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(54) **ENHANCING PROPERTIES BY THE USE OF NANOPARTICLES**

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(57) **ABSTRACT**

Composite materials comprising nanoparticles functionalized with metals are disclosed. The composite materials may be used in a variety of applications, including in coating compositions, cosmetic and pharmaceutical compositions, absorbent articles, and the like.

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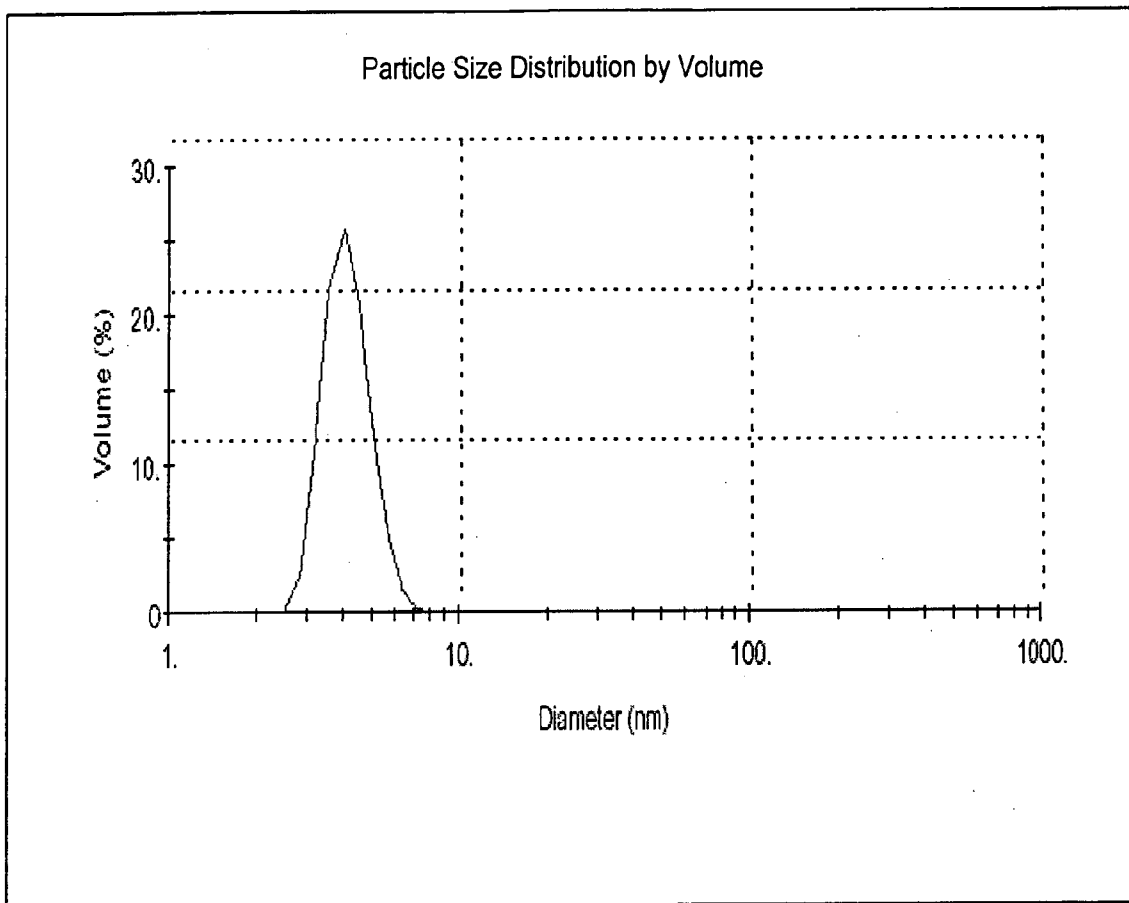


FIGURE 1

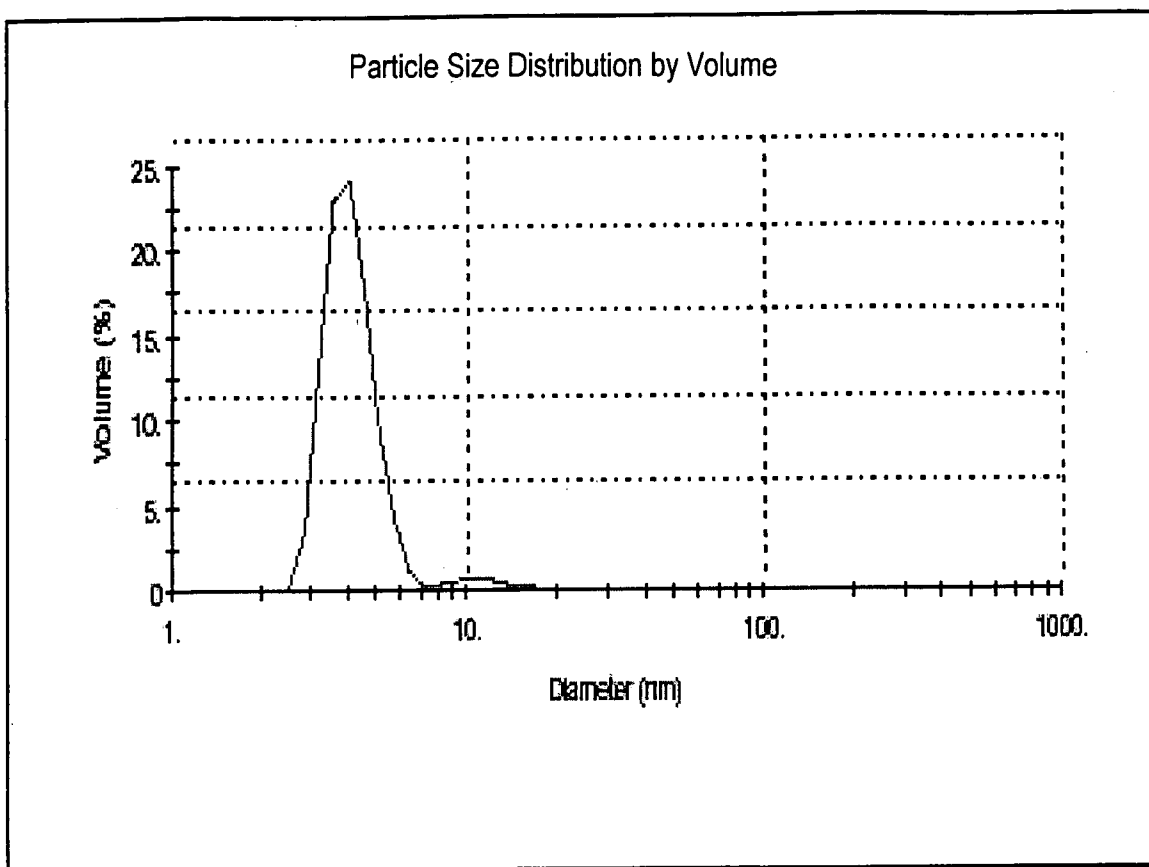


FIGURE 2

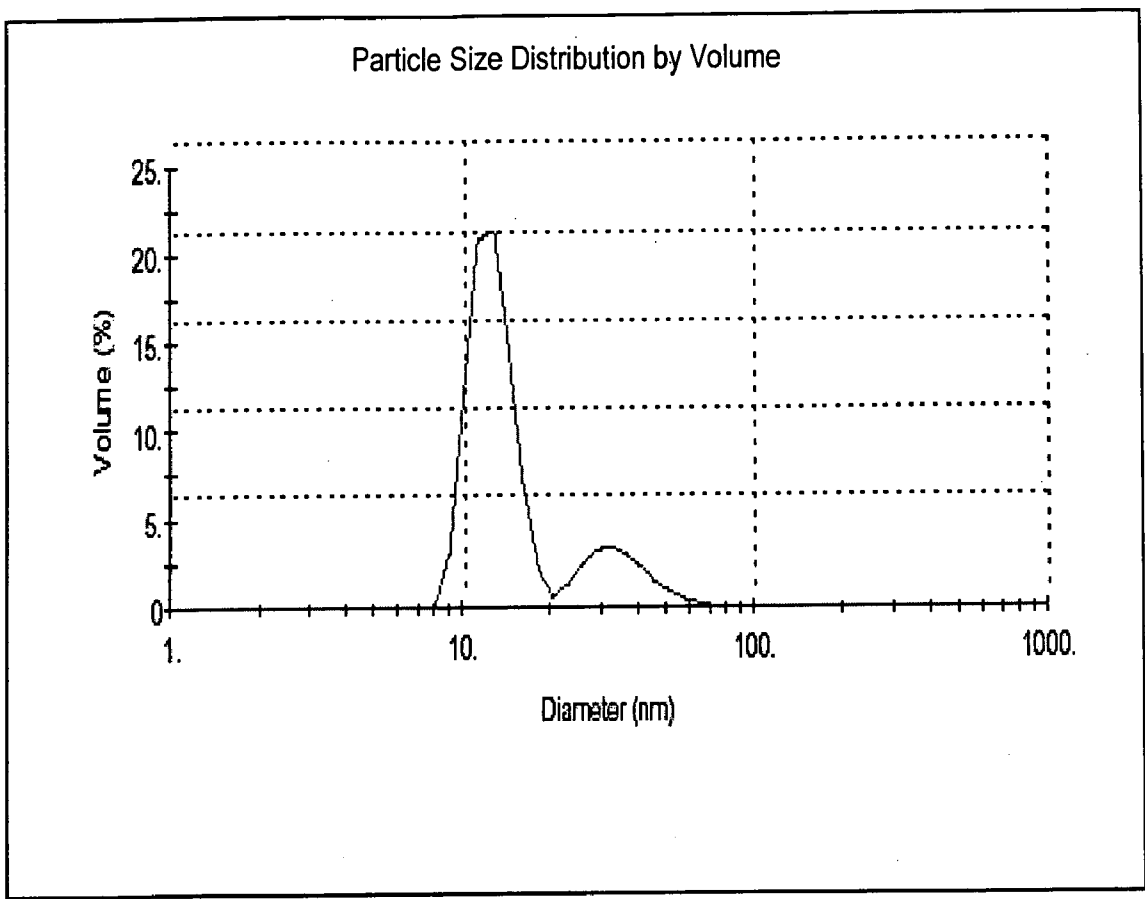


FIGURE 3

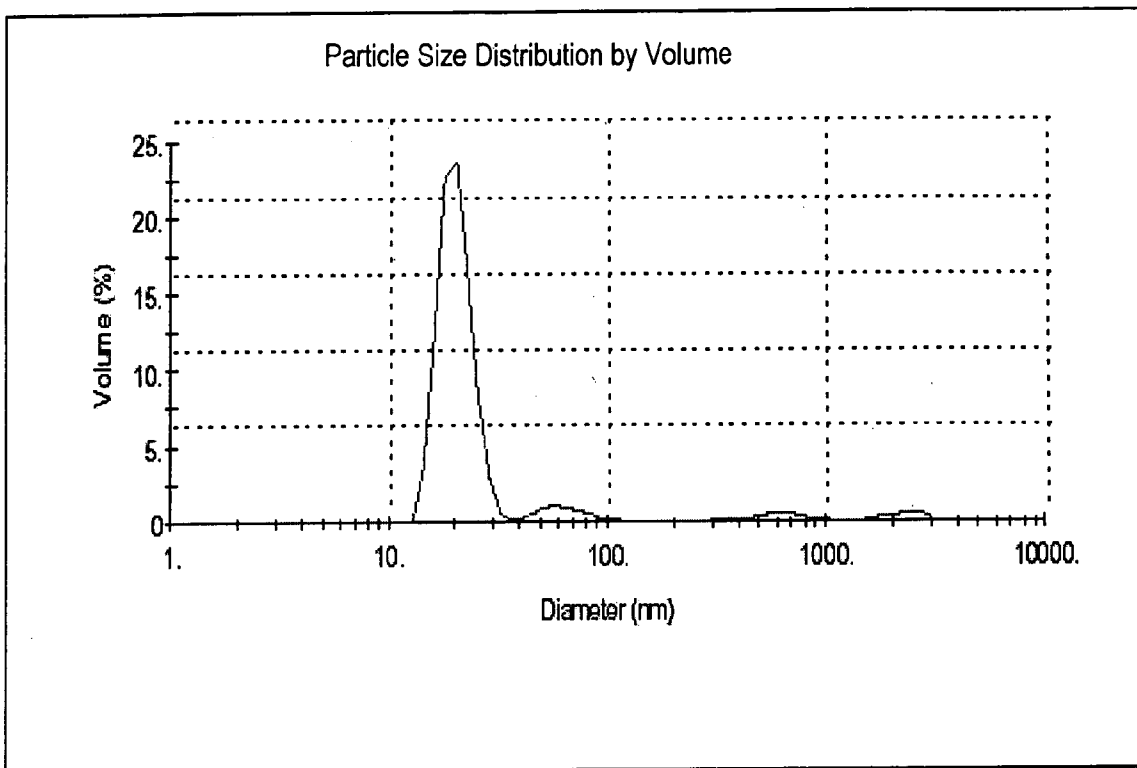


FIGURE 4

## ENHANCING PROPERTIES BY THE USE OF NANOPARTICLES

### CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority from U.S. provisional application Ser. No. 60/515,758 filed Oct. 30, 2003.

### FIELD OF THE INVENTION

[0002] The present invention relates to composite materials that are functionalized nanoparticles and in particular, metal-loaded nanoclays. Additionally, the present invention relates to a method of forming such composite materials.

### BACKGROUND OF THE INVENTION

[0003] For centuries, silver metal has been known to be an agent capable of killing many different microbial species. It was commonly used to purify drinking solutions or administered to sick individuals before the existence of modern antibiotics. Even after the discovery of penicillin and its descendants, colloidal silver solutions were often used in cases in which troublesome bacteria had become resistant to antibiotics.

[0004] Colloidal silver solutions are commercially available today. They are often unstable, however, and have a short shelf life. This is due to the tendency of the silver particles to aggregate and form clusters so large that they are no longer suspended in solution. For this reason, undesirable gelling agents are added to solutions to keep the silver particles suspended by preventing particle aggregation. Another problem of the commercially available solutions is that the majority of the silver content is usually found to be silver ions. This poses a large problem in medical applications where silver ions rapidly combine with ubiquitous chloride to form an insoluble white precipitate.

[0005] Nanoparticles have been known to be used as fillers as disclosed in U.S. Pat. No. 6,492,453, as coatings as disclosed in U.S. 2003/0185964 and as foam components as disclosed in U.S. Pat. No. 6,518,324.

[0006] Nanoparticle systems are disclosed in U.S. 2002/0150678 as being used in a composition and a method to impart surface modifying benefits to soft and hard surfaces. In particular, this application discloses a soft surface coating for articles such as fabrics and garments.

[0007] Inorganic particulates, such as, clays, silicates, and alumina have been widely used in combination with adjunct detergent and laundry compounds to impart some form of antistatic control and/or fabric softening benefit.

[0008] The present invention relates to composite materials comprising metal loaded onto exfoliated nanoparticles. Such functionalized nanoparticles may be incorporated into solid and liquid materials to enhance or modify their bulk physical and performance characteristics. In one embodiment, the metal is silver and the nanoparticle comprises a nanoclay. Silver ion is reduced to its neutral metal state ( $\text{Ag}^0$ ) and loaded onto the nanoclay. Silver-coated nanoclays in particular have excellent antimicrobial properties, and represent a less expensive alternative to the use of colloidal silver solutions. Such nanoparticles made according to the

invention are stable and use less silver metal to generate the same surface area as solid silver particles, making them more cost efficient.

### SUMMARY OF THE INVENTION

[0009] The invention provides a composite material comprising (a) an exfoliated nanoparticle having a surface and (b) a metal selected from Groups 3 to 12, aluminum and magnesium, wherein the metal is loaded onto the surface of the nanoparticle.

[0010] The invention also provides a method of making a composite material comprising an exfoliated nanoparticle having a metal coating, which method comprises: (a) reducing a metal ion to metal; (b) exfoliating a starting material to form a nanoparticle; and (c) contacting the metal with the exfoliated nanoparticle, whereby steps (a) and (b) may be performed sequentially in any order or simultaneously and the metal is loaded onto the surface of the exfoliated nanoparticle.

[0011] The invention further provides solutions, solids, gels, coating compositions, cosmetic and pharmaceutical compositions, and articles of manufacture comprising such a composite material.

### BRIEF DESCRIPTION OF THE DRAWINGS

[0012] FIG. 1 shows the particle size distribution of the material of Example 1.

[0013] FIG. 2 shows the particle size distribution of the material of Example 5.

[0014] FIG. 3 shows the particle size distribution of the material of Example 6.

[0015] FIG. 4 shows the particle size distribution of the material of Example 7.

### DETAILED DESCRIPTION OF THE INVENTION

[0016] Every limit given throughout this specification includes every lower or higher limit, as the case may be, as if such lower or higher limit was expressly written herein. Every range given throughout this specification includes every narrower range that falls within such broader range, as if such narrower ranges were all expressly written herein.

[0017] Nanoparticles as used herein means particles (including but not limited to rod-shaped particles, disc-shaped particles, platelet-shaped particles, tetrahedral-shaped particles), fibers, nanotubes, or any other materials having dimensions on the nano scale. In one embodiment, the nanoparticles have an average particle size of about 1 to about 1000 nanometers, preferably 2 to about 750 nanometers. That is, the nanoparticles have a largest dimension (e.g., a diameter or length) of about 1 to 1000 nm. Nanotubes can include structures up to 1 centimeter long, alternatively with a particle size from about 2 to about 50 nanometers. Nanoparticles have very high surface-to-volume ratios. The nanoparticles may be crystalline or amorphous. A single type of nanoparticle may be used, or mixtures of different types of nanoparticles may be used. If a mixture of nanoparticles is used they may be homogeneously or non-homogeneously distributed in the composite material or a system or composition containing the composite material.

[0018] Non-limiting examples of suitable particle size distributions of nanoparticles are those within the range of about 2 nm to less than about 750 nm, alternatively from about 2 nm to less than about 200 nm, and alternatively from about 2 nm to less than about 150 nm. It should also be understood that certain particle size distributions may be useful to provide certain benefits, and other ranges of particle size distributions may be useful to provide other benefits (for instance, color enhancement requires a different particle size range than the other properties). The average particle size of a batch of nanoparticles may differ from the particle size distribution of those nanoparticles. For example, a layered synthetic silicate can have an average particle size of about 25 nanometers while its particle size distribution can generally vary between about 10 nm to about 40 nm. It should be understood that the particle size distributions described herein are for nanoparticles when they are dispersed in an aqueous medium and the average particle size is based on the mean of the particle size distribution.

[0019] According to the invention, the nanoparticles are exfoliated. In particular, a starting material is exfoliated or disbursed to form the nanoparticles. Such starting material may have an average size of up to about 50 microns (50,000 nanometers).

[0020] The nanoparticle may comprise for example natural or synthetic nanoclays, including those made from amorphous or structured clays.

[0021] In one embodiment, the exfoliated nanoparticle is a nanoclay. In a further embodiment, the nanoparticle is a swellable nanoclay or adduct thereof. A swellable nanoclay has weakly bound ions in interlayer positions that may be hydrated or may absorb organic solvents. These swellable nanoclays generally possess a low cationic or anionic charge, i.e. less than about 0.9 units of charge per unit cell.

[0022] As used herein, "adducts" means oil swellable nanoclays, i.e. those that swell in organic, non-aqueous solvents such as polar and nonpolar solvents. They may be prepared by reacting a water swellable nanoclay with an organic material that binds to the swellable nanoclay. Examples of such binding organic materials include, but are not limited to, a quaternary ammonium compound having the structure:



[0023] wherein

[0024]  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are each independently selected from H, a  $C_1$  to  $C_{22}$  alkyl, a  $C_1$  to  $C_{22}$  alkenyl, and a  $C_1$  to  $C_{22}$  aralkyl, provided that at least one of the R groups is such an alkyl, alkenyl or aralkyl; and

[0025] X is the water swellable nanoclay.

[0026] The swellable nanoclay may be amorphous or structured, i.e., including sheets or layers, wherein a combination of such layers is referred to as a lattice structure. Examples of suitable nanoclays having lattice structures include the pyrophyllite (dioctahedral) type, the talc (trioctahedral) type, or mixtures thereof. Classes of suitable structured swellable nanoclays include, but are not limited to the smectite nanoclays, sepiolite nanoclays, zeolite nanoclays, palygorskite nanoclays, or mixtures thereof.

[0027] Examples of amorphous swellable nanoclays include allophone and imogolite.

[0028] In one embodiment, the nanoparticles are made from a starting material such as Nanomer 1.34TCN (available from Nanocor) having a particle size of 10 to 18 microns (10000-18000 nanometers). In another embodiment, the nanoparticles are made from PGV (also available from Nanocor) having a particle size of 20 to 25 microns. In another embodiment, exfoliated PGV having a particle size range of 1-3 nanometers is used. In other embodiments, Nanomer 1.34TCN and Nanomer 1.30E having a particle size range of 1-9 nanometers is used.

[0029] Boehmite alumina can have an average particle size distribution from 2 to 750 nm.

[0030] Layered clay minerals can be used as starting materials for the exfoliated nanoparticles. The layered clay minerals suitable for use in the present invention include those in the geological classes of the smectites, the kaolins, the illites, the chlorites, the attapulgites and the mixed layer clays. Typical examples of specific clays belonging to these classes are the smectices, kaolins, illites, chlorites, attapulgites and mixed layer clays. Smectites, for example, include montmorillonite, bentonite, pyrophyllite, hectorite, saponite, sauconite, nontronite, talc, beidellite, volchonskoite, stevensite, and vermiculite. In one embodiment, montmorillonite nanoclay is preferred. See U.S. Pat. No. 5,869,033, which is incorporated by reference herein. Kaolins include kaolinite, dickite, nacrite, antigorite, anauxite, halloysite, indellite and chrysotile. Illites include bravaisite, muscovite, paragonite, phlogopite and biotite. Chlorites include corrensite, penninite, donbassite, sudoite, pennine and clinochlore. Attapulgites include sepiolite and polygorskite. Mixed layer clays include allevardite and vermiculitebiotite. Variants and isomorphous substitutions of these layered clay minerals offer unique applications.

[0031] Layered clay minerals may be either naturally occurring or synthetic. For example, natural or synthetic hectorites, montmorillonites and bentonites may be used as the starting material for the nanoparticles.

[0032] Natural clay minerals typically exist as layered silicate minerals and less frequently as amorphous minerals. A layered silicate mineral has  $SiO_4$  tetrahedral sheets arranged into a two-dimensional network structure. A 2:1 type layered silicate mineral has a laminated structure of several to several tens of silicate sheets having a three layered structure in which a magnesium octahedral sheet or an aluminum octahedral sheet is sandwiched between two sheets of silica tetrahedral sheets.

[0033] A sheet of an expandable layer silicate has a negative electric charge, and the electric charge is neutralized by the existence of alkali metal cations and/or alkaline earth metal cations. Smectite or expandable mica can be dispersed in water to form a sol with thixotropic properties. Further, a complex variant of the smectite type clay can be formed by the reaction with various cationic organic or inorganic compounds. An example of such an organic complex, an organophilic clay in which a dimethyldioctadecyl ammonium ion (a quaternary ammonium ion) is introduced by cation exchange. This has been industrially produced and used as a gellant of a coating.

[0034] Synthetic nanoclays may be employed in the invention. With appropriate process control, the processes for the

production of synthetic nanoclays does indeed yield primary particles that are nanoscale. However, the particles are not usually present in the form of discrete particles, but instead predominantly assume the form of agglomerates due to consolidation of the primary particles. Such agglomerates may reach diameters of several thousand nanometers, such that the desired characteristics associated with the nanoscale nature of the particles cannot be achieved. The particles may be deagglomerated, for example, by grinding as described in EP-A 637,616 or by dispersion in a suitable carrier medium, such as water or water/alcohol and mixtures thereof.

[0035] Synthetic materials for making suitable nanoclays include layered hydrous silicate, layered hydrous aluminum silicate, fluorosilicate, mica-montmorillonite, hydroalcalite, lithium magnesium silicate and lithium magnesium fluorosilicate. An example of a substituted variant of lithium magnesium silicate is where the hydroxyl group is partially substituted with fluorine. Lithium and magnesium may also be partially substituted by aluminum. Lithium magnesium silicate may be isomorphically substituted by any member selected from the group consisting of magnesium, aluminum, lithium, iron, chromium, zinc and mixtures thereof.

[0036] Synthetic hectorite, for example as commercially marketed under the trade name LAPONITE™ by Southern Clay Products, Inc., may be used as a starting material for the nanoparticles. There are many grades or variants and isomorphous substitutions of LAPONITE™ marketed. Examples of commercial hectorites are LAPONITE B™, LAPONITE S™, LAPONITE XLS™, LAPONITE RD™, LAPONITE XLG™, and LAPONITE RDS™.

[0037] Synthetic hectorites do not contain any fluorine. An isomorphous substitution of the hydroxyl group with fluorine will produce synthetic clays referred to as sodium magnesium lithium fluorosilicates, which may also be used as the starting material. These sodium magnesium lithium fluorosilicates, marketed as LAPONITE™ and LAPONITE S™, may contain fluoride ions of up to approximately 10% by weight. The fluoride ion content useful in the compositions described herein is up to about 10 or more percent. LAPONITE B™, a sodium magnesium lithium fluorosilicate, has a flat, circular, plate-like shape, with an average particle size, depending on fluoride ion content, of about 25-100 nanometers. For example, in one non-limiting embodiment, LAPONITE B™ having a diameter of about 25-40 nm and thickness of about 1 nm may be used. Another variant, called LAPONITE S™, contains about 6% of tetrasodium pyrophosphate as an additive.

[0038] In one embodiment, Laponite XLS™ is used as the starting material for the nanoparticle, and silver is loaded thereon as the metal. Laponite XLS has tetrahedral silicate layers joined by octahedral magnesium and lithium hydroxyl bridges. This structure allows for exfoliation and modification by either intercalation or adsorption of metal to the nanoclay surface. In the case of intercalation, the metal is inserted between the layers of nanoclay. In the case of surface adsorption, the metal binds to the surface of the nanoclay. Laponite XLS is advantageous because it is synthetically consistent and pure, and exfoliates to form nanoparticles with minimal effort. The surface of the nanoparticle is covered with sodium ions to balance out the negative charge of the many silicate groups.

[0039] The aspect ratio of the exfoliated nanoparticles, in some cases, is of interest in forming films comprising the

composite material with desired characteristics. The aspect ratio of dispersions can be adequately characterized by TEM (transmission electron microscopy).

[0040] The aspect ratio of nanoparticles in one embodiment can be in the range of 100 to 250. In another embodiment, the aspect ratio of the nanoparticles is 200 to 350.

[0041] For example, the average aspect ratio of individual particles of LAPONITE B™ is approximately 20-40 and the average aspect ratio of individual particles of LAPONITE RD™ is approximately 10-15. LAPONITE B™ occurs in dispersions as essentially single clay particles or stacks of two clay particles. LAPONITE RD™ occurs essentially as stacks of two or more single clay particles.

[0042] In some embodiments, a high aspect ratio may be desirable for film formation. The aspect ratio of exfoliated nanoparticles dispersed in a suitable carrier medium, such as water, is also of interest. The aspect ratio of the nanoparticles in a dispersed medium is lower where several of the particles are aggregated.

[0043] In certain embodiments, it may be desirable for at least some individual (non-aggregated) platelet and disc-shaped nanoparticles to have at least one dimension that is greater than or equal to about 0.5 nm, and an aspect ratio of greater than or equal to about 15. Larger aspect ratios may be more desirable for platelet and disc-shaped nanoparticles than for rod-shaped nanoparticles.

[0044] The aspect ratio of rod-shaped nanoparticles can be lower than that of disc-shaped or platelet-shaped nanoparticles while maintaining adequate film-forming properties. In certain non-limiting embodiments, it may be desirable for at least some of the individual rod-shaped nanoparticles to have at least one dimension that is greater than or equal to about 0.5 nm, and an aspect ratio of greater than or equal to about 3.

[0045] The aspect ratio of spheroid-shaped nanoparticles is generally less than or equal to about 5. Nanoparticles preferred for the embodiments presented here have aspect ratios of less than or equal to about 250. In other non-limiting embodiments, it may be desirable for the nanoparticles to have an aspect ratio of less than about 10.

[0046] According to the invention, one or more metals are used to functionalize the nanoparticle. In particular, they are loaded onto the exfoliated nanoparticle by one of a variety of methods including intercalation, adsorption, or ion exchange. Advantageously, the metal retains its valuable properties, for example in the case of silver its anti-microbial properties, while on the nanoparticle. The term loaded, as used herein, includes complete coverage of the surface of the nanoparticle, or alternatively, only a portion thereof.

[0047] In one embodiment, the metal is selected from Groups 3 to 12 of the Periodic Table of Elements, aluminum, and magnesium. Preferably, the metal is selected from silver, copper, zinc, manganese, platinum, palladium, gold, calcium, barium, aluminum, iron, and mixtures thereof. In a particularly preferred embodiment, the metal is silver.

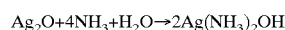
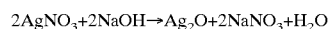
[0048] The metal or metals may be selected based on the desired effect to be achieved through use of the composite material. For example, silver may be selected for its known anti-microbial properties.



[0049] The metal may be loaded onto the nanoparticle via intercalation. For example, silver ions, in particular, can be inserted among the various layers of layered nanoclay by positioning in a "hole" to maximize favorable interactions between the positively charged silver ion and the various types of oxygen in the silicate structure. Silver ions have been shown to have anti-microbial properties and Laponite that contains intercalated ionic silver, retains these properties. Intercalation is also possible with other metal ions, such as copper, zinc, manganese, etc.

[0050] The metal may also be loaded onto the nanoparticle via ion exchange. For example, the surface of Laponite platelets is composed mainly of sodium ions, which exist to balance out the negatively charged oxygen atoms donated by the silicate structure in the layer below. When positively charged metal ions are added to a solution of exfoliated Laponite, a fraction of the surface sodium ions are displaced by the added metal cations.

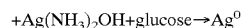
[0051] The metal may also be loaded onto the nanoparticle by adsorption. For example, certain functional groups such as amine, ammonium, and carboxyl groups are strong binders to the face or edge of a platelet of Laponite. Metal ions can be modified by the addition of these ligands so that they are able to bind strongly to the surface of Laponite. The reaction sequence for one example is shown below:



[0052] The final product,  $\text{Ag}(\text{NH}_3)_2\text{OH}$ , is contacted with Laponite, whereby the  $\text{Ag}(\text{NH}_3)_2\text{OH}$  binds to the face of the Laponite.

[0053] In one embodiment of the invention a metal ion is reduced to a metal (0) in the presence of a starting material, which is exfoliated to form a nanoparticle. Reduction and exfoliation may take place in sequence (either step happening first) or simultaneously upon contacting of the metal with the starting material/exfoliated nanoparticle. The metal is thereby loaded onto the surface of the exfoliated nanoparticle.

[0054] In one embodiment of the invention, the metal is silver, which is loaded onto the nanoparticle via intercalation using the Tollen's reagent. The Tollen's reagent is a known silver species able to undergo reduction by either an aldehyde or ketone to form silver metal (0):



[0055] The composite material may be incorporated into a variety of systems, materials and compositions, including liquids, solids, gels, coating compositions, cosmetic and pharmaceutical compositions and the like. The composite material may be incorporated into structures or articles of manufacture such as absorbent articles, wound care articles, soft surfaces, or hard surfaces. Compositions containing the composite material may be solutions or dry materials, that are coated, applied, extruded, sprayed, and so forth as further described below. Such compositions may have end uses in manufacturing, commercial, industrial, personal, or domestic applications.

[0056] Systems comprising the composite material can be employed to bring about certain, desired benefits, for example improved fluid absorbency, wettability, strike-through, comfort, malodor control, lubricity, anti-inflamma-

tory properties, anti-microbial properties, anti-fungal properties, modification of surface friction, flexibility, transparency, modulus, tensile strength, color enhancement, viscosity, smoothness, or gel strength.

[0057] In certain embodiments, the presence of the composite material in a composition does not affect the desirable properties of the composition, for example transparency. Addition of the composite material to a liquid composition, for instance, will not alter the transparency or color of the resultant composition as compared to the original, liquid material not containing the composite material. Moreover, since nanoparticles possess large surface areas, the composite material will also allow for higher concentrations of metals to be included in the overall formulation, such as in the treatment of infections.

[0058] Compositions of the invention may comprise the composite material and any other ingredients appropriate for the intended use of the compositions. Some compositions of the invention may comprise: (a) the composite material, which may be an effective amount of the composite material; (b) a suitable carrier medium; and (c) optionally one or more adjunct ingredients. The adjunct ingredients may be, for example, surfactants or charged functionalized molecules exhibiting properties selected from the group consisting of hydrophilic, hydrophobic and mixtures thereof associated with at least some of the composite material, or both.

[0059] Alternatively, an effective amount of composite material described above can be included in compositions useful for coating a variety of soft surfaces in need of treatment. As used herein, an effective amount of composite material refers to the quantity of composite material necessary to impart the desired benefit to the soft surface. Such effective amounts are readily ascertained by one of ordinary skill in the art and is based on many factors, such as the particular composite material used, the nature of the soft surface whether a liquid or dry (e.g., granular, powder) composition is required, and the like.

[0060] The composition may be applied to the surface(s) by washing, spraying, dipping, painting, wiping, or by other manner in order to deliver a coating, especially a transparent coating that covers at least about 0.5% of the surface, or any greater percentage of the surface, including but not limited to: at least about 5%, at least about 10%, at least about 30%, at least about 50%, at least about 80%, and at least about 100% of the surface. Accordingly, the coating may be continuous or discontinuous.

[0061] If the coating composition is to be sprayed onto the surface, the viscosity of the coating composition should be such that it will be capable of passing through the nozzle of a spray device. Such viscosities are well known, and are incorporated herein by reference. The composition may be capable of undergoing shear thinning so that it is capable of being sprayed.

[0062] Suitable carrier mediums for the compositions containing the composite material include liquids, solids and gases. One suitable carrier medium is water, which can be distilled, deionized, or tap water. Water is valuable due to its low cost, availability, safety, and compatibility. The pH of the liquid, in particular water, may be adjusted through the addition of acid or base. Aqueous carrier mediums are also easy apply to a substrate and then dried. Though aqueous

carrier mediums are more common than dry, nonaqueous mediums, the composition can exist as a dry powder, granule or tablet or encapsulated complex form.

[0063] Optionally, in addition to or in place of water, the carrier medium can comprise a low molecular weight organic solvent. Preferably, the solvent is highly soluble in water, e.g., ethanol, methanol, propanol, isopropanol, ethylene glycol, acetone, and the like, and mixtures thereof. The solvent can be used at any suitable level. Several non-limiting examples, include a level of up to about 50%, or more; from about 0.1% to about 25%; from about 2% to about 15%, and from about 5% to about 10%, by weight of the total composition. Factors to consider when a high level of solvent is used in the composition are odor, flammability, dispersancy of the nanoparticles and environmental impact.

[0064] The carrier medium may also comprise a film former, which when dried, forms a continuous film. Examples of film formers are polyvinyl alcohol, polyethylene oxide, polypropylene oxide, acrylic emulsions, hydroxypropylmethyl cellulose.

[0065] Adjunct ingredients that may be used in compositions containing the composite material include polymers and copolymers with at least one segment or group which comprises functionality that serves to anchor the composite material to a substrate. These polymers may also comprise at least one segment or group that serves to provide additional character to the polymer, such as hydrophilic or hydrophobic properties.

[0066] Examples of the anchoring segments or groups include: polyamines, quaternized polyamines, amino groups, quaternized amino groups, and corresponding amine oxides; zwitterionic polymers; polycarboxylates; polyethers; polyhydroxylated polymers; polyphosphonates and polyphosphates; and polymeric chelants.

[0067] Examples of the hydrophilizing segments or groups include: ethoxylated or alkoxyated polyamines; polyamines; polycarboxylated polyamines; water soluble polyethers; water soluble polyhydroxylated groups or polymers, including saccharides and polysaccharides; water soluble carboxylates and polycarboxylates; water soluble anionic groups such as carboxylates, sulfonates, sulfates, phosphates, phosphonates and polymers thereof; water soluble amines, quaternaries, amine oxides and polymers thereof; water soluble zwitterionic groups and polymers thereof; water soluble amides and polyamides; and water soluble polymers and copolymers of vinylimidazole and vinylpyrrolidone.

[0068] Examples of the hydrophobizing segments or groups include: alkyl, alkylene, and aryl groups, and polymeric aliphatic or aromatic hydrocarbons; fluorocarbons and polymers comprising fluorocarbons; silicones; hydrophobic polyethers such as poly(styrene oxide), poly(propylene oxide), poly(butylene oxide), poly(tetramethylene oxide), and poly(dodecyl glycidyl ether); and hydrophobic polyesters such as polycaprolactone and poly(3-hydroxycarboxylic acids).

[0069] Examples of hydrophilic surface polymers that may be incorporated into the compositions of the invention include, but are not limited to: ethoxylated or alkoxyated polyamines; polycarboxylated polyamines; polycarboxy-

lates including but not limited to polyacrylate; polyethers; polyhydroxyl materials; polyphosphates and phosphonates.

[0070] Examples of hydrophobic surface polymers that may be incorporated into the compositions of the invention include alkylated polyamines include, but are not limited to: polyethyleneimine alkylated with fatty alkylating agents such as dodecyl bromide, octadecyl bromide, oleyl chloride, dodecyl glycidyl ether and benzyl chloride or mixtures thereof; and polyethyleneimine acylated with fatty acylating agents such as methyl dodecanoate and oleoyl chloride; silicones including, but not limited to: polydimethylsiloxane having pendant aminopropyl or aminoethylaminopropyl groups and fluorinated polymers including, but not limited to: polymers including as monomers (meth)acrylate esters of perfluorinated or highly fluorinated alkyl groups.

[0071] Non-polymeric surface modifying materials that may be used as adjunct ingredients include fatty amines and quaternized amines including: ditallowdimethylammonium chloride; octadecyltrimethylammonium bromide; dioleil amine; and benzyltetradecyldimethylammonium chloride. Silicone-based surfactants, fatty zwitterionic surfactants and fatty amine oxides may also be incorporated into the composition.

[0072] Surfactants are also optional adjunct ingredients. Surfactants are especially useful in the composition as wetting agents to facilitate the dispersion.

[0073] Suitable surfactants can be selected from the group including anionic surfactants, cationic surfactants, nonionic surfactants, amphoteric surfactants, ampholytic surfactants, zwitterionic surfactants and mixtures thereof. Examples of suitable nonionic, anionic, cationic, ampholytic, zwitterionic and semi-polar nonionic surfactants are disclosed in U.S. Pat. Nos. 5,707,950 and 5,576,282. Nonionic surfactants may be characterized by an HLB (hydrophilic-lipophilic balance) of from 5 to 20, alternatively from 6 to 15.

[0074] Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are listed in standard texts.

[0075] Another class of adjunct ingredients that may be useful are silicone surfactants and/or silicones. They can be used alone and/or alternatively in combination with other surfactants described herein above. Nonlimiting examples of silicone surfactants are the polyalkylene oxide polysiloxanes having a dimethyl polysiloxane hydrophobic moiety and one or more hydrophilic polyalkylene side chains

[0076] If used, the surfactant should be formulated to be compatible with the composite material, carrier medium and other adjunct ingredients present in the composition.

[0077] The compositions can contain other adjunct ingredients, including but not limited to alkalinity sources, antioxidants, anti-static agents, chelating agents, aminocarboxylate chelators, metallic salts, photoactive inorganic metal oxides, odor-controlling materials, perfumes, photoactivators, polymers, preservatives, processing aids, pigments, and pH control agents, solubilizing agents, zeolites, and mixtures thereof. These optional ingredients may be included at any desired level.

[0078] Coating compositions comprising the composite material can be used on all types of soft surfaces, including but not limited to woven fibers, nonwoven fibers, leather,

plastic (for example, toothbrush handles, synthetic film, filaments, toothbrush bristles), and mixtures thereof. The soft surfaces of interest herein may comprise any known type of soft surface, including but not limited to those associated with disposable absorbent articles including but not limited to covers or topsheets, absorbent cores, transfer layers, absorbent inserts, and backsheets including those outer layers made from breathable and nonbreathable films.

[0079] It should be understood that in certain embodiments, such a coating composition can be applied to hard surfaces, and provide benefits thereto.

[0080] In certain embodiments, the soft surface may comprise one or more fibers. A fiber is defined as a fine hairlike structure, of vegetable, mineral, or synthetic origin. Commercially available fibers have diameters ranging from less than about 0.001 mm (about 0.00004 in) to more than about 0.2 mm (about 0.008 in) and they come in several different forms: short fibers (known as staple, or chopped), continuous single fibers (filaments or monofilaments), untwisted bundles of continuous filaments (tow), and twisted bundles of continuous filaments (yarn). Fibers are classified according to their origin, chemical structure, or both. They can be braided into ropes and cordage, made into felts (also called nonwovens or nonwoven fabrics), woven or knitted into textile fabrics, or, in the case of high-strength fibers, used as reinforcements in composites—that is, products made of two or more different materials.

[0081] The soft surfaces may comprise fibers made by nature (natural fibers), made by man (synthetic or man-made), or combinations thereof. Example of natural fibers include but are not limited to: animal fibers such as wool, silk, fur, and hair; vegetable fibers such as cellulose, cotton, flax, linen, and hemp; and certain naturally occurring mineral fibers. Synthetic fibers can be derived from natural fibers or not. Examples of synthetic fibers which are derived from natural fibers include but are not limited to rayon and lyocell, both of which are derived from cellulose, a natural polysaccharide fiber. Synthetic fibers which are not derived from natural fibers can be derived from other natural sources or from mineral sources. Example synthetic fibers derived from natural sources include but are not limited to polysaccharides such as starch. Example fibers from mineral sources include but are not limited to polyolefin fibers such as polypropylene and polyethylene fibers, which are derived from petroleum, and silicate fibers such as glass and asbestos. Synthetic fibers are commonly formed, when possible, by fluid handling processes (e.g., extruding, drawing, or spinning a fluid such as a resin or a solution). Synthetic fibers are also formed by solid handling size reduction processes (e.g., mechanical chopping or cutting of a larger object such as a monolith, a film, or a fabric).

[0082] Disposable absorbent articles, such as pantliners, sanitary napkins, interlabial devices, adult incontinent devices, breast pads, shoe insoles, bandages, and diapers typically are made from absorbent, nonwoven materials (including fibers) and are well known in the art. These articles typically have a fluid permeable body-facing side and fluid impermeable garment facing side. Additionally, such articles may include an absorbent core for retaining fluids therebetween. Addition of the composite material to an article of manufacture such as the absorbent core of a disposable, absorbent article may help control malodor formation and increase absorbency.

[0083] Other uses for the composite material include but are not limited to use in dental abrasives for toothpaste, odor absorbents, and oral rinses. Other uses for the composite material include ophthalmic solutions and devices such as contact lenses.

[0084] Another embodiment of the invention relates to cosmetic and pharmaceutical compositions comprising the composite material. These may be in the form of creams, lotions, gels, foams, oils, ointments, or powders for application to tissues including skin, hair, nails, and mucosa such as vaginal or oral mucosa. Such compositions may be formulated as either leave-on products or rinse-off products. Alternatively, such compositions may also be in the form of ophthalmic solutions or ointments, which are applied directly to the eye.

[0085] In one embodiment, the composition contains an anti-acne agent such as salicylic acid or benzoyl peroxide.

[0086] In another embodiment, the composition is a personal lubricant such as those disclosed in U.S. Ser. Nos. 10/137,509; 10/390,511; and 10/389,871, filed May 1, 2002; Mar. 17, 2003; Mar. 17, 2003, respectively. These applications describe warming lubricant compositions that are non-toxic and non-irritating and that can be used as personal lubricants designed to come into contact with the skin or mucosa. When mixed with water, such compositions increase in temperature or generate warmth. This has a soothing effect on the tissues to which these compositions are applied. These compositions are preferably substantially anhydrous and preferably contain at least one polyhydric alcohol. By incorporating the composite material into these personal lubrications, the resultant compositions have a smoother characteristic and remain as clear solutions, as the composite material does not detract from the transparency of the compositions.

[0087] Cosmetic and pharmaceutical compositions may contain a variety of active agents known in the art such as skin lightening agents, skin pigmentation darkening agents, anti-acne agents, sebum modulators, shine control agents, anti-microbial agents, anti-fungals, anti-inflammatory agents, anti-mycotic agents, anti-parasite agents, external analgesics, sunscreens, photoprotectors, antioxidants, keratolytic agents, detergents, surfactants, moisturizers, nutrients, vitamins, energy enhancers, anti-perspiration agents, astringents, deodorants, hair removers, firming agents, anti-callous agents, and agents for hair, nail, or skin conditioning.

[0088] Formulations for topical or mucosal application are well known in the art. Excipients used by those skilled in the art in such formulations may be used with the composite material herein, provided they are compatible.

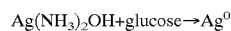
[0089] The compositions of the present invention can be applied to a surface and optionally allowed to dry on the surface, optionally repeating the application and drying steps as needed. In some embodiments of the methods described herein, including, but not limited to when applying more than one coating, it is not necessarily required to dry the coating(s) between applications.

## EXAMPLES

### Example 1

[0090] In order to deposit silver metal on nanoclay, silver ions were reduced in the presence of Laponite using the

Tollen's reagent, which is able to undergo reduction by either an aldehyde or ketone to form silver metal via the following reaction:



[0091] The Tollen's reagent was prepared by adding two drops of 10% NaOH to 5 mL of 5% AgNO<sub>3</sub> to form a gray-brown precipitate. This precipitate was then dissolved by the dropwise addition of 2% NH<sub>4</sub>OH to yield a total Tollen's reagent volume of 30 mL.

[0092] A solution of silver-loaded Laponite XLS was prepared by adding 600 mg of Laponite XLS to 50 mL of distilled water and using a magnetic stirrer to exfoliate for 20 minutes. To this solution, 800 mg of glucose were added and the stirring continued for 10 minutes to ensure complete dissolution of the glucose. To this, 10 mL of Tollen's reagent as prepared above were added. After two hours of continuous stirring, the solution turned golden yellow in color. Further reaction time yielded a dark amber-brown solution. Samples prepared for particle size analysis and TEM analysis were diluted by a factor of 10 to prevent particle aggregation. The particle size of the nanoparticles dictates the color of the solution caused by a surface plasmon resonance phenomenon. For silver particles, a yellow color has been determined to have the smallest particle size possible. The particle size distribution of the resulting nanoparticles is shown in FIG. 1.

#### Example 2

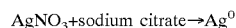
[0093] The formation of silver metal from silver ions was also investigated using NaBH<sub>4</sub>:



[0094] Dropwise addition of 32 mg of AgNO<sub>3</sub> dissolved in 5 mL of H<sub>2</sub>O to a solution containing 500 mg of exfoliated Laponite XLS and 4 mg NaBH<sub>4</sub> yielded a golden yellow solution. This addition order for this particular reaction was determined to give the smallest particle size.

#### Example 3

[0095] Nanoparticles of silver-laponite were prepared by reduction with sodium citrate, although the reduction by this method was more difficult to control. Citric acid was added to an exfoliated Laponite XLS solution, followed by the addition of silver nitrate. 10% NaOH was added dropwise to form the sodium salt of citric acid until the solution turned faintly yellow. In many cases, the over-addition of sodium hydroxide caused the silver particles to fall out of solution.



#### Example 4

[0096] Nanoparticles of silver-loaded Laponite XLS can be prepared by hydrazine reduction as follows: 5 g of Laponite XLS are added to 995 g of deionized water and stirred for 20 minutes to exfoliate the Laponite XLS. 20 mg of 55% hydrazine hydrate is added to the Laponite XLS dispersion and the solution is stirred for 1 minute. 77 mg of AgNO<sub>3</sub> is dissolved in deionized water. The AgNO<sub>3</sub> solution is added dropwise to the Laponite—hydrazine solution to form a golden-yellow solution containing 0.005% silver-loaded Laponite XLS.

#### Example 5

[0097] Another solution of silver-loaded Laponite XLS was prepared similarly to Example 1, but the order of the components was altered. Glucose and Tollen's reagent were mixed in a separate vessel and once the color of the solution turned faintly gray, this mixture was added to the solution of exfoliated Laponite XLS. After a short period of stirring, the solution turned amber-yellow. This solution was diluted by a factor of 10 for particle size analysis. The particle size distribution of the resulting material is shown in FIG. 2.

#### Example 6

[0098] A sample was prepared by adding 200 mg of Laponite XLS to 100 mL of water and stirring to exfoliate. The sample was analyzed for particle size. The results are shown in FIG. 3.

#### Example 7

[0099] The sample of Example 6 was diluted by a factor of 50. The sample was analyzed for particle size. The results are shown in FIG. 4.

[0100] The results of Examples 1-7 indicate that as a solution of Laponite XLS in water is diluted, the distribution of particle sizes changes. The particle size of silver-loaded Laponite XLS was smaller, on average, than Laponite XLS alone, indicating that the addition of silver to the solution aided in the Laponite XLS exfoliation process.

[0101] The data for Example 1 shows a single particle size distribution, averaging 4.1 nm in size. Example 5, on the other hand, showed a bimodal particle size distribution with the averages centered on 4.1 nm and 11 nm. This indicates the formation of two different types of particles. It is possible that this solution contained silver-loaded Laponite XLS and colloidal silver with no Laponite core.

#### Example 8

[0102] To verify that the Laponite XLS was being coated with silver, TEM (transmission electron microscopic) images and EDX (Energy Dispersive X-Ray) analysis were performed on Examples 1 and 6. The data confirmed that the composite material of Example 1 contained silver-loaded Laponite XLS particles, as opposed to a mixture of colloidal silver and Laponite XLS. Elemental analysis showed the presence of Na, Mg, Si, and Ag (Cu was present in the TEM grid). The data also revealed that particles of very small size (≈1 nm), determined to be uncoated Laponite XLS, were also present.

#### Example 9

[0103] A solution containing silver-loaded Laponite XLS particles was prepared as follows. 4.51 g of Laponite XLS was added to 900 mL of deionized water. The solution was stirred for 1 hour and labeled Solution A. To 400 mL of Solution A, 15 mg of NaBH<sub>4</sub> was added. This solution was labeled Solution B. 124 mg of AgNO<sub>3</sub> was dissolved in 5 mL of deionized water; and this was added dropwise to Solution B to form an amber brown solution of 0.02% silver loaded onto Laponite XLS. Following the above procedure, 0.01 %, 0.005% and 0.0025% silver loaded Laponite XLS solutions were prepared. These solutions were analyzed for biocidal activity against the organisms *Staphylococcus aureus* and

*Escherichia coli* as follows. The silver-loaded Laponite XLS solutions were inoculated with the bacteria and neutralized with Lethen Broth containing 1.5% to neutralize the activity after the appropriate time. Aliquots were plated using Lethen Agar. The bacterial log reduction is given in the Table below.

Sample Conc.	E.c. - 5			
	S.a. - 5 minute	S.a. - 10 min	minutes	E.c. - 10 min.
0.0025%	0.8	2.2	3.2	5.3
0.005%	4.8	4.8	5.3	5.3
0.01%	2.2	4.8	5.3	5.3
0.02%	4.8	4.8	5.3	5.3

We claim:

1. A composite material comprising (a) an exfoliated nanoparticle having a surface and (b) a metal selected from Groups 3 to 12, aluminum and magnesium, wherein the metal is loaded onto the surface of the nanoparticle.

2. The composite material of claim 1, wherein the metal is loaded onto the surface of the nanoparticle by intercalation.

3. The composite material of claim 1, wherein the metal is loaded onto the surface of the nanoparticle by adsorption.

4. The composite material of claim 1, wherein the metal is loaded onto the surface of the nanoparticle by ion exchange.

5. The composite material of claim 1, wherein the metal is selected from the group consisting of silver, copper, zinc, manganese, platinum, palladium, gold, calcium, barium, aluminum, iron, and mixtures thereof.

6. The composite material of claim 1, wherein the nanoparticle comprises a nanoclay.

7. The composite material of claim 1, wherein the nanoparticle comprises exfoliated Laponite.

8. A solution comprising the composite material of claim 1.

9. A solid comprising the composite material of claim 1.

10. A gel comprising the composite material of claim 1.

11. A composition comprising the composite material of claim 1.

12. The composition of claim 11, further comprising one or more adjunct ingredients and a carrier medium.

13. The composition of claim 12, wherein the adjunct ingredients are selected from surfactants and charged functionalized molecules.

14. The composition of claim 12, wherein the carrier medium comprises is an aqueous carrier medium.

15. A cosmetic or pharmaceutical composition comprising the composite material of claim 1.

16. The composition of claim 15, further comprising an active agent selected from skin lightening agents, skin pigmentation darkening agents, anti-acne agents, sebum modulators, shine control agents, anti-microbial agents, anti-fungals, anti-inflammatory agents, anti-mycotic agents, anti-parasite agents, external analgesics, sunscreens, photoprotectors, antioxidants, keratolytic agents, detergents, surfactants, moisturizers, nutrients, vitamins, energy enhancers, anti-perspiration agents, astringents, deodorants, hair removers, firming agents, anti-callous agents, and agents for hair, nail, or skin conditioning.

17. A method of making a composite material comprising an exfoliated nanoparticle having a metal coating, which method comprises: (a) reducing a metal ion to metal; (b) exfoliating a starting material to form an exfoliated nanoparticle; and (c) contacting the metal with the exfoliated nanoparticle, whereby steps (a) and (b) may be performed sequentially in any order or simultaneously and the metal is loaded onto the surface of the exfoliated nanoparticle.

18. The method of claim 17, wherein the metal is loaded onto the surface of the nanoparticle by intercalation.

19. The method of claim 17, wherein the metal is loaded onto the surface of the nanoparticle by adsorption.

20. The method of claim 17, wherein the metal is loaded onto the surface of the nanoparticle by ion exchange.

21. The method of claim 17, wherein the metal is selected from the group consisting of silver, copper, zinc, manganese, platinum, palladium, gold, calcium, barium, aluminum, iron, and mixtures thereof.

22. The method of claim 17, wherein the nanoparticle comprises a nanoclay.

23. The method of claim 22, wherein the nanoparticle comprises exfoliated Laponite.

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