

CLAIMS

What is claimed is:

1. A self-limiting electrospray composition comprising a non-charge-dissipative component and a charge-dissipative component,

wherein the non-charge-dissipative component is non-volatile under electrospray deposition conditions, and

wherein the charge-dissipative component is non-volatile under electrospray deposition conditions.
2. The self-limiting electrospray composition according to Claim 1, wherein the non-charge-dissipative component is selected from the group consisting of a non-charge-dissipative polymer, a non-charge-dissipative organosilicon compound, a non-charge-dissipative polysaccharide, a non-charge-dissipative polypeptide, a non-charge-dissipative collagen derivative, a non-charge-dissipative cellulose derivative, a non-charge-dissipative compound containing an epoxide functional group, a non-charge-dissipative urethane, and combinations thereof.
3. The self-limiting electrospray composition according to Claim 2, wherein the non-charge-dissipative component comprises the non-charge-dissipative polymer, and wherein the non-charge-dissipative polymer is selected from the group consisting of a poly(styrene), a poly(methyl methacrylate), a poly(vinyl pyrrolidone), a temperature responsive polymer, a poly(N,N-diethylacrylamide), a poly(N-vinylcaprolactam), a poly(vinyl alcohol), a poly(tetrafluoroethylene), a poly(acrylic acid), a poly(propylene oxide), a poly(dimethylamino ethyl methacrylate), a poly(N-(L)-(1-hydroxymethyl)propylmethacrylamide), a polyamide, a polyimide, a poly(oxazoline), a poly(propylene), and combinations thereof.

4. The self-limiting electrospray composition according to Claim 2, wherein non-charge-dissipative organosilicon compound is selected from the group consisting of a poly(silsesquioxane), an oligomeric silsesquioxane, and combinations thereof.
5. The self-limiting electrospray composition according to Claim 2, wherein non-charge-dissipative polysaccharide is selected from the group consisting of dextran, agarose, chitosan, and combinations thereof.
6. The self-limiting electrospray composition according to Claim 2, wherein non-charge-dissipative polypeptide is a poly(pentapeptide) of elastin.
7. The self-limiting electrospray composition according to Claim 2, wherein non-charge-dissipative collagen derivative is gelatin.
8. The self-limiting electrospray composition according to Claim 2, wherein non-charge-dissipative cellulose derivative is selected from the group consisting of methylcellulose, cellulose acetate, nitro cellulose, hydroxypropyl cellulose, and combinations thereof.
9. The self-limiting electrospray composition according to Claim 2, wherein non-charge-dissipative compound containing an epoxide functional group is selected from the group consisting of an epoxide, an epoxy, an oxirane, an ethoxyline, an epoxy-based resin, and combinations thereof.
10. The self-limiting electrospray composition according to Claim 2, wherein non-charge-dissipative urethane is selected from the group consisting of an ethyl carbamate, a polyurethane, a carbamate, and combinations thereof.
11. The self-limiting electrospray composition according to Claim 1, wherein the charge-dissipative component is selected from the group consisting of a charge-dissipative polymer, a charge-dissipative curing agent or photoinitiator, a charge-dissipative organic compound, a charge-dissipative ionic compound, a charge-dissipative chalcogenide glass, a charge-

dissipative oil, a charge-dissipative saccharide, a charge-dissipative surfactant, a charge-dissipative polymer, a charge-dissipative protein, a nucleic acid, and combinations thereof.

12. The self-limiting electrospray composition according to Claim 11, wherein the charge-dissipative polymer is selected from the group consisting of a poly(ethylene), a poly(ethylene oxide), a poly(isoprene), a poly(butadiene), a poly(vinyl methyl ether), a poly(dimethyl siloxane), a poly(ethylene glycol), a poly(propylene), a poly(propyleneglycol), a poly(caprolactone), an epoxy, and combinations thereof.

13. The self-limiting electrospray composition according to Claim 11, wherein the charge-dissipative curing agent or photoinitiator is selected from the group consisting of isopropylthioxanthone, benzoyl peroxide, a polyamide, and combinations thereof.

14. The self-limiting electrospray composition according to Claim 11, wherein the charge-dissipative organic compound is selected from the group consisting of terpineol, cinnamaldehyde, citric acid, 1-(2,5-dimethyl-4-(2,5-dimethylphenyl) phenyldiazenyl) azonaphthalen-2-ol, sodium bicarbonate, sodium chloride, potassium hydroxide, phenyl-C61-butyric acid methyl ester, a polymerizable monomer, and combinations thereof.

15. The self-limiting electrospray composition according to Claim 11, wherein the charge-dissipative ionic compound is selected from the group consisting of citric acid, 1-(2,5-dimethyl-4-(2,5-dimethylphenyl) phenyldiazenyl) azonaphthalen-2-ol, silver nitrate, calcium nitrate, calcium carbonate, sodium carbonate, gold hexachloroaurate, iron nitride, sodium chloride, potassium hydroxide, sodium bicarbonate, triphenylsulfonium salts, a metal organic framework, and combinations thereof.

16. The self-limiting electrospray composition according to Claim 11, wherein the charge-dissipative chalcogenide glass is selected from the group consisting of GeSbTe, AgInSbTe, InSe, SbSe, SbTe, InSbSe, InSbTe, GeSbSe, GeSbTeSe, AgInSbSeTe, and combinations thereof.

17. The self-limiting electrospray composition according to Claim 11, wherein the charge-dissipative oil is selected from the group consisting of a vegetable oil, a silicone oil, an epoxidized soybean oil, a hexadecane, a butyl glycidal ether, and combinations thereof.
18. The self-limiting electrospray composition according to Claim 11, wherein the charge-dissipative saccharide is selected from the group consisting of trehalose, sucrose, dextrose, fructose, glucose, and combinations thereof.
19. The self-limiting electrospray composition according to Claim 11, wherein the charge-dissipative surfactant is selected from the group consisting of lauryl mono-ethanol, abietic acid, and combinations thereof.
20. The self-limiting electrospray composition according to Claim 11, wherein the charge-dissipative polymer is selected from the group consisting of a poly(3,4-ethylenedioxythiophene), a poly(pyrrole), a poly(acetylene), a poly(ethylene oxide), a poly(3-hexylthiophene), and combinations thereof.
21. The self-limiting electrospray composition according to Claim 11, wherein the charge-dissipative protein is selected from the group consisting of lecithin, hemoglobin, a structural protein, a signaling protein, a regulatory protein, a transport protein, a sensory protein, a motor protein, a defense protein, a storage protein, an enzyme, and combinations thereof.
22. The self-limiting electrospray composition according to Claim 11, wherein the nucleic acid is selected from the group consisting of DNA, RNA, and combinations thereof.
23. The self-limiting electrospray composition according to Claim 1, wherein the self-limiting electrospray composition further comprises a solvent.
24. The self-limiting electrospray composition according to Claim 23, wherein the solvent is selected from the group consisting of water, alcohol, ethanol, isopropanol, 2-butanone, acetone, ethyl acetate, an alkane, a cycloalkane, an ether, benzene, xylene, toluene, dimethylformamide, dimethyl sulfoxide, chloroform, chlorobenzene, dichlorobenzene,

dichloroethane, trichlorobenzene, a chlorofluorocarbon, an ionic liquid, a fluorinated oil, N,N-dimethylformamide, tetrahydrofuran, methylene chloride, pyridine, cyclohexyl chloride, anisole, benzaldehyde, and combinations thereof.

25. The self-limiting electrospray composition according to Claim 24, wherein the ionic liquid is selected from the group consisting of dicyanamine, 1-alkyl-3-methylimidazolium, and combinations thereof.

26. The self-limiting electrospray composition according to Claim 1, wherein the self-limiting electrospray composition further comprises a plurality of filler particles.

27. The self-limiting electrospray composition according to Claim 26, wherein the plurality of filler particles is conductive.

28. The self-limiting electrospray composition according to Claim 26, wherein the self-limiting electrospray composition comprises from about 50 to about 90 percent by volume of the plurality of filler particles.

29. The self-limiting electrospray composition according to Claim 26, wherein the plurality of filler particles is selected from the group consisting of an inorganic compound, a carbon allotrope, a ceramic, a bacteria, a virus, a pollen, a cell, a protein, a polymer particle, a crystalline powder, a metal, and combinations thereof.

30. The self-limiting electrospray composition according to Claim 29, wherein the inorganic compound is selected from the group consisting of a MXene, zinc oxide, cadmium selenide, boron nitride, molybdenum disulfide, silver disulfide, titanium dioxide, hydroxyapatite, alumina, barium titanate, iron oxide, magnesium oxide, zinc oxide, silicon dioxide, a silica compound, a silica xerogel, a silicate, and combinations thereof.

31. The self-limiting electrospray composition according to Claim 29, wherein the carbon allotrope is selected from the group consisting of graphite, graphene, carbon nanotubes, activated carbon, carbon foam, and combinations thereof.

32. The self-limiting electrospray composition according to Claim 29, wherein the cell is selected from the group consisting of a human cell, an animal cell, a plant cell, and combinations thereof.
33. The self-limiting electrospray composition according to Claim 29, wherein the protein is selected from the group consisting of a protein powder, an antibody, an enzyme, a hormone, and combinations thereof.
34. The self-limiting electrospray composition according to Claim 29, wherein the polymer particle is selected from the group consisting of a polymer powder, polyethylene beads, polystyrene beads, a rubber, and combinations thereof.
35. The self-limiting electrospray composition according to Claim 29, wherein the crystalline powder is selected from the group consisting of sugar crystals, salt crystals, metal organic framework crystals, and combinations thereof.
36. The self-limiting electrospray composition according to Claim 29, wherein the metal is selected from the group consisting of aluminum, copper, gold, silver, iron, and combinations thereof.
37. A self-limiting electrospray composition comprising a plurality of charge-dissipative components and excluding a non-charge-dissipative component,
- wherein each of the plurality of charge-dissipative components is not capable of forming a layer of self-limiting thickness when electrosprayed without a component selected from the group consisting of at least one other member of the plurality of charge-dissipative components, the non-charge-dissipative component, and combinations thereof.
38. The self-limiting electrospray composition according to Claim 37, wherein each of the plurality of charge-dissipative components is selected from the group consisting of a charge-dissipative liquid, a charge-dissipative crystalline material, a charge-dissipative protein, a nucleic acid, a lyotropic material, and combinations thereof.

39. The self-limiting electrospray composition according to Claim 38, wherein the charge-dissipative liquid is selected from the group consisting of water, sulfuric acid, terpineol, a poly(ethylene), a poly(ethylene oxide), a poly(isoprene), a poly(butadiene), a poly(vinyl methyl ether), a poly(dimethyl siloxane), a poly(ethylene glycol), a poly(propylene), a poly(propyleneglycol), a poly(caprolactone), an epoxy, a surfactant, and combinations thereof.
40. The self-limiting electrospray composition according to Claim 38, wherein the charge-dissipative crystalline material is selected from the group consisting of citric acid, 1-(2,5-dimethyl-4-(2,5-dimethylphenyl) phenyldiazenyl) azonaphthalen-2-ol, silver nitrate, calcium nitrate, calcium carbonate, sodium carbonate, gold hexachloroaurate, iron nitride, sodium chloride, potassium hydroxide, sodium bicarbonate, triphenylsulfonium salts, a metal organic framework, trehalose, sucrose, dextrose, fructose, glucose, and combinations thereof.
41. The self-limiting electrospray composition according to Claim 38, wherein the charge-dissipative proteins selected from the group consisting of bovine serum albumin, lecithin, hemoglobin, structural protein, signaling protein, a regulatory protein, a transport protein, a sensory protein, a motor protein, a defense protein, a storage protein, an enzyme, and combinations thereof.
42. The self-limiting electrospray composition according to Claim 38, wherein the nucleic acid is selected from the group consisting of DNA, RNA, and combinations thereof.
43. The self-limiting electrospray composition according to Claim 38, wherein the lyotropic material is selected from the group consisting of phytantriol, DNA, a block copolymer, a synthetic aramid, and combinations thereof.
44. The self-limiting electrospray composition according to Claim 37, wherein the self-limiting electrospray composition further comprises a solvent.
45. The self-limiting electrospray composition according to Claim 44, wherein the solvent is selected from the group consisting of water, alcohol, ethanol, isopropanol, 2-

butanone, acetone, ethyl acetate, an alkane, a cycloalkane, an ether, benzene, xylene, toluene, dimethylformamide, dimethyl sulfoxide, chloroform, chlorobenzene, dichlorobenzene, dichloroethane, trichlorobenzene, a chlorofluorocarbon, an ionic liquid, a fluorinated oil, N,N-dimethylformamide, tetrahydrofuran, methylene chloride, pyridine, cyclohexyl chloride, anisole, benzaldehyde, and combinations thereof.

46. The self-limiting electrospray composition according to Claim 45, wherein the ionic liquid is selected from the group consisting of dicyanamine, 1-alkyl-3-methylimidazolium, and combinations thereof.

47. The self-limiting electrospray composition according to Claim 37, wherein the self-limiting electrospray composition further comprises a plurality of filler particles.

48. The self-limiting electrospray composition according to Claim 47, wherein the plurality of filler particles are conductive.

49. The self-limiting electrospray composition according to Claim 47, wherein the self-limiting electrospray composition comprises from about 50 to about 90 percent by volume of the plurality of filler particles.

50. The self-limiting electrospray composition according to Claim 47, wherein the plurality of filler particles are selected from the group consisting of an inorganic compound, a carbon allotrope, a ceramic, a bacteria, a virus, a pollen, a cell, a protein, a polymer particle, a crystalline powder, a metal, and combinations thereof.

51. The self-limiting electrospray composition according to Claim 50, wherein the inorganic compound is selected from the group consisting of a MXene, zinc oxide, cadmium selenide, boron nitride, molybdenum disulfide, silver disulfide, titanium dioxide, hydroxyapatite, alumina, barium titanate, iron oxide, magnesium oxide, zinc oxide, silicon dioxide, a silica compound, a silica xerogel, a silicate, and combinations thereof.

52. The self-limiting electrospray composition according to Claim 50, wherein the carbon allotrope is selected from the group consisting of graphite, graphene, carbon nanotubes, activated carbon, carbon foam, and combinations thereof.
53. The self-limiting electrospray composition according to Claim 50, wherein the cell is selected from the group consisting of a human cell, an animal cell, a plant cell, and combinations thereof.
54. The self-limiting electrospray composition according to Claim 50, wherein the protein is selected from the group consisting of a protein powder, an antibody, an enzyme, a hormone, and combinations thereof.
55. The self-limiting electrospray composition according to Claim 50, wherein the polymer particle is selected from the group consisting of a polymer powder, polyethylene beads, polystyrene beads, a rubber, and combinations thereof.
56. The self-limiting electrospray composition according to Claim 50, wherein the crystalline powder is selected from the group consisting of sugar crystals, salt crystals, metal organic framework crystals, and combinations thereof.
57. The self-limiting electrospray composition according to Claim 50, wherein the metal is selected from the group consisting of aluminum, copper, gold, silver, iron, and combinations thereof.
58. A method for forming a layer of self-limiting thickness, the method comprising:
exposing a target to a spray in the presence of an electric field, wherein the spray comprises a self-limiting electrospray composition; and
allowing the spray to accumulate on a surface of the target to form the layer of self-limiting thickness, wherein the self-limiting thickness is sufficient to allow the layer to hinder further accumulation of the spray on the conductive target.

59. The method according to Claim 58, wherein the target is conductive.
60. The method according to Claim 58, wherein the target is not conductive, and wherein the method further comprises rendering the target conductive by one selected from the group consisting of exposing the target to a conductive liquid, exposing the target to a conduction-inducing environment, and combinations thereof.
61. The method according to Claim 58, wherein the self-limiting thickness is less than 1 mm.
62. The method according to Claim 58, wherein the self-limiting electrospray composition comprises a non-charge-dissipative component and a charge-dissipative component.
63. The method according to Claim 62, wherein the charge-dissipative component alone is incapable of forming a layer of self-limiting thickness.
64. The method according to Claim 62, wherein the non-charge-dissipative component becomes immobilized on the surface of the conductive target.
65. The method according to Claim 64, wherein the non-charge-dissipative component becomes immobilized on the surface of the conductive target via a temperature transition.
66. The method according to Claim 64, wherein the non-charge-dissipative component becomes immobilized on the surface of the conductive target via a spinodal decomposition.
67. The method according to Claim 64, wherein the non-charge-dissipative component becomes immobilized on the surface of the conductive target via a polymerization.
68. The method according to Claim 58, wherein the self-limiting electrospray composition further comprises a solvent.
69. The method according to Claim 58, wherein the self-limiting electrospray composition further comprises a plurality of filler particles.

70. The method according to Claim 69, wherein the self-limiting electrospray composition further comprises a plurality of conductive filler particles, and wherein the method further comprises thermally densifying the layer of self-limiting thickness to at least partially remove the non-charge-dissipative component to form a continuous network of the conductive filler particles.

71. The method according to Claim 58, wherein the self-limiting electrospray composition comprises a plurality of charge-dissipative components and excludes a non-charge-dissipative component, and wherein each of the plurality of charge-dissipative components is not capable of forming a layer of self-limiting thickness when electrosprayed without a component selected from the group consisting of at least one other member of the plurality of charge-dissipative components, the non-charge-dissipative component, and combinations thereof.

72. A three-dimensional structure conformally-coated with a thin film, wherein the thin film comprises a self-limiting electrospray composition, and wherein the thin film conformally coats the three-dimensional structure such that a thickness of the thin film varies by less than 75% across a surface of the three-dimensional structure.

73. The three-dimensional structure according to Claim 72, wherein the thin film has a thickness of less than 1 mm.

74. The three-dimensional structure according to Claim 72, wherein the self-limiting electrospray composition comprises a non-charge-dissipative component and a charge-dissipative component.

75. The three-dimensional structure according to Claim 74, wherein the non-charge-dissipative component is a non-conductive polymer in the form of a plurality of elongated strands, wherein each of the plurality of elongated strands has at least one dimension less than 100 micrometers.

76. The three-dimensional structure according to Claim 74, wherein the non-charge-dissipative component is a non-conductive polymer in the form of a plurality of spheroidal particles comprising the non-conductive polymer, wherein each of the plurality of spheroidal particles has at least one dimension less than 100 micrometers.

77. The three-dimensional structure according to Claim 74, wherein the non-charge-dissipative component is at least partially densified, and wherein the thin film further comprises a continuous network of conductive filler particles that is at least partially exposed on a surface of the thin film.

78. The three-dimensional structure according to Claim 72, wherein the self-limiting electrospray composition comprises a plurality of charge-dissipative components and excludes a non-charge-dissipative component, and wherein each of the plurality of charge-dissipative components is not capable of forming a layer of self-limiting thickness when electrosprayed without a component selected from the group consisting of at least one other member of the plurality of charge-dissipative components, the non-charge-dissipative component, and combinations thereof.

79. The three-dimensional structure according to Claim 72, wherein the self-limiting electrospray composition further comprises a plurality of filler particles.

80. A method of thickness-limited, electrospray deposition comprising:

exposing an electrically conductive target to an incident spray comprising a thermo-responsive polymer solution, in the presence of an electric field,

wherein the electrically conductive target has a surface temperature,

wherein the thermo-responsive polymer solution comprises a non-conductive polymer,

wherein the thermo-responsive polymer solution has a solution temperature;

allowing the solution temperature to deviate toward the surface temperature to a deposited temperature at which the non-conductive polymer is immobile; and

allowing the non-conductive polymer to accumulate on the electrically conductive target to form a layer, having a thickness sufficient to repulse the incident spray.

81. The method according to Claim 80, wherein the layer has a spherical shell surface morphology.

82. The method according to Claim 81, wherein the spherical shell surface morphology comprises a plurality of spheroidal particles comprising the non-conductive polymer, wherein each of the plurality of spheroidal particles has at least one dimension less than 100 micrometers.

83. The method according to Claim 80, wherein allowing the solution temperature to deviate toward the surface temperature to the deposited temperature at which the non-conductive polymer is immobile prompts a spinodal decomposition of the thermo-responsive polymer solution.

84. The method according to Claim 83, wherein the layer has a nanowire surface morphology.

85. The method according to Claim 84, wherein the nanowire surface morphology comprises a plurality of elongated strands comprising the non-conductive polymer, wherein each of the plurality of elongated strands has at least one dimension less than 100 micrometers.

86. The method according to Claim 83, wherein the deposited temperature is greater than a lower critical solution temperature of the thermo-responsive polymer solution.

87. The method according to Claim 83, wherein the deposited temperature is less than an upper critical solution temperature of the thermo-responsive polymer solution.

88. The method according to Claim 80, wherein the thermo-responsive polymer solution further comprises a plurality of filler particles.

89. The method according to Claim 88, wherein the filler particles are conductive filler particles, and wherein the method further comprises thermally densifying the layer to at least partially remove the non-conductive polymer to form a continuous network of the conductive filler particles.

90. The method according to Claim 88, wherein the layer has a particle volume content of from about 50 to about 90 percent.

91. The method according to Claim 88, wherein each of the plurality of filler particles has at least one dimension less than 10 micrometers.

92. The method according to Claim 80, wherein non-conductive polymer is selected from the group consisting of poly(n-isopropylacrylamide) and methylcellulose.

93. The method according to Claim 80, wherein the thermo-responsive polymer solution further comprises water in an amount of from about 0.0001 to about 80 percent by weight.

94. A method for determining a conductivity of a material, the method comprising
exposing a material to a spray in the presence of an electric field, wherein the spray comprises a self-limiting electrospray composition;
allowing the spray to accumulate on a surface of the material to form the layer of self-limiting thickness, wherein the self-limiting thickness is sufficient to allow the layer to hinder further accumulation of the spray on the material;
measuring the self-limiting thickness of the layer; and
determining the conductivity of the material by comparing the self-limiting thickness to a thickness achieved by exposing a test material having a known conductivity to the spray in the presence of the electric field.

95. The method according to Claim 94, wherein the self-limiting electrospray composition comprises a charge-dissipative component and a non-charge-dissipative component.

96. The method according to Claim 94, wherein the self-limiting electrospray composition comprises a thermo-responsive polymer solution.

97. The method according to Claim 94, wherein the self-limiting electrospray composition comprises a plurality of charge-dissipative components and excludes a non-charge-dissipative component,

wherein each of the plurality of charge-dissipative components is not capable of forming a layer of self-limiting thickness when electrosprayed without a component selected from the group consisting of at least one other member of the plurality of charge-dissipative components, the non-charge-dissipative component, and combinations thereof.

98. A method for repairing a flaw in a layer on a surface of an object, the method comprising

applying a charge to the layer;

exposing the flaw to a spray in the presence of an electric field, wherein the spray comprises a self-limiting electrospray composition; and

allowing the spray to accumulate on the flaw to form a repair layer having a self-limiting thickness, wherein the self-limiting thickness is sufficient to hinder further accumulation of the spray on the repair layer.

99. The method according to Claim 98, wherein the self-limiting electrospray composition comprises a charge-dissipative component and a non-charge-dissipative component.

100. The method according to Claim 98, wherein the self-limiting electrospray composition comprises a thermo-responsive polymer solution.

101. The method according to Claim 98, wherein the self-limiting electrospray composition comprises a plurality of charge-dissipative components and excludes a non-charge-dissipative component,

wherein each of the plurality of charge-dissipative components is not capable of forming a layer of self-limiting thickness when electrosprayed without a component selected from the group consisting of at least one other member of the plurality of charge-dissipative components, the non-charge-dissipative component, and combinations thereof.

102. The method according to Claim 98, wherein the layer on the surface of the object is not conductive, and wherein the step of applying a charge to the layer comprises applying a solids-free spray to the layer.

103. The method according to Claim 98, wherein the layer on the surface of the object is conductive, and wherein the step of applying a charge to the layer comprises contacting the layer with a voltage source.

104. The method according to Claim 98, wherein the spray further comprises a charge-dissipative component, and optionally a plurality of filler particles.

105. A self-limiting electrospray composition comprising
a first charge-dissipative component selected from the group consisting of DNA, RNA, and combinations thereof,

an additional component selected from the group consisting of a second charge-dissipative component, a non-charge-dissipative component, and combinations thereof,

wherein the first charge-dissipative components is incapable of forming a layer of self-limiting thickness when electrosprayed without the additional component.