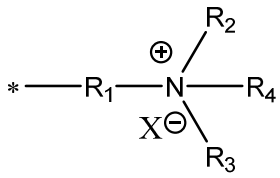
Claims

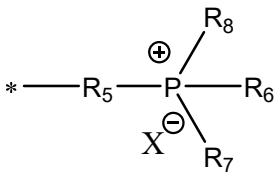
1. A positively charged acid- and alkali-resistant composite nanofiltration membrane, which is characterized in that, the positively charged acid- and alkali-resistant composite nanofiltration membrane sequentially comprises a bottom layer, a porous intermediate layer, and an acid- and alkali-resistant separation layer;

wherein, the acid- and alkali-resistant separation layer comprises:

(1) a quaternary ammonium salt group represented by Formula I and/or a quaternary phosphonium salt group represented by Formula II, which are grafted onto the acid- and alkali-resistant separation layer via a N atom;



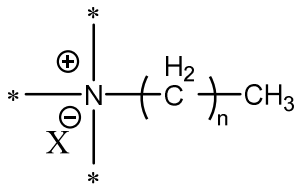
Formula I;



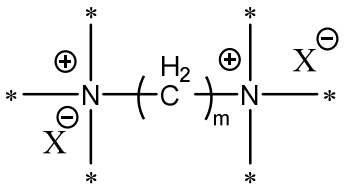
Formula II;

wherein, R_1 is a substituted or unsubstituted C1-C9 alkylene group or phenylene group; R_2, R_3, and R_4 are each independently selected from a C1-C3 alkyl group or phenyl group; R_5 is a C1-C6 alkylene group, phenylene group, or C7-C10 aralkylene group; R_6, R_7, and R_8 are each independently a phenyl group or C7-C10 aralkyl group; X is a halogen; or

(2) a quaternary ammonium salt structure, which comprises a structural formula represented by Formula III and/or a structural formula represented by Formula IV,



Formula III;



Formula IV;

X is a halogen; n is an integer ranging from 0 to 10; m is an integer ranging from 2 to 10;

wherein, the acid- and alkali-resistant separation layer is at least one

selected from a polyurea separation layer, a polytriazine amine separation layer, a polysulfonamide separation layer, a poly(triazine amine-urea) separation layer, a poly(sulfonamide-urea) separation layer, a poly(triazine amine-sulfonamide) separation layer, and a poly(triazine amine-sulfonamide-urea) separation layer.

2. The positively charged acid- and alkali-resistant composite nanofiltration membrane as claimed in claim 1, wherein, with regard to (1),

R_1 is a substituted or unsubstituted C1-C9 alkylene group or phenylene group, the substituent being a carboxyl, nitro, amino, silyl, carbonyl, ether or ester group; preferably, R_1 is an unsubstituted C1-C9 alkylene group or phenylene group; preferably, R_1 is an unsubstituted C1-C6 alkylene group or phenylene group; preferably, R_1 is an unsubstituted C1-C3 alkylene group; and/or

R_2, R_3, R_4 are each independently selected from a C1-C3 alkyl group; preferably, R_2, R_3, R_4 are each independently CH_3; and/or

R_5 is a C1-C3 alkylene group, phenylene group, or C8-C10 aralkylene group; preferably, R_5 is a C1-C3 alkylene group or C8-C10 aralkylene group; and/or

R_6, R_7, R_8 are each independently a phenyl group or C8-C10 aralkyl group; preferably, R_6, R_7, R_8 are each independently a phenyl group; and/or

X is Cl, Br or I; and/or

with regard to (2),

X is Cl, Br or I; and/or

n is an integer ranging from 0 to 7; and/or

m is an integer ranging from 2 to 8.

3. The positively charged acid- and alkali-resistant composite nanofiltration membrane as claimed in any one of claims 1-2, wherein, the acid- and alkali-resistant separation layer is at least one selected from a polyurea

separation layer, a polytriazine amine separation layer and a polysulfonamide separation layer.

4. The positively charged acid- and alkali-resistant composite nanofiltration membrane as claimed in any one of claims 1-3, wherein,

the content of nitrogen atoms in the quaternary ammonium salt group or quaternary ammonium salt structure of the positively charged acid- and alkali-resistant composite nanofiltration membrane is 0.5-20 at.%, preferably 2-15 at.%; and/or

the content of phosphorus atoms in the quaternary phosphonium salt group of the positively charged acid- and alkali-resistant composite nanofiltration membrane is 0.4-3 at.%, preferably 0.5-2 at.%; and/or

with regard to (1), the content of nitrogen atoms in the quaternary ammonium salt group of the positively charged acid- and alkali-resistant composite nanofiltration membrane is 10-20 at.%, or 10-15 at.%; or

with regard to (1), the content of nitrogen atoms in the quaternary ammonium salt group of the positively charged acid- and alkali-resistant composite nanofiltration membrane is 0.5-6 at.%, or 2-5 at.%; and/or

with regard to (2), the content of nitrogen atoms in the quaternary ammonium salt structure of the positively charged acid- and alkali-resistant composite nanofiltration membrane is 0.5-5 at.%, preferably 2-5 at.%.

5. The positively charged acid- and alkali-resistant composite nanofiltration membrane as claimed in any one of claims 1-4, wherein, the surface Zeta potential of the positively charged acid- and alkali-resistant composite nanofiltration membrane is 0-30 mV, preferably 5-25 mV, preferably 5-20 mV; and/or

the average pore size of the positively charged acid- and alkali-resistant composite nanofiltration membrane is 0.1-0.5 nm, preferably 0.1-0.4 nm,

preferably 0.15-0.3 nm, preferably 0.2-0.3 nm; and/or

the contact angle of the positively charged acid- and alkali-resistant composite nanofiltration membrane is 20-80°, preferably 30-80°, preferably 30-60°; and/or

the thickness of the bottom layer is 30-150 μm, preferably 50-120 μm; and/or

the thickness of the porous support layer is 10-100 μm, preferably 30-60 μm; and/or

the thickness of the acid- and alkali-resistant separation layer is 10-500 nm, preferably 50-300 nm.

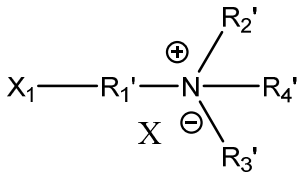
6. A method for preparing a positively charged acid- and alkali-resistant composite nanofiltration membrane, wherein the preparation method comprises the following steps:

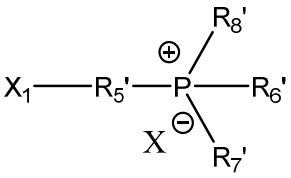
S1. under stirring conditions, adding a first solution containing a halogenated quaternary ammonium salt and/or a halogenated quaternary phosphonium salt, and a catalyst to a second solution containing a polyamine, and carrying out a reaction to obtain a modified polyamine;

S2. preparing a porous support layer on a bottom layer;

S3. bringing the surface of the porous support layer into a first contact with an aqueous phase containing the modified polyamine obtained in Step S1, and then a second contact with an organic phase containing a polyfunctional polar monomer, and performing heat treatment to obtain the positively charged acid- and alkali-resistant composite nanofiltration membrane;

the halogenated quaternary ammonium salt has a structure represented by Formula 1; the halogenated quaternary phosphonium salt has a structure represented by Formula 2;



Formula 1;


Formula 2;

wherein, R_1' is a substituted or unsubstituted C1-C9 alkylene group or phenylene group; R_2', R_3', R_4' are each independently selected from a C1-C3 alkyl group or phenyl group; R_5' is a C1-C6 alkylene group, phenylene group, or C7-C10 aralkylene group; R_6', R_7', R_8' are each independently a phenyl group or C7-C10 aralkyl group;

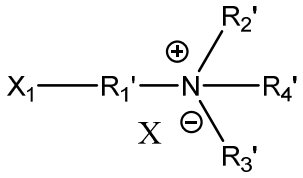
X and X_1 are each independently a halogen.

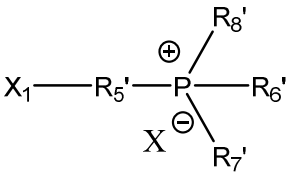
7. A method for preparing a positively charged acid- and alkali-resistant composite nanofiltration membrane, wherein the preparation method comprises the following steps:

S1': sequentially preparing a porous support layer and an acid- and alkali-resistant separation layer on a bottom layer to obtain a composite membrane;

S2': bringing the composite membrane into contact with an aqueous solution containing a catalyst, a halogenated quaternary ammonium salt and/or a halogenated quaternary phosphonium salt, and drying, to obtain the positively charged acid- and alkali-resistant composite nanofiltration membrane;

the halogenated quaternary ammonium salt has a structure represented by Formula 1; the halogenated quaternary phosphonium salt has a structure represented by Formula 2;



Formula 1;


Formula 2;

wherein, R_1' is a substituted or unsubstituted C1-C9 alkylene group or phenylene group; R_2', R_3', R_4' are each independently selected from a C1-C3

alkyl group or phenyl group; R_5' is a C1-C6 alkylene group, phenylene group, or C7-C10 aralkylene group; R_6', R_7', R_8' are each independently a phenyl group or C7-C10 aralkyl group;

X and X_1 are each independently a halogen.

8. The preparation method as claimed in claim 6 or 7, wherein,

R_1' is a substituted or unsubstituted C1-C9 alkylene group or phenylene group, the substituent being a hydroxy, carboxyl, nitro, amino, silyl, carbonyl, ether or ester group; preferably, R_1' is an unsubstituted C1-C9 alkylene group or phenylene group; preferably, R_1' is an unsubstituted C1-C6 alkylene group or phenylene group; preferably, R_1' is an unsubstituted C1-C3 alkylene group; and/or

R_2', R_3', R_4' are each independently selected from a C1-C3 alkyl group; preferably, R_2', R_3', R_4' are each independently CH_3; and/or

R_5' is a C1-C3 alkylene group, phenylene group, or C8-C10 aralkylene group; preferably, R_5' is a C1-C3 alkylene group or C8-C10 aralkylene group;

R_6', R_7', R_8' are each independently a phenyl group or C8-C10 aralkyl group; preferably, R_6', R_7', R_8' are each independently a phenyl group; and/or

X is Cl, Br or I; and/or

X_1 is F, Cl, Br or I; and/or

the halogenated quaternary ammonium salt is at least one selected from 2-chloroethyltrimethylammonium chloride, 2-chloroethyltriethylammonium chloride, 2-chloroethyltriphenylammonium chloride, 3-chloro-2-hydroxypropyltrimethylammonium chloride, 3-chloropropyltrimethylammonium chloride, 4-chlorobutyltrimethylammonium chloride, 5-chloropentyltrimethylammonium chloride, 6-chlorohexyltrimethylammonium chloride, 2-bromoethyltrimethylammonium bromide, 3-bromopropyltrimethylammonium bromide, 4-bromobutyltrimethylammonium bromide, 5-bromopentyltrimethylammonium

bromide, 6-bromohexyltrimethylammonium bromide, iodomethyltrimethylammonium iodide, 2-iodoethyltrimethylammonium iodide, 3-iodopropyltrimethylammonium iodide, 4-iodobutyltrimethylammonium iodide, 5-iodopentyltrimethylammonium iodide, and 6-iodohexyltrimethylammonium iodide; preferably 2-chloroethyltrimethylammonium chloride and/or 3-bromopropyltrimethylammonium bromide; and/or

the halogenated quaternary phosphonium salt is at least one selected from 3-bromopropyltriphenylphosphonium bromide, 2-bromoethyltriphenylphosphonium bromide, 1-bromoethyltriphenylphosphonium bromide, bromomethyltriphenylphosphonium bromide, 3-chloropropyltriphenylphosphonium chloride, 2-chloroethyltriphenylphosphonium chloride, 1-chloroethyltriphenylphosphonium chloride, chloromethyltriphenylphosphonium chloride, 3-iodopropyltriphenylphosphonium iodide, 2-iodoethyltriphenylphosphonium iodide, 1-iodoethyltriphenylphosphonium iodide, iodomethyltriphenylphosphonium bromide, 4-bromomethylbenzyltriphenylphosphonium bromide, 2-bromomethylbenzyltriphenylphosphonium bromide, 3-bromomethylbenzyltriphenylphosphonium bromide, 4-chloromethylbenzyltriphenylphosphonium chloride, 2-chloromethylbenzyltriphenylphosphonium chloride, 3-chloromethylbenzyltriphenylphosphonium chloride, 4-iodomethylbenzyltriphenylphosphonium iodide, 2-iodomethylbenzyltriphenylphosphonium iodide, and 3-iodomethylbenzyltriphenylphosphonium iodide; preferably 3-bromopropyltriphenylphosphonium bromide and/or 4-bromomethylbenzyltriphenylphosphonium bromide; and/or

the catalyst is at least one selected from sodium hydroxide, potassium hydroxide, potassium carbonate, sodium carbonate, sodium bicarbonate, potassium bicarbonate, disodium hydrogen phosphate, and dipotassium hydrogen phosphate; preferably potassium hydroxide.

9. The preparation method as claimed in claim 7, wherein, step S1' includes:

S1-1': preparing a porous support layer on the bottom layer; and

S1-2': first bringing the surface of the porous support layer into a first contact with an aqueous phase containing the polyamine, and then a second contact with an organic phase containing the polyfunctional polar monomer, and performing heat treatment to obtaining the composite membrane and/or

in step S2',

the contact method is immersion; and/or

the contact time is 10 s-10 min, preferably 20 s-1 min; the contact temperature is 20-80°C, preferably 30-50°C; and/or

the drying time is 0.5-10 min, preferably 3-5 min; the drying temperature is 40-80°C, preferably 50-70°C; and/or

the concentration of the catalyst in the aqueous solution is 0.01 wt%-5 wt%, preferably 0.1 wt%-1 wt%; and/or

the concentration of the halogenated quaternary ammonium salt and/or halogenated quaternary phosphonium salt in the aqueous solution is 1 wt%-20 wt%, preferably 5 wt%-10 wt%.

10. The preparation method as claimed in any one of claims 6 and 9, wherein, the polyamine is at least one selected from polyethyleneimine, polyvinylamine, triethylenetetramine, tetraethylenepentamine, diethylenetriamine, polyethylenepolyamine, piperazine, m-phenylenediamine, and p-phenylenediamine; preferably polyethyleneimine and/or

polyethylenepolyamine; and/or

the polyfunctional polar monomer is at least one selected from polyisocyanate, a triazine compound containing at least two C-Cl bonds, and polysulfonyl chloride;

preferably, the polyisocyanate is at least one selected from m-xylylene diisocyanate, isophorone diisocyanate, 1,6-hexamethylene diisocyanate, toluene-2,6-diisocyanate, 1,4-phenylene diisocyanate, toluene-2,4-diisocyanate, 4,4'-methylene bis(phenyl isocyanate), 1,3-phenylene diisocyanate, 3,3'-dichloro-4,4'-biphenyl diisocyanate, dicyclohexylmethane-4,4'-diisocyanate, trimethylhexamethylene diisocyanate, L-lysine ethyl ester diisocyanate, 1,4-cyclohexyl diisocyanate, and 4-chloro-6-methyl-m-phenylene diisocyanate; preferably 1,4-phenylene diisocyanate and/or 1,3-phenylene diisocyanate;

preferably, the triazine compound containing at least two C-Cl bonds is at least one selected from cyanuric chloride, 2,4-dichloro-1,3,5-triazine, 2,5-dichloro-1,3,5-triazine, and 2,4-dichloro-6-phenyl-1,3,5-triazine; preferably cyanuric chloride;

preferably, the polysulfonyl chloride is at least one selected from 1,3-benzenedisulfonyl chloride, 1,2-benzenedisulfonyl chloride, 1,4-benzenedisulfonyl chloride, 2,4-disulfonyl chloride mesitylene, biphenyl-4,4'-disulfonyl chloride, 4,5-dichloro-1,3-benzenedisulfonyl chloride, 2,6-naphthalenedisulfonyl chloride, 1,3-naphthalenedisulfonyl chloride, 2,7-naphthalenedisulfonyl chloride, 1,3,5-benzenetrisulfonyl chloride, and 1,3,6-naphthalenetrisulfonyl chloride; preferably 1,3-benzenedisulfonyl chloride.

11. The preparation method as claimed in any one of claims 6-8 and 10, wherein, in step S1,

the concentration of the halogenated quaternary ammonium salt and/or halogenated quaternary phosphonium salt in the first solution is 0.5 wt%-20

wt%, preferably 1 wt%-10 wt%; and/or

the concentration of the catalyst in the first solution is 0.01 wt%-5 wt%, preferably 0.1 wt%-1 wt%; and/or

the concentration of the polyamine in the second solution is 1 wt%-20 wt%, preferably 5 wt%-10 wt%; and/or

the amounts of the first solution and the second solution are such that the mass ratio of the polyamine, the halogenated quaternary ammonium salt and/or halogenated quaternary phosphonium salt, and the catalyst is 1-1000:1-100:1, preferably 1-200:1-50:1; and/or

the reaction conditions include: a reaction temperature of 25-90°C, preferably 40-60°C; and a reaction time of 1-48 h, preferably 6-24 h; and/or

wherein, in step S3,

the concentration of the modified polyamine in the aqueous phase is 0.1 wt%-10 wt%, preferably 0.5 wt%-2.5 wt%; and/or

the concentration of the polyfunctional polar monomer in the organic phase is 0.01 wt%-2 wt%, preferably 0.05 wt%-1 wt%; and/or

the first contact time is 5-100 s, preferably 10-60 s; and/or

the second contact time is 10-200 s, preferably 20-120 s; and/or

the heat treatment conditions include: a heat treatment temperature of 40-150°C, preferably 50-120°C; and a heat treatment time of 0.5-10 min, preferably 1-5 min.

12. A method for preparing a positively charged acid- and alkali-resistant composite nanofiltration membrane, wherein the preparation method comprises the following steps:

S1": preparing a porous support layer on a bottom layer;

S2": sequentially bringing the membrane layer obtained in step S1" into a first contact with an aqueous phase of a polyamine containing a tertiary amine group, and a second contact with an organic phase containing a polyfunctional

polar monomer, and performing heat treatment to obtain a composite nanofiltration membrane including an acid- and alkali-resistant separation layer;

S3": bringing the composite nanofiltration membrane into a third contact with an organic solution containing a halogenated alkane and a catalyst, and drying to obtain the positively charged acid- and alkali-resistant composite nanofiltration membrane.

13. The preparation method as claimed in claim 12, wherein, in step S2", the polyamine containing the tertiary amine group is at least one selected from polyethyleneimine, polyethylenepolyamine, 1-aminopiperazine, 1,4-diaminopiperazine, 1,4-piperazinediethylamine, and 1,4-bis(aminopropyl)piperazine, preferably polyethyleneimine and/or polyethylenepolyamine; and/or

in the aqueous phase of the polyamine containing the tertiary amine group, the concentration of the polyamine containing the tertiary amine group is 0.1 wt%-10 wt%, preferably 0.5 wt%-2.5 wt%; and/or

the polyfunctional polar monomer is at least one selected from polyisocyanate, a triazine compound containing at least two C-Cl bonds, and polysulfonyl chloride;

preferably, the polyisocyanate is at least one selected from m-xylylene diisocyanate, isophorone diisocyanate, 1,6-hexamethylene diisocyanate, toluene-2,6-diisocyanate, 1,4-phenylene diisocyanate, toluene-2,4-diisocyanate, 4,4'-methylene bis(phenyl isocyanate), 1,3-phenylene diisocyanate, 3,3'-dichloro-4,4'-biphenyl diisocyanate, dicyclohexylmethane-4,4'-diisocyanate, trimethylhexamethylene diisocyanate, L-lysine ethyl ester diisocyanate, 1,4-cyclohexyl diisocyanate, and 4-chloro-6-methyl-m-phenylene diisocyanate; preferably 1,4-phenylene diisocyanate and/or 1,3-phenylene diisocyanate;

preferably, the triazine compound containing at least two C-Cl bonds is at least one selected from cyanuric chloride, 2,4-dichloro-1,3,5-triazine,

2,5-dichloro-1,3,5-triazine, and 2,4-dichloro-6-phenyl-1,3,5-triazine; preferably cyanuric chloride;

preferably, the polysulfonyl chloride is at least one selected from 1,3-benzenedisulfonyl chloride, 1,2-benzenedisulfonyl chloride, 1,4-benzenedisulfonyl chloride, 2,4-disulfonyl chloride mesitylene, biphenyl-4,4'-disulfonyl chloride, 4,5-dichloro-1,3-benzenedisulfonyl chloride, 2,6-naphthalenedisulfonyl chloride, 1,3-naphthalenedisulfonyl chloride, 2,7-naphthalenedisulfonyl chloride, 1,3,5-benzenetrisulfonyl chloride, and 1,3,6-naphthalenetrisulfonyl chloride; preferably 1,3-benzenedisulfonyl chloride; and/or

in the organic phase, the concentration of the polyfunctional polar monomer is 0.01 wt%-2 wt%, preferably 0.05 wt%-1 wt%; and/or

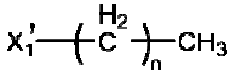
the amounts of the aqueous phase of the polyamine containing the tertiary amine group and the organic phase containing the polyfunctional polar monomer are such that the weight ratio of the polyamine containing the tertiary amine group to the polyfunctional polar monomer is 2-200:1, preferably 5-80:1; and/or

the first contact time is 5-100 s, preferably 10-60 s; and/or

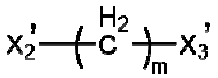
the second contact time is 10-200 s, preferably 20-120 s; and/or

the heat treatment conditions include: a heat treatment temperature of 40-150°C, preferably 50-120°C; and a heat treatment time of 0.5-10 min, preferably 1-5 min; and/or

in step S3", the halogenated alkane is selected from a halogenated alkane represented by Formula 3 and/or a halogenated alkane represented by Formula 4;



Formula 3,



Formula 4;

X_1', X_2' and X_3' are each independently a halogen; n is an integer ranging from 0 to 10; m is an integer ranging from 2 to 10;

preferably, X_1', X_2' and X_3' are each independently Cl, Br or I;

preferably, n is an integer ranging from 0 to 7; m is an integer ranging from 2 to 8;

preferably, the halogenated alkane is at least one selected from methyl iodide, ethyl iodide, propyl iodide, butyl iodide, pentyl iodide, hexyl iodide, heptyl iodide, octyl iodide, nonyl iodide, decyl iodide, cyclopropyl iodide, cyclobutyl iodide, cyclopentyl iodide, cycloheptyl iodide, cyclooctyl iodide, 1,2-diiodoethane, 1,3-diiodopropane, 1,4-diiodobutane, 1,5-diiodopentane, 1,6-diiodohexane, 1,7-diiodoheptane, 1,8-diiodooctane, methyl chloride, ethyl chloride, propyl chloride, butyl chloride, pentyl chloride, hexyl chloride, heptyl chloride, octyl chloride, nonyl chloride, decyl chloride, cyclopropyl chloride, cyclobutyl chloride, cyclopentyl chloride, cycloheptyl chloride, cyclooctyl chloride, 1,2-dichloroethane, 1,3-dichloropropane, 1,4-dichlorobutane, 1,5-dichloropentane, 1,6-dichlorohexane, 1,7-dichloroheptane, 1,8-dichlorooctane, methyl bromide, ethyl bromide, propyl bromide, butyl bromide, pentyl bromide, hexyl bromide, heptyl bromide, octyl bromide, nonyl bromide, decyl bromide, cyclopropyl bromide, cyclobutyl bromide, cyclopentyl bromide, cycloheptyl bromide, cyclooctyl bromide, 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane, 1,5-dibromopentane, 1,6-dibromohexane, 1,7-dibromoheptane and 1,8-dibromooctane, preferably at least one selected from ethyl bromide, propyl chloride and methyl iodide; and/or

the catalyst is at least one selected from sodium hydroxide, potassium hydroxide, potassium carbonate, sodium carbonate, sodium bicarbonate, potassium bicarbonate, potassium tert-butoxide and sodium tert-butoxide, preferably selected from sodium hydroxide and/or sodium tert-butoxide; and/or

the organic solution is an alcohol solvent; and/or

in step S3", in the organic solution, the concentration of the halogenated alkane is 1 wt%-20 wt%, preferably 5-10 wt%; and/or

in the organic solution, the concentration of the catalyst is 0.01 wt%-5 wt%, preferably 0.1 wt%-1 wt%; and/or

the weight ratio of the halogenated alkane to the catalyst is 2-50:1, preferably 5-30:1; and/or

the ratio of the volume of the organic solution to the membrane area of the composite nanofiltration membrane is 0.1-1 mL/cm^2, preferably 0.3-0.5 mL/cm^2; and/or

the conditions for the third contact include: a third contact time of 1-120 min, preferably 5-60 min; and/or

the drying conditions include: a drying temperature of 30-80°C, preferably 40-60°C; and a drying time of 0.5-5 min, preferably 1-3 min.

14. A positively charged acid- and alkali-resistant composite nanofiltration membrane prepared by the preparation method as claimed in any one of claims 6-13.

15. A use of the positively charged acid- and alkali-resistant composite nanofiltration membrane as claimed in any one of claims 1-5 and 14 in a field of water treatment.