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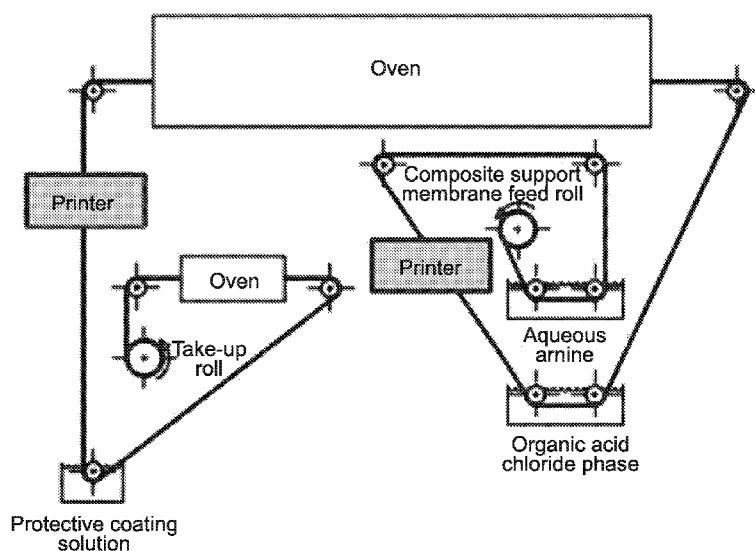
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(54) Title: FABRICATION AND MODIFICATION OF POLYMER MEMBRANES USING INK-JET PRINTING

Fig. 18



(57) Abstract: The present invention relates to methods for fabrication or modification of polymer membranes for water treatment utilizing ink-jet printing. The methods of the invention provide substantial advantages over the current state of the art including, *inter alia*, accurately delivering precise amounts of liquids to surfaces; quickly changing coating parameters; quickly controlling and changing coating compositions; and tailor-making membranes according to customer needs.

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FABRICATION AND MODIFICATION OF POLYMER MEMBRANES USING INK-JET PRINTING

FIELD OF THE INVENTION

[0001] The present invention generally relates to methods for fabrication or modification of different types of polymer membranes for water treatment by using ink-jet printing.

BACKGROUND OF THE INVENTION

[0002] Dense homogeneous polymer films can separate various gaseous or liquid mixtures very effectively; however, normal thicknesses (20-200 μm) lead to very low permeation rates. Such membranes cannot be made thin enough (of the order of 0.1-1 μm) to improve permeation because they are very difficult to handle (no mechanical strength), and since such thin layers need to be supported. The development of asymmetric integrally skinned membranes by the Loeb Sourirajan method could be used to improve flux, but selectivity and rejections are reduced. A major breakthrough in the history of membrane technology was the development of composite membranes with an asymmetric structure, where a thin, dense top-layer of one material is supported by a porous sub-layer of another material, and the two layers originate from different polymeric materials. The advantage of composite membranes is that each layer can be optimized independently to obtain optimal membrane performance with respect to selectivity, permeation rate, and chemical and thermal stability.

[0003] Thin film composite (TFC) membranes are currently manufactured using interfacial polymerization, which is a technique used to apply an ultra-thin top-layer upon a porous support, wherein a polymerization reaction occurs between two very reactive monomers at the interface of two immiscible solvents. Polymers currently used as porous supports include polysulfone (PSf), polyethersulfone (PES) and polyacrylonitrile (PAN). The support layer, which is generally an ultrafiltration (UF) or microfiltration membrane, is immersed in an aqueous solution containing a reactive monomer, frequently an aliphatic or aromatic amine-type; the wet amine containing film is then immersed in a second bath containing a water-immiscible solvent in which another reactive, often an aliphatic or aromatic acid chloride, has been dissolved; and the two reactive monomers

react at the interface with each other to form a dense polymeric top-layer. Heat treatments are often applied to complete the interfacial reaction and to crosslink the water-soluble monomer. This process is currently optimized for roll-to-roll fabrication facilities. The advantage of interfacial polymerization is that the reaction is self-controlled through passage of a limited supply of reactants through the already formed layer, resulting in an extremely thin film of thickness within the 50 nm range. The nature of the solvents and monomers, as well as the monomer concentrations, reaction time and heat curing, define the porosity, pore size and thickness of the selective layer.

[0004] Graft polymerization is an effective way to functionalize the surface of a TFC membrane, wherein surface charge and hydrophobicity can be varied using variable amounts of positively, negatively, or neutral monomer building blocks. For example, polyethyleneglycol based coatings act as a hydrophilic barrier between the selective reverse osmosis (RO) surface and the bulk solution inhibiting and delaying surface attachment of bacteria. Moreover, variable amounts of differently charged monomers can increase the effectiveness of the polymer coatings and different end group functionality on modified membranes can effectively reduce the amount of fouling and ease of cleaning. Roughness can be controlled by parameters in the polymerization reaction itself, e.g., solvent mixture composition, initial monomer concentration, reaction temperature, and reaction time or types of reaction initiation employed. Redox-initiated, ionizing radiation, oxidation by ozone, low-temperature plasma and UV radiation have been the initiation methods employed, although all involve membrane modification from a bulk solution of monomers.

[0005] Water desalination is currently a relatively expensive process that is done in most cases by RO technology and to a lesser extent utilizing nanofiltration (NF). The leading RO technology uses polymeric TFC membranes typically including a selective thin polyamide layer that is permeable to water but impermeable to larger molecules or salt ions, on an ultrafiltration support. Such TFC membranes have a limited life span due to degradation by oxidants (hypochlorite), mineral scaling and (bio)fouling; however, new membrane compositions or modifications to the thin polyamide top layer may lead to more durable stable membranes, membranes with unique separation characteristics, or membranes having enhanced performance characteristics such as improved water flux.

SUMMARY OF THE INVENTION

[0006] Ink-jet printing has been developed to accurately deliver pico-liter quantities of ink or other substances onto numerous types of surfaces, and is currently utilized in many applications, e.g., electronics, ceramics, protein and nucleic acid arrays, and polymers.

[0007] It has now been found, in accordance with the present invention, that using ink-jet printing for fabrication or modification of membranes for water treatment provides substantial advantages over the current state of the art. Those advantages include the ability to accurately deliver precise amounts of liquids to surfaces, which results in consistent and reproducible coatings; quickly changing coating parameters; quickly controlling and changing coating compositions; and tailor-making membranes according to customer needs. Further advantages of such a process derive from the reduced amount of monomers consumed; reduced amount of waste which results in a more environmentally friendly process and lower waste disposal costs.

[0008] In one aspect, the present invention thus provides a method for fabrication of a membrane for reverse osmosis, nanofiltration or ultrafiltration by forming either a polyamide layer or a nanoparticle layer on a surface of a support membrane, said method comprising a step selected from:

- (i) ink-jet printing on said surface of said support membrane a polyfunctional amine or polyamine functionalized nanoparticles which, upon reacting on said surface with a polyfunctional acyl halide or anhydride functional group, forms said polyamide layer; or
- (ii) ink-jet printing on said surface of said support membrane nanoparticles which, upon reacting on said surface with a matrix and a crosslinker, forms said nanoparticle layer.

[0009] In one particular such aspect, the present invention provides a method as defined above, for fabrication of a TFC polyamide membrane, said method comprising:

- (i) ink-jet printing of an aqueous solution of a polyfunctional amine or polyamine functionalized nanoparticles on a surface of a support membrane; and
- (ii) treating the printed surface of said support membrane with a water-immiscible organic solution of a polyfunctional acyl halide or anhydride

functional group thereby interfacially polymerizing said polyfunctional amine or polyamine functionalized nanoparticles with said polyfunctional acyl halide or anhydride functional group on said surface of said support membrane, thus forming a polyamide layer on said surface of said support membrane.

[0010] In another particular such aspect, the present invention provides a method as defined above, for fabrication of a membrane coated with nanoparticles, said method comprising ink-jet printing of a solution of said nanoparticles on a surface of a support membrane to thereby form, upon reaction of said nanoparticles with a matrix and a crosslinker, a nanoparticle layer on said surface of said support membrane, wherein (i) a matrix solution comprising said matrix and a crosslinking solution comprising said crosslinker are ink-jet printed on said surface of said support membrane simultaneously with said nanoparticle solution; or (ii) said surface of said support membrane is pretreated with said matrix solution, and said crosslinking solution is ink-jet printed on said surface of said support membrane simultaneously with said nanoparticle solution; or (iii) said surface of said support membrane is pretreated with said matrix solution and said crosslinking solution; or (iv) said matrix solution is ink-jet printed on said surface of said support membrane, optionally simultaneously with said nanoparticle solution, and said surface of said support membrane is then submersed in said crosslinker solution.

[0011] In another aspect, the present invention provides a membrane fabricated according to the fabrication methods defined above.

[0012] In a further aspect, the present invention provides a method for modification of a membrane, said method comprising:

- (i) activating a surface of said membrane, preferably with plasma, atmospheric plasma, chemical radical initiators, or UV activated initiators; and
- (ii) ink-jet printing of an aqueous solution containing monomers capable of polymerizing with each other and onto the surface of said membrane, thus forming a modified TFC membrane having improved antifouling properties while maintaining or improving salt rejection.

[0013] In yet another aspect, the present invention provides a modified membrane obtained according to the modification method defined above.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] **Figs. 1A-1D** show SEM top surface images ($\times 80,000$) of a control PAN-HV3 UF support membrane (**1A**); a conventional way made polyamide TFC membrane (**1B**); a 2-times MPD printed membrane (**1C**); and a 4-times MPD printed membrane (**1D**), as well as FTIR spectra of control PAN-HV3 UF support membrane (CON) and 2-times MPD printed membrane (2MPD) (**1E**); and of control PAN-HV3 UF support membrane (CON) and 4-times MPD printed membrane (4MPD) (**1F**).

[0015] **Figs. 2A-2B** show SEM top surface images (**2A**, $\times 100,000$) of PES support membrane (control-no printing, panel A); polysulfone support membranes fabricated by interfacial polymerization of two reactive monomers (panels B-E show 1, 2, 4 and 5 prints, respectively); and PES support membrane fabricated by the conventional method using the same monomers (panel F); and the FTIR spectra of the membrane surfaces shown in 2A, panels B-E (**2B**).

[0016] **Figs. 3A-3E** show different patterns of printed polyamide (**3A**); SEM images ($\times 50,000$) of printed TFC membranes (**3B**), where "monomer 1" images are areas where only MPD were applied and "printed monomer 2" images are areas where congo red/MPD mixtures were printed; an image of a dry membrane (**3C**); an image of a membrane after immersion in aqueous acid solution (HCl) (**3D**); and an image of a membrane after subsequent immersion in aqueous base solution (NaOH) (**3E**) (actual size of each one of the colored squares in 3C-3E is 3×3 mm).

[0017] **Figs. 4A-4D** show a schematic representation of interfacial polymerization using ink-jet printing by first soaking the support in one monomer, and printing a second monomer on top before adding TMC (**4A**); the contact angle measurements on polyamide patterned membrane surface, wherein the "white" area represents polyamide made of MPD+TMC (**4B**), and the "black" area represents polyamide made of MPD+printed fluorinated diamine+TMC (**4C**); an XPS analysis of MPD/fluorinated diamine-polyamide printed membranes (PA - control membrane; FPA - membrane printed with fluorinated diamine) (**4D**); a graph showing flux measurements of different types of membranes as indicated (**4E**); and a graph showing NaCl rejection with ink-jet printed membranes compared to conventionally made membranes (**4F**).

[0018] **Figs. 5A-5B** show graphs demonstrating the salt rejection (**5A**) and water permeability (**5B**) of control polyamide membrane (CPA) and printed polyamide membranes made by variable number of full surface cover prints of amine-functionalized nanodiamonds. Test conditions: feed: [NaCl]=1500 ppm aqueous solution, transmembrane pressure (TMP)=20 bar, T=25°C.

[0019] **Fig. 6** schematically illustrates a membrane modification process, wherein the membrane surface is first activated by either atmospheric plasma or chemical initiators, and graft polymerization process is then carried out by either dip-coating method (a) or ink jet printing (b).

[0020] **Fig. 7** shows a FTIR characterization of ESPA-1 RO membranes treated with atmospheric plasma activation and ink-jet printed with methacrylic acid (MA) and polyethylene glycol methacrylate (PEGMA) aqueous solution. The number of prints varied from 1 to 5.

[0021] **Fig. 8** shows the peak ratio ($1719\text{ cm}^{-1}/1488\text{ cm}^{-1}$) and contact angle of ESPA-1 membranes treated with atmospheric plasma after the monomer solution (MA:PEGMA) has been deposited thereon by ink-jet printing a different number of times (1, 3 and 5).

[0022] **Fig. 9** shows the permeability and rejection of ESPA-1 membranes treated with atmospheric plasma after the monomer solution (MA:PEGMA) has been deposited thereon by ink-jet printing a different number of times (1, 3 and 5).

[0023] **Fig. 10** illustrates a fully filled black square, i.e., a fully covered membrane (left panel, no pattern), black squares $0.2\times 0.2\text{ cm}$ covering 50% of the total space (a checkerboard pattern, "pattern 1") (middle panel), and a zig-zag covering 85% of the space (striped pattern, "pattern 2") (right panel).

[0024] **Fig. 11** shows the peak ratio ($1719\text{ cm}^{-1}/1488\text{ cm}^{-1}$) and contact angle of ESPA-1 membranes treated with atmospheric plasma after monomer aqueous solution MA/PEGMA has been deposited thereon by ink-jet printing with an Epson L110 printer using different types of patterns: checkerboard covering 50% of the total space ("pattern 1"); zig-zag covering 85% of the total space ("pattern 2"); full cover (no pattern); and control (unmodified membrane).

[0025] **Figs. 12A-12B** show the permeability and rejection of ESPA-1 membranes treated with atmospheric plasma after monomer aqueous solution MA/PEGMA has been

deposited thereon by ink-jet printing with an Epson L110 printer using different types of patterns: checkerboard covering 50% of the total space ("pattern 1"); zig-zag covering 85% of the total space ("pattern 2"); full cover (no pattern); and control (unmodified membrane) (12A); and AFM images showing the roughness of the above membranes (area measured, 50 μm ×50 μm) (12B).

[0026] Fig. 13 shows the peak ratio (1719 cm^{-1} /1488 cm^{-1}) and contact angle of ESPA-1 membranes treated with redox initiators ($\text{K}_2\text{S}_2\text{O}_8$, and $\text{K}_2\text{S}_2\text{O}_5$) by soaking for different times (between 10 to 90 min), and after the monomer solution (MA:PEGMA) has been deposited thereon by ink-jet printing as a full coverage (100%).

[0027] Fig. 14 shows the peak ratio (1719 cm^{-1} /1488 cm^{-1}) and contact angle of ESPA-1 membranes treated with redox initiators ($\text{K}_2\text{S}_2\text{O}_8$, and $\text{K}_2\text{S}_2\text{O}_5$) by soaking for different times (between 10 to 30 min), after MA:PEGMA aqueous solution has been deposited thereon by ink-jet printing using different types of patterns: checkerboard covering 50% of the total space (pattern 1); zig-zag covering 85% of the total space (pattern 2); and control (unmodified membrane).

[0028] Fig. 15 shows the permeability and rejection of ESPA-1 membranes treated with redox initiators ($\text{K}_2\text{S}_2\text{O}_8$, and $\text{K}_2\text{S}_2\text{O}_5$) by soaking at different times (between 10 to 90 min) after the monomer solution (MA:PEGMA) has been deposited thereon by ink-jet printing as a full (100%) coverage (no pattern).

[0029] Fig. 16 shows the permeability and rejection of ESPA-1 membranes treated with redox initiators ($\text{K}_2\text{S}_2\text{O}_8$, and $\text{K}_2\text{S}_2\text{O}_5$) by soaking at different times (between 10 to 30 min) after MA:PEGMA aqueous solution has been deposited thereon by ink-jet printing by using different types of patterns: checkerboard covering 50% of the total space (pattern 1); zig-zag covering 85% of the total space (pattern 2); and control (unmodified membrane).

[0030] Fig. 17 shows a graph demonstrating sheet resistance of modified RO membranes vs. amount of printed CNTs.

[0031] Fig. 18 shows a schematic representation of a process for fabrication of a TFC membrane including novel printer modules.

DETAILED DESCRIPTION OF THE INVENTION

[0032] The present invention provides various methods for fabrication or modification of membrane surfaces precisely in the micro-domain, utilizing ink-jet printing to give a greater control over the placement of nano- and micro-heterogeneity of the membrane composition, and resulting in improved properties. Any ink-jet system that can deliver solvents to substrates may be employed in the method of the invention. These solvents may be either aqueous or organic, and may contain, e.g., dissolved compounds, monomers, polymers, or nanoparticles. Membranes fabricated or modified in this way may consist of multiple compositions in micro domains that show novel separation properties, novel functionality, and enhanced membrane performance over the state of art.

[0033] According to the present invention, multiple materials are grafted to the surface in patterns. While the main limitation of the current membranes consisting of a grafted layer on top of the separation layer is a less controllable reaction, the present invention overcomes this limitation by depositing precise amounts of reactants to the surface, which results in differing amounts of modification, where surface properties can be set and controlled.

[0034] Because of the nature of the ink-jet printer, incompatible materials may be loaded in separate cartridges or reservoirs and printed on the substrate when this is not possible with other coating methods for example dip coating. "Mosaic" membranes are an example of this possibility.

[0035] In one aspect, the present invention provides a method for fabrication of a membrane for reverse osmosis or nanofiltration by forming either a polyamide layer or a nanoparticle layer on a surface of a support membrane, said method comprising a step selected from: (i) ink-jet printing on said surface of said support membrane a polyfunctional amine or polyamine functionalized nanoparticles which, upon reacting on said surface with a polyfunctional acyl halide or anhydride functional group, forms said polyamide layer; or (ii) ink-jet printing on said surface of said support membrane nanoparticles which, upon reacting on said surface with a matrix and a crosslinker, forms said nanoparticle layer.

[0036] In certain embodiments, the support membrane used according to this method is a polymer membrane composed of, e.g., polysulfone (PSf), polyethersulfone (PES), polyacrylonitrile (PAN), polyester, polyphenyleneoxide, polyphenylenesulfide, polyvinyl chloride, polyvinylidene fluoride, polytetrafluoroethylene, polycarbonate, polyetherketone, or polyetheretherketone, or a TFC membrane including reverse osmosis and nanofiltration membranes having a polyamide surface.

[0037] In certain embodiments, the membrane fabricated by this method, as defined above, has salt rejection of 40% or more, i.e., 40%-50%, 50%-60%, 60%-70%, 70%-80%, 80%-90%, 90%-95%, 95%-99.5%, or more, and flux of 0.3-40 L/h m² bar.

[0038] In one particular such aspect, the present invention provides a method as defined above, for fabrication of a TFC polyamide membrane (hereinafter "***Fabrication Method A***"), said method comprising: (i) ink-jet printing of an aqueous solution of a polyfunctional amine or polyamine functionalized nanoparticles on a surface of a support membrane; and (ii) treating the printed surface of said support membrane with a water-immiscible organic solution of a polyfunctional acyl halide or anhydride functional group thereby interfacially polymerizing said polyfunctional amine or polyamine functionalized nanoparticles with said polyfunctional acyl halide or anhydride functional group on said surface of said support membrane, thus forming a polyamide layer on said surface of said support membrane.

[0039] In certain embodiments, step (i) of Fabrication Method A is repeated n times prior to step (ii), wherein n is an integer from 1 to 5.

[0040] In certain embodiments, the ink-jet printing in step (i) of Fabrication Method A is carried out from one or more reservoirs. In particular such embodiments, the ink-jet printing is carried out from more than one reservoir, e.g., two, three, four or more reservoirs, wherein each one of said reservoirs contains an aqueous solution of identical or different polyfunctional amine or polyamine functionalized nanoparticles.

[0041] In certain embodiments, the ink-jet printing in step (i) of Fabrication Method A is carried out according to a predetermined pattern.

[0042] In certain embodiments, the treating in step (ii) of Fabrication Method A is conducted by immersing the printed surface of said support membrane in said organic solution; or by ink-jet printing of the organic solution on the printed surface of said

support membrane. In certain particular such embodiments, the ink-jet printing of the organic solution on the printed surface of the support membrane is carried out from either one reservoir or more than one, e.g., two, three, four or more, reservoirs, wherein each one of the reservoirs contains an organic solution of identical or different polyfunctional acyl halide or anhydride functional group. In other particular such embodiments, the ink-jet printing of the organic solution on the printed surface of said support membrane is carried out according to a predetermined pattern. In more particular such embodiments, the treating in step (ii) of this method is conducted by ink-jet printing of the organic solution on the printed surface of the support membrane, and simultaneously with the ink-jet printing of step (i).

[0043] In certain embodiments, heat treatment is applied in step (ii) of Fabrication Method A to complete the interfacial polymerization.

[0044] In certain embodiments, the support membrane used according to Fabrication Method A is composed of polysulfone, polyethersulfone, polyacrylonitrile, polyester, polyphenyleneoxide, polyphenylenesulfide, polyvinyl chloride, polyvinylidene fluoride, polytetrafluoroethylene, polycarbonate, polyetherketone, or polyetheretherketone.

[0045] According to certain embodiments of Fabrication Method A, the support membrane is first printed with an aqueous solution of a polyfunctional amine or polyamine functionalized nanoparticles, and the printed support membrane is then treated with a water-immiscible organic solution of a polyfunctional acyl halide or anhydride functional group.

[0046] Examples of polyfunctional amines include, without being limited to, *m*-phenylenediamine (MPD), *p*-phenylenediamine, 2,4-diaminotoluene, 2,5-diaminotoluene, N,N'-diphenylethylene diamine, 4-methoxy-*m*-phenylenediamine, 1,3,4-triaminobenzene, 1,3,5-triaminobenzene, 3,5-diaminobenzoic acid, 2,4-diaminoanisole, xylylenediamine, ethylenediamine, propylenediamine, tris(2-diaminoethyl)amine, piperazine, a fluorinated aromatic polyamine such as 5-fluoro-*m*-phenylenediamine and 2,5-difluoro-*m*-phenylenediamine, a fluorinated non-aromatic polyamine, a fluorinated alkane substituted with one or more aromatic groups, e.g., phenyl groups, each containing at least one amino group such as 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane, a fluorinated alkane diol interrupted by one or more aromatic groups each containing at least one

amino group such as 2,2'-(methylenebis(3-amino-6,1-phenylene))bis(1,1,1,3,3,3-hexafluoropropan-2-ol), a chiral polyamine, and mixtures thereof.

[0047] Examples of polyamine functionalized nanoparticles include, without limiting, carbon nanotubes (CNTs), metallic nanoparticles such as silver, copper and titanium (including titanium oxide) containing nanoparticles, nanodiamonds, or graphene quantum dots, which are polyamine functionalized.

[0048] Non-limiting examples of polyfunctional acyl halides include trimesoyl chloride (TMC), trimellitic acid chloride, terephthaloyl chloride, isophthaloyl chloride, cyclohexane-1,3,5-tricarbonyl chloride, 1,3,5,7-tetracarboxylic acid chloride, adamantane-2,6-dione, 1-isocyanato-3,5-benzenedicarbonyl chloride (5-isocyanato-isophthaloyl chloride), aromatic polyfunctional acyl halides such as trimesic acid chloride, terephthalic acid chloride, isophthalic acid chloride, biphenyl dicarboxylic acid chloride and naphthalene dicarboxylic acid dichloride, alicyclic polyfunctional acyl halides such as cyclopropane tricarboxylic acid chloride, cyclobutane tetracarboxylic acid chloride, cyclopentane tricarboxylic acid chloride, cyclopentane tetracarboxylic acid chloride, tetrahydrofuran tetracarboxylic acid chloride, cyclopentane dicarboxylic acid chloride, cyclobutane dicarboxylic acid chloride, cyclohexane dicarboxylic acid chloride and tetrahydrofuran dicarboxylic acid chloride, and mixtures thereof.

[0049] Examples of anhydride functional groups include, without being limited to, polyfunctional acid anhydrides such as mellitic anhydride, or polyfunctional acid anhydride halides such as 4-chloroformyl phthalic anhydride.

[0050] According to Fabrication Method A, the water-immiscible organic solution of the polyfunctional acyl halide or anhydride functional group may be based on any suitable organic solvent in which the polyfunctional acyl halide or anhydride functional group is dissolved. Particular such solvents comprise, without being limited to, a hydrocarbon selected from a straight or iso-(C₅-C₁₂)alkane such as pentane, isopentane, hexane, isohexane, heptane, isoheptane, octane, isooctane, nonane, isononane, decane, isodecane, undecane isoundecane, dodecane, and isododecane, a (C₅-C₁₂)cycloalkane such as cyclopentane, cyclohexane, cycloheptane, cyclooctane, cyclononane, cyclodecane, cycloundecane and cyclododecane, or a mixture thereof. Such hydrocarbons may optionally be halogenated, i.e., substituted with one, two, three, four or more, halogen

atoms, i.e., fluorine, chlorine, bromine, or iodine but preferably fluorine. The hydrocarbons may be substituted at any position. In a particular embodiment, the organic solvent in which the polyfunctional acyl halide or anhydride functional group is dissolved comprises a mixture of alkanes and/or isoalkanes, e.g., a commercially available mixture of (C₁₀-C₁₂)isoalkanes such as IsoparTM G Fluid.

[0051] According to Fabrication Method A, upon treatment of the printed support membrane with a water-immiscible organic solution of said polyfunctional acyl halide or anhydride functional group, and consequently interfacial polymerization of the polyfunctional amine or polyamine functionalized nanoparticles with the polyfunctional acyl halide or anhydride functional group, a polyamide layer is formed on top of the support membrane. In certain embodiments, the polyamide layer formed has a thickness in the range of 0.01-1, preferably 0.01-0.2, μm .

[0052] In certain embodiments, the surface of the support membrane ink-jet printed in step (i) of Fabrication Method A, according to any one of the embodiments defined above, is soaked in an aqueous solution of a polyfunctional amine or polyamine functionalized nanoparticles, and the excess solution is then removed if necessary, e.g., by rolling the membrane with a rubber roller or using an air knife, prior to step (i) and/or after step (i). The support membrane can be soaked in said aqueous solution of polyfunctional amine or polyamine functionalized nanoparticles for any sufficient period of time, e.g., for 1-30 minutes, wherein the concentration of the polyfunctional amine or polyamine functionalized nanoparticles in said solution may be in the range of 0.1-20% (w/v %), preferably in the range of 0.5-10% (w/v %). In particular such embodiments, the polyfunctional amine or polyamine functionalized nanoparticles in the aqueous solution ink-jet printed in step (i), and the polyfunctional amine or polyamine functionalized nanoparticles in the aqueous solution in which the surface of the support membrane is soaked prior to step (i) are identical or different.

[0053] In a particular embodiment exemplified herein, the present invention relates to a method for fabrication of a TFC polyamide membrane as defined above, said method comprising (i) ink-jet printing of an aqueous solution of MPD or 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane on a surface of a porous support membrane n times, wherein n is an integer of 1 to 5, and said support membrane is composed of PSf, PES or

PAN; and (ii) treating the printed surface of the support membrane with a solution of TMC in *n*-hexane thereby interfacially polymerizing said MPD with said TMC on the surface of said support membrane, thus forming a polyamide layer on top of said surface of said support membrane. In a more particular such embodiment, said support membrane is soaked in an aqueous solution of MPD and the excess solution is then removed, if necessary, prior to step (i).

[0054] In another particular such aspect, the present invention provides a method as defined above, for fabrication of a membrane coated with nanoparticles (hereinafter "***Fabrication Method B***"), said method comprising ink-jet printing of a solution of said nanoparticles on a surface of a support membrane to thereby form, upon reaction of said nanoparticles with a matrix and a crosslinker, a nanoparticle layer on said surface of said support membrane, wherein (i) a matrix solution comprising said matrix and a crosslinking solution comprising said crosslinker are ink-jet printed on said surface of said support membrane simultaneously with said nanoparticle solution; or (ii) said surface of said support membrane is pretreated with said matrix solution, and said crosslinking solution is ink-jet printed on said surface of said support membrane simultaneously with said nanoparticle solution; or (iii) said surface of said support membrane is pretreated with said matrix solution and said crosslinking solution; or (iv) said matrix solution is ink-jet printed on said surface of said support membrane, optionally simultaneously with said nanoparticle solution, and said surface of said support membrane is then submersed in said crosslinker solution.

[0055] In certain embodiments, the ink-jet printing of the nanoparticle solution according to Fabrication Method B is repeated *n* times, wherein *n* is an integer from 1 to 300.

[0056] In certain embodiments, the ink-jet printing of the nanoparticle solution according to Fabrication Method B is carried out from one or more reservoirs. In particular such embodiments, the ink-jet printing is carried out from more than one reservoir, e.g., two, three, four or more reservoirs, wherein each one of said reservoirs contains a solution of identical or different nanoparticles.

[0057] In certain embodiments, the ink-jet printing of the nanoparticle solution according to Fabrication Method B is carried out according to a predetermined pattern.

[0058] In all cases wherein Fabrication Method B comprises ink-jet printing of the matrix solution on said support membrane, i.e., when carried out according to options (i) or (iv) described hereinabove, the nanoparticle solution and the matrix solution can be ink-jet printed from two different reservoirs or, alternatively, together from one or more reservoirs.

[0059] In certain embodiments, Fabrication Method B further comprises heat treatment aimed at allowing the crosslinker to completely react with the matrix and the nanoparticles. Such treatment may be carried out, e.g., in a temperature ranging from room temperature to about 100°C.

[0060] In certain embodiments, the support membrane utilized according to Fabrication Method B is composed of polysulfone, polyethersulfone, polyacrylonitrile, polyester, polyphenyleneoxide, polyphenylenesulfide, polyvinyl chloride, polyvinylidene fluoride, polytetrafluoroethylene, polycarbonate, polyetherketone, polyetheretherketone, or a TFC membrane including reverse osmosis and nanofiltration membranes having a polyamide surface.

[0061] The crosslinker utilized according to Fabrication Method B is a compound capable of cross-linking with both an alcohol and a carboxylic or amine moiety. Examples of such crosslinkers include, without limiting, dialdehydes such as glyoxal, malondialdehyde, succindialdehyde, glutaraldehyde and phthalaldehyde. The matrix utilized according to this method is a hydrophilic polymer capable of cross-linking with said crosslinker, e.g., polyvinylalcohol.

[0062] Examples of nanoparticles that may be ink-jet printed according to Fabrication Method B include, without being limited to, CNTs, metallic nanoparticles such as silver, copper and titanium (including titanium oxide) containing nanoparticles, nanodiamonds, graphene quantum dots, or other carbon based nanoparticles. Upon crosslinking said matrix and said cross-linker, such nanoparticles will be embedded within the matrix-cross-linker layer formed on top of said support membrane. According to Fabrication Method B, the nanoparticles ink-jet printed may also be functionalized with any functional groups capable of reacting with said cross-linker and linking to said matrix, e.g., with hydroxyl and/or carboxyl groups. Particular such functionalized nanoparticles are CNTs having hydroxyl and carboxyl groups. In case functionalized nanoparticles are

utilized, upon crosslinking said matrix and said cross-linker, such nanoparticles will be covalently linked into the matrix coating formed on top of said support membrane.

[0063] In another aspect, the present invention provides a membrane fabricated according to the fabrication method defined herein, more particularly a TFC polyamide membrane fabricated by the Fabrication Method A or a nanoparticles-coated membrane fabricated by the Fabrication Method B.

[0064] In certain embodiments, the membrane of the present invention is a TFC polyamide membrane having salt rejection of 40-99.5% and flux of 0.3-40 L/h m² bar; or wherein the thickness of said polyamide layer is in the range of 10-500 nm, e.g., in the range of 10-200, 10-300, 10-400 or 10-450 nm.

[0065] The membrane fabricated according to the any of the fabrication methods may be used for water treatment, e.g., for reverse osmosis, nanofiltration or ultrafiltration. It should be noted that while nanofiltration TFC membranes have salt rejection of about 50%, reverse osmosis membranes have salt rejection that is remarkably higher and may reach 80%, 90%, 95% and even 99.5%.

[0066] In a further aspect, the present invention provides a method for modification of a membrane (hereinafter "**Modification Method**"), said method comprising: (i) activating a surface of said membrane, preferably with plasma, atmospheric plasma, chemical radical initiators, or UV activated initiators; and (ii) ink-jet printing of an aqueous solution containing monomers capable of polymerizing with each other and onto the surface of said membrane, thus forming a modified TFC membrane having improved antifouling properties while maintaining or improving salt rejection.

[0067] In certain embodiments, the membrane modified according to the Modification Method is a polymer membrane selected from TFC membranes including TFC polyamide membranes fabricated according to the method defined above, reverse osmosis membranes, nanofiltration membranes, ultrafiltration membranes, or microfiltration membranes.

[0068] In certain embodiments, the monomers contained in the aqueous solution ink-jet printed in step (ii) of the Modification Method are either charged or neutral organic molecules containing an acrylic moiety. Examples of such charged or neutral organic molecules include, without being limited to, methacrylic acid (MA), polyethylene glycol

methacrylate (PEGMA), 2-[methacryloyloxyethyl] trimethylammonium chloride, 3-sulfopropyl methacrylate potassium salt, N-(3-sulfopropyl)-N-methacryloyloxyethyl-N,N-dimethylammonium betaine, and neutral acrylic-containing monomers including fluorine such as 3-pentafluoropropyl acrylate. According to the method of the present invention, these monomers may be present in the aqueous solution in any ratio.

[0069] In yet another aspect, the present invention provides a modified membrane obtained according to the modification method defined above.

[0070] The various methods described herein are envisioned to be used as stand-alone membrane fabrication and/or modification technologies, or implemented into current membrane fabrication and modification facilities as shown schematically in **Fig. 18**. For instance, the device or technique of the present invention may be engineered or modified to fit into currently available fabrication infrastructures for tailored-made membranes with customer defined characteristics.

[0071] The invention will now be illustrated by the following non-limiting Examples.

EXAMPLES

Example 1. Membrane fabrication via ink-jet printing

[0072] In general, an Epson L110 printer was used with the front paper feed roller removed to prevent damage to the membrane surface. The middle portion of the rear roller was removed as well. Optionally, if oxygen sensitive compounds are used, a flexible tube was attached onto the print head for application of nitrogen gas in the vicinity of the print head. The amine monomer meta-phenylenediamine (MPD) was dissolved in water at different concentrations and to this 0-100 ppm Na_2CO_3 was added to ensure that the MPD amine groups would not become protonated as HCl is generated in the polymerization process, and 0-5% (w/v) ethylene glycol. This solution was poured into the 4 color reservoirs of the Epson L110 printer instead of the CMYK inks. The aqueous MPD solution was printed onto an ultra-filtration (UF) polymer support membrane. The number of prints as well as pattern can be controlled using Photoshop software or other programs such as GNU Image Manipulation Program (GIMP). Percent or each color can be adjusted to control the amount of each substance to be printed. The trimesoyl chloride (TMC) solution (0.05-0.13% in hexane) was poured on top, or

alternatively added to the color reservoirs and printed on the surface. Alternatively, the amine monomers and nanoparticles may be added to a commercially available printing ink "base" solution, consisting of 55% distilled water, 35% glycerol and 10% Kodak Photo-Flo 200 solution (containing 60-70% water, 25-30% propylene glycol, and 5-10% p-tert-octylphenoxy polyethoxyethyl alcohol).

Interfacial polymerization printing on polyethersulfone (PES) UF supports

[0073] TFC polyamide printed membranes were made using 5% (w/v) MPD/water solution containing 100 ppm Na_2CO_3 and 5% (w/v) ethylene glycol. This solution was added to all the tanks in the printer and "100% black" was then printed 5 times on the PES UF support. Once printed, the membranes were treated with 0.05% (w/v) TMC/*n*-hexane solution, similar to the conventional method. As observed, a polyamide layer was formed with increased salt rejection from 5% to 54%, with associated loss in flux. The hydrophilicity increased as seen from the contact angle decrease from 104 degrees to 80 degrees. The test results of the membranes fabricated by the above method compared to the support membrane are shown in **Table 1**.

Table 1

	Flux (LMH)	Salt rejection (%)	Contact angle (°)
5 kDa PES UF support	425.51	5	104±3
5 times MPD printed membrane	3.94	54	80±6

Interfacial polymerization printing on polyacrylonitrile (PAN) UF supports

[0074] TFC polyamide printed membranes were made using 10% (w/v) MPD/water solution containing 100 ppm Na_2CO_3 and 2.5% (w/v) ethylene glycol (**Fig. 1**). This solution was added to all the tanks in the printer and "100% black" was then printed various number of times on the PAN UF support. Once printed, the membranes were treated with 0.13% (w/v) TMC/*n*-hexane solution, similar to the conventional method. As observed, a polyamide layer was formed with increased salt rejection from 0% to 79%, with associated loss in flux (**Table 2** below). These were compared to membranes made in the conventional way using these solutions. As shown in **Fig. 1** and summarized in **Table 2**, the membranes prepared according to the method of the invention had a unique morphology which gives unique performance characteristics such as reduced

fouling and higher flux. As particularly shown in **Figs. 1E** and **1F**, fourier transform infrared spectroscopy (FTIR) measurements showed an appearance of 4 new peaks at approximately 1664, 1612, 1543 and 1490 cm^{-1} , characterizing an aromatic polyamide polymer. Four times printing gave stronger signals than two times printing, indicating a thicker or denser layer.

Table 2

	Flux (LMH)	Salt rejection (%)
PAN-HV3 support	2025.07	0
Conventional method membrane	6.04	33.06
2-times MPD printed membrane	6.66	48.99
4-times MPD printed membrane	10.19	79.23

Interfacial polymerization printing on PES UF supports

[0075] TFC polyamide printed membranes were made using 2.5% (w/v) MPD/water solution containing 100 ppm Na_2CO_3 and 5% (w/v) ethylene glycol (**Fig. 2**). This solution was added to all the tanks in the printer and "100% black" was then printed various number of times on the PES UF support. Once printed, the membranes were treated with 0.13% (w/v) TMC/*n*-hexane solution, similar to the conventional method. As observed, a polyamide layer was formed with differing morphology based on the number of prints. These were compared to membranes made in the conventional way using these solutions. Morphology of 4 and 5 prints was similar to that of a membrane made in the conventional way. FTIR spectra showed also an appearance of peaks at approximately 1611 and 1543 cm^{-1} , which are characteristic of an aromatic polyamide polymer.

[0076] In a different case, TFC polyamide printed membranes were made using 2% (w/v) MPD/water solution containing 2% triethylamine and 0.1% (w/v) sodium dodecylsulfate (SDS). This solution was added to all the tanks in the printer and "100% black" was then printed various number of times on the polysulfone (PSf) UF support. Once printed, the membranes were treated with 0.1% (w/v) TMC/*n*-hexane solution, similar to the conventional method.

Interfacial polymerization printing on PES UF supports after soaking in MPD solution

[0077] TFC polyamide printed membranes were made using 2% (w/v) MPD/water solution containing 5% ethylene glycol and 100 ppm Na_2CO_3 including 5% N-methyl-2-pyrrolidone (NMP). The membranes were pre-soaked in this solution for 5 min and were then rolled with a rubber roller to remove excess drops. This soaked support was printed using (a) 2% MPD solution in the C, M and Y ink reservoir tanks, and (b) 0.15% aqueous congo red solution in the K ink reservoir. Different "black and white" patterns were printed (**Fig. 3**). Once printed, the membranes were treated with 0.2% (w/v) TMC/*n*-hexane solution, similar to the conventional method. The "white" and "black" portions of the membrane were analyzed with SEM and different morphology and structure were observed in the areas with congo red. The nanostructure was approximately twice as large as the nanostructure of the polyamide polymer. Also, the parts of the membrane that incorporated congo red were more hydrophobic (contact angle $83^\circ \pm 6^\circ$) compared with the areas that did not have congo red (contact angle $54^\circ \pm 5^\circ$). Congo red is a pH sensitive dye. After incorporation into the polyamide thin film with this process, the membrane was subjected to aqueous acid and base solutions. The membrane areas where the dye was incorporated changed to blue upon immersion in HCl solution, and back to red when immersed in NaOH solution. This color change process was repeated more than 50 times with no deterioration of the membrane or color, after which it was deemed to show robust switching properties.

Interfacial polymerization printing on polysulfone (PSf) UF supports after soaking in MPD solution using MPD and a fluorinated diamine

[0078] TFC polyamide printed membranes were made using 2% (w/v) MPD/water solution. As illustrated in **Fig. 4A**, the membranes were pre-soaked in this solution for 5 min and were then rolled with a rubber roller to remove excess drops. This soaked support was printed using (a) 5% 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (a fluorinated diamine) in alkaline solution, in the K ink reservoir tank, and (b) Milli-Q water in the C, M and Y ink reservoir tanks. Different "black and white" patterns were printed (checkerboard patterns as shown in **Fig. 3A**). Once printed, the membranes were treated with 0.1% (w/v) TMC/*n*-hexane solution, similar to the conventional methods above. After 1 min, the TMC solution was decanted, and the resulting membrane was

subsequently dried for 5 min in air at ambient temperature, rinsed with an aqueous 0.2% (w/v) Na_2CO_3 solution for 5 min, and stored in deionized (DI) water until use. The "white" and "black" portions of the membrane were analyzed with X-ray photoelectron spectroscopic (XPS) analysis in order to confirm the new patterned fluorinated-polyamide that was formed on the surface, and as observed, a newly generated fluorine peak was formed (dashed arrow in **Fig. 4D**) due to the fluorine-containing diamine used, while the control membrane prepared without pattern printing of the fluorinated diamine showed only three major peaks originated from the regular aromatic polyamide. As shown in **Fig. 4D**, since the control membranes (PA) do not contain fluorine, no fluorine is observed in the XPS. On the other hand, in membranes printed with fluorinated diamine (FPA), fluorine is clearly detected, which is an indication of a successful reaction.

[0079] "Checkerboard" patterns were printed in which the membrane was 25%, 50%, 75% or 100% covered with the fluorinated diamine polymerized as described above. Contact angle was slightly increased in the fluorinated diamine covered areas ($71^\circ \pm 4$) as compared with MPD covered area ($54^\circ \pm 5$) (**Figs. 4C and 4B**, respectively).

[0080] Flux and salt rejection were measured for these membranes and an increase in salt rejection was generally observed (**Fig. 4F**) as the coverage of the fluorinated diamine increased: 0% fluorinated diamine FPA coverage gave NaCl rejection of about 92%, whereas increasing area of fluorinated diamine lead to NaCl rejection as high as 98%. Flux was measured to be similar or greater for fluorinated diamine membranes as compared to membranes fabricated without fluorinated diamine (**Fig. 4E**). Other advantages of fluorinated membranes might be increased chlorine resistance, increased boron rejections, increased salt rejections, and decreased scaling and biofouling.

Interfacial polymerization printing on PSf UF supports after soaking in MPD solution using amine-functionalized nanodiamonds

[0081] In this particular process, different polyfunctional amines, including nanoparticles, could be printed to give a variable polymer composition or polymer composite. The nanoparticles can be either amine-functionalized nanoparticles, e.g., amine functionalized nanodiamonds, to get covalent attachment, or non-functionalized to get composite material. For example, TFC polyamide printed membranes were made

using 2% (w/v) MPD/water solution. The PSf UF support membranes (PS-20, 20kDa, Sepro) were pre-soaked in this solution for 5 min (excess droplets on the surface were removed). This soaked support was printed using 2.5% dispersed amine functionalized nanodiamonds aqueous solution (contains: amine modified surface nanodiamonds purchased from Ray Techniques Ltd., distilled water and "Paul Roark's Generic clear base C6A (distilled water, glycerol and Kodak photo-Flo 200 formula)), that was poured to all the ink reservoirs tanks (C, M, Y, K). "100% black" (designed by Adobe Photoshop CS6) as a full surface cover was then printed various number of times (1-3 times) on the PSf UF support. Excess droplets on the printed surface were rolled flat with the soft rubber roller. Once printed, the membranes were treated with 0.1% (w/v) TMC/*n*-hexane solution, similar to the conventional method. After 1 min, the TMC solution was decanted, and the resulting membrane was rinsed with an aqueous solution of 0.2% (w/v) sodium carbonate and stored in DI water until use. Nanodiamonds were incorporated covalently into the polyamide matrix and a higher concentration of nanodiamonds (more prints) led to higher permeability and lower NaCl rejection (**Fig. 5**). This process may be useful for fabrication of catalytic surfaces or membranes where the catalysts are nanoparticles and differing permeability and flux are needed.

Preliminary membrane testing methods

[0082] Separation efficacy. Permeate-flux and salt-rejection of the membranes were measured using dead-end cell. The 25°C aqueous feed contained 1500 or 2000 ppm (0.026 or 0.034 M, respectively) NaCl, and the pH was between 6 and 7 (the transmembrane pressure (TMP) difference was 19.5-20 bar and the permeate pressure was essentially atmospheric).

[0083] Contact Angle. Contact angles may be those of DI water at room temperature. Membranes may be thoroughly rinsed with water, and then allowed to dry in a vacuum desiccator to dryness. Due to the occasional variability in contact angle measurements, 6 angles were measured and averaged with reported standard deviation.

Example 2. Membrane modification via ink-jet printing

[0084] In general, an Epson L110 printer was used with the front paper feed roller removed to prevent damage to the membrane surface. The middle portion of the rear

roller was removed as well. Optionally, a flexible tube was attached onto the print head for application of nitrogen gas in the vicinity of the print head. Reverse osmosis membrane surfaces were activated with atmospheric plasma and printed a number of times with a monomer solution, at room temperature. The solution was composed of methacrylic acid (MA) and polyethylene glycol methacrylate (PEGMA) in a ratio of 4:1 in water (0.8 M MA and 0.2 M PEGMA). This solution was poured into the 4 color reservoirs of the Epson L110 printer instead of the CMYK inks. After reaction, the membrane was washed between 15-20 min with DI water with stirring. The membranes were dried at atmospheric pressure and room temperature. An overview of the activation, and coating application methods are schematically shown in **Fig. 6**.

[0085] In particular, the surface of a commercially available reverse osmosis membrane (ESPA-1) was activated with atmospheric plasma (Surfx technologies) O₂ and He gas at 100 W, scanning at a rate of 40 mm/min and at a height of 1 to 3 cm from the wet membrane. Graft polymerization was then achieved by application of the monomers MA and PEGMA with the ink-jet printer. As shown in **Fig. 7**, the appearance of a new peak at value of about 1715 cm⁻¹ is an evidence of a successful graft polymerization. Accordingly, FTIR measurements showed that a polymer layer of increasing thickness was added to the surface of the membrane with an increasing number of prints, as determined by analysis of the characteristic signals of the new grafted layer polymer at ca. 1715 cm⁻¹ and at ca. 950 cm⁻¹. A decrease of contact angle was also observed from 64° for the untreated membrane to about 30° as the number of prints increased (**Fig. 8**). Flux and rejection values were measured and salt rejection increased, and flux decreased as number of prints increased (**Fig. 9**).

[0086] In particular, the surface of a commercially available reverse osmosis membrane (ESPA-1) was activated with atmospheric plasma (Surfx technologies) O₂ and He gas at 100 W, scanning at a rate of 40 mm/min and at a height of 1 cm from the wet membrane. Graft polymerization was then achieved by application of the monomers MA and PEGMA with the ink-jet printer printed as a full cover, a checkerboard pattern where printed areas comprised 50% of the membrane ("pattern 1"), and a zig-zag pattern where printed areas comprised 85% of the membrane ("pattern 2") (**Fig. 10**). Similarly as above, the FTIR and contact angle changes indicated a successful reaction (**Fig. 11**). The flux

decreased on modified membranes and the rejection remained the same or increased (**Fig. 12A**). Atomic force microscope (AFM) was used to give an indication of surface roughness, and the patterned membranes showed a smoother surface compared to the fully covered modified membrane as shown in **Fig. 12B** and summarized in **Table 3**.

Table 3

	Roughness R_a (nm)	Roughness RMS (nm)
Unmodified	67 ± 2	85 ± 3
Fully modified	117 ± 4	166 ± 2
Pattern 1	90 ± 2	135 ± 5
Pattern 2	100 ± 1	133 ± 3

Membrane modification using ink jet printing and redox activation

[0087] In general, an Epson L110 printer was used with the front paper feed roller removed to prevent damage to the membrane surface. The middle portion of the rear roller was removed as well. Reverse osmosis membrane surfaces were activated by soaking the membranes in aqueous solutions of potassium persulfate and potassium metabisulfite (equimolar concentration of 0.01M) for 10, 20, 30 and 90 minutes, and the membrane was then removed from the solution and loaded into the printer. A solution of monomers composed of MA and PEGMA in a ratio of 4:1 in water (0.8 M MA and 0.2 M PEGMA) was prepared at room temperature. This monomer solution was poured into the 4 color reservoirs of the Epson L110 printer instead of the CMYK inks, and was printed onto the potassium persulfate and potassium metabisulfite activated surface. One full covering was printed, as well as 50% covering in a checkerboard patterned manner ("Pattern 1"), and a 85% covering in a zig-zag pattern ("Pattern 2") (**Fig. 10**). After printing, the membrane was kept in a closed petri dish container for 20 min, and was then washed for 15-20 min with DI water while stirring. The membranes were dried at atmospheric pressure and room temperature. FTIR and contact angle were measured on places where monomers were deposited. A general trend emerged, where increased FTIR $1720/1588\text{ cm}^{-1}$ peak ratio correlated to a lower contact angle. In addition, an increased membrane soaking time in potassium persulfate and potassium metabisulfite solution gave increased modification (**Figs. 13-14**). The membrane coupon size was 11.3 cm^2 , and

flux and rejection were measured. For the different activation times and different patterns printed, flux ranged from 88-135 L/m².h with NaCl rejection of 82-96% (**Figs. 15-16**). In general, these longer membrane-activation/soaking times gave increased roughness as observed in atomic force microscopy (AFM). In particular, while the root mean square (RMS) roughness measured for ESPA-1 control membrane was 84 nm, the RMS roughness measured for 10, 20 and 90 min activation/soaking was 154, 202, and 240 nm, respectively.

Example 3. Membrane modification with nanoparticles using ink-jet printing

[0088] In general, an Epson L110 printer is used with the front paper feed roller removed to prevent damage to the membrane surface. For disposal of excess solution, the ink pump is rerouted from the internal waste ink tank to an external container. 16 cm square membranes are taped to the center of laminated sheets of A4 paper preventing any part of the printer from physically touching the membranes. The middle portion of the rear roller is removed as well. Reverse osmosis membrane surfaces are used as the substrate to print a solution of carbon nanotubes (CNTs) (0.1-1.0 mg/ml) either as a full coverage coating (may be printed 1-50 times to increase CNTs density) or in different patterns, e.g., checkerboard or lines. For multiple printings, 5 minutes is allowed in between printings in order for the solution to dry, leaving only CNTs on the membrane before another layer is printed. The CNT solution is placed in one of the four ink reserve tanks, and a crosslinking solution, e.g., glutaraldehyde solution or other known crosslinkers, and a matrix solution, e.g., polyvinylalcohol solution or another suitable polymer, are placed in available ink reserve tanks. The three solutions are simultaneously printed on the reverse osmosis membrane. Heating of the membrane after printing may be necessary to allow crosslinker to completely react with the matrix and the CNTs, and temperatures from room temperature to about 100°C may be used. Electrical conductivity of the surface due to the CNTs may prevent fouling upon application of an electric potential. Conductivity of modified membranes can be checked with a multimeter or, more accurately, with a four point conductivity meter. By printing multiple layers of CNTs on the polymer surface, increasing amounts of CNT-coated membranes could be achieved (**Fig. 17**). As a result, conductivity was increased as more CNTs were deposited.

[0089] In alternative processes, the membrane is pretreated with the matrix solution, and the CNT and crosslinking solutions are then printed on the pretreated membrane; or the membrane is pretreated with both the matrix and crosslinking solutions, and the CNT solution is then printed on the pretreated membrane. The matrix solution may also be mixed with the nanoparticle solution within the same ink tank. Alternatively in the crosslinking process the membrane can be submersed within a bath of crosslinker solution and heated.

[0090] Modification of membranes with nanoparticles as described above is not limited to CNT, and other nanoparticles such as silver, copper or titanium containing nanoparticles, nanodiamonds, graphene quantum dots, or other carbon-based nanoparticles, or any functionalized derivatives of those nanoparticles, can be utilized as well.

CLAIMS

1. A method for fabrication of a membrane for reverse osmosis, nanofiltration or ultrafiltration by forming either a polyamide layer or a nanoparticle layer on a surface of a support membrane, said method comprising a step selected from:
 - (i) ink-jet printing on said surface of said support membrane a polyfunctional amine or polyamine functionalized nanoparticles which, upon reacting on said surface with a polyfunctional acyl halide or anhydride functional group, forms said polyamide layer; or
 - (ii) ink-jet printing on said surface of said support membrane nanoparticles which, upon reacting on said surface with a matrix and a crosslinker, forms said nanoparticle layer.
2. The method of claim 1, wherein said support membrane is a polymer membrane.
3. The method of claim 1 or 2, wherein the membrane fabricated has salt rejection of 40-99.5%, and flux of 0.3-40 L/h m² bar.
4. A method according to any one of claims 1 to 3, for fabrication of a thin film composite (TFC) polyamide membrane, said method comprising:
 - (iii) ink-jet printing of an aqueous solution of a polyfunctional amine or polyamine functionalized nanoparticles on a surface of a support membrane; and
 - (iv) treating the printed surface of said support membrane with a water-immiscible organic solution of a polyfunctional acyl halide or anhydride functional group thereby interfacially polymerizing said polyfunctional amine or polyamine functionalized nanoparticles with said polyfunctional acyl halide or anhydride functional group on said surface of said support membrane, thus forming a polyamide layer on said surface of said support membrane.
5. The method of claim 4, wherein step (i) is repeated n times prior to step (ii), and wherein n is an integer from 1 to 5.

6. The method of claim 4, wherein said ink-jet printing is carried out from (i) one reservoir; or (ii) more than one reservoir, wherein each one of said reservoirs contains an aqueous solution of identical or different polyfunctional amine or polyamine functionalized nanoparticles.
7. The method of claim 4, wherein said ink-jet printing is carried out according to a predetermined pattern.
8. The method of claim 4, wherein said treating in step (ii) is conducted by immersing the printed surface of said support membrane in said organic solution; or by ink-jet printing of said organic solution on the printed surface of said support membrane.
9. The method of claim 8, wherein said ink-jet printing is carried out from (i) one reservoir; or (ii) more than one reservoirs, wherein each one of said reservoirs contains an organic solution of identical or different polyfunctional acyl halide or anhydride functional group.
10. The method of claim 8, wherein said ink-jet printing is carried out according to a predetermined pattern.
11. The method of any one of claims 8 to 10, wherein said treating in step (ii) is conducted by ink-jet printing of said organic solution on the printed surface of said support membrane, and simultaneously with said ink-jet printing of step (i).
12. The method of claim 4, wherein heat treatment is applied in step (ii) to complete the interfacial polymerization.
13. The method of claim 4, wherein:
 - (i) said support membrane is composed of polysulfone (PSf), polyethersulfone (PES), polyacrylonitrile (PAN), polyester, polyphenyleneoxide, polyphenylenesulfide, polyvinyl chloride, polyvinylidene fluoride, polytetrafluoroethylene, polycarbonate, polyetherketone, or polyetheretherketone; or

- (ii) wherein said polyfunctional amine is *m*-phenylenediamine (MPD), *p*-phenylenediamine, 2,4-diaminotoluene, 2,5-diaminotoluene, N,N'-diphenylethylene diamine, 4-methoxy-*m*-phenylenediamine, 1,3,4-triaminobenzene, 1,3,5-triaminobenzene, 3,5-diaminobenzoic acid, 2,4-diaminoanisole, xylylenediamine, ethylenediamine, propylenediamine, tris(2-diaminoethyl)amine, piperazine, a fluorinated aromatic polyamine such as 5-fluoro-*m*-phenylenediamine and 2,5-difluoro-*m*-phenylenediamine, a fluorinated non-aromatic polyamine, a fluorinated alkane substituted with one or more aromatic groups each containing at least one amino group such as 2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane, a fluorinated alkane diol interrupted by one or more aromatic groups each containing at least one amino group such as 2,2'-(methylenebis(3-amino-6,1-phenylene))bis(1,1,1,3,3,3-hexafluoropropan-2-ol), a chiral polyamine, or a mixture thereof; or
- (iii) said nanoparticles are carbon nanotubes (CNTs), metallic nanoparticles such as silver, copper and titanium containing (titanium dioxide) nanoparticles, nanodiamonds, or graphene quantum dots; or
- (iv) said polyfunctional acyl halide is trimesoyl chloride (TMC), trimellitic acid chloride, terephthaloyl chloride, isophthaloyl chloride, cyclohexane-1,3,5-tricarbonyl chloride, 1,3,5,7-tetracarboxyl chloride, adamantane-2,6-dione, 1-isocyanato-3,5-benzenedicarbonyl chloride (5-isocyanato-isophthaloyl chloride), an aromatic polyfunctional acyl halide such as trimesic acid chloride, terephthalic acid chloride, isophthalic acid chloride, biphenyl dicarboxylic acid chloride and naphthalene dicarboxylic acid dichloride, an alicyclic polyfunctional acyl halide such as cyclopropane tricarboxylic acid chloride, cyclobutane tetracarboxylic acid chloride, cyclopentane tricarboxylic acid chloride, cyclopentane tetracarboxylic acid chloride, tetrahydrofuran tetracarboxylic acid chloride, cyclopentane dicarboxylic acid chloride, cyclobutane dicarboxylic acid chloride, cyclohexane dicarboxylic acid chloride and tetrahydrofuran dicarboxylic acid chloride, or a mixture thereof; or

- (v) said anhydride functional group is a polyfunctional acid anhydride such as mellitic anhydride, or a polyfunctional acid anhydride halide such as 4-chloroformyl phthalic anhydride; or
- (vi) the organic solvent in said organic solution comprises a straight or iso- (C₅-C₁₂)alkane such as pentane, isopentane, hexane, isohexane, heptane, isoheptane, octane, isooctane, nonane, isononane, decane, isodecane, undecane isoundecane, dodecane, and isododecane, a (C₅-C₁₂)cycloalkane such as cyclopentane, cyclohexane, cycloheptane, cyclooctane, cyclononane, cyclodecane, cycloundecane and cyclododecane, or a mixture thereof, wherein said (C₅-C₁₂)alkane and (C₅-C₁₂)cycloalkane is optionally halogenated.

14. The method of claim 4, wherein the polyamide layer formed on said surface of said support membrane has a thickness in the range of 0.01-1 μ m, preferably 0.01-0.2 μ m.

15. The method of any one of claims 4 to 14, wherein said support membrane is soaked in an aqueous solution of a polyfunctional amine or polyamine functionalized nanoparticles prior to step (i).

16. The method of claim 15, wherein the concentration of said aqueous solution is in a range of 0.5-10% (w/v%).

17. The method of claim 15, wherein the polyfunctional amine or polyamine functionalized nanoparticles in the aqueous solution ink-jet printed in step (i) and the polyfunctional amine or polyamine functionalized nanoparticles in the aqueous solution in which the surface of said support membrane is soaked prior to step (i) are identical or different.

18. The method of any one of claims 4 to 14, comprising the steps of:

- (i) ink-jet printing of an aqueous solution of MPD or 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane on a surface of a porous support

membrane n times, wherein n is an integer of 1 to 5, and said support membrane is composed of PSf, PES or PAN; and

- (ii) treating the printed surface of said support membrane with a solution of TMC in n -hexane thereby interfacially polymerizing said MPD with said TMC on the surface of said support membrane, thus forming a polyamide layer on said surface of said support membrane.

19. The method of claim 18, wherein said support membrane is soaked in an aqueous solution of MPD prior to step (i).

20. A method according to any one of claims 1 to 3, for fabrication of a membrane coated with nanoparticles, said method comprising ink-jet printing of a solution of said nanoparticles on a surface of a support membrane to thereby form, upon reaction of said nanoparticles with a matrix and a crosslinker, a nanoparticle layer on said surface of said support membrane,

wherein (i) a matrix solution comprising said matrix and a crosslinking solution comprising said crosslinker are ink-jet printed on said surface of said support membrane simultaneously with said nanoparticle solution; or (ii) said surface of said support membrane is pretreated with said matrix solution, and said crosslinking solution is ink-jet printed on said surface of said support membrane simultaneously with said nanoparticle solution; or (iii) said surface of said support membrane is pretreated with said matrix solution and said crosslinking solution; or (iv) said matrix solution is ink-jet printed on said surface of said support membrane, optionally simultaneously with said nanoparticle solution, and said surface of said support membrane is then submersed in said crosslinker solution.

21. The method of claim 20, wherein said ink-jet printing of said nanoparticle solution is repeated n times, wherein n is an integer from 1 to 300.

22. The method of claim 20, wherein said ink-jet printing of said nanoparticle solution is carried out from (i) one reservoir; or (ii) more than one reservoir, wherein each one of said reservoirs contains a solution of identical or different nanoparticles.

23. The method of claim 20, wherein said ink-jet printing of said nanoparticle solution is carried out according to a predetermined pattern.

24. The method of claim 20, wherein said nanoparticle solution and said matrix solution are ink-jet printed together from one reservoir.

25. The method of claim 20, wherein heat treatment is applied to allow said crosslinker to completely react with said matrix and said nanoparticles.

26. The method of claim 20, wherein:

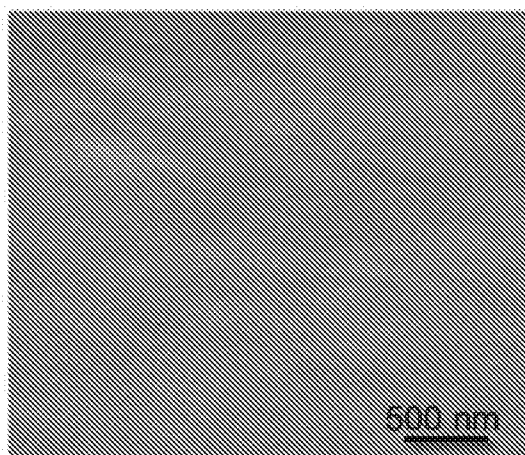
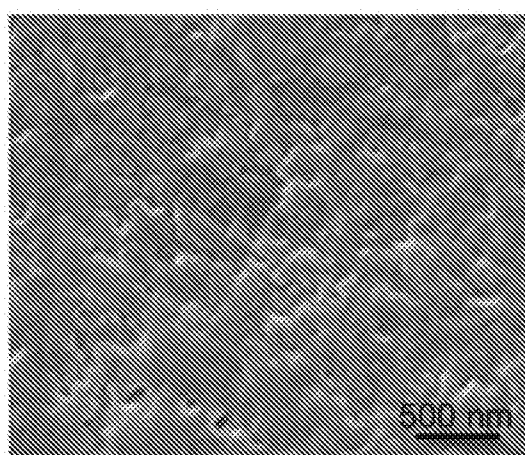
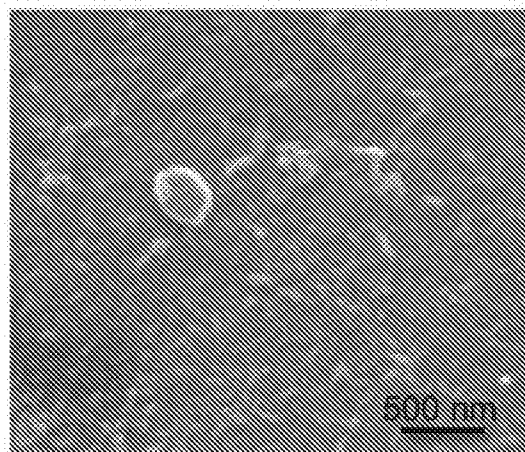
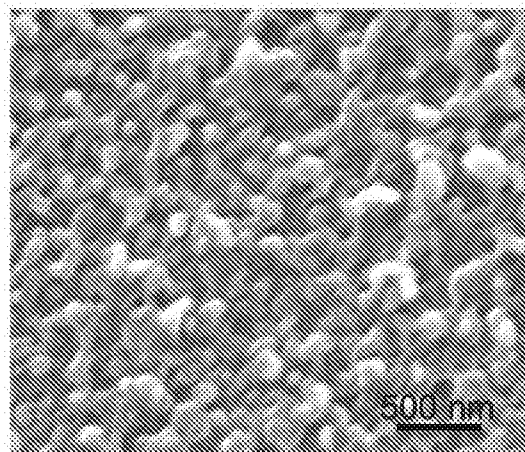
- (i) said support membrane is composed of polysulfone (PSf), polyethersulfone (PES), polyacrylonitrile (PAN), polyester, polyphenyleneoxide, polyphenylenesulfide, polyvinyl chloride, polyvinylidene fluoride, polytetrafluoroethylene, polycarbonate, polyetherketone, polyetheretherketone, or a thin film composite (TFC) membrane including reverse osmosis and nanofiltration membranes having a polyamide surface; or
- (ii) said crosslinker is a compound capable of cross-linking with both an alcohol and a carboxylic or amine moiety; and said matrix is a hydrophilic polymer capable of cross-linking with said crosslinker; or
- (iii) said nanoparticles are carbon nanotubes (CNTs), metallic nanoparticles such as silver, copper and titanium containing nanoparticles, nanodiamonds, or graphene quantum dots, and are optionally functionalized with functional groups capable of reacting with said crosslinker and linking to said matrix.

27. The method of claim 26, wherein said crosslinker is a dialdehyde selected from glyoxal, malondialdehyde, succindialdehyde, glutaraldehyde or phthalaldehyde; and said matrix is polyvinylalcohol.

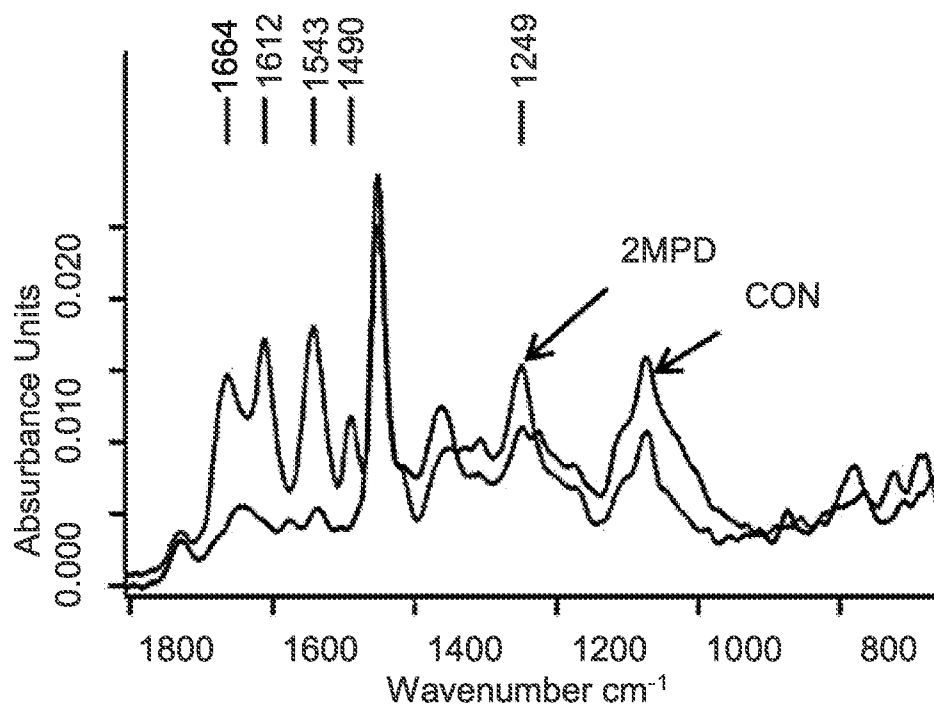
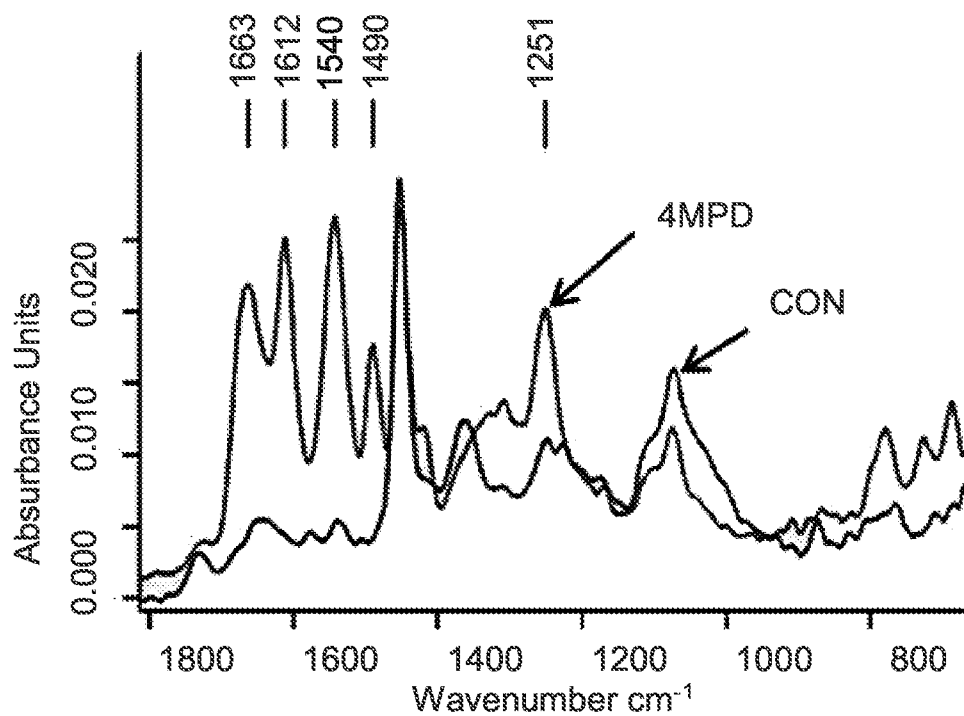
28. A membrane fabricated according to the method of any one of claims 1 to 27.

29. A TFC polyamide membrane according to claim 28, wherein said polyamide layer has a thickness in the range of 10-500 nm.

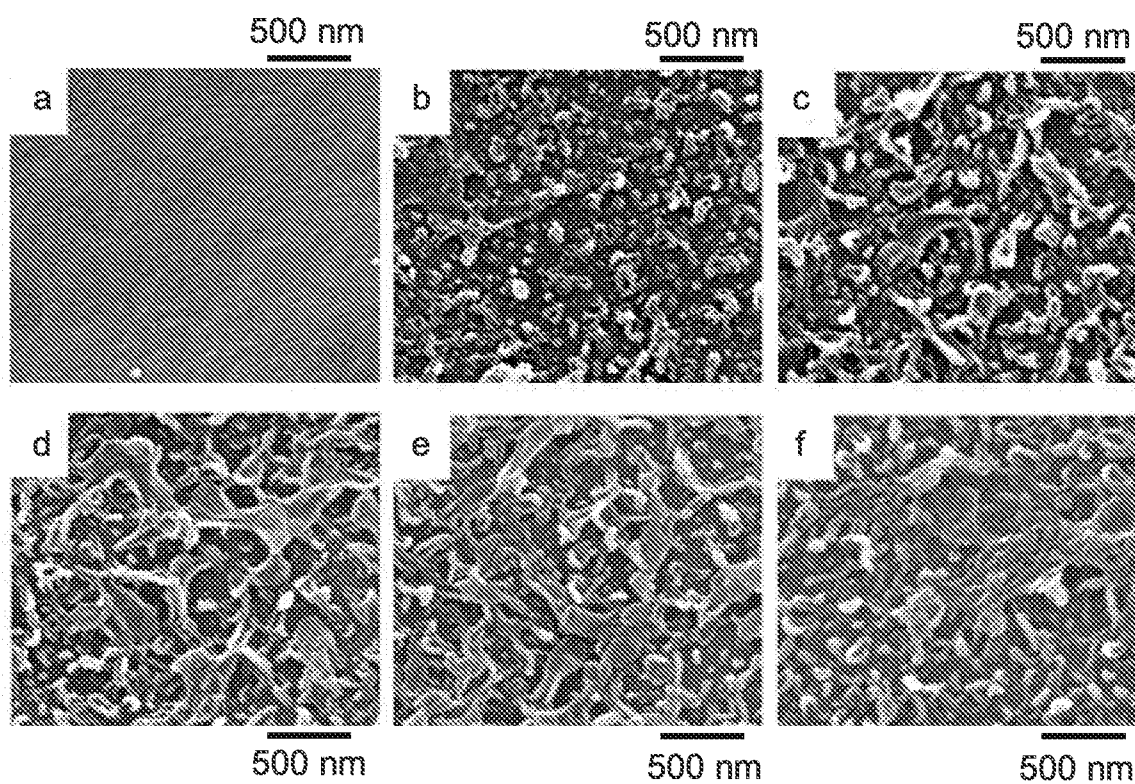
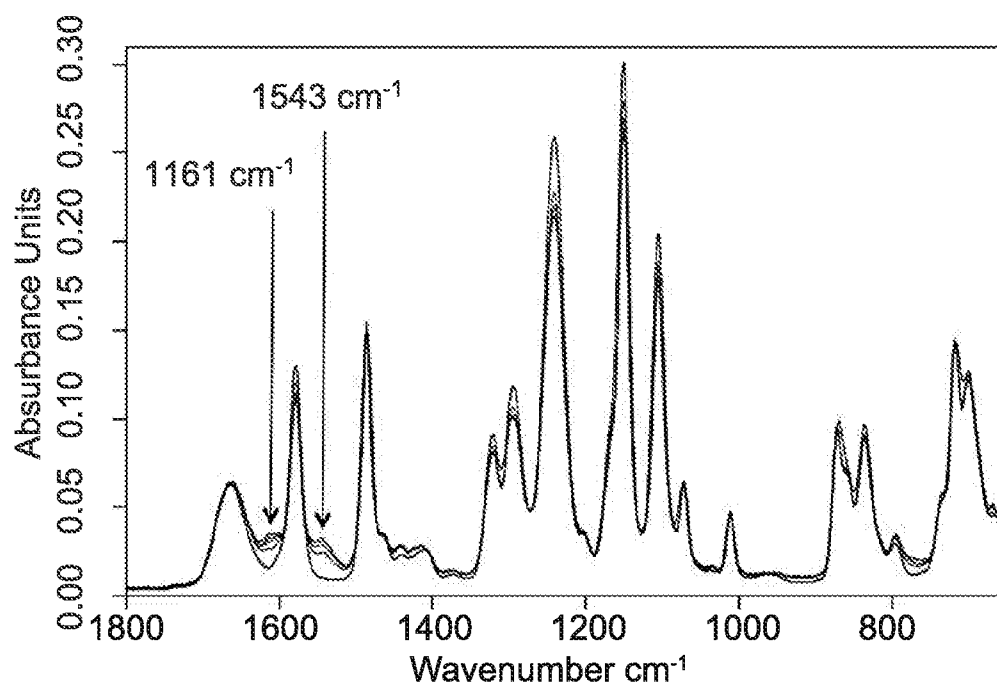
30. The membrane of claim 28 or 29, for use in reverse osmosis or nanofiltration.
31. A method for modification of a membrane, said method comprising:
- (iii) activating a surface of said membrane, preferably with plasma, atmospheric plasma, chemical radical initiators, or UV activated initiators; and
 - (iv) ink-jet printing of an aqueous solution containing monomers capable of polymerizing with each other and onto the surface of said membrane, thus forming a modified TFC membrane having improved antifouling properties while maintaining or improving salt rejection.
32. The method of claim 31, wherein:
- (i) said membrane is a polymer membrane selected from thin film composite (TFC) membranes, reverse osmosis membranes, nanofiltration membranes, ultrafiltration membranes, or microfiltration membranes; or
 - (ii) said monomers are either charged or neutral organic molecules containing an acrylic moiety and selected from methacrylic acid (MA), polyethylene glycol methacrylate (PEGMA), 2-[methacryloyloxyethyl] trimethylammonium chloride, 3-sulfopropyl methacrylate potassium salt, N-(3-sulfopropyl)-N-methacryloyloxyethyl-N,N-dimethylammonium betaine, neutral acrylic-containing monomers including fluorine such as 3-pentafluoropropyl acrylate; or
 - (iii) said monomers are present in said aqueous solution in any ratio.
33. A modified membrane obtained according to the method of claim 31 or 32.

Fig. 1A**Fig. 1B****Fig. 1C****Fig. 1D**

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Fig. 1E**Fig. 1F**

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Fig. 2A**Fig. 2B**

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Fig. 3A

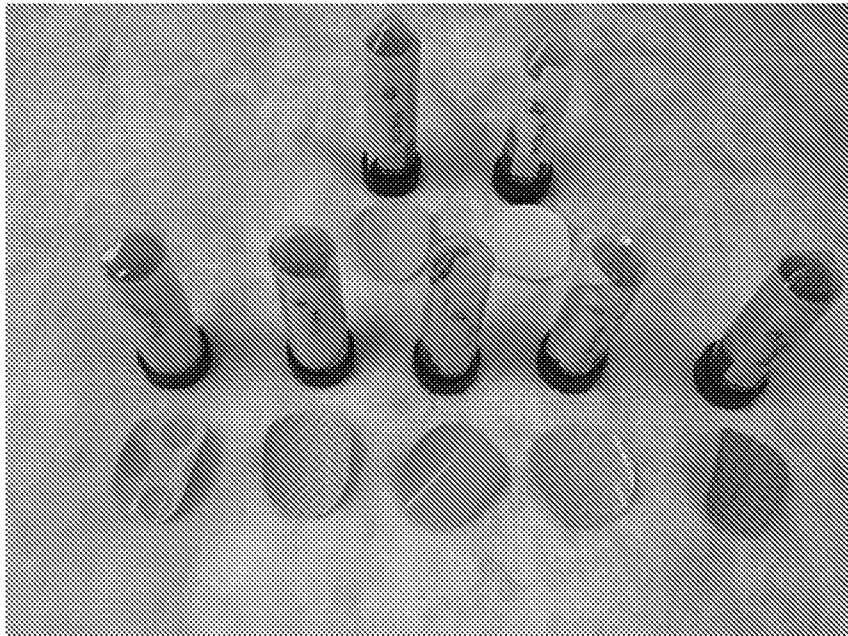


Fig. 3B

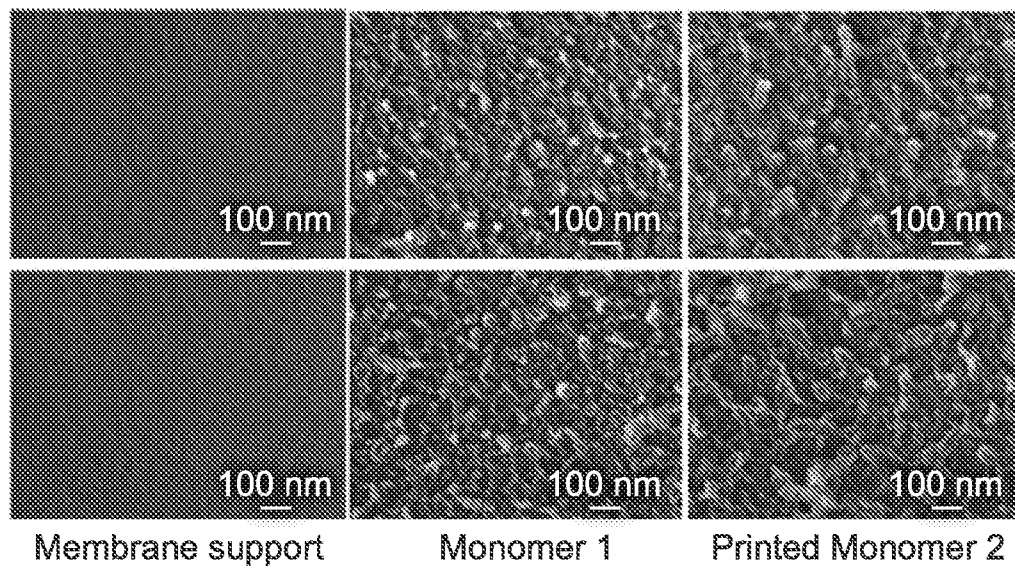


Fig. 3C

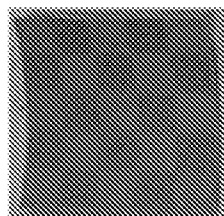


Fig. 3D

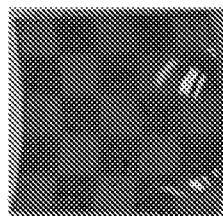
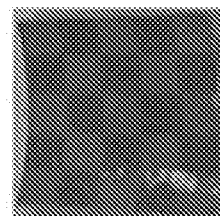
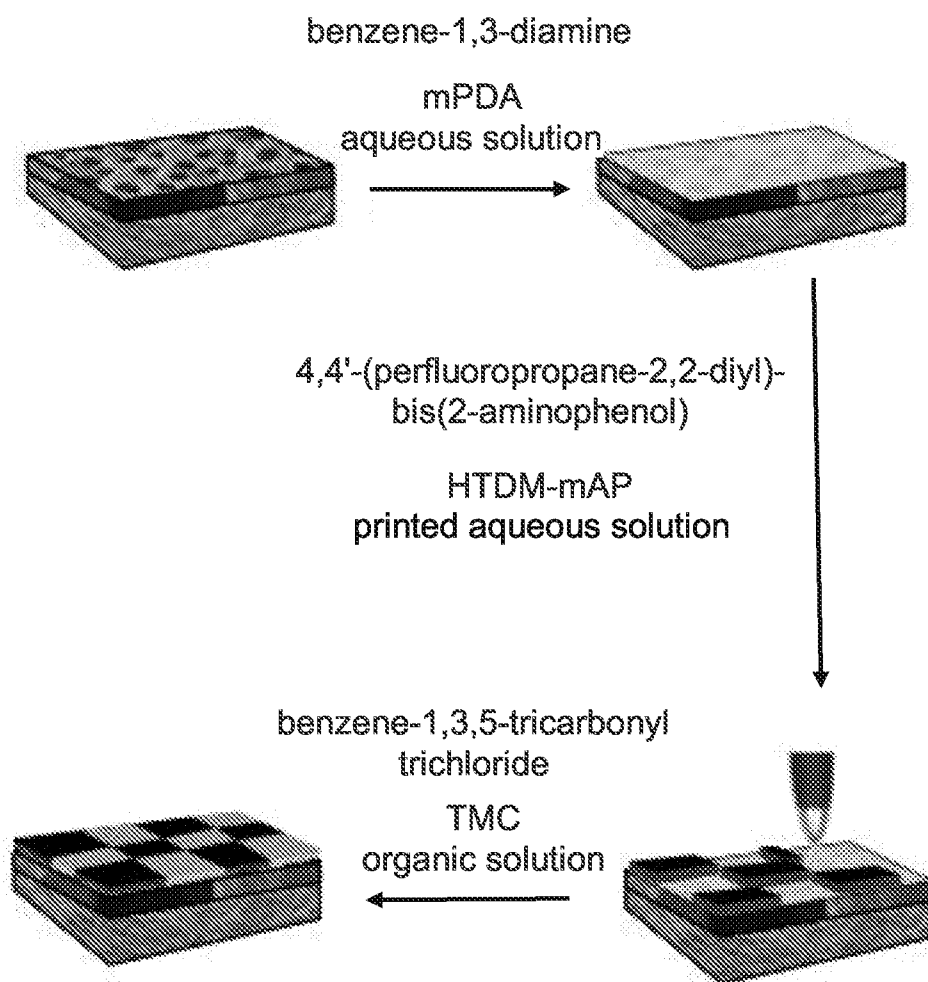
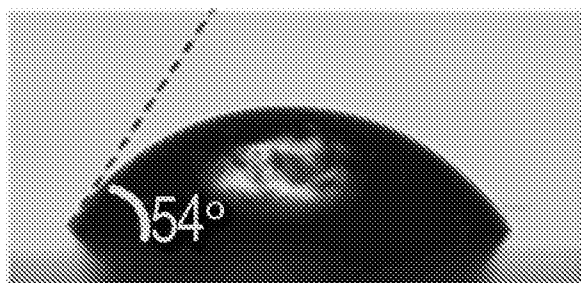
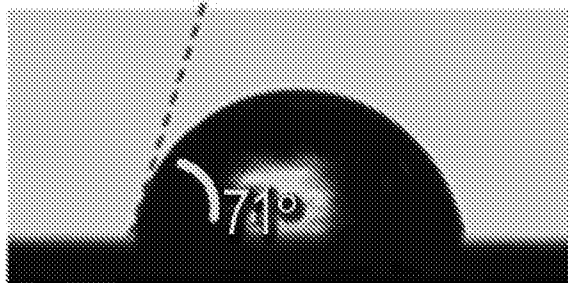


Fig. 3E



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Fig. 4A**Fig. 4B****Fig. 4C**

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Fig. 4D

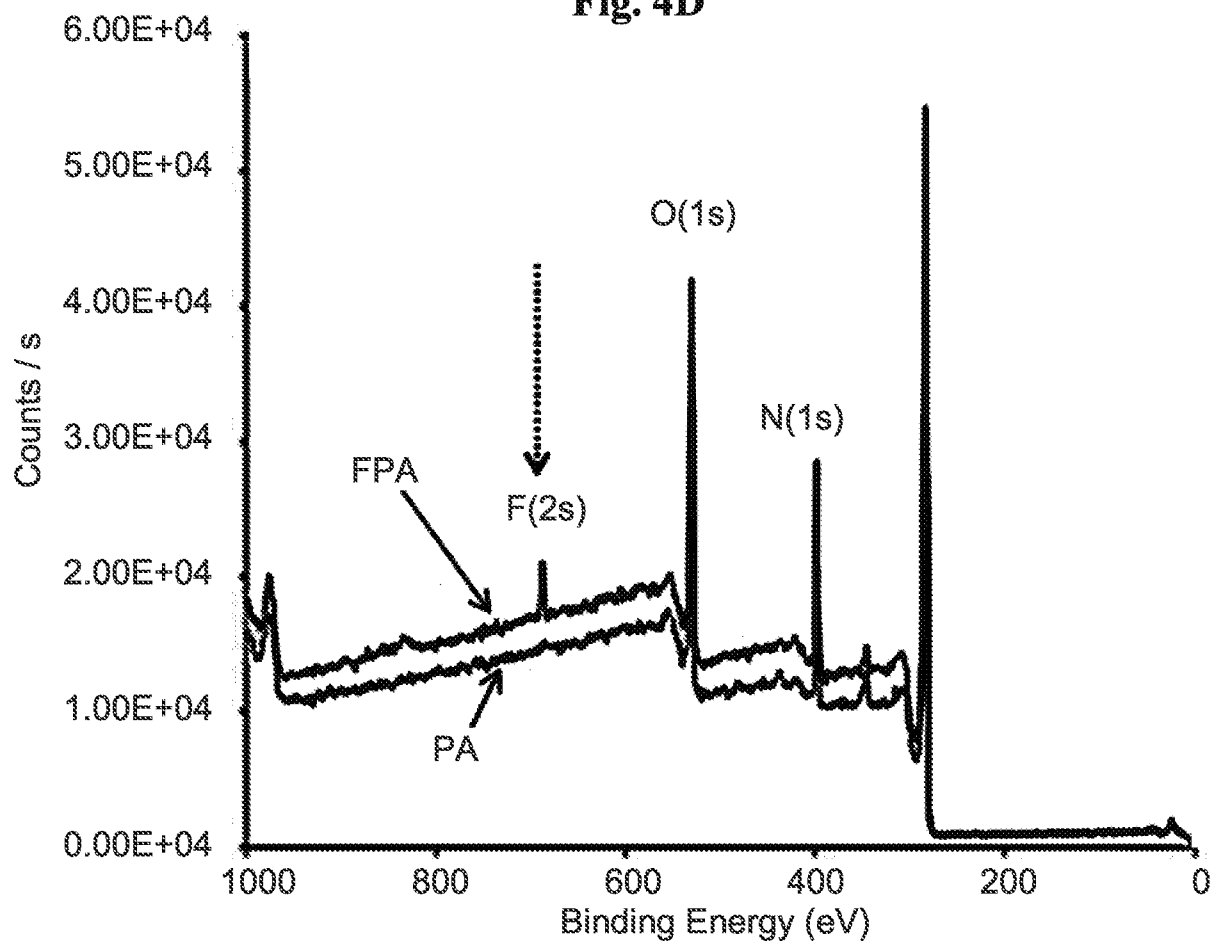
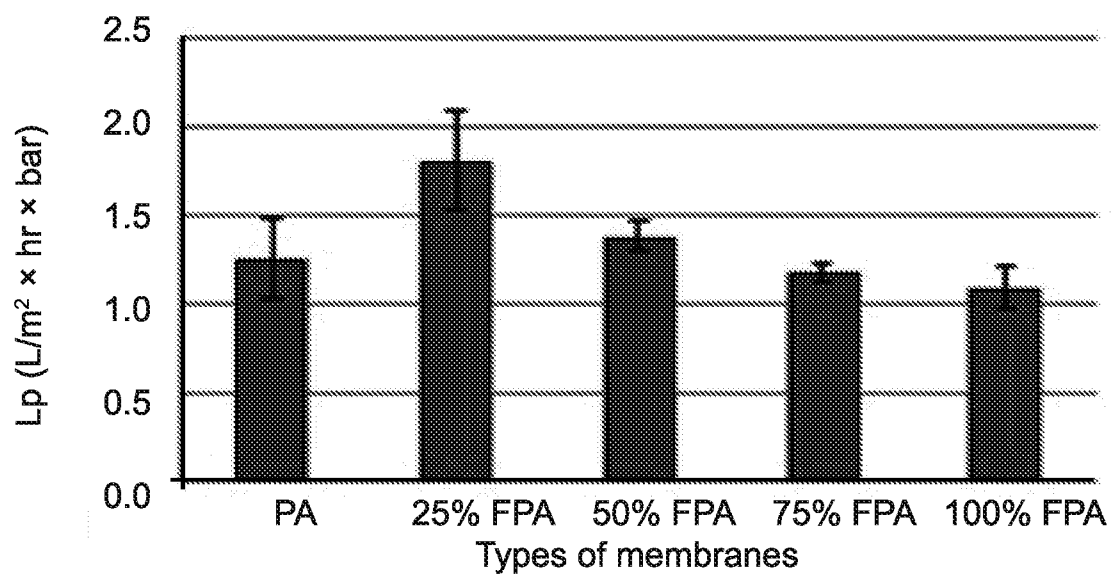
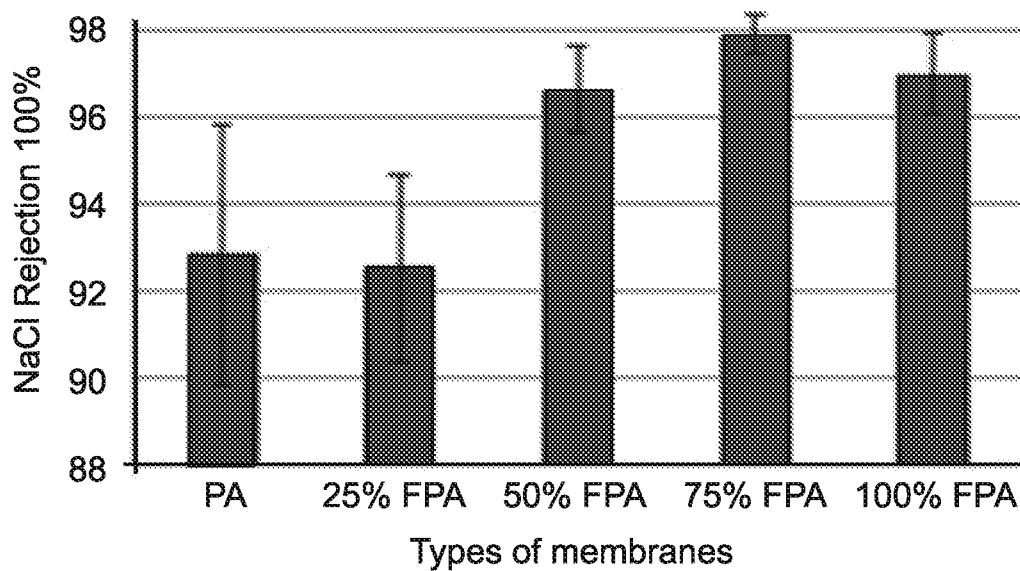
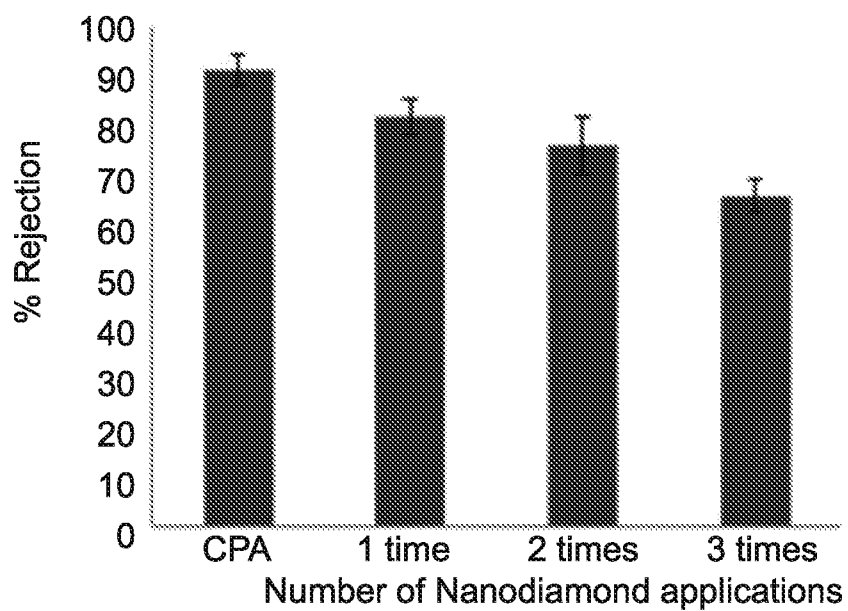


Fig. 4E



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Fig. 4F**Fig. 5A**

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Fig. 5B

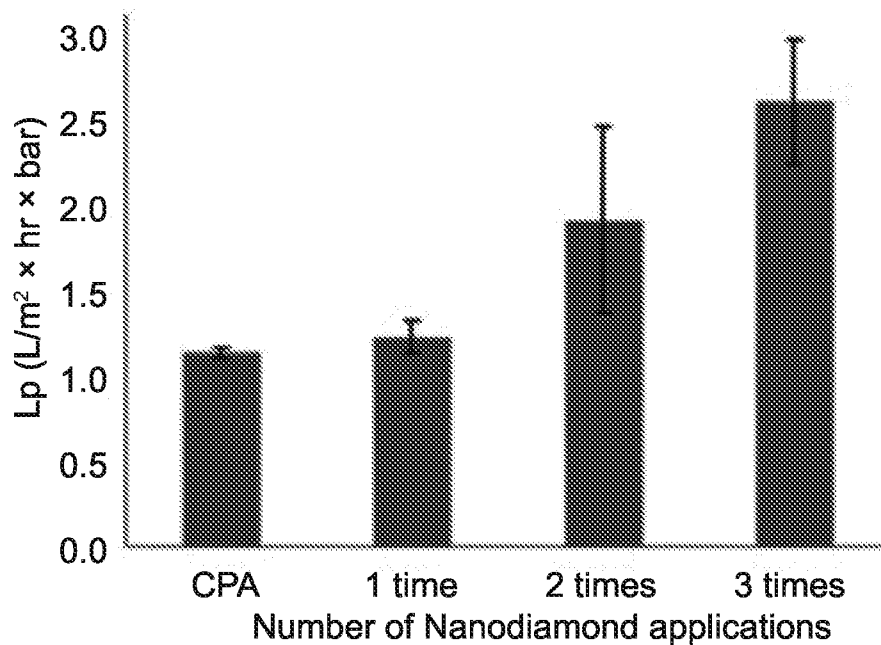
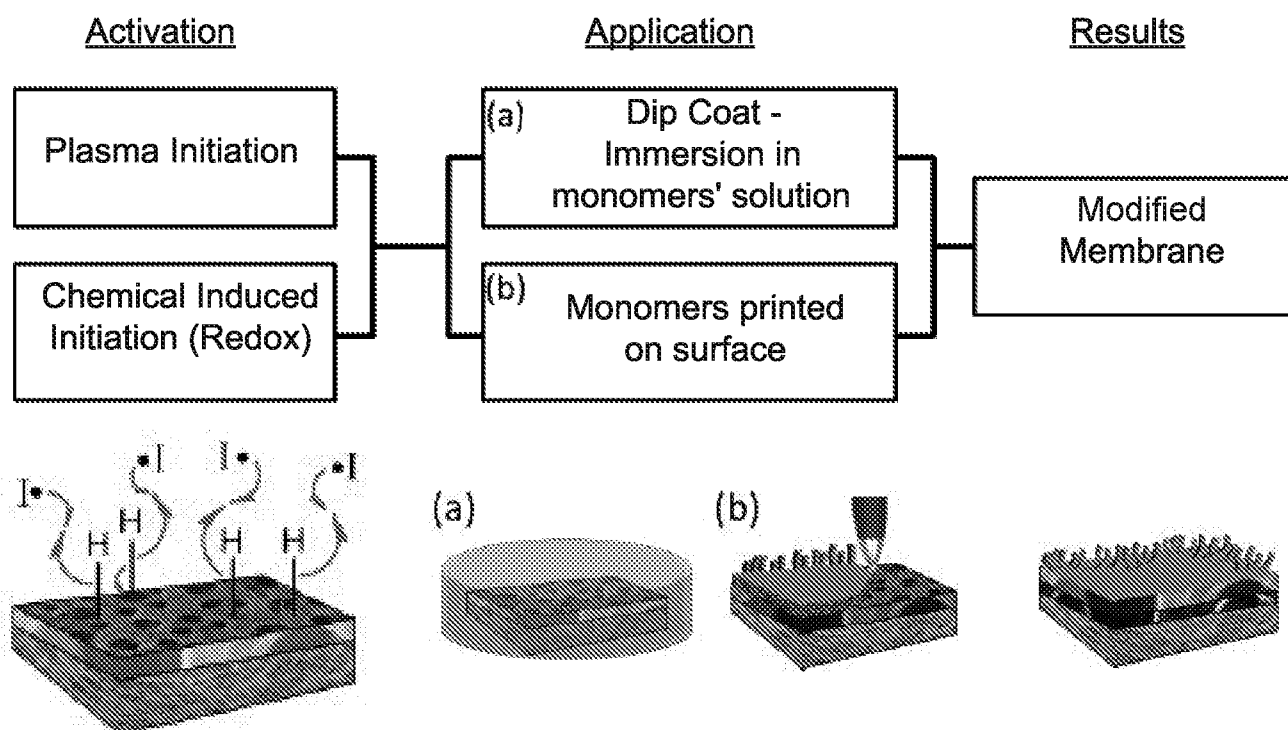


Fig. 6



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Fig. 7

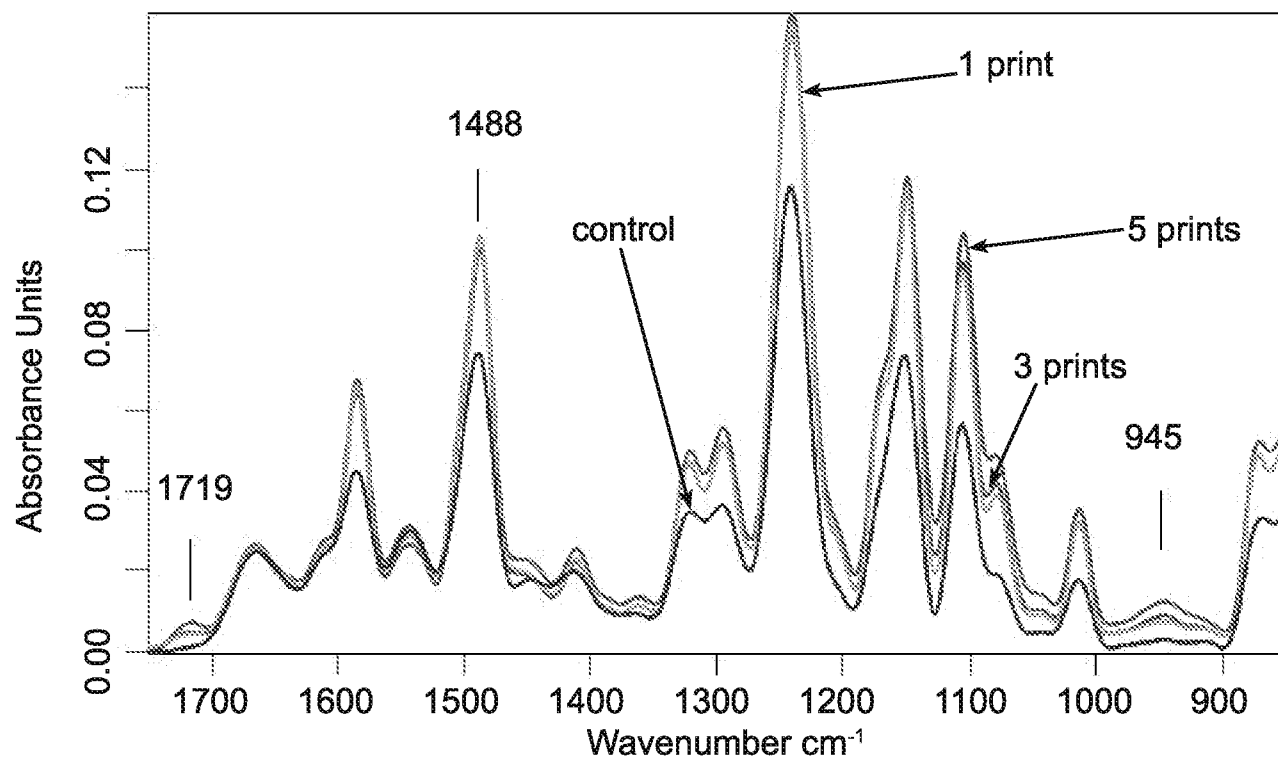
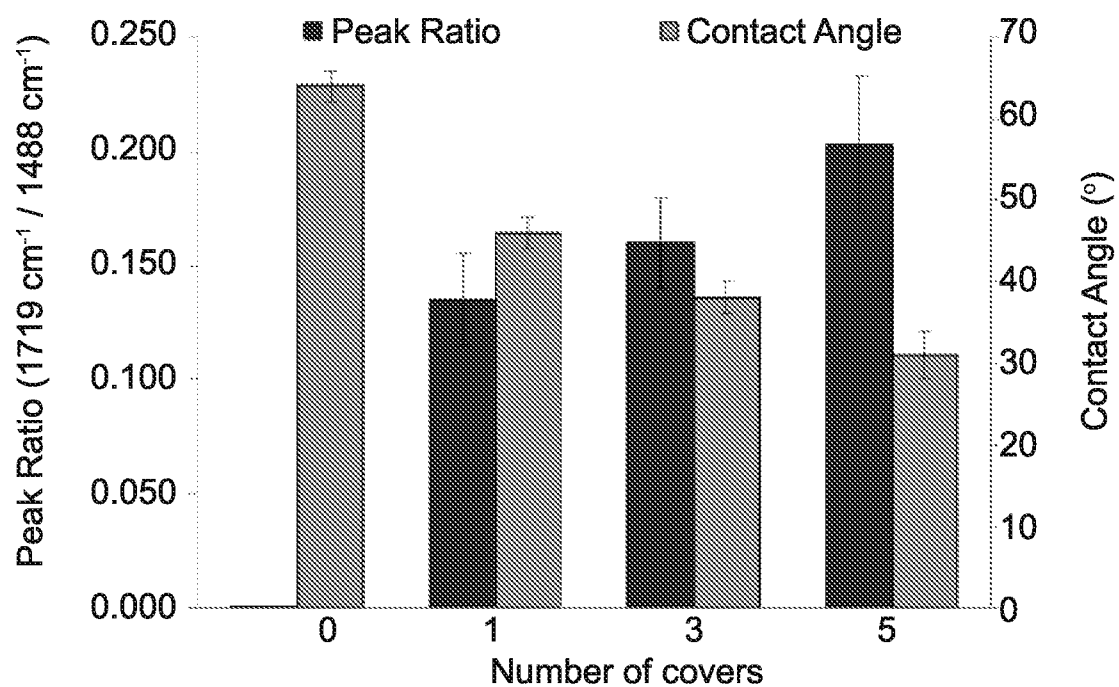


Fig. 8



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Fig. 9

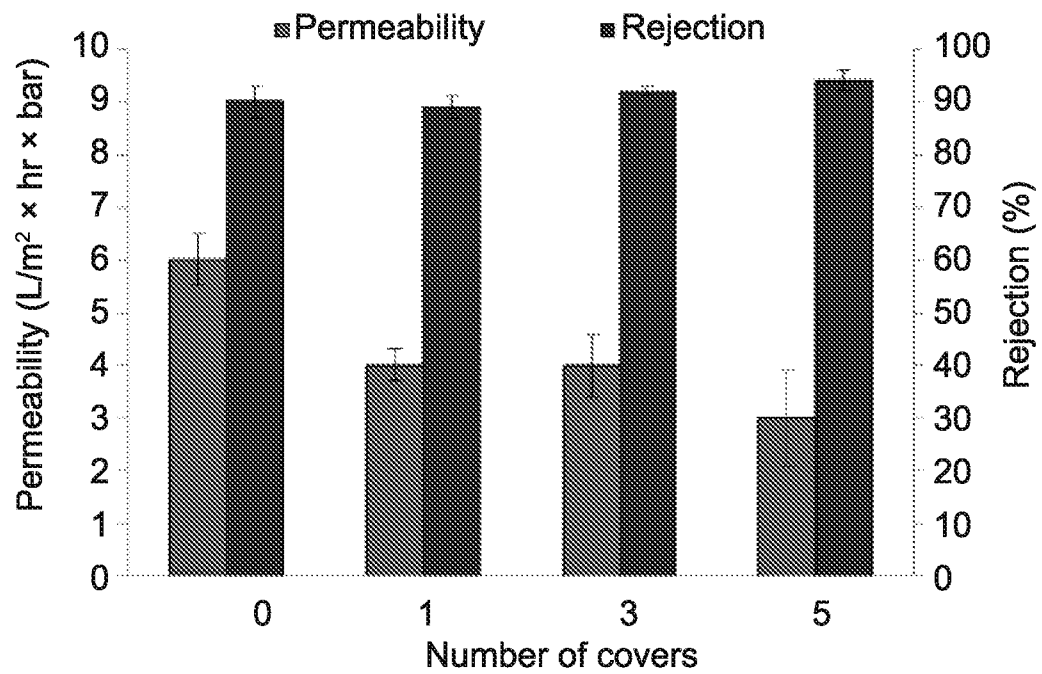
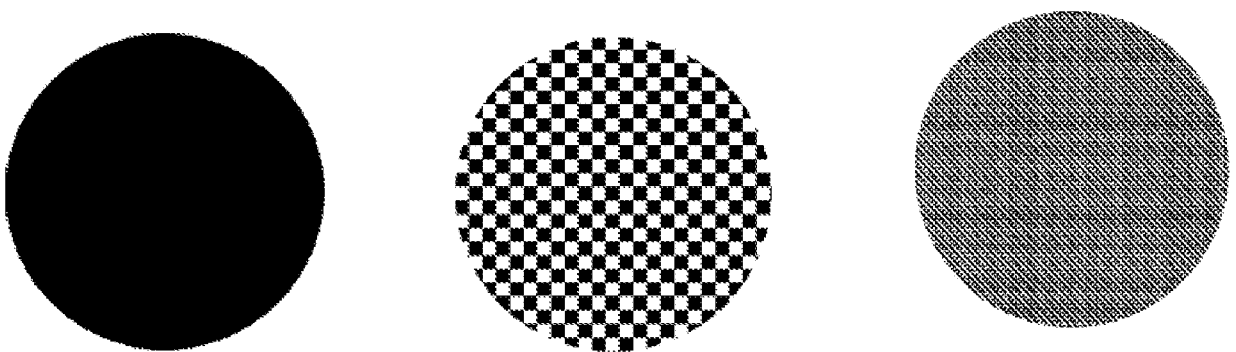


Fig. 10



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Fig. 11

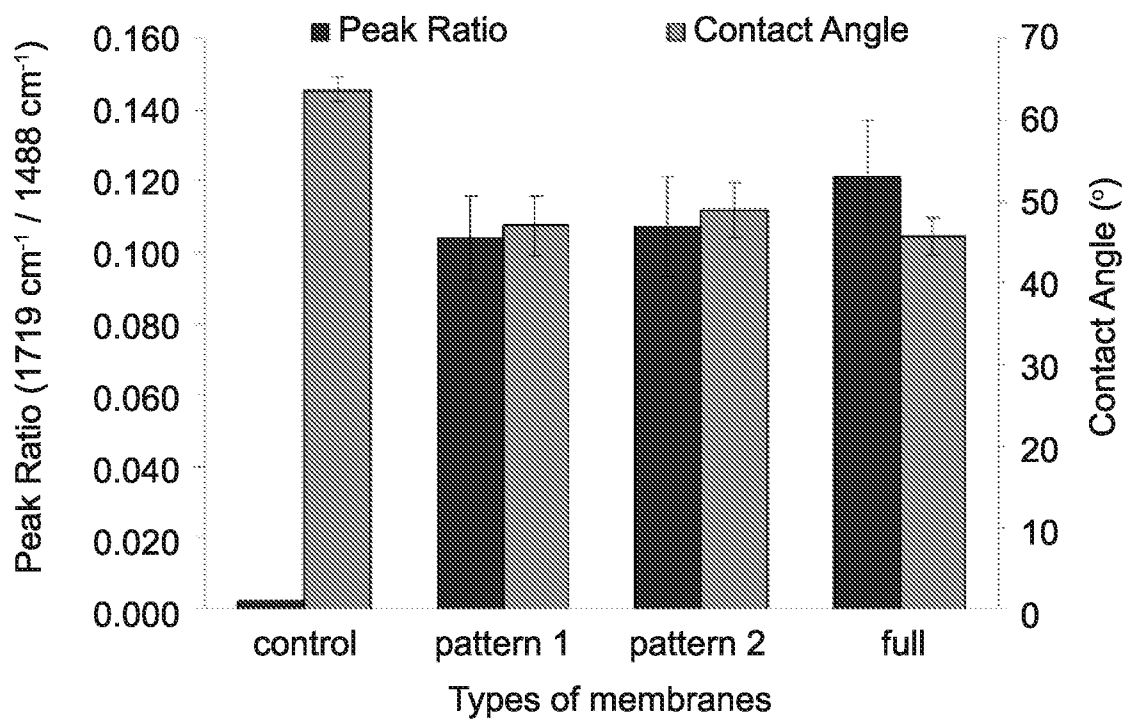
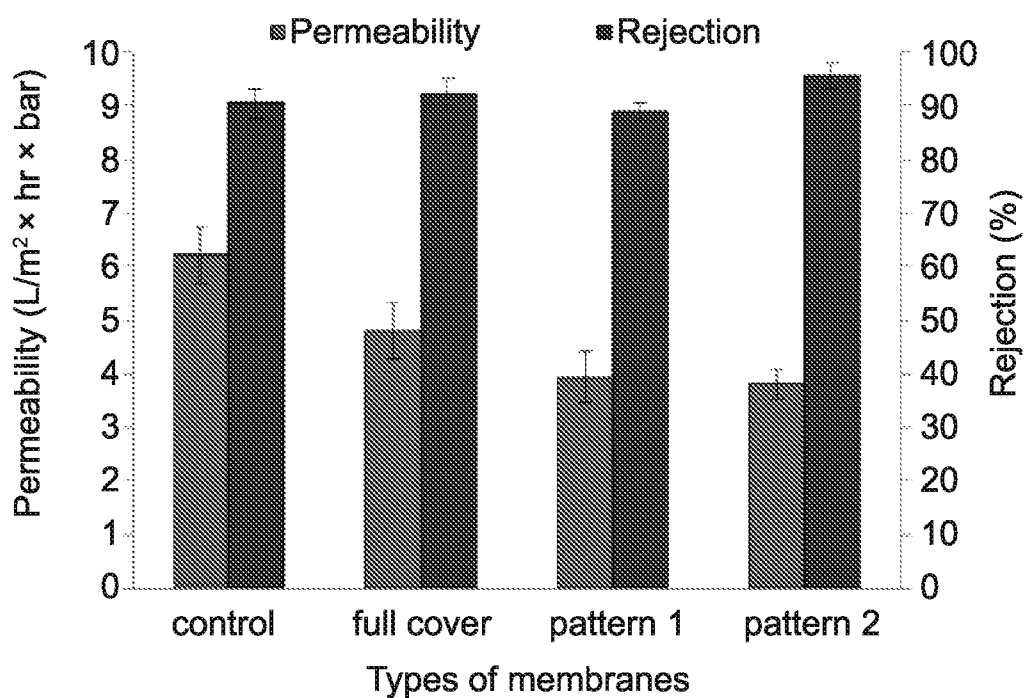


Fig. 12A



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Fig. 12B

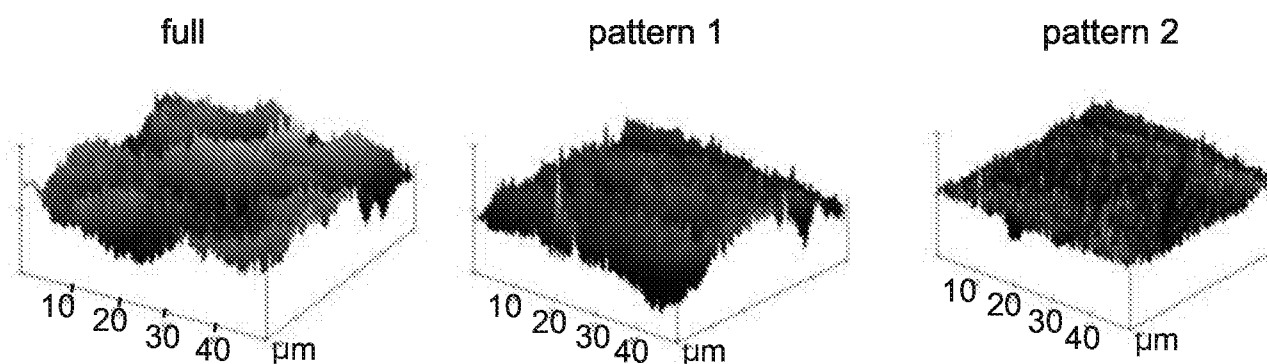
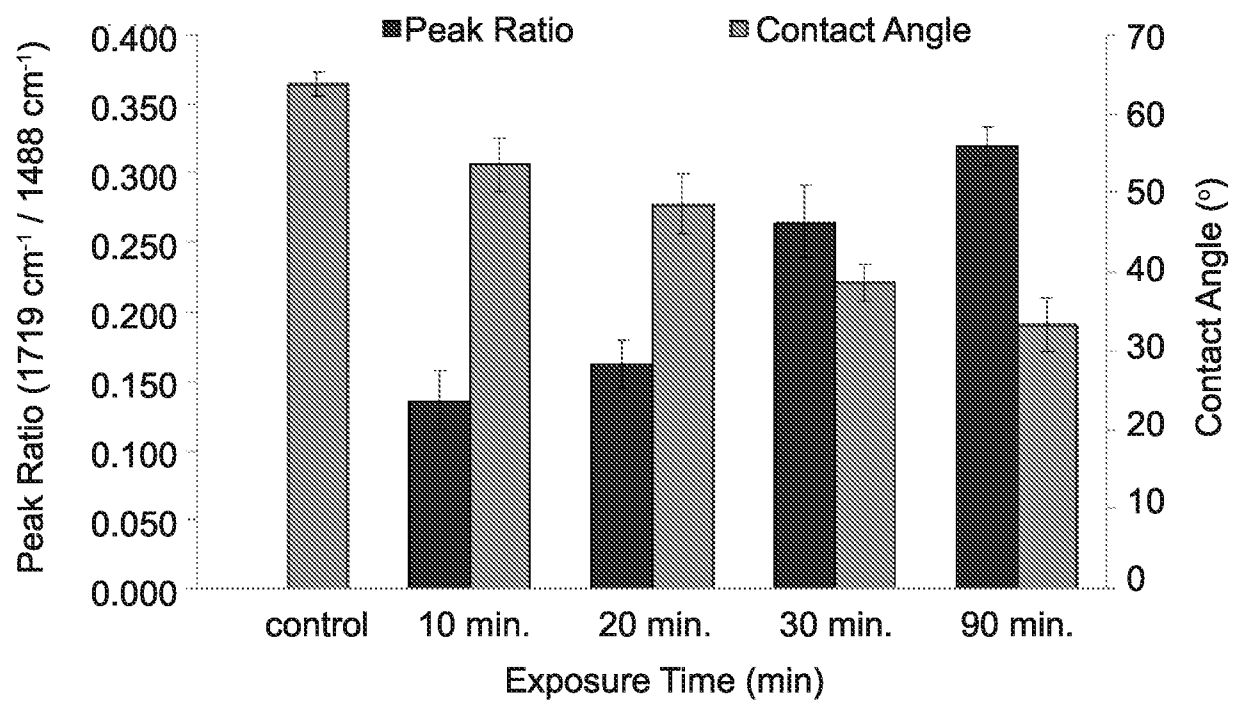


Fig. 13



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Fig. 14

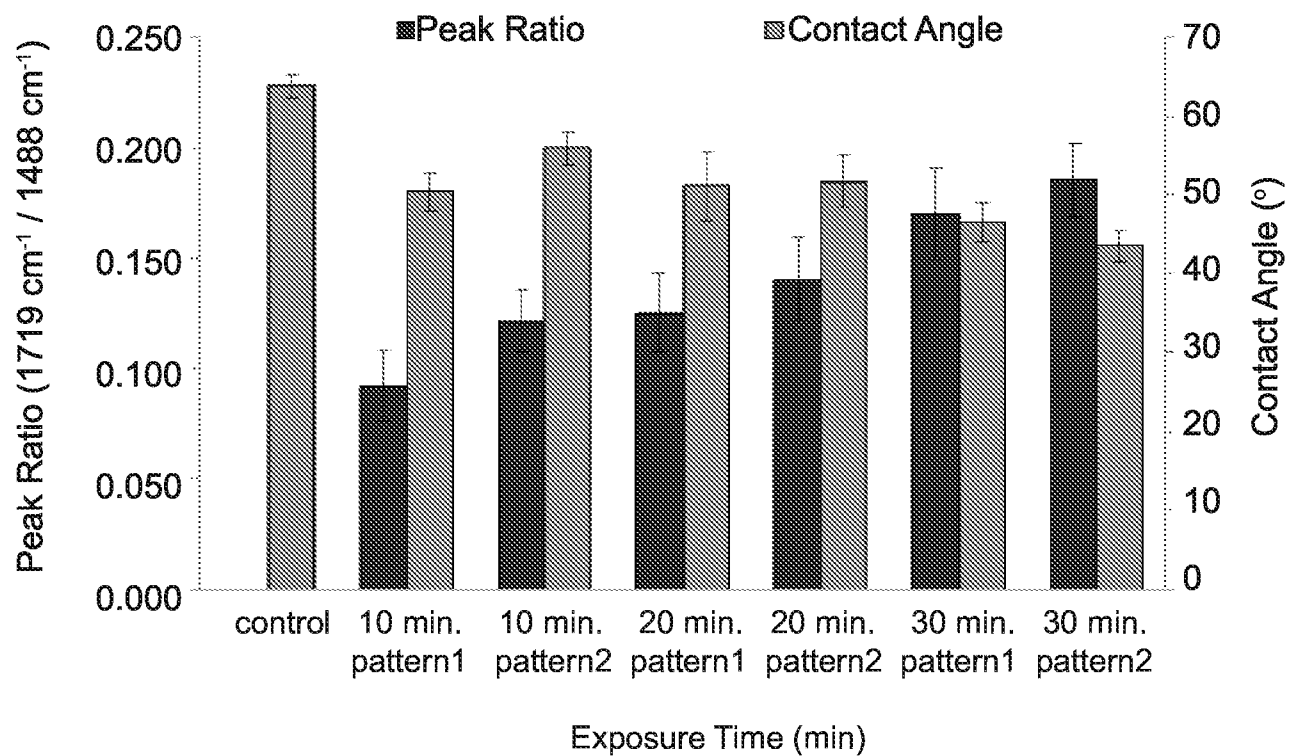
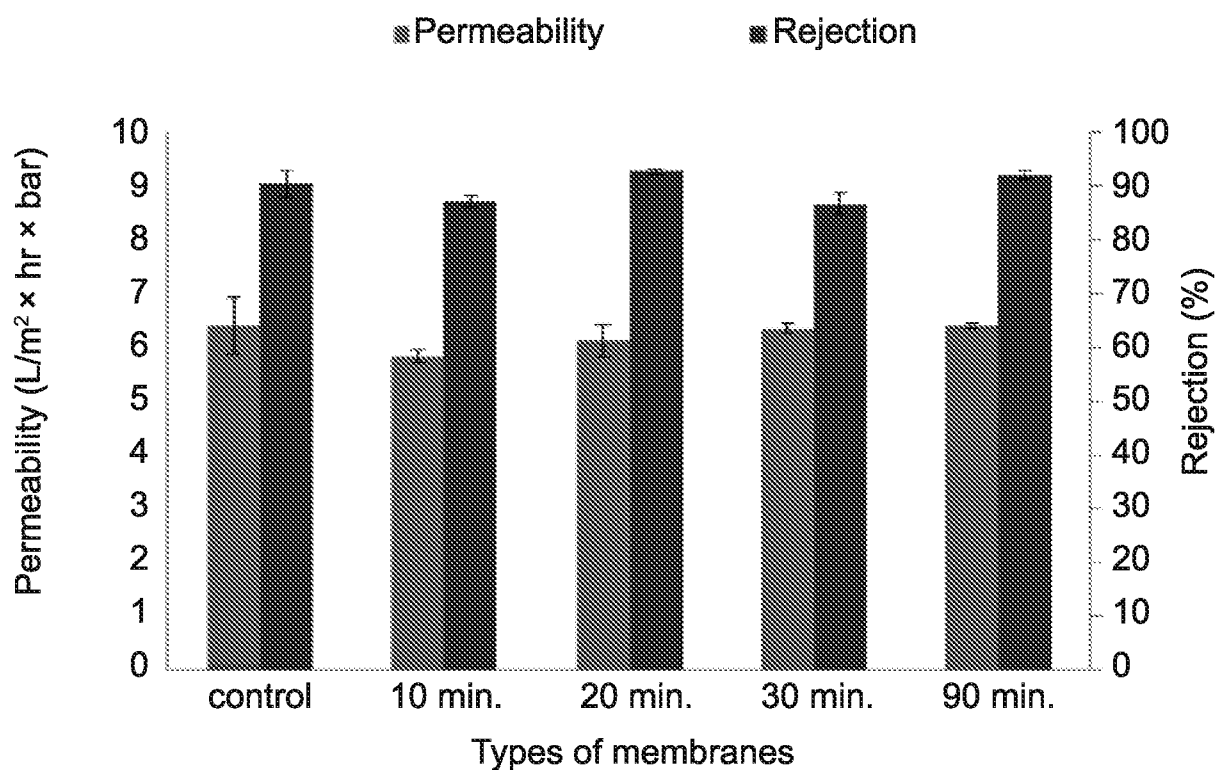


Fig. 15



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Fig. 16

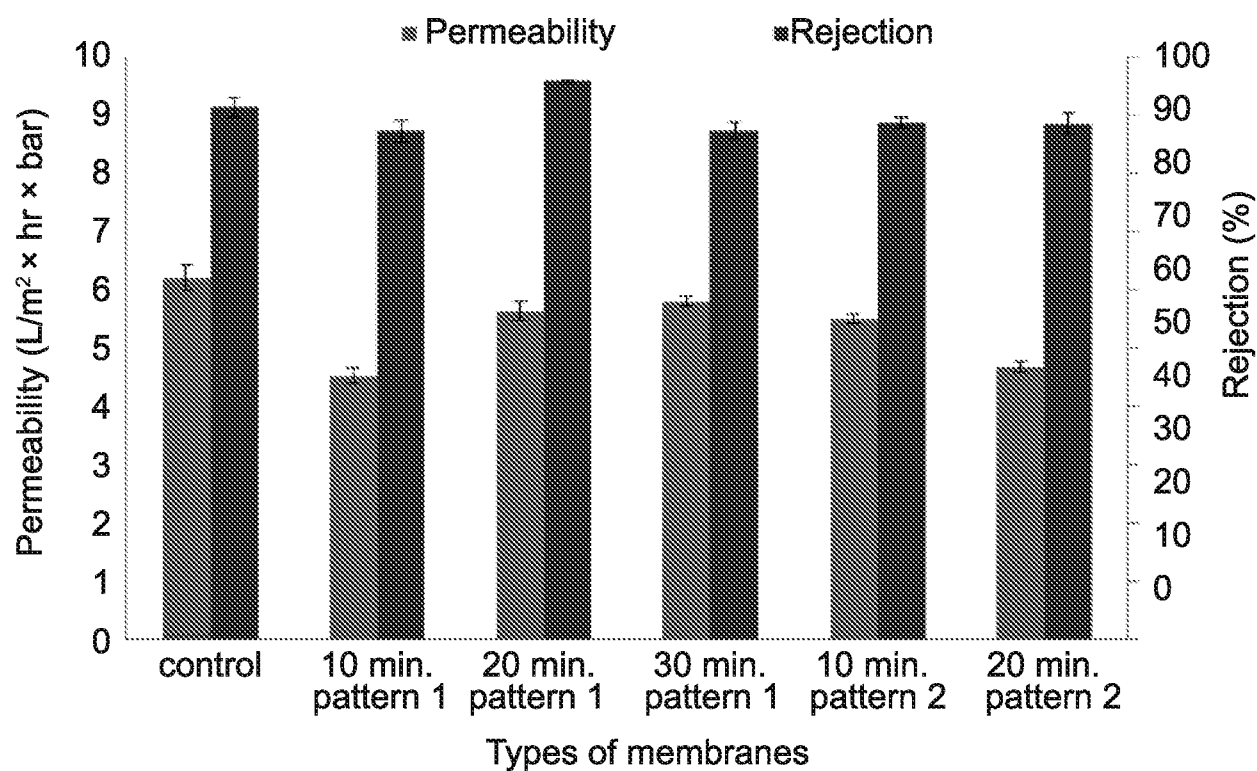
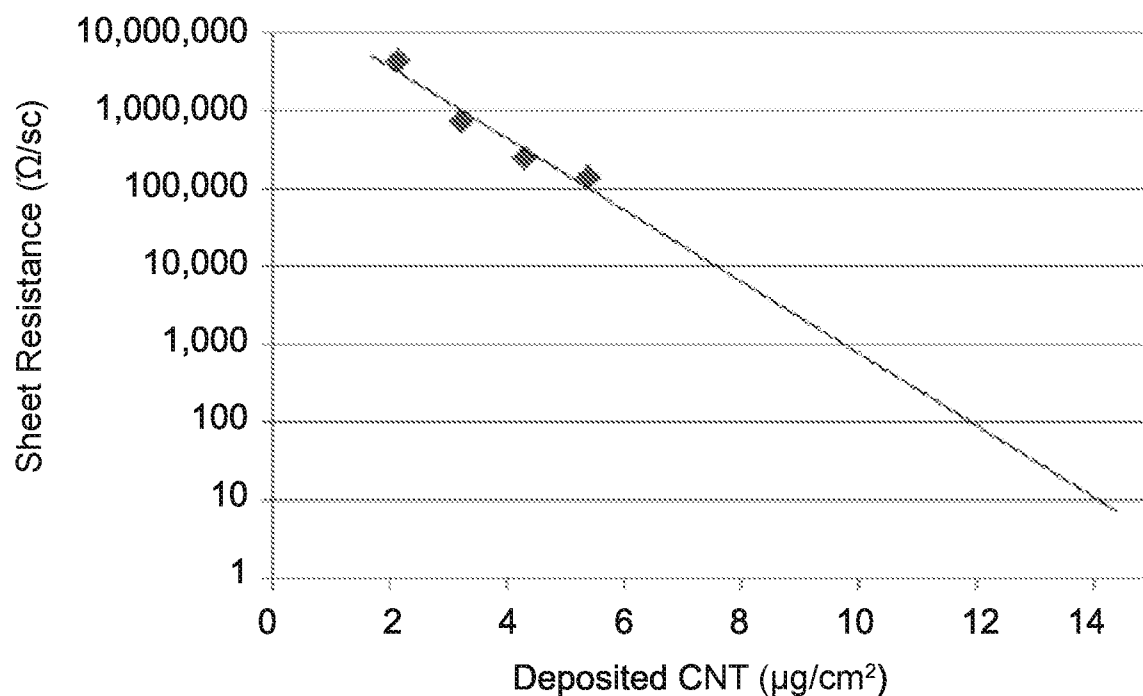


Fig. 17



INTERNATIONAL SEARCH REPORT

International application No.

PCT/IL2014/051029

A. CLASSIFICATION OF SUBJECT MATTER See extra sheet. 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 (2015.01) B01D, B05D, B41J, B41M Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) Databases consulted: THOMSON INNOVATION, Esp@cenet, Google Patents		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009139650 A1 (GENERAL ELECTRIC COMPANY) 04 Jun 2009 (2009/06/04) The whole document	1-30
Y		31-33
X	US 8313560 B1 (COTE A. P. et al) 20 Nov 2012 (2012/11/20) The whole document	31-33
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Y	WO 2013155453 A1 (THE REGENTS OF THE UNIVERSITY OF CALIFORNIA et al) 17 Oct 2013 (2013/10/17) The whole document	1-33
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Date of the actual completion of the international search 12 Mar 2015		Date of mailing of the international search report 15 Mar 2015
Name and mailing address of the ISA: Israel Patent Office Technology Park, Bldg.5, Malcha, Jerusalem, 9695101, Israel Facsimile No. 972-2-5651616		Authorized officer ZAKHARIA Imad Telephone No. 972-2-5651686

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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Y	WO 0220142 A1 (MIOX CORPORATION et al) 14 Mar 2002 (2002/03/14) The whole document	I-33
A	US 8529997 B2 (HEUFT M. A. et al) 10 Sep 2013 (2013/09/10) The whole document	I-33

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A. CLASSIFICATION OF SUBJECT MATTER:

IPC (2015.01) B01D 67/00, B01D 69/12, B01D 71/56, B05D 1/26, B05D 1/42, B05D 3/10, B05D 5/04, B05D 7/04, B41J 2/01, B41M 1/30