Claims

1. A composite material suitable for use in surface-enhanced Raman scattering, the material comprising:

a substrate layer having a surface;

a plurality of layers of core-shell particles formed on the surface of the substrate layer, wherein:

the core-shell particles comprise:

a core formed from a plasmonic metal nanoparticle; and

a shell formed from a metal-organic framework; and

the plurality of layers of core-shell particles provides a thickness of from 0.5 to 10 μm on the surface of the substrate layer.

2. The composite material according to Claim 1, wherein the plasmonic metal nanoparticles are selected from one or more of the group consisting of plasmonic gold nanoparticles, plasmonic silver nanoparticles, plasmonic platinum nanoparticles, and plasmonic palladium nanoparticles, optionally wherein the plasmonic metal nanoparticles are plasmonic silver nanoparticles.

~~3. The composite material according to Claim 2, wherein the plasmonic metal nanoparticles are plasmonic silver nanoparticles.~~

4~~3~~. The composite material according to ~~any one of the preceding claims~~Claim 1 or Claim 2, wherein the plasmonic metal nanoparticles are provided as one or more of the group selected from nanopolyhedra, nanospheres, nanowires, nanorods, nanobowls, and nanoplates, optionally wherein the plasmonic metal nanoparticles are nanoporous, optionally wherein, when the plasmonic metal nanoparticles are provided as nanopolyhedra, they have four or more faces, optionally wherein the nanopolyhedra are selected from one or more nanopolyhedra having from 5 to 30 faces, for example the nanopolyhedra are nanocubes or nanooctahedra.

~~5. The composite material according to Claim 4, wherein, when the plasmonic metal nanoparticles are provided as nanopolyhedra, they have four or more faces, optionally wherein the nanopolyhedra are selected from one or more nanopolyhedra having from 5 to 30 faces, for example the nanopolyhedra are nanocubes or nanooctahedra.~~

~~64~~. The composite material according to Claim ~~53~~, wherein the nanopolyhedra are provided as nanocubes.

~~75~~. The composite material according to any one of the preceding claims, wherein:

(aa) the metal organic framework is selected from one or more of the group consisting of UIO-66, ZIF-8, **kag**-MOF-1, MFM-300, HKUST-1, SIFSIX-1-Cu, and ZIF-71; and/or

(ab) the plurality of layers of core-shell particles provides a thickness of from 0.8 to 5 μm on the surface of the substrate layer or at least 1.3 μm on the surface of the substrate layer, optionally wherein the plurality of layers of core-shell particles provides a thickness of from 0.8 to 5 μm on the surface of the substrate layer or at least 1.3 μm on the surface of the substrate layer, further optionally wherein the plurality of layers of core-shell particles provides a thickness of from 1 to 2 μm on the surface of the substrate layer, yet further optionally wherein the plurality of layers of core-shell particles provides a thickness of about 1.3 μm on the surface of the substrate layer; and/or.

~~8. The composite material according to any one of the preceding claims, wherein the plurality of layers of core-shell particles provides a thickness of from 0.8 to 5 μm on the surface of the substrate layer or at least 1.3 μm on the surface of the substrate layer.~~

~~9. The composite material according to Claim 8, wherein the plurality of layers of core-shell particles provides a thickness of from 1 to 2 μm on the surface of the substrate layer.~~

~~10. The composite material according to Claim 9, wherein the plurality of layers of core-shell particles provides a thickness of about 1.3 μm on the surface of the substrate layer.~~

~~116~~. The composite material according to any one of the preceding claims, wherein the plurality of layers of core-shell particles provide from 5 to 30 layers of core-shell particles on the surface of the substrate layer, optionally wherein the plurality of layers of core-shell particles provide from 8 to 20 layers of core-shell particles on the surface of the substrate layer, further optionally wherein the plurality of layers of core-shell particles provide from 10 to 15 layers of core-shell particles on the surface of the substrate layer.

~~12. The composite material according to Claim 11, wherein the plurality of layers of core-shell particles provide from 8 to 20 layers of core-shell particles on the surface of the substrate layer.~~

~~13. The composite material according to Claim 12, wherein the plurality of layers of core-shell particles provide from 10 to 15 layers of core-shell particles on the surface of the substrate layer.~~

~~14~~7. The composite material according to any one of the preceding claims, wherein:

(a) the core-shell particles in the plurality of layers are packed with an interparticle distance of less than 10 nm, such as from 0.1 to 9.8 nm; and/or

(b) the core-shell particles have a size of from 100 nm to 1,000 nm, such as from 200 to 600 nm, such as from 300 to 500 nm; and/or

(c) the shell layer has a thickness of from 5 nm to 100 nm, such as from 10 to 80 nm; and/or

(d) a surface of the plasmonic metal nanoparticles is bonded to 4-methylbenzene thiol; and/or

(e) the substrate is a silicon substrate.

~~15~~8. The composite material according to any one of the preceding claims, wherein:

(ai) the plasmonic metal nanoparticles are silver nanocubes; and/or

(aii) the metal organic framework is selected from one of the group consisting of UIO-66, ZIF-8, **kag**-MOF-1, MFM-300, HKUST-1, SIFSIX-1-Cu, and ZIF-71; and/or

(aiii) the plurality of layers of core-shell particles provide a thickness of about 1.3 μm on the surface of the substrate layer; and/or

(aiv) the plurality of layers of core-shell particles provide from 10 to 15 layers of core-shell particles on the surface of the substrate layer.

~~16~~9. The composite material according to Claim ~~15~~8, wherein:

the plasmonic metal nanoparticles are silver nanocubes;

the metal organic framework is ZIF-8; and

the plurality of layers of core-shell particles are provided in from 10 to 15 layers and provide a thickness of about 1.3 μm, optionally wherein a surface of the silver nanocubes are bonded to 4-methylbenzene thiol.

~~17~~10. A method of forming a composite material according to any one of Claims 1 to ~~16~~9, which method comprises:

(ci) providing a substrate having a surface and a solution comprising a solvent and core-shell particles comprising:

a core formed from a plasmonic metal nanoparticle; and

a shell formed from a metal-organic framework; and

(cii) placing a portion of the solution onto the surface of the substrate and allowing the solvent to evaporate to provide the composite material.

~~18~~11. The method according to Claim ~~17~~10, wherein:

(ba) the solvent in the solution is an organic alcohol; and/or

(bb) the solvent in the solution is an organic alcohol that has three or more carbon atoms and is linear or branched, optionally wherein the organic alcohol is 1-propanol; and/or

(bc) the concentration of the core-shell particles is from 0.5 to 20 mg/mL and the substrate has a surface area of from 0.5 x 0.5 cm.

~~19. The method according to Claim 18, wherein the solvent in the solution is an organic alcohol that has three or more carbon atoms and is linear or branched, optionally wherein the organic alcohol is 1-propanol.~~

~~20. The method according to any one of Claims 17 to 19, wherein the concentration of the core-shell particles is from 0.5 to 20 mg/mL and the substrate has a surface area of from 0.5 x 0.5 cm.~~

~~21~~12. A composite material suitable for use in surface-enhanced Raman scattering, the material comprising:

a substrate layer having a surface;

a plurality of layers of plasmonic metal nanoparticles formed on the surface of the substrate layer, wherein:

the plurality of layers of plasmonic metal nanoparticles provide a thickness of from 0.3 to 10 μm on the surface of the substrate layer.

~~22~~13. The composite material according to Claim ~~21~~12, wherein the composite material further comprises a layer of a metal-organic framework, which is formed on a surface provided by the plurality of layers of plasmonic metal nanoparticles, optionally wherein the total thickness of the plurality of layers of plasmonic metal nanoparticles and the layer of a metal-organic framework is from 0.4 to 10 μm on the surface of the substrate layer.

~~23~~14. The composite material according to Claim ~~21~~ 12 or Claim ~~22~~13, wherein:

(ca) the plasmonic metal nanoparticles are selected from one or more of the group consisting of plasmonic gold nanoparticles, plasmonic silver nanoparticles, plasmonic platinum nanoparticles, and plasmonic palladium nanoparticles, optionally wherein the plasmonic metal nanoparticles are plasmonic silver nanoparticles; and/or

(cb) the plasmonic metal nanoparticles are provided as one or more of the group selected from nanopolyhedra, nanospheres, nanowires, nanorods, nanobowls, and nanoplates, optionally wherein the plasmonic metal nanoparticles are nanoporous, optionally wherein, when the plasmonic metal nanoparticles are provided as nanopolyhedra, they have four or more faces, optionally wherein the nanopolyhedra are selected from one or more nanopolyhedra having from 5 to 30 faces, for example the nanopolyhedra are nanocubes or nanooctahedra, further optionally wherein the nanopolyhedra are provided as nanocubes; and/or

(cc) the plurality of layers of plasmonic metal nanoparticles provide a thickness of from 0.4 to 1.5 μm, such as from 0.5 to 1 μm, on the surface of the substrate layer; and/or

(cd) the plurality of layers of plasmonic metal nanoparticles provide from 5 to 30 layers of plasmonic metal nanoparticles on the surface of the substrate layer, optionally wherein the plurality of layers of plasmonic metal nanoparticles provide from 8 to 20 layers of plasmonic metal nanoparticles on the surface of the substrate layer, further optionally wherein the plurality of layers of plasmonic metal nanoparticles provide from 10 to 15 layers of plasmonic metal nanoparticles on the surface of the substrate layer; and/or

(ce) the plasmonic metal nanoparticles have a size of from 100 nm to 1,000 nm, such as from 150 to 500 nm, such as from 170 to 250 nm; and/or

(cf) a surface of the plasmonic metal nanoparticles is bonded to 4-methylbenzene thiol; and/or

(cg) the substrate is a silicon substrate.

~~24. The composite material according to Claim 23, wherein the plasmonic metal nanoparticles are plasmonic silver nanoparticles.~~

~~25. The composite material according to any one of Claims 21 to 24, wherein the plasmonic metal nanoparticles are provided as one or more of the group selected from nanopolyhedra, nanospheres, nanowires, nanorods, nanobowls, and nanoplates, optionally wherein the plasmonic metal nanoparticles are nanoporous.~~

~~26. The composite material according to Claim 25, wherein, when the plasmonic metal nanoparticles are provided as nanopolyhedra, they have four or more faces, optionally wherein the nanopolyhedra are selected from one or more nanopolyhedra having from 5 to 30 faces, for example the nanopolyhedra are nanocubes or nanooctahedra.~~

~~27. The composite material according to Claim 26, wherein the nanopolyhedra are provided as nanocubes.~~

2815. The composite material according to any one of Claims 2213 and or Claims 23 to 2714 as dependent upon Claim 2213, wherein:

(da) the metal organic framework is selected from one or more of the group consisting of UIO-66, ZIF-8, **kag**-MOF-1, MFM-300, HKUST-1, SIFSIX-1-Cu, and ZIF-71; and/or

(db) the plurality of layers of plasmonic metal nanoparticles and the layer of a metal organic framework together provide a thickness of from 0.4 to 1.5 μm, such as from 0.5 to 1 μm on the surface of the substrate layer; and/or

(dc) the layer of a metal organic framework has a thickness of from 50 nm to 500 nm, such as from 100 to 300 nm, such as 200 nm; and/or

(dd) the layer of a metal organic framework has a thickness of from 50 nm to 500 nm, such as from 100 to 300 nm, such as 200 nm.

29. The composite material according to any one of Claims 21 to 28, wherein the plurality of layers of plasmonic metal nanoparticles provide a thickness of from 0.4 to 1.5 μm, such as from 0.5 to 1 μm, on the surface of the substrate layer.

30. The composite material according to any one of Claims 22 and Claims 23 to 29 as dependent upon Claim 22, wherein the plurality of layers of plasmonic metal nanoparticles and the layer of a metal organic framework together provide a thickness of from 0.4 to 1.5 μm, such as from 0.5 to 1 μm on the surface of the substrate layer.

31. The composite material according to any one of Claims 21 to 30, wherein the plurality of layers of plasmonic metal nanoparticles provide from 5 to 30 layers of plasmonic metal nanoparticles on the surface of the substrate layer.

32. The composite material according to Claim 31, wherein the plurality of layers of plasmonic metal nanoparticles provide from 8 to 20 layers of plasmonic metal nanoparticles on the surface of the substrate layer.

33. The composite material according to Claim 32, wherein the plurality of layers of plasmonic metal nanoparticles provide from 10 to 15 layers of plasmonic metal nanoparticles on the surface of the substrate layer.

34. The composite material according to any one of Claims 21 to 33, wherein:

(A) the plasmonic metal nanoparticles have a size of from 100 nm to 1,000 nm, such as from 150 to 500 nm, such as from 170 to 250 nm; and/or

(B) a surface of the plasmonic metal nanoparticles is bonded to 4-methylbenzene thiol; and/or

(C) the substrate is a silicon substrate.

35. The composite material according to any one of Claims 22 and Claims 23 to 34 as dependent upon Claim 22, wherein:

(AAi) the layer of a metal organic framework has a thickness of from 50 nm to 500 nm, such as from 100 to 300 nm, such as 200 nm; and/or

(AAii) the metal organic framework is selected from one of the group consisting of UIO-66, ZIF-8, **kag** MOF-1, MFM-300, HKUST-1, SIFSIX-1-Cu, and ZIF-71.

3616. The composite material according to any one of Claims 21 12 to 3515, wherein:

(di) the plasmonic metal nanoparticles are silver nanocubes; and/or

(dii) the plurality of layers of plasmonic metal nanoparticles provide from 10 to 15 layers of plasmonic metal nanoparticles on the surface of the substrate layer, optionally wherein:

the plasmonic metal nanoparticles are silver nanocubes;

the metal organic framework is ZIF-8;

the plurality of layers of silver nanocubes are provided in from 10 to 15 layers, optionally wherein a surface of the silver nanocubes are bonded to 4-methylbenzene thiol.

37. The composite material according to Claim 35 or Claim 36, wherein:

the plasmonic metal nanoparticles are silver nanocubes;

the metal organic framework is ZIF-8;

the plurality of layers of silver nanocubes are provided in from 10 to 15 layers, optionally wherein a surface of the silver nanocubes are bonded to 4-methylbenzene thiol.

3817. A kit of parts comprising:

(bi) a composite material as described in any one of one of Claims 1 to 16 9 or Claims 21 12 to 3716; and

(bii) an excitation and detection means or apparatus, optionally wherein the excitation and detection means or apparatus comprises a spectrophotometer, a laser and a lens; and/or

the kit further comprises a target housing for the composite material.

39. The kit of parts according to Claim 38, wherein:

the excitation and detection means or apparatus comprises a spectrophotometer, a laser and a lens; and/or

~~the kit further comprises a target housing for the composite material.~~

~~40~~18. A method of detecting one or more of a gas and a volatile organic chemical, the method comprising the steps of:

(i) placing a composite material as described in any one of Claims 1 to ~~16~~ 9 or Claims ~~21~~ 12 to ~~37~~ 16 at a target site for a period of time;

(ii) using an excitation and detection means or apparatus to provide an excitation signal to the composite material at the target site; and

(iii) detecting a surface-enhanced Raman scattering signal produced by the excitation signal in the composite material at the target site and determining whether the one or more of a gas and a volatile organic compound is present in the composite material, wherein

the detection means or apparatus is set at a distance of from 1 to 20 metres away from the composite material at the target site, optionally wherein:

(Ci) the detection means or apparatus is set at a distance of from 2 to 10 metres away from the composite material at the target site; and/or

(Cii) the composite material at the target site is placed within a target housing; and/or

(Ciii) the one or more of a gas and a volatile organic chemical is selected from one or more of CO, CO_2, H_2S, SO_x, and small volatile organic compounds selected from one or more of the group consisting of aromatic hydrocarbons, and aliphatic compounds having up to 10 carbon atoms in a linear chain, optionally wherein the one or more of a gas and a volatile organic chemical is selected from CO_2, H_2S, SO_2, and small volatile organic compounds selected from one or more of the group consisting of xylene, 4-methylbenzenethiol, toluene, and naphthalene (e.g. 4-methylbenzenethiol, toluene, and naphthalene); and/or

(Civ) the method of detection makes use of a composite material according to any one of Claims 1 to 9 or Claims 12 to 16.

~~41. The method of detecting one or more of a gas and a volatile organic chemical according to Claim 40, wherein:~~

~~(Ci) the detection means or apparatus is set at a distance of from 2 to 10 metres away from the composite material at the target site; and/or~~

~~(Cii) the composite material at the target site is placed within a target housing.~~

~~42. The method of detecting one or more of a gas and a volatile organic chemical according to Claim 40 or Claim 41, wherein the one or more of a gas and a volatile organic chemical is selected from one or more of CO, CO_2, H_2S, SO_x, and small volatile organic compounds selected from one or more of the group consisting of aromatic hydrocarbons, and aliphatic compounds having up to 10 carbon atoms in a linear chain.~~

~~43. The method of detecting one or more of a gas and a volatile organic chemical according to Claim 42, wherein the one or more of a gas and a volatile organic chemical is selected from CO_2, H_2S, SO_2, and small volatile organic compounds selected from one or more of the group consisting of xylene, 4-methylbenzenethiol, toluene, and naphthalene (e.g. 4-methylbenzenethiol, toluene, and naphthalene).~~

~~44. The method of detecting one or more of a gas and a volatile organic chemical according to any one of Claims 40 to 43, wherein the method of detection makes use of a composite material according to any one of Claims 1 to 16 or Claims 21 to 37.~~

~~45~~19. A method of forming a composite material according to any one of Claims ~~21~~ 12 and ~~23~~ 14 to ~~37~~ 16 as dependent upon Claim ~~21~~12, which method comprises:

(ei) providing a substrate having a surface and a solution comprising a solvent and plasmonic metal nanoparticles; and

(eii) placing a portion of the solution onto the surface of the substrate and allowing the solvent to evaporate to provide the composite material, optionally wherein the solvent in the solution is an organic alcohol, optionally wherein the solvent in the solution is an organic alcohol that has three or more carbon atoms and is linear or branched, optionally wherein the organic alcohol is 1-propanol.

~~46. The method according to Claim 45, wherein the solvent in the solution is an organic alcohol.~~

~~47. The method according to Claim 46, wherein the solvent in the solution is an organic alcohol that has three or more carbon atoms and is linear or branched, optionally wherein the organic alcohol is 1-propanol.~~

~~48~~20. A method of forming a composite material according to any one of Claims ~~22~~ 13 and ~~23~~ 14 to ~~37~~ 16 as dependent upon Claim ~~22~~13, which method comprises:

(fi) placing a substrate coated with a plurality of layers of plasmonic metal nanoparticles into a solution comprising a solvent, a metal organic framework metal salt precursor and a metal organic framework organic precursor compound to form an intermediate material;

(fii) removing the intermediate material from the solution, washing and drying it; and

(fii) repeating step (fi) and (fii) from 0 to 5 times with the intermediate material to form the composite material, optionally wherein:

(gi) the solvent in the solution is an organic alcohol, optionally wherein the second solvent is methanol; and/or

(gii) the substrate coated with a plurality of layers of plasmonic metal nanoparticles is obtained by the method described in Claim 19.

~~49. The method according to Claim 48, wherein the solvent in the solution is an organic alcohol, optionally wherein the second solvent is methanol.~~

~~50. The method according to Claim 48 or Claim 49, wherein the substrate coated with a plurality of layers of plasmonic metal nanoparticles is obtained by the method described in any one of Claims 45 to 47.~~