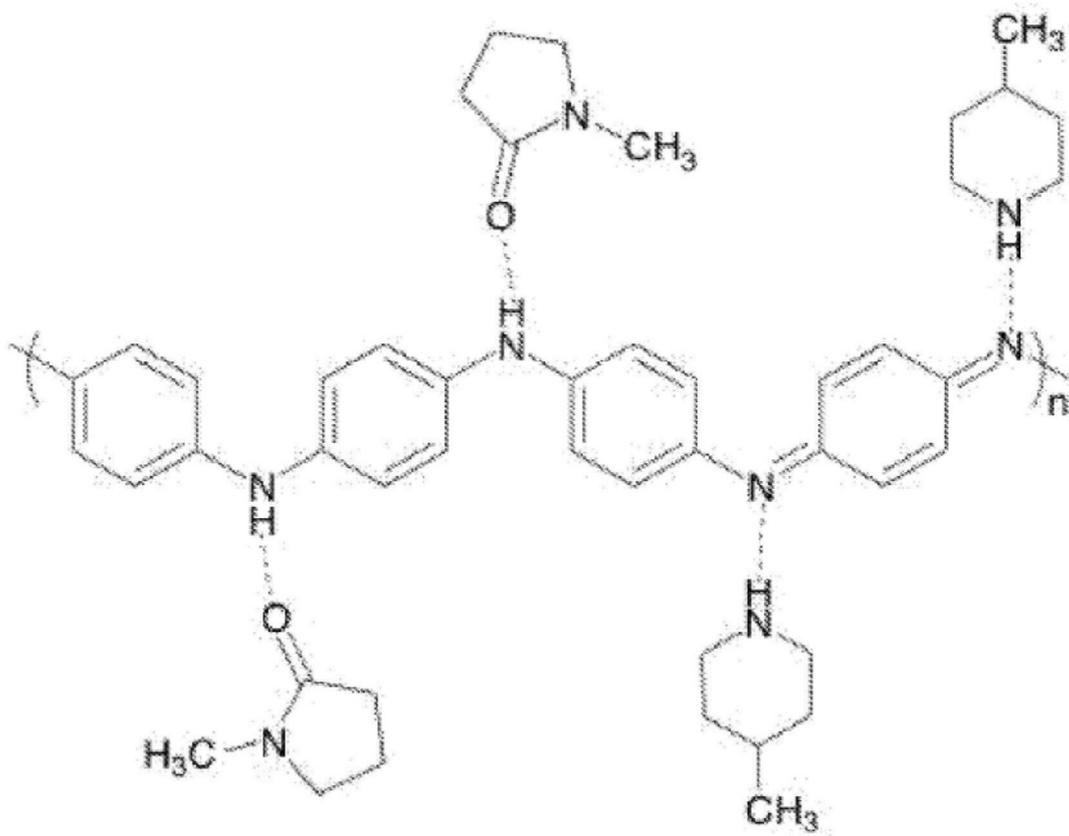


图 1

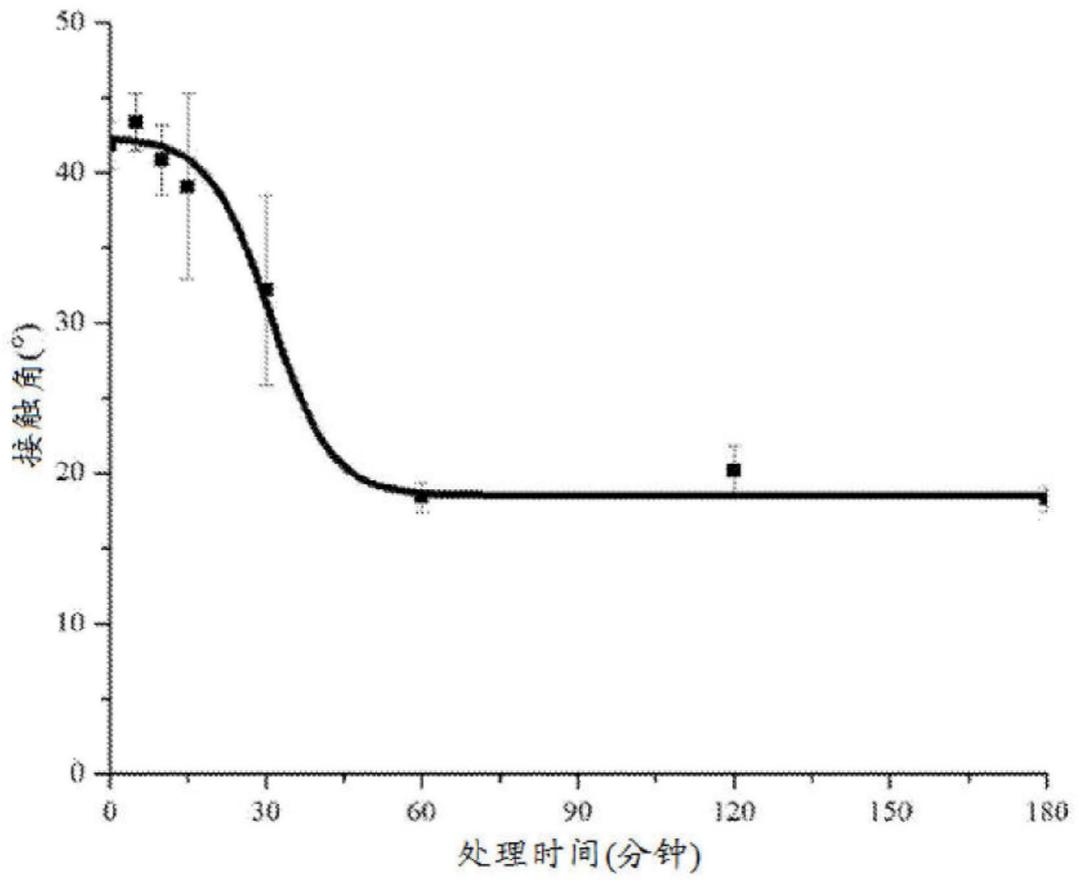


图 2

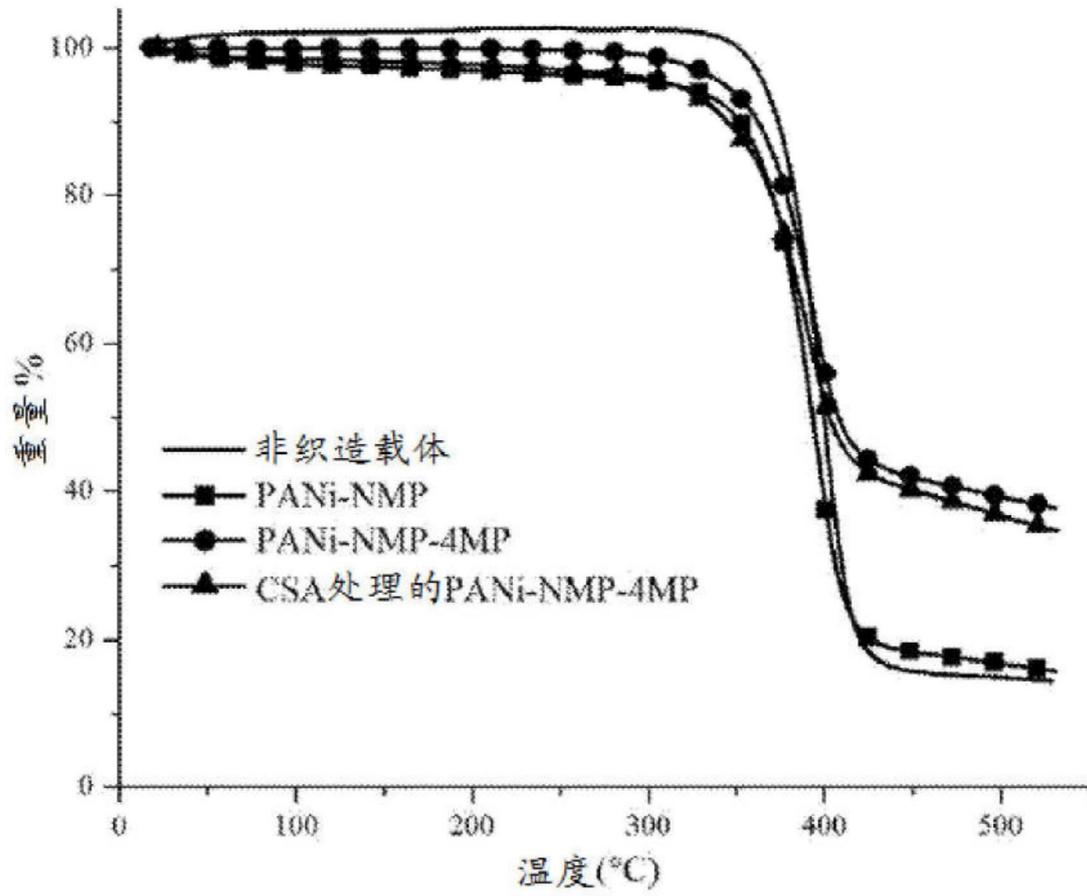


图 3

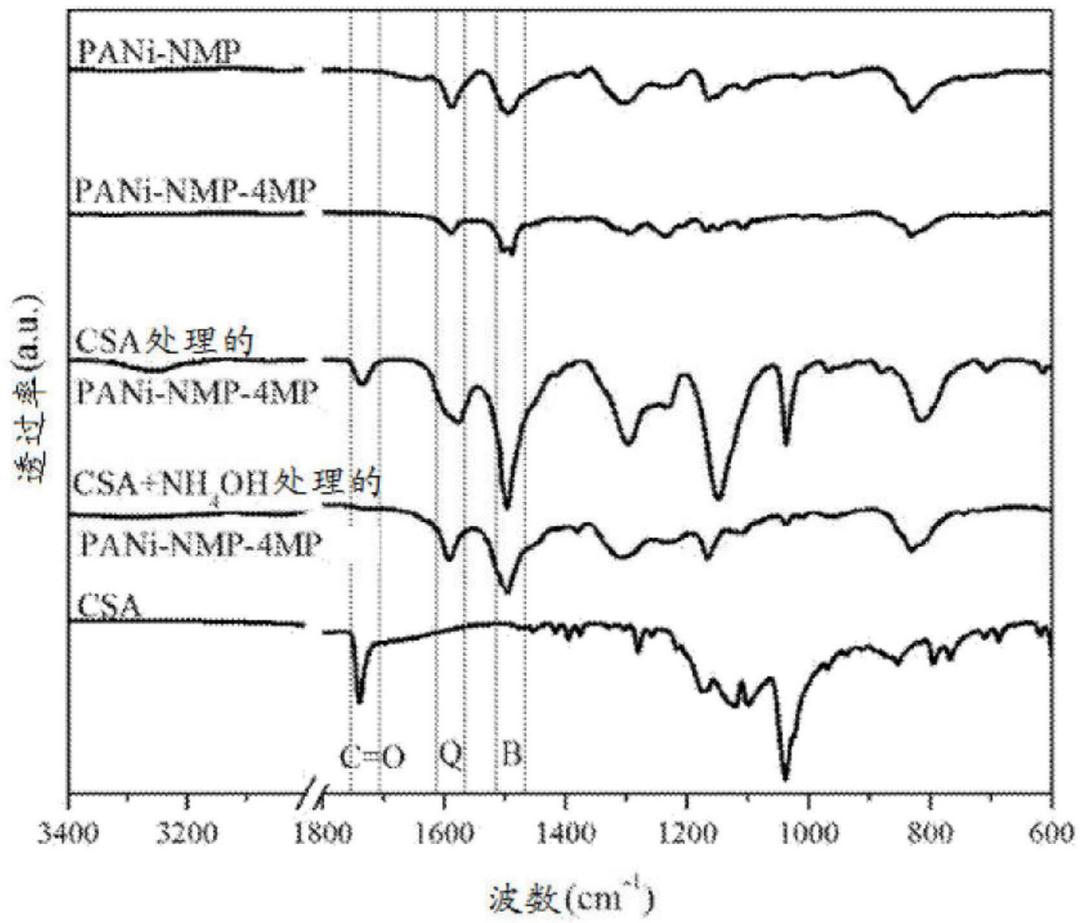


图 4

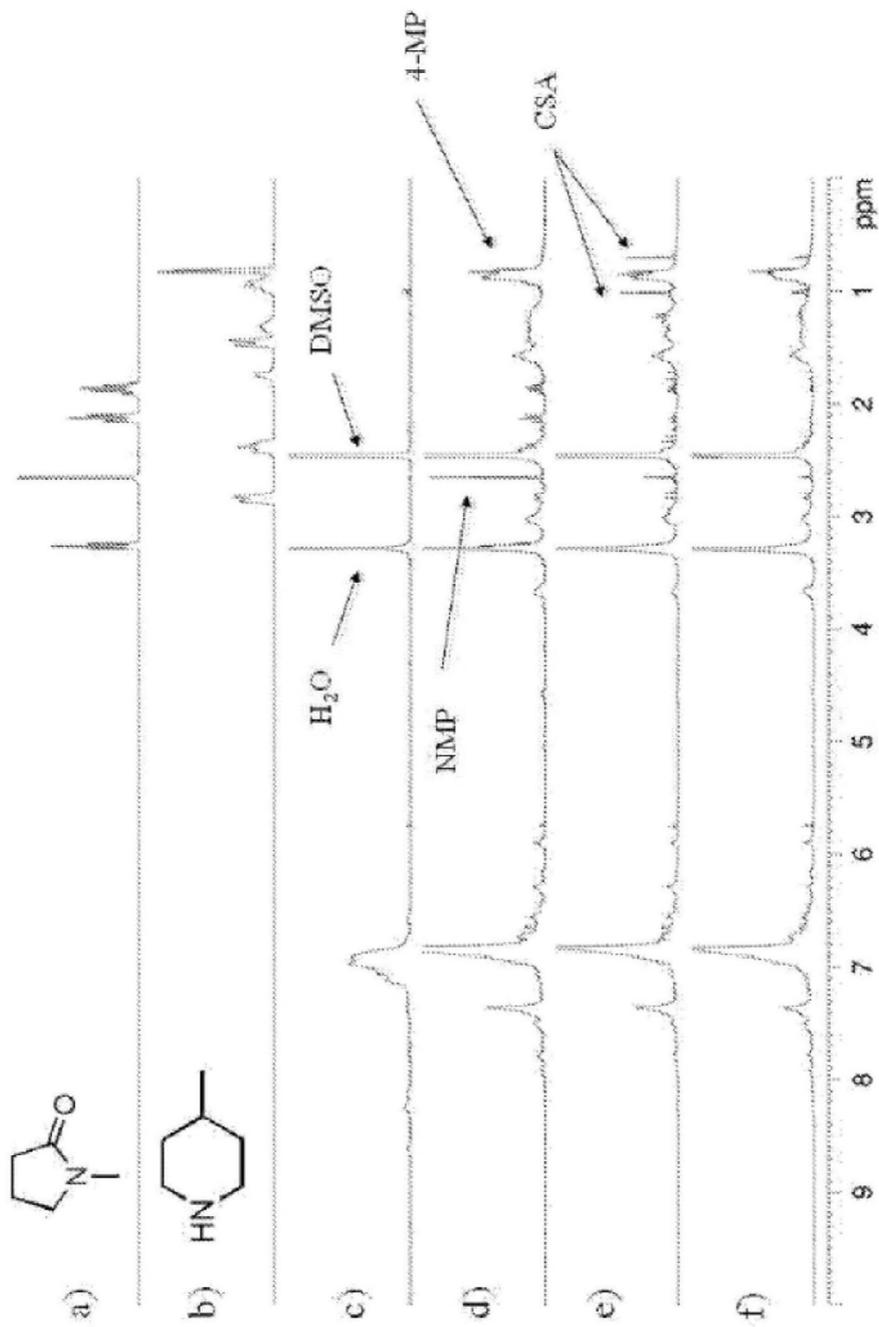


图 5

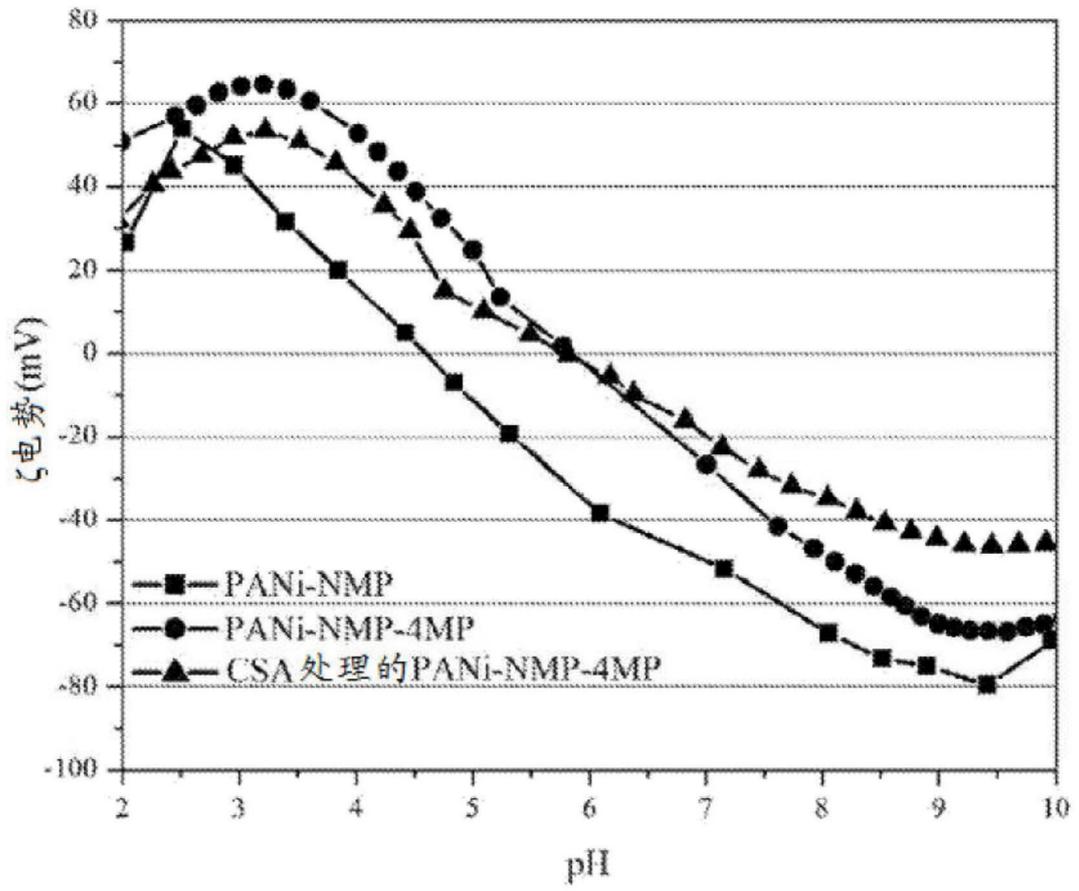


图 6

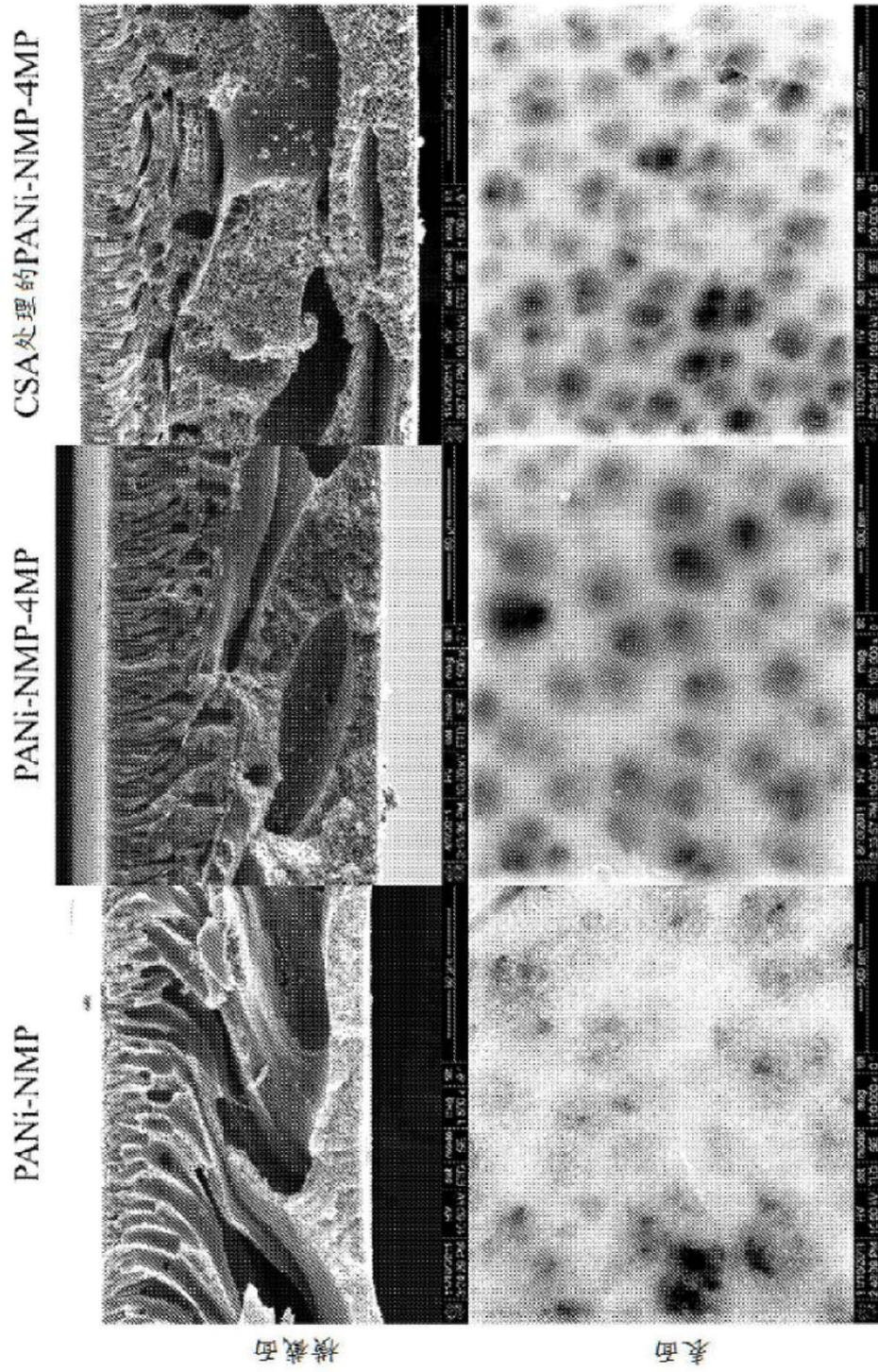


图 7

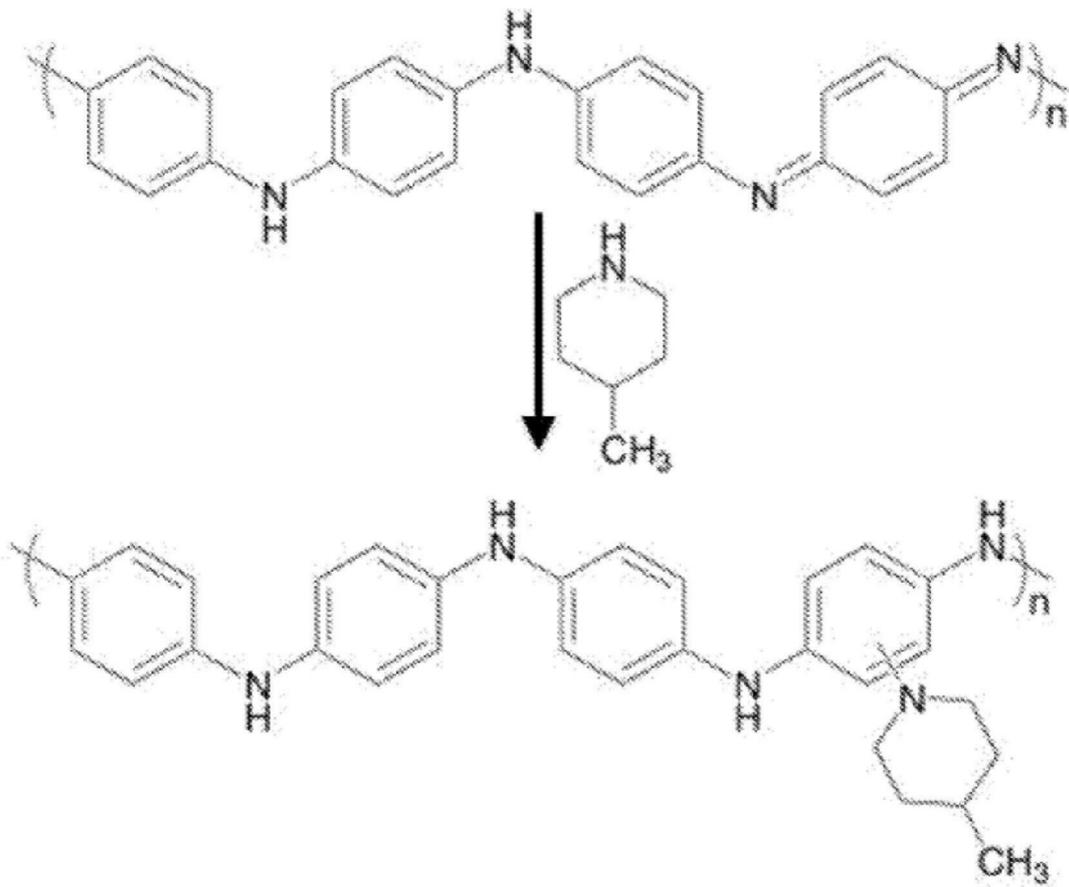


图 8

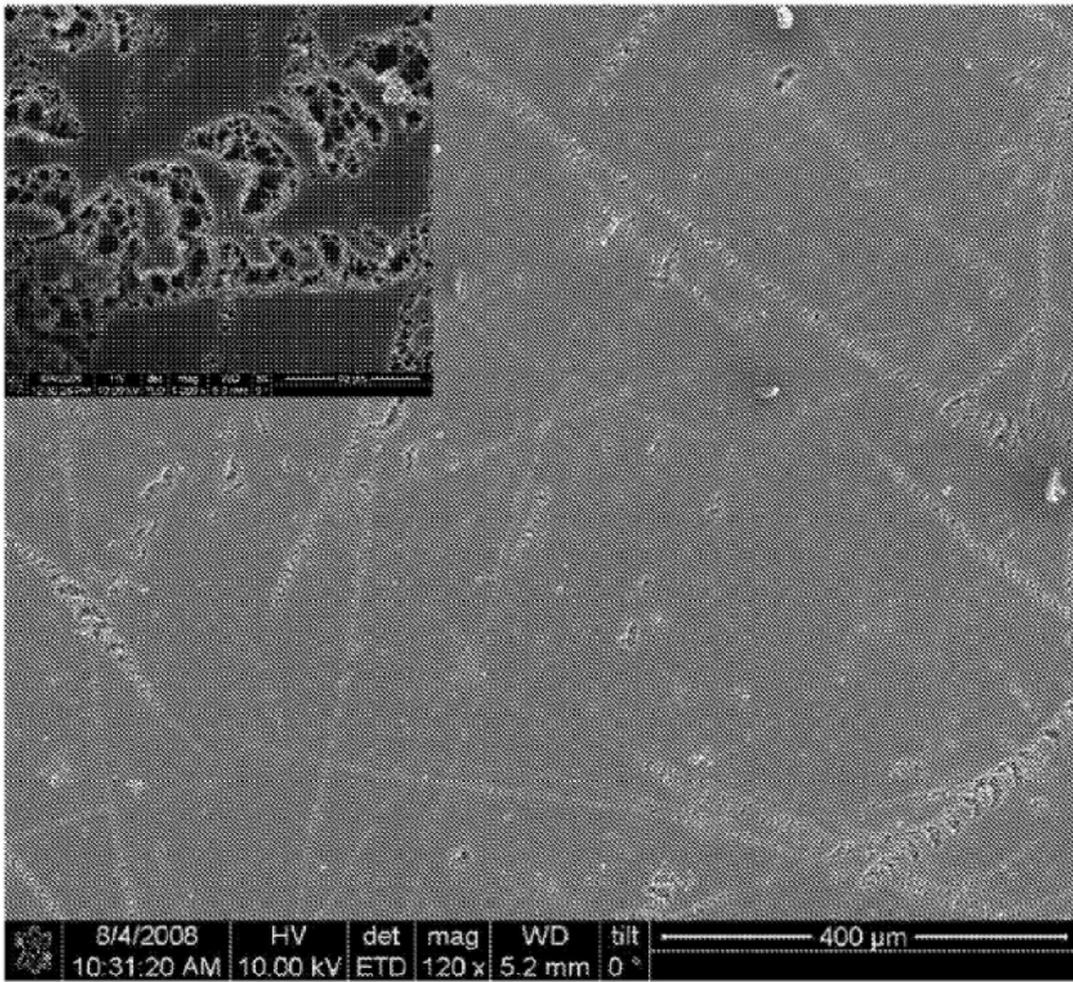


图 9

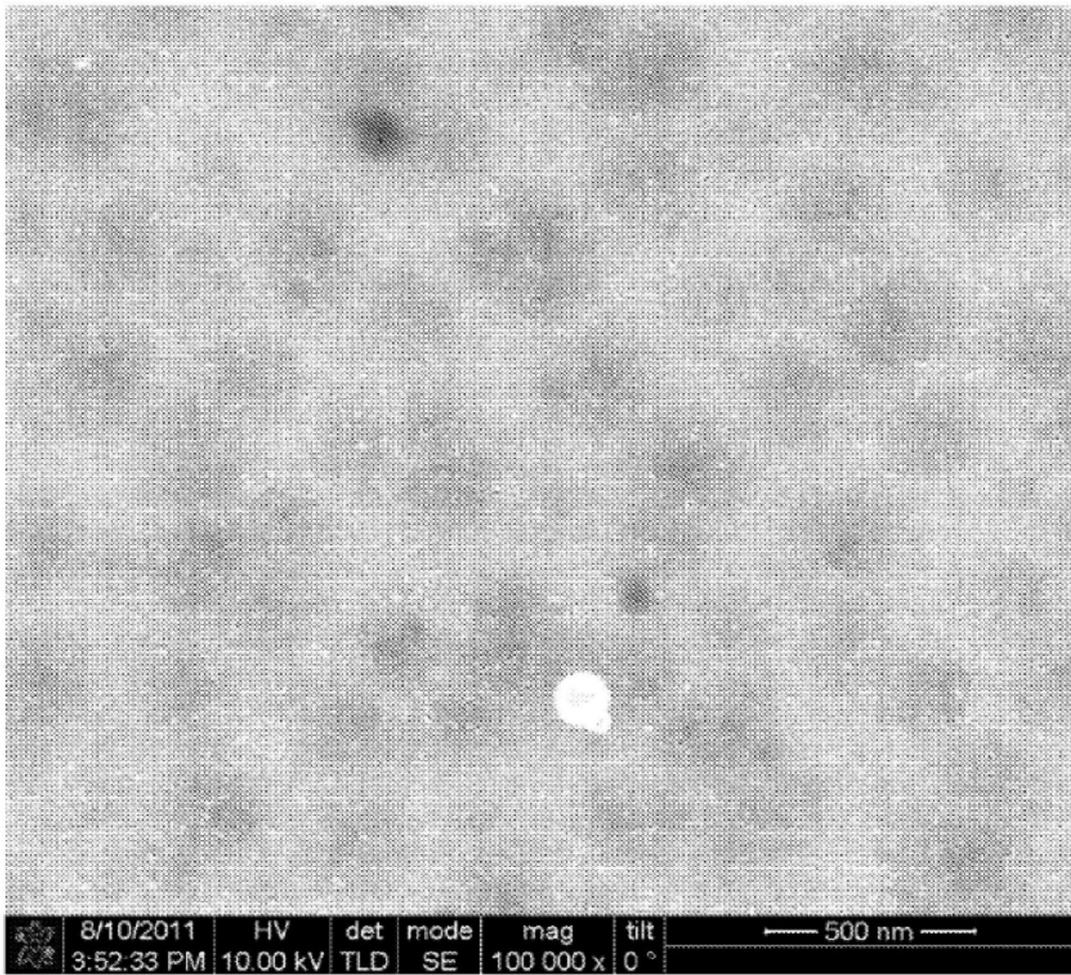


图 10

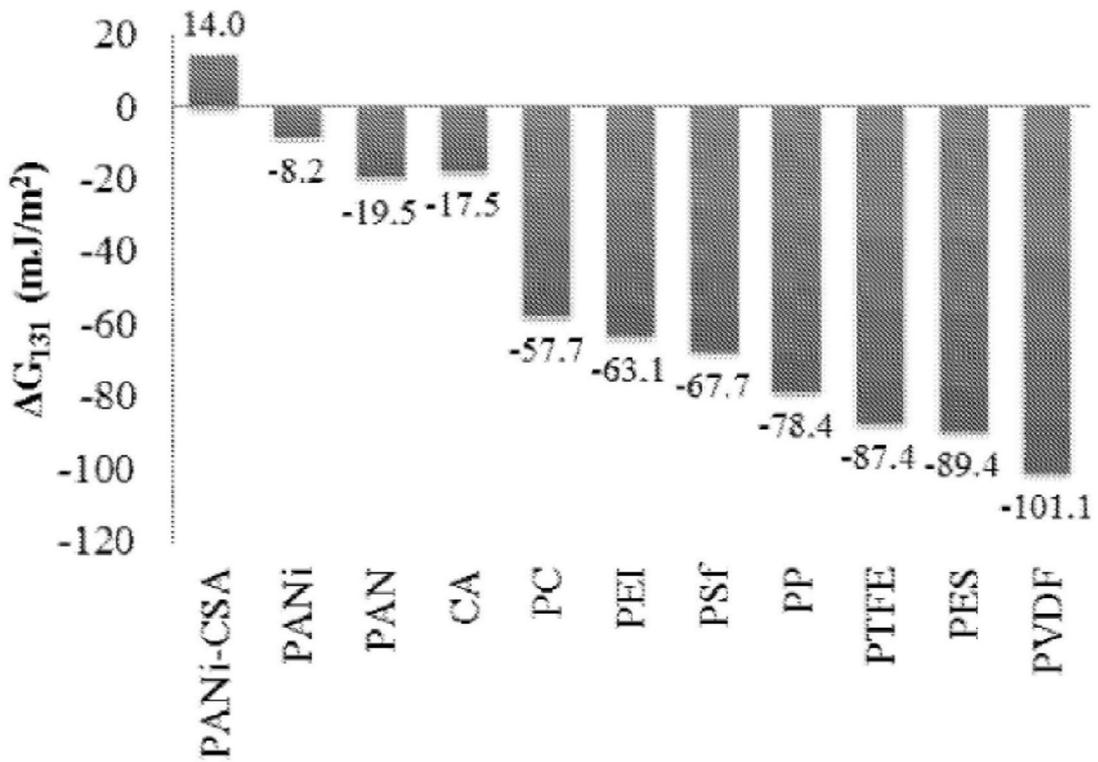


图 11

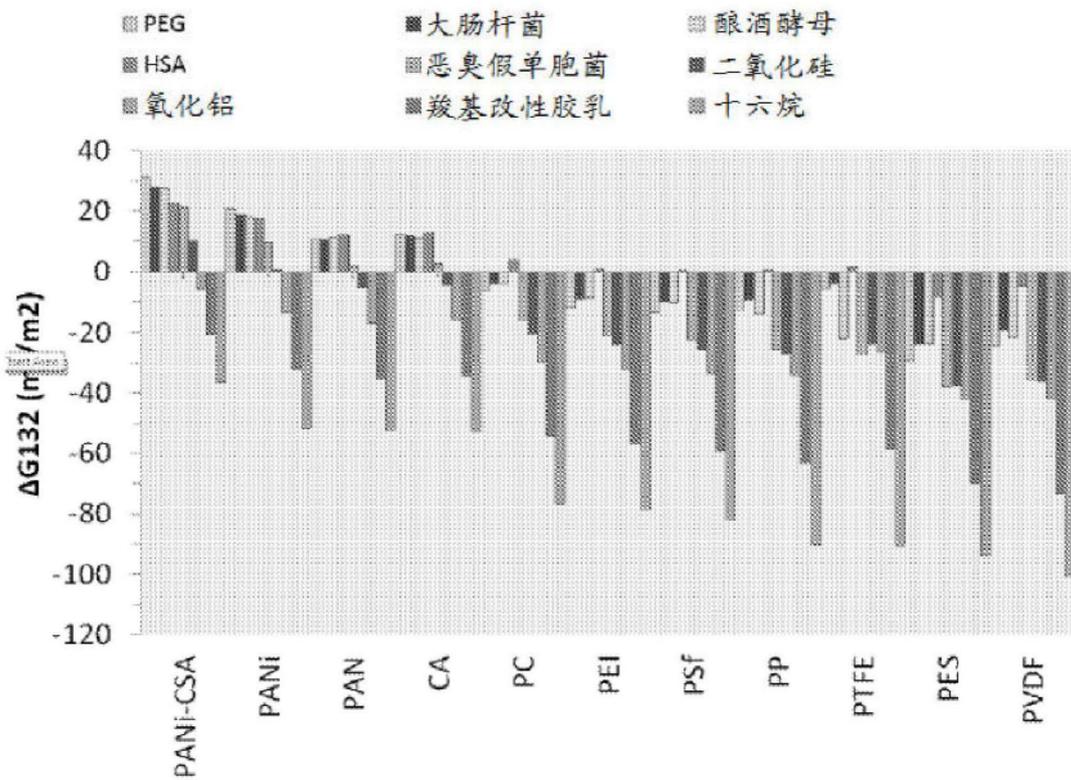


图 12