solvents may include, but are not limited to, methanol, ethanol, *n*-propanol, isopropanol, n-butanol, isobutanol, acetone, acetonitrile, dioxane, tetrahydrofuran, tetrachloroethylene, *n*-propyl bromide, dimethylformamide, dimethyl sulfoxide and water. Other chemical agents may also be used alone or in conjunction with alkoxyalkylsilanes to perform similar tasks to render the surface hydrophobic and/or to generate nanoscopic topography.

[0039] In some embodiments, the alkoxyalkylsilane $[CH_3(CH_2)_a]_bSiR_c[alkoxy]_d$ is chemically converted from alkylsilane $[CH_3(CH_2)_a]_bSiR_cX_d$ by mixing and heating the alkylsilane in the correspondent solvent(s) (e.g. methanol, ethanol, isopropanol and water). The mixture of the thereof chemical agents is preferred to be stirred at elevated temperature equal to or between 50 to 100 °C for about 1 hour to 7 days in an acidic environment ($pH \leq 1$) and the solutions were neutralized with KOH (may contain up to 15% (w/w) of water) until the pH level is equal to or between 6 and 8. The hydrophobic solutions were used directly or further diluted in appropriate solvent(s) (e.g. methanol, ethanol, isopropanol, denatured ethanol, water, etc.).

[0040] Notably, the components of the composite coatings discussed herein, including the various additives, are fluorine-free and do not comprise any fluorine. The use of chemical compositions that are fluorine-free avoids the associated environmental and health risks of fluorine containing materials.

[0041] In some embodiments, the target surface of materials may be activated before the deposition of the organic/inorganic composite solution. The surface activation may be achieved by reaction with ozone, oxygen, hydrogen peroxide, halogens, other reactive oxidizing species, or combinations thereof. The purpose is to create an energetically reactive surface, increase the concentration of free radicals and to bind molecules on the surface covalently. In some embodiments, the surface activation may be achieved by ozone plasma generated by intense UV

CLAIMS

1. A fluorine-free method for treating a substrate for improved soil-resistance or stain-resistance, the method comprising:

selecting a substrate to be coated, wherein the substrate is a textile or flexible material;

preparing a composite solution that is fluorine-free, wherein the composite solution is prepared by mixing at least water, acid, first solvent, base chemical reagent, plasticizer and bonding agent,

wherein further the base chemical reagent is selected from an alkoxysilane, metal oxide precursor, or a combination thereof having a general formula of $M(OR)_4$, where M = Si, Al, Ti, In, Sn or Zr, and R comprises hydrogen, a substituted or unsubstituted alkyl,

the plasticizer is selected from an alkoxysilane, metal oxide precursor, or a combination thereof having a general formula of $M(OR)_{4-x}R'_x$ (M = Si, Al, In, Sn or Ti; x is the integer 1, 2 or 3), where R comprise hydrogen, a substituted or unsubstituted alkyl or derivatives thereof and R′ comprise a substituted or unsubstituted alkyl, a substituted or unsubstituted alkenyl, a substituted or unsubstituted alkynyl, a substituted or unsubstituted aryl or derivatives thereof, and

the bonding agent is selected from an alkoxysilane, metal oxide precursor, or a combination thereof having a general formula of $M(OR)_x\ R'_y\ R''_z$ (M = Si, Al, In, Sn or Ti; x is the integer 1, 2 or 3; y is the integer 0, 1 or 2; z is the integer 1, 2 or 3, provided that the sum of x, y and z equals 4), where R comprises hydrogen, a substituted or unsubstituted alkyl or derivatives thereof; R′ comprises hydrogen, a substituted or unsubstituted alkyl or derivatives thereof and R″ comprises a substituted or unsubstituted epoxy or glycidoxy;

utilizing the composite solution to coat the substrate;

drying or curing the substrate to allow a composite coating to form on the substrate; and

coating the substrate with a hydrophobic solution that is fluorine-free to provide a hydrophobic coating, wherein the hydrophobic solution comprises a hydrophobic chemical agent and a third solvent, and the composite coating and the hydrophobic coating formed on the substrate are both fluorine-free.

2. The method of claim 1, wherein the composite solution comprises 3-8 vol. % of the water, 20-30 vol. % of the first solvent, 40-60 vol. % of the base chemical reagent, 15-20 vol. % of the plasticizer, and 5-10 vol. % of the bonding agent; and

diluting the composite solution further with a second solvent to a final concentration equal to or between 5 to 60 vol. %.

3. The method of claim 1, wherein the composite solution is prepared under acidic condition where pH is equal to or less than 5.

4. The method of claim 1, wherein the preparation step further comprises stirring the composite solution at an elevated temperature in a range of 50-100 °C, and the stirring at the elevated temperature is performed for ½ hour to 12 hours.

5. The method of claim 1, wherein the composite coating formed on the substrate does not change the feel and texture of the substrate before coating.

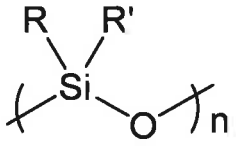
6. The method of claim 1, wherein a degree of polymerization of the composite solution is equal to or less than 100.

7. The method of claim 1, wherein the first solvent is selected from water, methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, ethylene glycol, glycerol acetone, acetonitrile, dioxane, tetrahydrofuran, dimethylformamide, dimethyl sulfoxide or a mixture thereof.

8. The method of claim 1, wherein the composite solution further comprises a chelating agent, wherein the chelating agent is selected from an alkoxysilane, metal oxide precursor, or a combination thereof having a general formula of $M(OR)_x R'_y R''_z$ (M = Si, Al, In, Sn or Ti; x is the integer 1, 2 or 3; y is the integer 0, 1 or 2; z is the integer 1, 2 or 3, provided that the sum of x, y and z equals 4), where R comprises hydrogen, a substituted or unsubstituted alkyl or derivatives thereof; R′ comprises hydrogen, a substituted or unsubstituted alkyl or derivatives thereof and R″ comprises a substituted or unsubstituted alky or alkenyl group comprising from 3 to 20 carbon atoms, or

the chelating agent is selected from an alkoxysilane, metal oxide precursor, or a combination thereof having a general formula of $M(OR)_x R'_y R''_z$ (M = Si, Al, In, Sn or Ti; x is the integer 1, 2 or 3; y is the integer 0, 1 or 2; z is the integer 1, 2 or 3, provided that the sum of x, y and z equals 4), where R comprises hydrogen, a substituted or unsubstituted alkyl or derivatives thereof; R′ comprises hydrogen, a substituted or unsubstituted alkyl or derivatives thereof and R″ comprises a substituted or unsubstituted amine (including primary, secondary and tertiary) or thiol.

9. The method of claim 1, wherein the composite solution further comprises a viscosity modifier selected from an alkylsiloxane in oligomer/co-oligomer form, polymer/co-polymer form, or a combination thereof having a general formula of



where R and R′ can be the same or different and comprise hydrogen, a substituted or unsubstituted alkyl or derivatives thereof.

10. The method of claim 1, wherein the composite solution further comprises a functional additive that provides UV absorbing or blocking, anti-reflective, anti-abrasion, fire-retardant, conducting, anti-microbial, anti-bacterial, anti-fungal, or pigmentation properties.

11. The method of claim 1, wherein the hydrophobic chemical agent is an alkylsilane $[CH_3(CH_2)_a]_bSiR_cX_d$; where X comprise Cl, Br, I or other suitable organic leaving groups, R comprise a substituted or unsubstituted alkyl, a substituted or unsubstituted alkenyl, a substituted or unsubstituted alkynyl, a substituted or unsubstituted aryl or derivatives thereof, and a is the integer 0, 1, 2, 3… to 20, b is the integer 1, 2 or 3, c is the integer 0, 1, 2, 3 and d is the integer 1, 2 or 3, provided that the sum of b, c and d equals 4, or

the hydrophobic chemical agent is an alkoxyalkylsilane $[CH_3(CH_2)_a]_bSiR_c[alkoxy]_d$; where [alkoxy] comprise methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, or a combination thereof; R comprise a substituted or unsubstituted alkyl, a substituted or unsubstituted alkenyl, a substituted or unsubstituted alkynyl, a substituted or unsubstituted aryl

or derivatives thereof, and a is the integer 0, 1, 2, 3... to 20, b is the integer 1, 2 or 3, c is the integer 0, 1, 2, 3 and d is the integer 1, 2 or 3, provided that the sum of b, c and d equals 4.

12. The method of claim 1, wherein the third solvent is selected from toluene, benzene, xylene, trichloroethylene, 1,2-dichloroethane, dichloromethane, chloroform, carbon tetrachloride, tetrachloroethylene, *n*-propyl bromide, diethyl ether, acetone, diisopropyl ether, methyl-*t*-butyl ether, petroleum ethers or petroleum hydrocarbons, or

the third solvent is selected from methanol, ethanol, *n*-propanol, isopropanol, n-butanol, isobutanol, acetone, acetonitrile, dioxane, tetrahydrofuran, tetrachloroethylene, dimethylformamide, dimethyl sulfoxide, or water.

13. The method of claim 11, wherein the alkylsilane is selected from chlorosilane, dichlorosilane, trichlorosilane, chlorotrimethylsilane, dichlorodimethylsilane, trichloromethylsilane, chlorophenylsilane, dichlorophenylsilane, trichlorophenylsilane, chloromethylphenylsilane, chlorodimethylphenylsilane, dichloromethylphenylsilane, chlorodimethylphenethylsilane, dichloromethylphenethylsilane, trichlorophenethylsilane, chlorodimethyloctylsilane, dichloromethyloctylsilane trichlorooctylsilane, chlorodimethyldodecylsilane, dichloromethyldodecylsilane, trichlorododecylsilane, chlorodecyldimethylsilane, dichlorodecylmethylsilane, trichlorodecylsilane, chlorodimethyloctadecylsilane, dichloromethyloctadecylsilane, trichlorooctadecylsilane, chlorodimethylthexylsilane, dichloromethylthexylsilane, trichlorothexylsilane, allyldichloromethylsilane, allylchlorodimethylsilane, allyltrichlorosilane,

(cyclohexylmethyl)chlorodimethylsilane, (cyclohexylmethyl)dichloromethylsilane, or (cyclohexylmethyl)trichlorosilane; or

the alkoxyalkylsilane is selected from trimethoxyisobutylsilane, triethoxyisobutylsilane, dimethoxydiisobutylsilane, diethoxydiisobutylsilane, trimethoxyphenylsilane, triethoxyphenylsilane, dimethoxydiphenylsilane, diethoxydiphenylsilane, dimethoxymethylphenylsilane, diethoxymethylphenylsilane, methoxydimethylphenylsilane, ethoxydimethylphenylsilane, trimethoxy(hexyl)silane, triethoxy(hexyl)silane, tripropoxy(hexyl)silane, triisopropoxy(hexyl)silane, trimethoxy(octyl)silane, triethoxy(octyl)silane, tripropoxy(octyl)silane, triisopropoxy(octyl)silane, trimethoxy(decyl)silane, triethoxy(decyl)silane, tripropoxy(decyl)silane, triisopropoxy(decyl)silane, trimethoxy(dodecyl)silane, triethoxy(dodecyl)silane, tripropoxy(dodecyl)silane, or triisopropoxy(dodecyl)silane.

14. The method of claim 11, wherein the hydrophobic chemical agent is prepared by mixing and heating the hydrophobic chemical agent and the third solvent, the mixing and heating of the hydrophobic chemical agent and the third solvent occurs in an acidic environment with pH equal to or less than 1, the mixing and heating of the hydrophobic chemical agent and the third solvent occurs at an elevated temperature equal to or between 50 to 100 °C, and the mixing and heating the hydrophobic chemical agent and the third solvent occurs for equal to or between 1 hour to 7 days.

15. A two stage fluorine-free solution for a substrate to improve soil-resistance or stain-resistance, the two stage solution comprising:

a first stage solution that is fluorine-free, the first stage solution comprises

water,

an acid,

a first solvent,

a base chemical reagent, wherein the base chemical reagent is selected from an alkoxysilane, metal oxide precursor, or a combination thereof having a general formula of $M(OR)_4$, where M = Si, Al, Ti, In, Sn or Zr, and R comprises hydrogen, a substituted or unsubstituted alkyl,

a plasticizer, wherein the plasticizer is selected from an alkoxysilane, metal oxide precursor, or a combination thereof having a general formula of $M(OR)_{4-x}R'_x$ (M = Si, Al, In, Sn or Ti; x is the integer 1, 2 or 3), where R comprise hydrogen, a substituted or unsubstituted alkyl or derivatives thereof and R′ comprise a substituted or unsubstituted alkyl, a substituted or unsubstituted alkenyl, a substituted or unsubstituted alkynyl, a substituted or unsubstituted aryl or derivatives thereof, and

a bonding agent, wherein the bonding agent is selected from an alkoxysilane, metal oxide precursor, or a combination thereof having a general formula of $M(OR)_x R'_y R''_z$ (M = Si, Al, In, Sn or Ti; x is the integer 1, 2 or 3; y is the integer 0, 1 or 2; z is the integer 1, 2 or 3, provided that the sum of x, y and z equals 4), where R comprises hydrogen, a substituted or unsubstituted alkyl or derivatives thereof; R′ comprises hydrogen, a substituted or unsubstituted alkyl or derivatives thereof and R″ comprises

a substituted or unsubstituted epoxy or glycidoxy, and the composite solution is utilized to coat a substrate; and

a hydrophobic solution that is fluorine-free, the hydrophobic solution comprises

a hydrophobic chemical agent, and

a second solvent, wherein the hydrophobic solution is deposited on the substrate after the first stage solution.

16. The two stage solution of claim 15, wherein the first stage solution comprises 3-8 vol. % of the water, 20-30 vol. % of the first solvent, 40-60 vol. % of the base chemical reagent, 15-20 vol. % of the plasticizer, and 5-10 vol. % of the bonding agent, and the first stage solution is further diluted with a third solvent to a final concentration of equal to or between 5 to 60 vol. %.

17. The two stage solution of claim 15, wherein the first stage solution is stirred at an elevated temperature for ½ hour to 12 hours, and the first stage solution is prepared while stirring at the elevated temperature in a range of 50-100 °C.

18. The two stage solution of claim 15, wherein the composite solution is prepared under acidic condition where pH is equal to or less than 5.

19. The two stage solution of claim 15, wherein a coating formed with the two stage solution does not change the feel and texture of the substrate before coating.

20. The two stage solution of claim 15, wherein a degree of polymerization of the composite solution is equal to or less than 100.

21. The two stage solution of claim 15, wherein the first solvent is selected from water, methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, ethylene glycol, glycerol acetone, acetonitrile, dioxane, tetrahydrofuran, dimethylformamide, dimethyl sulfoxide or a mixture thereof.

22. The two stage solution of claim 15, wherein the composite solution further comprises a chelating agent, wherein the chelating agent is selected from an alkoxysilane, metal oxide precursor, or a combination thereof having a general formula of $M(OR)_x R'_y R''_z$ (M = Si, Al, In, Sn or Ti; x is the integer 1, 2 or 3; y is the integer 0, 1 or 2; z is the integer 1, 2 or 3, provided that the sum of x, y and z equals 4), where R comprises hydrogen, a substituted or unsubstituted alkyl or derivatives thereof; R′ comprises hydrogen, a substituted or unsubstituted alkyl or derivatives thereof and R″ comprises a substituted or unsubstituted alky or alkenyl group comprising from 3 to 20 carbon atoms, or

the chelating agent is selected from an alkoxysilane, metal oxide precursor, or a combination thereof having a general formula of $M(OR)_x R'_y R''_z$ (M = Si, Al, In, Sn or Ti; x is the integer 1, 2 or 3; y is the integer 0, 1 or 2; z is the integer 1, 2 or 3, provided that the sum of x, y and z equals 4), where R comprises hydrogen, a substituted or unsubstituted alkyl or derivatives thereof; R′ comprises hydrogen, a substituted or unsubstituted alkyl or derivatives thereof and R″ comprises a substituted or unsubstituted amine (including primary, secondary and tertiary) or thiol.

23. The two stage solution of claim 15, wherein the hydrophobic chemical agent is prepared by mixing and heating the hydrophobic chemical agent and the second solvent, the mixing and heating of the hydrophobic chemical agent and the second solvent occurs in an acidic environment with pH equal to or less than 1, the mixing and heating of the hydrophobic chemical agent and the second solvent occurs at an elevated temperature equal to or between 50 to 100 °C, and the mixing and heating of the hydrophobic chemical agent and the second solvent occurs for equal to or between 1 hour to 7 days.

24. The two stage solution of claim 15, wherein the hydrophobic chemical agent is an alkylsilane $[CH_3(CH_2)_a]_bSiR_cX_d$; where X comprise Cl, Br, I or other suitable organic leaving groups, R comprise a substituted or unsubstituted alkyl, a substituted or unsubstituted alkenyl, a substituted or unsubstituted alkynyl, a substituted or unsubstituted aryl or derivatives thereof, and a is the integer 0, 1, 2, 3... to 20, b is the integer 1, 2 or 3, c is the integer 0, 1, 2, 3 and d is the integer 1, 2 or 3, provided that the sum of b, c and d equals 4; or

the hydrophobic chemical agent is an alkoxyalkylsilane $[CH_3(CH_2)_a]_bSiR_c[alkoxy]_d$; where [alkoxy] comprise methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, or a combination thereof; R comprise a substituted or unsubstituted alkyl, a substituted or unsubstituted alkenyl, a substituted or unsubstituted alkynyl, a substituted or unsubstituted aryl or derivatives thereof, and a is the integer 0, 1, 2, 3... to 20, b is the integer 1, 2 or 3, c is the integer 0, 1, 2, 3 and d is the integer 1, 2 or 3, provided that the sum of b, c and d equals 4.

25. The two stage solution of claim 24, wherein the alkylsilane is selected from chlorosilane, dichlorosilane, trichlorosilane, chlorotrimethylsilane, dichlorodimethylsilane, trichloromethylsilane, chlorophenylsilane, dichlorophenylsilane, trichlorophenylsilane, chloromethylphenylsilane, chlorodimethylphenylsilane, dichloromethylphenylsilane, chlorodimethylphenethylsilane, dichloromethylphenethylsilane, trichlorophenethylsilane, chlorodimethyloctylsilane, dichloromethyloctylsilane trichlorooctylsilane, chlorodimethyldodecylsilane, dichloromethyldodecylsilane, trichlorododecylsilane, chlorodecyldimethylsilane, dichlorodecylmethylsilane, trichlorodecylsilane, chlorodimethyloctadecylsilane, dichloromethyloctadecylsilane, trichlorooctadecylsilane, chlorodimethylthexylsilane, dichloromethylthexylsilane, trichlorothexylsilane, allyldichloromethylsilane, allylchlorodimethylsilane, allyltrichlorosilane, (cyclohexylmethyl)chlorodimethylsilane, (cyclohexylmethyl)dichloromethylsilane, or (cyclohexylmethyl)trichlorosilane; and

the alkoxyalkylsilane is selected from trimethoxyisobutylsilane, triethoxyisobutylsilane, dimethoxydiisobutylsilane, diethoxydiisobutylsilane, trimethoxyphenylsilane, triethoxyphenylsilane, dimethoxydiphenylsilane, diethoxydiphenylsilane, dimethoxymethylphenylsilane, diethoxymethylphenylsilane, methoxydimethylphenylsilane, ethoxydimethylphenylsilane, trimethoxy(hexyl)silane, triethoxy(hexyl)silane, tripropoxy(hexyl)silane, triisopropoxy(hexyl)silane, trimethoxy(octyl)silane, triethoxy(octyl)silane, tripropoxy(octyl)silane, triisopropoxy(octyl)silane, trimethoxy(decyl)silane, triethoxy(decyl)silane, tripropoxy(decyl)silane, triisopropoxy(decyl)silane, trimethoxy(dodecyl)silane, triethoxy(dodecyl)silane, tripropoxy(dodecyl)silane, or triisopropoxy(dodecyl)silane.