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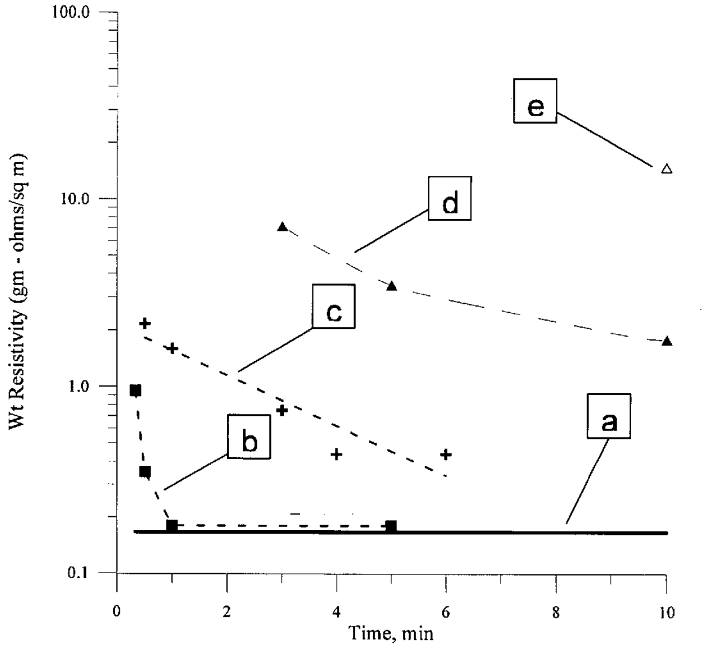
(54) **Title:** SYNTHESIS OF METALLIC NANOPARTICLE DISPERSIONS



(57) **Abstract:** Disclosed are compositions comprising metallic nanoparticles suitable for use in cohesive, highly conductive structures on substrates. Also disclosed are methods for synthesizing the compositions and methods for forming cohesive, highly conductive structures from the compositions.

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SYNTHESIS OF METALLIC NANOPARTICLE DISPERSIONS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Pat. App. No. 60/752,143, "Low Temperature Curing Inks Utilizing Metallic Nanoparticles As A Sintering Aid", filed December 20, 2005, U.S. Provisional Pat. App. No. 60/752,144, "Low Temperature Curing Inks Containing Metallic Nanoparticle Dispersions", filed December 20, 2005, U.S. Provisional Pat. App. No. 60/752,628, "Capacitance Coupled Interactive Electronics Using Printed Conductors", filed December 21, 2005, and U.S. Non-Provisional Pat. App. No. 11/613,136, "Synthesis of Metallic Nanoparticle Dispersions", filed December 19, 2006. The entirety of each of these applications is incorporated by reference herein in their entirety.

FIELD OF THE INVENTION

[0002] The present invention pertains to the field of nanoparticles. The present invention also pertains to the fields of conductive inks and of printable conductive features.

BACKGROUND OF THE INVENTION

[0003] Various scientific and patent publications are referred to herein. Each is incorporated by reference in its entirety.

[0004] Thin, conductive metal films have a wide range of uses, and have particular application as connectors in microelectronic devices, e.g., U.S. Pat. No. 6,855,378, to Subhash, N., and also as connectors in photovoltaic devices. Accordingly, the ability to make highly conductive traces and films at low temperatures and moderate cost is of enormous commercial interest to the electronics industry.

[0005] The economic feasibility of making devices such as radio frequency identification ("RFID") tags, flexible displays, low cost consumer electronics, and printed thin film transistors (TFTs) depends on the ability to efficiently and quickly manufacture such materials. Thus, application of printing technologies, such as inkjet printing, roll-to-roll, printing, gravure printing, and the like, to forming conductive traces and other structures is of keen interest to the electronics, display, and energy industries. As is known, e.g., Lee, et al., *Nanotechnology*, **2006**, 17, 2424, forming conductive structures via printing methods has clear advantages over conventional photolithography and etching processes for producing such structures. First, printing is more environmentally friendly than more traditional methods of manufacture. Second, printing involves relatively less material loss than traditional processes. Third, printing processes are customizable. Fourth, printing processes are capable of high productivity, and, in certain printing processes, furthermore, are also capable of depositing precise amount of material to a specified location via a non-contact and directed deposition process capable of being controlled by a computer.

[0006] Present methods of printing conductive compositions onto substrates have certain limitations. Commercial conductive ink systems, such as those used to print membrane touch switches, typically contain metal flake with a cross-sectional dimension of about 1000 nm as a conductive constituent and also contain polymers that function as binders. These flake-based inks, however, generally cannot be processed at temperatures lower than 120°C or at times less than 1 minute, regardless of temperature. Furthermore, these materials are only capable of achieving conductivities of only 2 to 10% of bulk metal conductivity because of the continuous polymeric matrix and the manner with which the flakes pack together.

[0007] Furthermore, metallic flakes do not sinter together, so a continuous metallic network is not formed by such materials and the network conducts electricity instead by incidental contact of the metal flakes, resulting in conductivity that often only 10% of the bulk metal conductivity. Further, ink systems containing flake as the metal constituent are limited in the ultimate thickness that can be obtained; because the nominal flake size is the range of 1-2 microns, the thinnest traces possible may be 3-4 microns.

[0008] Other conductive ink systems employ the use of metallo-organic additives, U.S. Pat. No. 5,071,826 to Anderson, J.T, et al, U.S. Pat. No. 5,338,507, to Anderson, J.T, et al; U.S. Pat. No. 4,599,277 to Brownlow, J.M., et al; U.S. Pat. No. 7,115,218, to Kydd, P.H., et al., which, upon decomposition, result in atomic metal that acts as a chemical binding agent for the metal flakes. Conductivities as high as 20% of the bulk metal are possible when using such additives, but high temperatures are needed to decompose the metallo-organic into a conductive structure, and these high temperatures accordingly limit the range substrates suitable for use in conjunction with such ink systems.

[0009] Many metallic nanoparticle systems have been described in the literature and there are accordingly many methods for preparing and stabilizing metallic nanoparticles. Haes, A.J. and Van Duyne, R.P., *J. Am. Chem. Soc.*, **2002**, 124 , 10596; Chen, S., et al, *J. Phys. Chem. B,* **1992**, 124, 9898; Li, Y., et al., *Langmuir*, **2002**, 18, 4921; Taleb, A., et al., Chem. Mat., **1997**, 9, 950; Yi, K.C., et al., *J. Phys. Chem. B.*, **1994**, 98, 38721 Esumi, K., et al, *Langmuir*, **2000**, 16, 2604; Harfensit, S.A., et al, J. Phys. Chem. B, **1996**, 100, 13904; Bunge, S.D., Boyle, T.J., et al., *Nano. Letters*, **2003**, 3, 901; Wang, W., et al, *Langmuir*, **1998**, 14, 602; Yamamoto, M., et al., *Langmuir*, **2006**, 22, 8581; Yamamoto, M., *Chem. Letters*, **2003**, 32, 452. Some of these methods include: condensation of metal vapor to create particles, thermal decomposition of atomized metal organic salts, and use of chemically reduced metal salt solutions to produce particles. All of these production or synthesis methods require that the produced nanoparticles be stabilized in order that the nanoparticles do not interact with each other or aggregate to form larger particles that become unsuitable for a given application. Thus, preventing metallic nanoparticle aggregation can be crucial to a ink composition having maximum utility.

[0010] The mechanism of stabilization is important in that the manner by which agents that stabilize metallic nanoparticles against aggregation also affect the ability of the metallic particles to sinter at a low temperature. A low temperature sintering process is critical to application of conductive inks to substrates, such as paper, that can not tolerate high temperatures. Affecting the ability of the metallic nanoparticles to sinter in turn defines the cure characteristics of the ink; systems that form conductive structures only after curing at temperatures above 150°C and only after long cure times may possess such suboptimal cure behavior in part because of the method used to stabilize the particles. Hence, an ideal stabilizing species prevents permanent aggregation of the particles while not interfering with the particle sintering process when heat is applied. Other considerations present in choosing a stabilizing agent or agents also include the effect of the stabilizer on the nanoparticles' shelf life and their cost.

[0011] An additional consideration in crafting a system for stabilizing metallic nanoparticles against aggregation is the choice of the medium in which the metallic nanoparticles are dispersed. Certain conductive ink compositions spread out on a substrate surface before curing, thus adversely impacting the ability to form structures of a certain, defined shape. In addition, certain compositions incorporate organic solvents, which are difficult to dispose of. Furthermore, systems comprising metallic nanoparticles dispersed in an organic solvent medium suffer from poor sintering characteristics once deposited onto a substrate, and may require comparatively long exposure to comparatively high temperatures in order to form conductive traces after deposition. E.g., Lee, et al., *J. of Colloid and Interface Sci*, **2006**, 304, 92-97.

[0012] One potential hindrance to metallic nanoparticles' use in conductive inks is their limited ability to form relatively thick conductive traces. While large metallic particles – typically characterized as having diameters of greater than about 500 nm – are limited in application because they do not sinter at low temperatures, large particles are nonetheless capable of forming thicker metal traces than metallic nanoparticles are capable of forming. Hence, because of large metallic particles' inability to sinter and form conductive structures at low temperatures, manufacturers are limited in their ability to form thick conductive structures on substrates that are incapable of withstanding the temperatures necessary for large particles to cohere into conductive structures.

[0013] Accordingly, based on the current state of the art, there is a need for an aqueous metallic nanoparticle composition, that exhibits little to no particle aggregation and is capable of forming a cohesive, conductive structure on a broad range of substrates after exposure to moderate temperatures for short periods of time following deposition via a printing process, and method of making such a composition. There is also a related need for a method of forming conductive structures by using such a composition.

[0014] Furthermore, the difficulty in inducing large metallic particles to form conductive structures under moderate processing conditions also gives rise to a need for a method for forming thick conductive structures on substrates capable of tolerating only low temperatures. There is also a related need for any compositions suitable for such a method.

SUMMARY OF THE INVENTION

[0015] In overcoming the challenges associated with providing an aqueous metallic nanoparticle composition capable of being deposited on a substrate and forming a cohesive conductive structure under moderate temperature conditions, the present invention provides, inter alia, a composition comprising a population of metallic nanoparticles dispersed in an aqueous medium, wherein at least a portion of the population comprising individual metallic nanoparticles characterized as having an average cross-sectional dimension in the range of from about 1 nm to about 100 nm.

[0016] In another aspect, the present invention provides a composition, comprising: a metallic nanoparticle mixture capable of forming a cohesive structure of less than about 10 μm in thickness following curing at a temperature of less than about 140°C for less than about 90 seconds, wherein the cohesive structure has a resistivity in the range of from about 2 times to about 15 times the bulk resistivity of the corresponding metal.

[0017] Additionally, the present invention provides methods for synthesizing a metallic nanoparticle dispersion. As will be disclosed in further detail, the methods include reacting in an aqueous medium: at least one ligand, wherein the ligand comprises a heteroatom head group bonded to a tail comprising from 1 to about 20 carbon atoms; at least one reducing agent; and, at least one metallic salt in an aqueous dispersing solution, wherein the metallic salt is present in the dispersion at a concentration in the range of from about 10 grams/liter to about 600 grams/liter based on volume of the dispersing solution, and wherein the metallic salt comprises at least one cation comprising silver, copper, gold, zinc, cadmium, palladium, iridium, ruthenium, osmium, rhodium, platinum, iron, nickel, cobalt, indium, or any combination thereof.

[0018] The present invention further provides methods for forming a conductive structure on a substrate. As will be set forth in greater detail, the methods comprise depositing a composition onto the substrate, wherein the composition comprises at least one population of metallic nanoparticles, wherein at least a portion of the population comprising individual metallic nanoparticles characterized as having an average cross-sectional dimension in the range of from about 1 nm to about 100 nm; wherein each of the nanoparticles comprise at least one ligand bound to its surface, the ligand comprising a heteroatom head group bound to the nanoparticle surface and a tail bound to the heteroatom head group; and, curing the deposited composition.

[0019] In additional aspects, the present invention provides methods for forming a conductive structure. These methods, as will be set forth in further detail, comprise depositing a metallic nanoparticle composition onto the substrate, wherein the composition is capable of forming, after curing at a temperature of less than about 140°C for less than about 90 seconds, a cohesive and conductive structure having a resistivity in the range of from about 2 times to about 15 times the bulk resistivity of the corresponding metal and having a thickness of less than about 20 μm, and curing the deposited composition.

[0020] The general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as defined in the appended claims. Other aspects of the present invention will be apparent to those skilled in the art in view of the detailed description of the invention as provided herein.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] The summary, as well as the following detailed description, is further understood when read in conjunction with the appended drawings. For the purpose of illustrating the invention, there are shown in the drawings exemplary embodiments of the invention; however, the invention is not limited to the specific methods, compositions, and devices disclosed. In addition, the drawings are not necessarily drawn to scale. In the drawings:

[0022] **FIG. 1(A)** depicts a transmission electron microscope ("TEM") micrograph of silver nanoparticles synthesized by the present invention;

[0023] **FIG. 1(B)** illustrates a scanning electron microscope ("SEM") micrograph of a trace comprised of a composition of the present invention cured for 1 minute at 100°C;

[0024] **FIG. 1(C)** depicts a SEM micrograph of a trace comprised of a composition of the present invention cured for 3 minutes at 85°C;

[0025] **FIG. 2** depicts a particle size distribution, on a weight basis, of a composition of the present invention; and,

[0026] **FIG. 3** depicts the weight resistivity versus cure time for certain compositions provided by the present invention and for certain prior art compositions.

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

[0027] The present invention may be understood more readily by reference to the following detailed description taken in connection with the accompanying figures and examples, which form a part of this disclosure. It is to be understood that this invention is not limited to the specific devices, methods, applications, conditions or parameters described and/or shown herein, and that the terminology used herein is for the purpose of describing particular embodiments by way of example only and is not intended to be limiting of the claimed invention. Also, as used in the specification including the appended claims, the singular forms "a," "an," and "the" include the plural, and reference to a particular numerical value includes at least that particular value, unless the context clearly dictates otherwise. The term "plurality", as used herein, means more than one. When a range of values is expressed, another embodiment includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent "about," it will be understood that the particular value forms another embodiment. All ranges are inclusive and combinable.

[0028] It is to be appreciated that certain features of the invention which are, for clarity, described herein in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features of the invention that are, for brevity, described in the context of a single embodiment, may also be provided separately or in any subcombination. Further, reference to values stated in ranges include each and every value within that range.

Terms

[0029] As used herein, the term "aqueous" means containing water.

[0030] As used herein, the term "bonding" means covalently bonding, ionically bonding, hydrogen bonding, coordinate bonding, and the like.

[0031] As used herein, the term "tail" means a straight, branched, or cyclic chain of carbon atoms, wherein the chain may be aliphatic, and wherein the chain may have one or more additional groups bound to one or more of its member carbon atoms. An example would be a chain of aliphatic carbon atoms with an alcohol group attached to one of the chain members.

[0032] As used herein, the term "heteroatomic head group" means a group including at least one atom wherein at least one atom within the group is atom other than carbon. Examples include nitrogen, sulfur, or oxygen.

[0033] As used herein, the term "cohesive" means united as a single entity and resisting separation.

[0034] As used herein, the term "complexing" means forming coordinating bonds with a metal atom or ion.

[0035] As used herein, the term "ligand" means a molecule or a molecular group that binds to another chemical entity to form a larger complex. Examples include a molecular group that becomes bound to a metal or metal ion by a coordinate covalent bond through donating electrons from a lone electron pair of the ligand into an empty metal electron orbital.

[0036] As used herein, the term "agglomeration" means two or more particles reversibly clustered together, wherein the surfaces of the particles do not come into contact with one another.

[0037] As used herein, the term "floc" means two or more particles reversibly clustered together, wherein the surfaces of the particles do not come into contact with one another.

[0038] As used herein, the term "bulk resistivity" means the inherent resistivity of a material that makes up a specified object. For example, the bulk resistivity of a ingot made of silver would be the inherent conductivity of silver. As another example, the bulk resistivity of an ingot made of an alloy comprising silver and gold would be the inherent conductivity of the silver and gold alloy.

[0039] As used herein, the terms "aggregate", "aggregation", and similar forms mean a unified structure comprised of two or more particles irreversibly fused, connected, or necked together.

[0040] Compositions of the present invention typically include a population of metallic nanoparticles dispersed in an aqueous medium, wherein at least a portion of the population comprising individual metallic nanoparticles characterized as having an average cross-sectional dimension in the range of from about 1 nm to about 100 nm; and, wherein each of the nanoparticles comprise at least one ligand bound to its surface, the ligand comprising a heteroatom head group bound to the nanoparticle surface and a tail bound to the heteroatom head group.

[0041] Nanoparticle populations typically comprise particle agglomerate comprised of two or more individual nanoparticles, nanoparticle floc comprised of two or more individual nanoparticles, or any combination thereof. The ratio, by weight, of the population of individual metallic nanoparticles to particle agglomerate is contemplated as being in the range of from about 1:99 to 99:1, and the ratio, by weight, of the population of individual metallic nanoparticles to particle floc is contemplated as being in the range of from about 1:99 to 99:1.

[0042] In certain embodiments, a nanoparticle agglomerate has an average cross-sectional dimension in the range of from about 100 nm to about 10000 nm; a nanoparticle floc has an average cross-sectional dimension in the range of from about 100 to about 10000 nm.

[0043] An individual metallic nanoparticle may include silver, copper, gold, zinc, cadmium, palladium, iridium, ruthenium, osmium, rhodium, platinum, iron, nickel, cobalt, indium, silver oxide, copper oxide, gold oxide, zinc oxide, cadmium oxide, palladium oxide, iridium oxide, ruthenium oxide, osmium oxide, rhodium oxide, platinum oxide, iron oxide, nickel oxide, cobalt oxide, indium oxide, or any combination thereof.

[0044] It is contemplated that the ligand tail comprises from about 1 to about 20 carbon atoms. The tail can comprise a straight-chain segment, a branched segment, a cyclic segment, or any combination thereof, and can further comprise an aliphatic chain, an acid group, an alcohol group, an amphiphillic group, an amine group, and the like, or any combination thereof.

[0045] Suitable heteroatom head groups comprise oxygen, sulfur, nitrogen, and the like.

[0046] The aqueous medium comprises water, and it is envisioned that the aqueous medium can further comprise one or more polar organic solvents, one or more non-polar organic solvents, or any combination thereof. A suitable polar organic solvent comprises an alcohol, a polyol, a glycol ether, 1-methyl pyrolidinone, pyridine, methylethylketone, or any combination thereof. A suitable non-polar organic solvent comprises tetrahydrofuran, toluene, xylene, a C_5 to C_{14} branched paraffin, a C_5 to C_{14} unbranched paraffin, N,N – dimethyl formamide, or any combination thereof.

[0047] The aqueous medium is typically capable of solvating the metallic salt in a range of from about 10 grams/liter to about 600 grams/liter, or even 50 to 200, or even 80 to 120.

[0048] It is envisioned that the nanoparticles are present in the range of from about 0.5 wt %to about 70 wt %, the ligand is present in the range of from about 0.5 wt % to about 75 wt %, and the medium is present in the range of from about 30 to about 98 wt %.

[0049] In some embodiments, the composition is capable of forming a cohesive structure of less than about 10 μm in thickness following curing at a temperature of less than about 110°C for less than about 90 seconds. The structure suitably has a resistivity in the range of from about 2 times to about 15 times the bulk resistivity of the corresponding metals present in the composition.

[0050] Compositions also comprise a metallic nanoparticle mixture capable of forming a cohesive structure of less than about 10 μm in thickness following curing at a temperature of less than about 110°C for less than about 60 seconds, or capable of forming a cohesive structure of less than about 5 μm in thickness following curing at a temperature of less than about 140°C for less than about 15 seconds, or capable of forming a cohesive structure of less than about 2 μm in thickness following curing at a temperature of less than about 110°C for less than about 10 seconds, or capable of forming a cohesive structure of less than about 2 μm in thickness following curing at a temperature of less than about 140°C for less than about 5 seconds, wherein the cohesive structure has a resistivity in the range of from about 2 times to about 15 times the bulk resistivity of the corresponding metal in the composition.

[0051] Suitable mixtures comprise a population of metallic nanoparticles, a ligand, an aqueous medium, or any combination thereof.

[0052] In some embodiments, the metallic nanoparticle populations can comprise individual nanoparticles, particle agglomerate comprised of two or more individual nanoparticles, particle floc comprised of two or more individual nanoparticles, or any combination thereof. The ratio, by weight, of the population of individual metallic nanoparticles to particle agglomerate can be in the range of from about 1:99 to 99:1, and the ratio, by weight, of the population of individual metallic nanoparticles to particle floc is typically in the range of from about 1:99 to 99:1. In other embodiments, substantially all of the nanoparticles are agglomerated. In other embodiments, substantially all of the nanoparticles are discrete individual nanoparticles.

[0053] In some embodiments of the invention, individual metallic nanoparticles have an average cross-sectional dimension in the range of from about 1 nm to about 100 nm; or even from about 5 nm to about 30 nm, or even from about 10 nm to about 20 nm. Particle size can be measured using an acoustic attenuation spectroscopy method substantiated by transmission electron microscopy. Particle agglomerates have an average cross-sectional dimension of at least about 2 nm, or even at least about 20 nm, or even at least about 200 nm, or in the range of from about 100 nm to about 10000 nm; and particle flocs have an average cross-sectional dimension in the range of from about 100 to about 10000 nm. Individual metallic nanoparticles and ligands are as described elsewhere herein; ligands are typically characterized as bound to a surface of one or more metallic nanoparticles by a heteroatom head group so as to give rise to one or more metallic nanoparticles stabilized against irreversible aggregation.

[0054] The aqueous medium of these compositions typically comprises water, and can further comprise one or more polar organic solvents, one or more non-polar organic solvents, or any combination thereof. The aqueous medium is typically capable of solvating the metallic salt in a range of from about 10 grams/liter to about 600 grams/liter, and suitable polar organic solvents include an alcohol, a polyol, a glycol ether, 1-methyl pyrolidinone, pyridine, methylethylketone, or any combination thereof. Suitable non-polar organic solvents comprises tetrahydrofuran, toluene, xylene, a C_5 to C_{14} branched paraffin, a C_5 to C_{14} unbranched paraffin, N,N – dimethyl formamide, or any combination thereof.

[0055] The nanoparticles can be present in the range of from about 0.5 to about 70 wt %, the ligand can be present in the range of from about 0.5 to about 75 wt %, and the medium can be present in the range of from about 30 to about 98 wt %. The nanoparticles can be present in the range of from about 10 to about 60 wt %, the ligand can be present in the range of from about 1 to about 30 wt %, and the medium is present in the range of from about 30 to about 98 wt %. The nanoparticles can be present in the range of from about 15 to about 55 wt %, the ligand is present in the range of from about 2 to about 25 wt %, and the medium is present in the range of from about 30 to about 98 wt %. Also, the amount of ligand can be about 10% based on weight relative to the weight of the nanoparticles.

[0056] In one embodiment, the present invention involves the chemical reduction of metal salt in the presence of a ligand, which ligand is capable of complexing or bonding to the metal in a dispersing medium. The metal salt can be solvated by the solvent or dispersed in the solvent as a solid if the salt is insoluble in the solvent phase. Suitable solvents include aqueous solvents substantially free of organic solvents. Suitable solvents also include some polar organic solvents, e.g., if the metal salt can be solvated in a sufficiently high concentration, e.g., about 0.3 to about 0.9 M, or about 0.45 to about 0.7 M, or about 0.55 to about 0.6 M. The metal may include silver, copper, gold, zinc, cadmium, palladium, iridium, ruthenium, osmium, rhodium, platinum, iron, nickel, cobalt, indium, or any combination thereof. The salt anion may include nitrates, carboxylates, sulfates, or chlorides. The reducing agent must be of sufficient electrochemical potential and concentration to effectively reduce the respective metal salt. Strong reducing agents such as hydrazine, hydrazine hydrate, or hydrogen, that do not produce undesirable ionic byproducts are suitable; other reducing agents such as sodium borohydride may be used.

[0057] Ligands can be chosen on their ability to complex with metal particles and stabilize the particles against aggregation; one consideration is the ability of the ligand to allow the particles to consolidate and sinter during drying and thermal treatment. The temperature at which the particles sinter is in some part controlled by the ligand adsorbed to the metal. The ligand can be characterized as bonding to the metal through a heteroatom such as oxygen, sulfur, or nitrogen. In some embodiments the heteroatom portion of the ligand is provided as a carboxyl, sulfonyl, thiol, and the like. Without being bound to any particular theory of operation, it is believed that based on the relative thermal stability of the complexing portion and aliphatic backbone of the ligand compound, an intermediate salt may result during thermal treatment that adversely affecting the sintering of the metal nanoparticles. Ligands having a straight-chain aliphatic backbone comprising from about 1 to about 20 carbon atoms are particularly suitable. Branched or cyclic backbones having up to about 20 carbon atoms may be used, for example, if the ligand is sufficiently stable in the solvent system. Suitable ligands can preferably have from about 5 to about 12 carbon atoms in the aliphatic tail.

[0058] In the present invention, no post-synthesis treatment such as washing or phase transfer is needed in order to remove residual byproducts such as the metal salt anion. Although this step is not needed, additional washing and post-processing steps can be used. The byproducts of the reaction are left in the nanoparticle mixtures to catalyze the decomposition of the ligands on the nanoparticles surface. In particular, nitrate anions can react with organic acid ligands in self-propagating chemical decomposition or anionic oxidation-reduction synthesis of superconducting oxides to prevent intermediate metal salts. Alternatively, a compound such as an amine could be added to the reaction product or be part of the ligand molecule which similarly catalyzes the decomposition of the ligands and sintering of the nanoparticles. The particles are sometimes allowed to settle in order to concentrate them for forming films.

[0059] Without being bound by a particular theory of operation, it is believed that the metallic nanoparticles are able to remain dispersed in the aqueous phase by the formation of self-assembled surfactant structures, e.g., an interdigitated bi-layer, of the ligand or vesicle structures around the metallic nanoparticles. In other cases, the nanoparticles can phase separate from the aqueous phase giving rise to an oily ligand-rich phase comprising concentrated nanoparticles and a second aqueous phase. The particles can be stabilized by ligands binding to the surface of the silver through nucleophilic head groups with the aliphatic portion extending outward. The aliphatic portion of ligands not bound to the nanoparticle surface can associate with the aliphatic portion of the bound ligands forming a vesicle around the nanoparticle. Also without being bound to any particular theory of operation, it is believed that if no bi-layer formed, the metallic nanoparticles may phase-separate into an oily phase. Accordingly, ligands can form a bi-layer around the particles. The bi-layer can be broken down causing the nanoparticles to form a hydrophobic phase by either modifying the pH or by adding a salt or to the aqueous sol.

[0060] Accordingly, methods for synthesizing a metallic nanoparticle dispersion include reacting in an aqueous medium: at least one ligand, wherein the ligand comprises a heteroatom head group bonded to a tail comprising from 1 to about 20 carbon atoms; at least one reducing agent; and, at least one metallic salt in an aqueous dispersing solution, wherein the metallic salt is present in the dispersion at a concentration in the range of from about 10 grams/liter to about 600 grams/liter based on volume of the dispersing solution, and wherein the metallic salt comprises at least one cation comprising copper, gold, zinc, cadmium, palladium, iridium, ruthenium, osmium, rhodium, platinum, iron, nickel, cobalt, indium, or any combination thereof. Preferably the metallic salt comprises silver.

[0061] Typically, the tail is as described elsewhere herein; suitable heteroatom head groups comprise oxygen, sulfur, nitrogen, and the like. A suitable ligand is characterized as being capable of binding by its heteroatom head group to a surface of a metallic nanoparticle so as to give rise to a metallic nanoparticle stabilized at least in part against aggregation.

[0062] Suitable reducing agents include strong reducing reagents that typically are capable of reducing metals in aqueous systems, e.g., hydrazine, hydrazine hydrate, hydrogen, sodium borohydride, lithium borohydride, ascorbic acid, a primary amine, a secondary amine, a secondary amine, a tertiary amine, and the like, or any combination thereof.

[0063] The metallic salt typically comprises at least one anion, wherein the anion comprises acetate, nitrate, carboxylate, sulfate, chloride, hydroxide, or any combination thereof.

[0064] A suitable dispersing solution comprises an aqueous medium. Another suitable dispersing solution comprises an aqueous medium substantially free of organic solvents, and can comprise water. The dispersing solution can further comprise one or more polar organic solvents, one or more non-polar organic solvents, or any combination thereof. Suitable polar and non-polar solvents are as described elsewhere herein.

[0065] Reacting can comprise contacting, mixing, stirring, sonicating, agitating, and the like; after reacting, one or more ligand heteroatom head groups are characterized as bound to a surface of one or more metallic nanoparticles so as to give rise to one or more metallic nanoparticles stabilized against irreversible aggregation.

[0066] The method typically comprises combining the ligand and metallic salt in a respective molar ratio in the range of from about 0.1:1 to about 0.2:0.7, or even in the range of from about 0.1:1 to about 0.3:0.5; combining the metallic salt and reducing agent in a respective molar ratio in the range of from about 0.7:1 to about 1:2, in other cases the metallic salt and reducing agent in a respective molar ratio in the range of from about 4:1 to about 1:2, in other cases the metallic salt and reducing agent in a respective molar ratio in the range of from about 0.6:1 to about 1.2:1. The method can, in some embodiments, include adjusting the relative amounts of ligand, reducing agent, metallic salt, aqueous dispersing solution, adjusting the pH of the aqueous medium, or any combination thereof, so as to give rise to a pH in the range of from about 3 to about 12. In certain embodiments, the pH can vary between the basic and acidic regimes during the reaction.

[0067] In some configurations, the method includes heating the aqueous medium, ligand, reducing agent, and metallic salt in aqueous dispersing solution, or any combination thereof, to a temperature of from about 5°C to about 200°C prior to reaction, to a temperature of from about 35°C to about 70°C prior to reaction, or to a temperature of from about 40°C to about 60°C prior to reaction.

[0068] The method typically includes a recovery step following reaction. The recovery step can include allowing the passage of sufficient time such that the concentration of nanoparticles in any aqueous medium present after reaction can be in the range of from about 0 wt % to about 70 wt%, or in the range of from about 0.5 wt % to about 30 wt.%, or in the range of from about 2 wt % to about 20 wt.%, or in the range of from about 3 wt % to about 7 wt.%, and then recovering the reaction products. In some cases, the recovery step comprises allowing the passage of sufficient time such that the concentration of nanoparticles in any aqueous medium present can be in the range of from about 0.5 wt % to about 70 wt.%, or in the range of from about 5 wt % to about 60 wt.%, decanting the aqueous medium, recovering the reaction products, and ultrafiltration of the decanted aqueous medium to recover any nanoparticles residing in the decanted medium. In some cases, a cake comprising nanoparticles will be formed. Such a cake can have from about 25 wt.% to about 70 wt.%. In other embodiments, a supernatant is formed, which can comprise from 0 wt.% up to about 30 wt.% nanoparticles. Distribution of the nanoparticles can be distributed between supernatant and cake. The recovery step can include ultrafiltration of any aqueous medium present following reaction when there are no settled reaction products so as to recover nanoparticles present in the medium.

[0069] In some embodiments, the reacting comprises continuously introducing the aqueous medium, ligand, and reducing agent into a first stirred reactor capable of fluid communication with the contents of a second stirred reactor. Suitable medium, ligand, and reducing agent are described elsewhere herein, as are the suitable ratios of these entities to one another. The aqueous medium, ligand, reducing agent, and metallic salt in aqueous dispersing solution may be heated as set forth elsewhere herein. Typically, the residence time of the first reactor is sufficient to as to give rise to the reaction progressing to substantial completion, and the method can include continuously transporting the contents of the first reactor to the second reactor; the residence time in the second reactor is envisioned as sufficient to allow the reaction to progress to essentially total completion.

[0070] The methods described herein can also include one or more recovery steps.

[0071] Metallic nanoparticles synthesized according to the present invention and the structures formed by curing these nanoparticles are shown in **FIGS 1(A), 1(B), and 1(C)**. **FIG. 1(A)** depicts silver nanoparticles made according to the present invention. As can be seen by comparison of the particles to the scale bar in **FIG. 1(A)**, typical nanoparticles made in accordance with the present invention have widths of well under 100 nm. **FIG 1(B)** depicts a structure formed by metallic nanoparticles made according to the present invention after curing at about 100°C for about 1 minute. **FIG. 1(C)** depicts a structure formed by metallic nanoparticles made according to the present invention after curing at about 85°C for about 3 minutes.

[0072] The existence of individual particles along with nanoparticle agglomerate in certain embodiments of the present invention is shown in **FIG. 2**. That figure depicts, on a weight basis, the proportion of individual metallic nanoparticles synthesized according to the present invention relative to nanoparticle agglomerate comprised of the individual nanoparticles.

[0073] Methods for forming a conductive structure on a substrate comprise depositing a composition onto the substrate, wherein the composition comprises at least one population of metallic nanoparticles, at least a portion of the population comprising individual metallic nanoparticles characterized as having an average cross-sectional dimension in the range of from about 1 nm to about 30 nm; wherein each of the nanoparticles comprise at least one ligand bound to its surface, the ligand comprising a heteroatom head group bound to the nanoparticle surface and a tail bound to the heteroatom head group; and, curing the deposited composition.

[0074] The depositing can include a printing method; suitable printing methods include flexographic printing, rotogravure printing, lithographic printing, intaglio printing, relief printing, screen printing, inkjet printing, laser printing, or any combination thereof.

[0075] As pertaining to the composition of these methods, typical populations of metallic nanoparticles are as described elsewhere herein, as are suitable ligands, and acceptable aqueous media.

[0076] A further consideration in formulating metallic nanoparticle-based inks is rheology. The ink rheology is influenced by the deformation behavior of the solid components and the flow behavior of the components. Mezger, T.G., *The Rheology Handbook*, 2002, published by Vincentz Verlag, Hannover, Germany; Verstrat, D.W., Research Report, Formulating with Associative Rheology Modifiers, Alco Chemical website, www.alcochemical.com, Alco Chemical Company, Division of National Starch and Chemical Company, Chattanooga, TN; Manshausen, P., Borchers GmbH, Monheim, Germany, *Presented* *at the 6th Nurnberg Congress*, April, 2001. These behaviors are responses to shear forces imparted on the ink during the process of depositing or printing the ink onto the desired substrate. Additives can modify the ink rheology such that the desired flow properties are achieved with minimal adverse affects on the electrical properties and adhesion of the metallic trace or film.

[0077] There are many choices for rheology modifiers, Manshausen, P., Borchers GmbH, Monheim, Germany, *Presented at the 6th Nurnberg Congress*, April, 2001; Young, V.L. and Hickman, A.D., *Dow Latex Technotes*, January 6, 1992, including associative and non-associative organic thickeners, as well as inorganic thickeners. Associative thickeners generally associate with ingredients in the inks such as the metal nanoparticles and the polymeric binder particles incorporated for adhesion. Non-associative thickeners interact with the aqueous phase, essentially thickening the water.

[0078] The composition of the method can include one or more rheology modifiers. Some such modifiers can include an associative thickener such as hydrophobically modified polyether polyurethane, hydrophobically modified polyether, hydrophobically modified acrylic thickener, hydrophobically modified cellulose ether, and the like. Alternatively, the rheology modifier can include a thickening agent such as an alkali-soluble emulsion, such as a polymer comprising units polymerized from (meth)acrylic acid, wherein a suitable polymer comprises a homopolymer of (meth)acrylic acid, a co-polymer of (meth)acrylic acid and (meth)acrylate esters, maleic acid, or any combination thereof. A thickening agent can also include a cellulose based material such as hydroxyethyl cellulose, hydroxypropyl cellulose, arabinogalactin, dextran, starches, an acid swellable emulsion, a polyvinyl alcohol, a polyacrylamide, polyethylene glycol, or any combination thereof. Typically, a rheology modifier can be present in the range of from about 0 wt% to about 15 wt%, or in the range of from about 0 wt% to about 7 wt%, or even in the range of from about 0 wt% to about 3 wt%.

[0079] Preparation of a formulation that is viable as an ink to be printed on commercial printing equipment also typically requires the addition of agents to enable or enhance adhesion of the cured ink to the desired substrate, to enhance the wetting of the ink on the substrate, and to modify the rheological or flow characteristics of the ink.

[0080] Typically, metallic nanoparticles will not adhere to untreated substrates that are commonly used such as polyester, polypropylene, and paper. Thus, adhesives, binders, or any combination thereof, may be added to the metallic nanoparticle dispersion such that additive establishes a chemical or physical bond with the surface of the desired substrate. Ideally, these additives do not prevent or hamper the process of curing or sintering the metallic nanoparticles into a continuous, conductive film or structure. In addition, the adhesion-enhancing additive should be chosen such that it does not affect the stability of the nanoparticles. Adhesion-promoting additives generally include surfactants that contribute to the ink wetting the substrate surface.

[0081] Accordingly, the composition of the disclosed method further comprises a binder, which can include a latex, any polymer soluble in the solvent medium of the nanoparticles, or compatible with the nanoparticles, a polymer latex, an emulsion polymer, polyimide, a silicone, a fluorocarbon, a polyamic acid, a polyurethane, a polyester, an epoxy, polyvinylalcohol, polyacrylamide, or any combination thereof. It is envisioned that the binder is present in the range of from about 0 wt% to about 20 wt%, or in the range of from about 0 wt% to about 7 wt%., or in the range of from about 0 wt% to about 5 wt%.

[0082] Substrates suitable for the method include a glass, a ceramic, a polymer, a silicon, a nitride, a carbides, a ceramic precursor, or any combination thereof. Suitable polymers include a polyester, a polyolefin, a polycarbonate, an acrylic polymer, polyethylene naphthalate, polyimide, polyamideimide, polyvinyl chloride, polypropylene, a liquid crystal polymer, polycarbonate, or any combination thereof. In some embodiments, the substrate comprises paper, synthetic engineered paper, cardboard, a coated corrugated cardboard, uncoated corrugated cardboard, a fabric, and the like.

[0083] In some instances, it is envisioned that at least a portion of a surface of the substrate is capable of being modified to give rise to a surface capable of adhering to the deposited composition.

[0084] In some embodiments of the invention, the composition further comprises metallic particles. Such particles typically have a width in the range of from about 200 nm to about 20000 nm, in the range of from about 500 nm to about 10000 nm, or in the range of from about 800 nm to about 3000 nm. Suitable particles comprise silver, copper, gold, zinc, cadmium, palladium, iridium, ruthenium, osmium, rhodium, platinum, iron, nickel, cobalt, indium, silver oxide, copper oxide, gold oxide, zinc oxide, cadmium oxide, palladium oxide, iridium oxide, ruthenium oxide, osmium oxide, rhodium oxide, platinum oxide, iron oxide, nickel oxide, cobalt oxide, indium oxide, or any combination thereof.

[0085] The curing aspect of the method typically comprises exposing the deposited composition to a temperature of less than about 110°C for less than about 90 seconds; a structure formed by the method typically has a thickness of less than about 20 μm; or exposing the deposited composition to a temperature of less than about 110°C for less than about 60 seconds; a structure formed by the method typically has a thickness of less than about 15 μm; or exposing the deposited composition to a temperature of less than about 140°C for less than about 30 seconds; a structure formed by the method typically has a thickness of less than about 15 μm; or exposing the deposited composition to a temperature of less than about 110°C for less than about 30 seconds; a structure formed by the method typically has a thickness of less than about 8 μm; or exposing the deposited composition to a temperature of less than about 140°C for less than about 20 seconds; a structure formed by the method typically has a thickness of less than about 8 μm.

[0086] Methods for forming a conductive structure include depositing a metallic nanoparticle composition onto the substrate, wherein the composition is capable of forming after curing at a temperature of less than about 110°C for less than about 90 seconds a cohesive and conductive structure having a resistivity in the range of from about 2 times to about 15 times the bulk resistivity of the corresponding metal and having a thickness of less than about 20 μm; and, curing the deposited composition.

[0087] Suitable deposition processes are described elsewhere herein. Nanoparticle compositions are envisioned as including a population of metallic nanoparticles, a ligand, a medium, or any combination thereof, all as discussed elsewhere herein.

[0088] Suitable compositions further can also include rheology modifiers as described elsewhere herein. The composition is envisioned as further comprising a binder, as described elsewhere herein. Suitable compositions may also include metallic particles, as detailed elsewhere.

[0089] **FIG.** 3 depicts resistivity as a function of cure time for prior art compositions and compositions provided by the present invention. As shown, the resistivity of a composition comprising metallic silver nanoparticles synthesized by the present invention (trace **(b)**) achieve a resistivity comparable to that of bulk silver (trace **(a)**) after curing at a temperature of about 85°C for about 1 minute. Trace **(c)** represents a composition comprising metallic silver nanoparticles synthesized by the present invention and certain additives such as rheology modifiers and binders; as shown, that composition also approaches the resistivity of bulk silver after curing at a temperature of about 100°C for about 6 minutes. Trace **(d)** represents a composition produced by Sumitomo Metal Mining Co (Japan), http:www.smm.co.jp/b_info_E/b10_E.html which composition, when cured at 150°C, achieved resistivity higher than that of compositions made according to the present invention at all cure times. Trace **(e)** represents a composition produced by Sumitomo (Japan), which, when cured at 100°C, and also is characterized as having a resistivity several orders of magnitude greater than that of compositions made according to the present invention at all cure times.

EXAMPLES

[0090] The following are non-limiting examples that are representative only and that do not necessarily restrict the scope of the present invention.

Example 1

[0091] An initial solution was prepared by adding 7.5 grams of ammonium hydroxide (30% ammonia by weight) to 275 grams of water; 13.5 grams of heptanoic acid was added to this solution followed by 20.9 grams of 50 % hydrazine hydrate aqueous solution. The ammonium hydroxide is necessary to allow the acid to dissolve in the water. Separately, 36 grams of silver nitrate was dissolved in 175 grams of water. The silver nitrate solution was added to the initial solution while stirring under nitrogen. The resultant product was flocculated and allowed to settle. Excess water was decanted off. The concentrated product was spread onto 5 mil polyester film with a 0.5 mil wire wound rod and then cured at 80°C and 100°C for 1-2 minutes resulting in cohesive and conductive silver films.

Example 2

[0092] An initial solution was prepared by adding 2.1 grams of ammonium hydroxide (30% ammonia by weight) to 50 grams of water; 7.8 grams of heptanoic acid was added to this solution followed by 3 grams of 50 % hydrazine hydrate aqueous solution. Separately, 10 grams of silver nitrate was dissolved in 50 grams of water. The silver nitrate solution was added to the initial solution while stirring under nitrogen. The resultant product was allowed to settle and the excess water decanted off.

[0093] The concentrated product was spread onto 5 mil polyester film with a 0.5 mil wire wound rod and then cured at 80°C and 100°C for 1-2 minutes resulting in cohesive and conductive silver films. The weight resistivity of a sample cured at 100°C for 1 minute was measured to be 0.39 gram-ohms/m^2 (~2x bulk silver).

Example 3

[0094] An ink composition was prepared by adding 50 grams of spherical silver powder (1-2 um mean diameter) to 50 grams of 35 wt% nanoparticle dispersion of Example 1 also

containing 3 wt% of an acrylic copolymer latex (55 wt% polymer), 2 wt% of polyvinyl alcohol (25 wt% in water, M_w of 8,000-9,000), and 1 wt% ethylene glycol. The materials were mixed well together, and were milled in a mortar and pestle until a homogeneous mixture was obtained. A film of the resulting ink was deposited onto 0.005" thick untreated polyester film with a 0.0015" Bird film applicator. The wet film was cured in a 100°C for 30 seconds followed by 60 seconds at 140°C. The weight resistivity of the resulting silver films was measured to be 1.3 gram-ohms/m^2, approximately 8 times the resistivity of bulk silver. The adhesion of the film to the substrate was tested by applying a 4" long strip of Scotch brand tape (3M Corporation) to the film, insuring good adhesion to the film by applying pressure with the index finger (not the fingernail). The tape is then rapidly removed, pulling upward at a 90° angle, perpendicular to the substrate. This tape test method is derived from the ASTM D3359-02 Standard Test Method for Measuring Adhesion by Tape Test. Slight removal of the silver from the bulk of the trace was observed (4.215,with 5 being a clean tape), but none of the silver was removed from the substrate. The failure was observed to be a cohesive failure between the silver particles.

Example 4

[0095] An ink composition was prepared by adding 50 grams of spherical silver powder (1 -2 micron mean diameter) to 50 grams of 35 wt% nanoparticle dispersion also containing 10 wt% polyvinlacetate-polyethylene copolymer latex (50 wt% polymer), 2 wt% of polyvinyl alcohol (25 wt% in water, Mw of 8,000-9,000), and 1 wt% ethylene glycol. The materials were mixed well together, and were milled in a mortar and pestle until a homogeneous mixture was obtained. A film of the resulting ink was deposited onto 0.005" thick untreated polyester film with a #16 wire wound rod (0.016" wire diameter, 0.001" wet film thickness).. The wet film was cured in a 100°C for 30 seconds followed by 30 seconds at 140°C. The weight resistivity of the resulting silver films was measured to be 1.0 gram-ohm/m^2, approximately 6.2 times the resistivity of bulk silver. The adhesion of the film to the substrate was evaluated by utilizing the tape test method previously described in Example 2. The adhesion of the film to the substrate was very good (4.8/5), with only a trace of silver removed from the surface (cohesive failure), and no silver removal from the substrate was observed.

Example 5

[0096] An ink composition was prepared by adding 25 grams of spherical silver powder (1 -2 um mean diameter) to 50 grams of 35 wt% nanoparticle dispersion also containing 3 wt% acrylic copolymer (55 wt% polymer), and 4 wt% of polyacrylamide (50 wt% in water). The materials were mixed well together, and were milled in a mortar and pestle until a homogeneous mixture was obtained. A film of the resulting ink was deposited onto 0.005" thick untreated polyester film with a #16 wire wound rod (0.01 6" wire diameter, 0.00 1" wet film thickness). The wet film was cured in a 100°C for 30 seconds followed by 60 seconds at 130°C. The weight resistivity of the resulting silver films was measured to be 1.71 gram-ohms/m^2, approximately 10.7 times the resistivity of bulk silver. The adhesion of the film to the substrate was evaluated by utilizing the tape test method previously described in Example 2. The adhesion of the film to the substrate was very good (4.8/5), with only a trace of silver removed from the surface (cohesive failure), and no silver removal from the substrate was observed.

Example 6

[0097] An ink composition was prepared by adding 65 grams of spherical silver powder (1-2 pm mean diameter) to 80 grams of 35 wt% nanoparticle dispersion also containing 3 wt% acrylic copolymer (55 wt% polymer), 1.5 wt% of polyacrylamide (50 wt% in water), and 1 wt% propylene glycol. The materials were mixed well together, and were milled in a mortar and pestle until a homogeneous mixture was obtained. A film of the resulting ink was deposited onto 0.005" thick untreated polyester film with a #16 wire wound rod (0.016" wire diameter, 0.001" wet film thickness). The wet film was cured in a 100°C for 30 seconds followed by 60 seconds at 130°C. The weight resistivity of the resulting silver films was measured to be 1.3 1 gram-ohms/m^2, aproximately 8 times the resistivity of bulk silver. The adhesion of the film to the substrate was evaluated by utilizing the tape test method previously described in Example 2. The adhesion of the film to the substrate was good (4.215), with some removal (cohesive failure) of the silver from the bulk of the trace (4.215, with 5 being a clean tape), but no silver removal from the substrate.

Example 7

[0098] An ink composition was prepared by adding 52 grams of spherical silver powder (1 -2 pm mean diameter) to 64 grams of 35 wt% nanoparticle dispersion also containing 3 wt% acrylic copolymer (55 wt% polymer), 1.5 wt% of polyacrylamide (50 wt% in water), and 1 wt% propylene glycol. The materials were mixed well together, and were further mixed in vortex paint mixer for 5 minutes. A film of the resulting ink was deposited onto 0.005" thick untreated polyester film with a #16 wire wound rod (0.016" wire diameter, 0.001" wet film thickness). The wet film was cured in a 60°C for 20 seconds followed by 40 seconds at 130°C. The weight resistivity of the resulting silver films was measured to be 1.00 gram-ohms/m^2, appproximately 6 times the resistivity of bulk silver. The adhesion of the film to the substrate was evaluated by utilizing the tape test method previously described in Example 2. The adhesion of the film to the substrate was very good (4.9/5), with only a slight trace of silver removed from the surface (cohesive failure), and no silver removal from the substrate was observed. Further, resulting samples were folded in expansive mode (single crease) and than compressive mode (single crease), and a hard crease was made with the tip of the finger (not the finger nail) on each sample. Minimal loss of conductivity was observed for each sample.

Example 8

[0099] An ink composition was prepared by adding 10 grams of Floetrol (The Flood Company) to 40 grams of 35 wt% nanoparticle dispersion. The materials were mixed well together and a film of the resulting ink was deposited onto 0.005" thick untreated polyester film with a 0.0005" diameter wire wound rod and then cured at 130°C for 90 seconds resulting in cohesive and conductive silver films. The adhesion of the film to the substrate was tested by applying a 4" long strip of Scotch brand tape (3M Corporation) to the film, insuring good adhesion to the film by applying pressure with the index finger (not the fingernail). The tape is then rapidly removed, pulling upward at a 90' angle, perpendicular to the substrate. This tape test method is derived from the ASTM D3359-02, Standard Test Method for Measuring Adhesion by Tape Test. No material was removed from the substrate.

Example 9

[0100] An ink composition was prepared by adding 10 grams of a 25 wt% solution ofpolyvinyl alcohol (9,000-10,000 Mw, 80% hydrolyzed) to 40 grams of 35 wt% silver nanoparticle dispersion. The materials were mixed well together and a film of the resulting ink was deposited onto 0.005" thick polyester film with a 0.0005" diameter wire wound rod and then cured at 130°C for 90 seconds resulting in cohesive and conductive silver films. The adhesion of the film to the substrate was evaluated by utilizing the tape test method previously described. Some material was removed from the substrate, however, most of the ink remained on the substrate.

Example 10

[0101] A film of the as-prepared, 35 wt% silver nanoparticle dispersion was deposited onto 5 mil polyester film with a 0.0005" diameter wire wound rod and then cured at 85°C for 60 seconds resulting in cohesive and conductive silver films. The resulting film had a weight resistivity of 0.38 gram-ohms/m2 (IPC-TM-650, number 2.5.17.2). The adhesion of the film to the substrate was evaluated by utilizing the tape test method previously described. All of the material was removed from the substrate.

Example 11

[0102] An ink composition was prepared by adding 2.6 grams of a 1 or 2 wt% solution of commercially available hydrophobically modified hydroxyethylcellulose to 19.2 grams of 40 wt% silver nanoparticle dispersion. The materials were mixed well together and a film of the resulting ink was deposited onto 0.005" thick polyester film with a 0.0003" diameter wire wound rod and then cured at 130°C for 90 seconds resulting in a cohesive and conductive silver film. The adhesion of the film to the substrate was evaluated by utilizing the tape test method previously described. All of the material was removed from the substrate.

Example 12

[0103] An ink composition was prepared by adding 0.5 grams of a solution of hydrophobically modified ethoxylated urethane rheology modifier to 10 grams of 34 wt% silver nanoparticle dispersion. The materials were mixed well together and a film of the resulting ink was deposited onto 0.005" thick polyester film with a 0.0003" diameter wire wound rod and then cured at 100°C for 60 seconds resulting in a cohesive and conductive silver film. The adhesion of the film to the substrate was tested using the tape test method described above. All of the material was removed from the substrate.

Example 13

[0104] An ink composition was prepared by adding 0.36 grams of Arabinogalactan wood gum (Larex Grade 100) to 18.2 grams of 35 wt% silver nanoparticle dispersion. The materials were mixed well together and a film of the resulting ink was deposited onto 0.005" thick polyester film with a 0.0003" diameter wire wound rod and then cured at 100°C for 60 seconds resulting in a cohesive and conductive silver film. The adhesion of the film to the substrate was tested using the tape test method described above. Some of the material was removed.

Example 14

[0105] An ink composition was prepared by adding 0.63 grams of a 50 wt. % polyacrylamide solution (Aldrich 10,000 Mw) to 12.57 grams of 40 wt% silver nanoparticle dispersion. The materials were mixed well together and a film of the resulting ink was deposited onto 0.005" thick polyester film with a 0.0003" diameter wire wound rod and then cured at 100°C for 60 seconds resulting in a cohesive and conductive silver film. The adhesion of the film to the substrate was evaluated by utilizing the tape test method previously described in Example 1. None of the material was removed from the substrate.

Example 15

[0106] An ink composition was prepared by adding 0.44 grams of a 25 wt. % polyvinyl alcohol solution (Aldrich 9,000-10,000 Mw) and 1.14 grams of an acrylic nanoparticle latex dispersion to 22.2 grams of 35 wt% silver nanoparticle dispersion. The materials were mixed well together and a film of the resulting ink was deposited onto 0.005" thick polyester film with a 0.0003" diameter wire wound rod and then cured at 130°C for 30 seconds resulting in a cohesive and conductive silver film. The adhesion of the film to the substrate was evaluated by utilizing the tape test method previously described in Example 2. Some of the material was removed from the substrate was removed from the substrate

COMPARATIVE EXAMPLES

[0107] The material of **Example 1** was transferred to hexane by sodium chloride induction similar to the method of Hirai. Hirai, et al., *Chemistry Letters*, **1992**, 1527-1530; Hirai, et al., *J. of Colloid and Interface Sci.*, **1993**, 161, 471-474. Hexane and a sodium chloride solution was added to concentrated material from Example 1 and the two phases mixed with a magnetic stir bar for 10 minutes. The silver nanoparticles transferred phases to the non-aqueous phase presumably leaving all ionic species in the aqueous phase. The solvent phase with the suspended silver particles was separated from the water phase. When an attempt was made to cure the phase transferred material at 120°C, the silver did not cure and an oily silver film remained even after extended periods at this temperature.

What is Claimed:

1. A composition, comprising:

a population of metallic nanoparticles dispersed in an aqueous medium, wherein at least a portion of the population comprising individual metallic nanoparticles characterized as having an average cross-sectional dimension in the range of from about 1 nm to about 100 nm; and,

wherein each of the nanoparticles comprise at least one ligand bound to its surface, the ligand comprising a heteroatom head group bound to the nanoparticle surface and a tail bound to the heteroatom head group.

2. The composition of claim 1, wherein the nanoparticle population further comprises particle agglomerate comprised of two or more individual nanoparticles, nanoparticle floc comprised of two or more individual nanoparticles, or any combination thereof.

3. The composition of claim 2, wherein the ratio, by weight, of the population of individual metallic nanoparticles to particle agglomerate is in the range of from about 1:99 to 99:1.

4. The composition of claim 2, wherein the ratio, by weight, of the population of individual metallic nanoparticles to particle floc is in the range of from about 1:99 to 99:1.

5. The composition of claim 2, a nanoparticle agglomerate has an average cross-sectional dimension in the range of from about 100 nm to about 10000 nm.

6. The composition of claim 2, wherein a nanoparticle floc has an average cross-sectional dimension in the range of from about 100 to about 10000 nm.

7. The composition of claim 1, wherein an individual metallic nanoparticle comprises silver, copper, gold, zinc, cadmium, palladium, iridium, ruthenium, osmium, rhodium, platinum, iron, nickel, cobalt, indium, silver oxide, copper oxide, gold oxide, zinc oxide, cadmium oxide, palladium oxide, iridium oxide, ruthenium oxide, osmium oxide, rhodium oxide, platinum oxide, iron oxide, nickel oxide, cobalt oxide, indium oxide, or any combination thereof.

8. The composition of claim 1, wherein the aqueous medium is capable of solvating the metallic salt in a range of from about 10 grams/liter to about 600 grams/liter.

9. The composition of claim 1, wherein the nanoparticles are present in the range of from about 0.5 wt % to about 70 wt %.

10. The composition of claim 1, wherein the ligand is present in the range of from about 0.5 wt % to about 75 wt %.

11. The composition of claim 1, wherein the medium is present in the range of from about 30 to about 98 wt %.

12. The composition of claim 1, wherein the composition is capable of forming a cohesive structure of less than about 10 μm in thickness following curing at a temperature of less than about 140°C for less than about 60 seconds.

13. The composition of claim 12, wherein the structure has a resistivity in the range of from about 2 times to about 15 times the bulk resistivity of the corresponding metal.

14. A composition, comprising:

a metallic nanoparticle mixture comprising at least one metallic nanoparticles, capable of forming a cohesive structure of less than about 10 μm in thickness following curing at a temperature of less than about 140°C for less than about 90 seconds, wherein the cohesive structure has a resistivity in the range of from about 2 times to about 15 times the bulk resistivity of the corresponding metal.

15. The composition of claim 14, wherein the mixture comprises a population of metallic nanoparticles, a ligand, an aqueous medium, or any combination thereof.

16. The composition of claim 15, wherein the nanoparticle population comprises individual nanoparticles, particle agglomerate comprised of two or more individual nanoparticles, particle floc comprised of two or more individual nanoparticles, or any combination thereof.

17. The composition of claim 16, wherein the ratio, by weight, of the population of individual metallic nanoparticles to particle agglomerate is in the range of from about 1:99 to 99:1.

18. The composition of claim 16, wherein the ratio, by weight, of the population of individual metallic nanoparticles to particle floc is in the range of from about 1:99 to 99:1.

19. The composition of claim 16, wherein individual metallic nanoparticles have an average cross-sectional dimension in the range of from about 1 nm to about 100 nm.

20. The composition of claim 16, wherein particle agglomerates have an average cross-sectional dimension in the range of from about 100 nm to about 10000 nm.

21. The composition of claim 16, wherein particle flocs have an average cross-sectional dimension in the range of from about 100 to about 10000 nm.

22. The composition of claim 16, wherein an individual metallic nanoparticle comprises silver, copper, gold, zinc, cadmium, palladium, iridium, ruthenium, osmium, rhodium, platinum, iron, nickel, cobalt, indium, silver oxide, copper oxide, gold oxide, zinc oxide, cadmium oxide, palladium oxide, iridium oxide, ruthenium oxide, osmium oxide, rhodium oxide, platinum oxide, iron oxide, nickel oxide, cobalt oxide, indium oxide, or any combination thereof.

23. The composition of claim 15, wherein the aqueous medium is capable of solvating the metallic salt in a range of from about 10 grams/liter to about 600 grams/liter.

24. The composition of claim 15, wherein the nanoparticles are present in the range of from about 0.5 to about 70 wt %.

25. The composition of claim 15, wherein the ligand is present in the range of from about 0.5 to about 75 wt %.

26. The composition of claim 15, wherein the medium is present in the range of from about 30 to about 98 wt %.

27. A method for synthesizing a metallic nanoparticle dispersion, comprising:

reacting in an aqueous medium:

at least one ligand, wherein the ligand comprises a heteroatom head group bonded to a tail comprising from 1 to about 20 carbon atoms;

at least one reducing agent; and,

at least one metallic salt in an aqueous dispersing solution, wherein the metallic salt is present in the dispersion at a concentration in the range of from about 10 grams/liter to about 600 grams/liter based on volume of the dispersing solution, and wherein the metallic salt comprises at least one cation comprising silver, copper, gold, zinc, cadmium, palladium, iridium, ruthenium, osmium, rhodium, platinum, iron, nickel, cobalt, indium, or any combination thereof.

28. The method of claim 27, wherein the ligand is characterized as being capable of binding by its heteroatom head group to a surface of a metallic nanoparticle so as to give rise to a metallic nanoparticle stabilized at least in part against aggregation.

29. The method of claim 27, wherein the metallic salt further comprises at least one anion.

30. The method of claim 27, wherein the reacting comprises contacting, mixing, stirring, sonicating, agitating, or any combination thereof.

31. The method of claim 30, wherein, after the reacting, one or more ligand heteratomic head groups are characterized as bound to a surface of one or more metallic nanoparticles so as to give rise to one or more metallic nanoparticles stabilized against irreversible aggregation.

32. The method of claim 30, wherein the method further comprises combining the ligand and metallic salt in a respective molar ratio in the range of from about 0.1:1 to about 1:1.

33. The method of claim 32, wherein the method further comprises combining the metallic salt and reducing agent in a respective molar ratio in the range of from about 1:10 to about 4:1.

34. The method of claim 32, wherein the method further comprises adjusting the relative amounts of ligand, reducing agent, metallic salt, aqueous dispersing solution, adjusting the pH of the aqueous medium, or any combination thereof, so as to give rise to a pH in the range of from about 3 to about 12.

35. The method of claim 27 wherein the method further comprises heating the aqueous medium, ligand, reducing agent, and metallic salt in aqueous dispersing solution, or any combination thereof, to a temperature of from about 5°C to about 200°C prior to reaction.

36. The method of claim 27, wherein the method further comprises heating the aqueous medium, ligand, reducing agent, and metallic salt in aqueous dispersing solution, or any combination thereof, to a temperature of from about 35°C to about 70°C prior to reaction.

37. The method of claim 27, wherein the method further comprises heating the aqueous medium, ligand, reducing agent, and metallic salt in aqueous dispersing solution, or any combination thereof, to a temperature of from about 40°C to about 60°C prior to reaction.

38. The method of claim 27, further comprising a recovery step following reaction.

39. The method of claim 38, wherein the recovery step comprises allowing the passage of sufficient time such that the concentration of nanoparticles in any aqueous medium present is in the range of from about 0 wt % to about 70 wt%.

40. The method of claim 38, wherein the recovery step comprises allowing the passage of sufficient time such that the concentration of nanoparticles in any aqueous medium present is about 5 wt% and decanting the aqueous medium.

41. The method of claim 27, wherein the reacting comprises continuously introducing the aqueous medium, ligand, and reducing agent into a first stirred reactor capable of fluid communication with the contents of a second stirred reactor.

42. The method of claim 41, wherein the ligand is characterized as being capable of binding by its heteroatom head group to a surface of a metallic nanoparticle so as to give rise to a metallic nanoparticle stabilized at least in part against irreversible aggregation.

43. The method of claim 41, further comprising continuously introducing the metallic salt dispersion to the first reactor.

44. The method of claim 43, wherein the metallic salt further comprises an anion.

45. The method of Claim 44, wherein the anion comprises acetate, nitrate, carboxylate, sulfate, chloride, hydroxide, or any combination thereof.

46. The method of claim 43, wherein the dispersing medium comprises an aqueous medium substantially free of organic solvents.

47. The method of claim 44, wherein the ligand and metallic salt are introduced to the first reactor at a respective molar ratio of from about 0.1:1 to about 1:1.

48. The method of claim 43, further comprising adjusting the relative amounts of ligand, reducing agent, metallic salt, aqueous dispersing solution, adjusting the pH of the aqueous medium, or any combination thereof, so as to give rise to a pH in the range of from about 3 to about 12.

49. The method of claim 48, wherein the method further comprises heating the aqueous medium, ligand, reducing agent, and metallic salt in aqueous dispersing solution, or any combination thereof, to a temperature of from about 5°C to about 200°C before reaction.

50. The method of claim 43, wherein the method further comprises heating the aqueous medium, ligand, reducing agent, and metallic salt in aqueous dispersing solution, or any combination thereof, to a temperature of from about 35°C to about 70°C before reaction.

51. The method of claim 43, wherein the method further comprises heating the aqueous medium, ligand, reducing agent, and metallic salt in aqueous dispersing solution, or any combination thereof, to a temperature of from about 40°C to about 60°C before reaction.

52. The method of claim 43, wherein the residence time of the first reactor is sufficient so as to give rise to the reaction progressing to substantial completion.

53. The method of claim 43, further comprising continuously transporting the contents of the first reactor to the second reactor.

54. The method of claim 53, wherein the residence time in the second reactor is sufficient to allow the reaction to progress to essentially total completion.

55. The method of claim 54, further comprising a recovery step following reaction.

56. The method of claim 55, wherein the recovery step comprises allowing the passage of sufficient time such that the concentration of nanoparticles in any aqueous medium present is about 5 wt%.

57. A method for forming a conductive structure on a substrate, comprising:

depositing a composition onto the substrate, wherein the composition comprises at least one population of metallic nanoparticles, wherein at least a portion of the population comprising individual metallic nanoparticles characterized as having an average cross-sectional dimension in the range of from about 1 nm to about 30 nm;

wherein each of the nanoparticles comprise at least one ligand bound to its surface, the ligand comprising a heteroatom head group bound to the nanoparticle surface and a tail bound to the heteroatom head group; and,

curing the deposited composition.

58. The method of claim 57, wherein depositing comprises a printing method.

59. The method of claim 58, wherein the printing method comprises flexographic printing, rotogravure printing, lithographic printing, intaglio printing, relief printing, screen printing, inkjet printing, laser printing, or any combination thereof.

60. The method of claim 57, wherein the nanoparticle population comprises individual particles, nanoparticle agglomerate comprised of at least two individual nanoparticles, nanoparticle floc comprised of at least two nanoparticles, or any combination thereof.

61. The method of claim 57, wherein an individual metallic nanoparticle comprises silver, copper, gold, zinc, cadmium, palladium, iridium, ruthenium, osmium, rhodium, platinum, iron, nickel, cobalt, indium, silver oxide, copper oxide, gold oxide, zinc oxide, cadmium oxide, palladium oxide, iridium oxide, ruthenium oxide, osmium oxide, rhodium oxide, platinum oxide, iron oxide, nickel oxide, cobalt oxide, indium oxide, or any combination thereof.

62. The method of claim 57, wherein one or more ligands are characterized as bound to a surface of one or more metallic nanoparticles so as to give rise to one or more metallic nanoparticles stabilized against aggregation.

63. The method of claim 57, wherein the nanoparticles are present in the range of from about 0.5 to about 70 wt %.

64. The method of claim 57, wherein the ligand is present in the range of from about 0.5 to about 75 wt %.

65. The method of claim 57, wherein the composition further comprises a rheology modifier.

66. The method of claim 65, wherein the rheology modifier comprises an associative thickener.

67. The method of claim 65, wherein the rheology modifier comprises a thickening agent.

68. The method of claim 67, wherein the thickening agent comprises an alkali-soluble emulsion.

69. The method of claim 65, wherein the rheology modifier is present in the range of from about 0 wt% to about 15 wt%.

70. The method of claim 57, wherein the composition further comprises a binder.

71. The method of claim 70, wherein the binder is present in the range of from about 0 wt% to about 20 wt%.

72 The method of claim 57, wherein the substrate comprises a glass, a ceramic, a polymer, a silicon, a nitride, a carbide, a ceramic precursor, fabric, or any combination thereof.

73 The method of claim 72, wherein the polymer comprises a polyester, a polyolefin, a polycarbonate, an acrylic polymer, polyethylene naphthalate, polyimide, polyamideimide, polyvinyl chloride, polypropylene, a liquid crystal polymer, polycarbonate, or any combination thereof.

74. The method of claim 72, wherein the substrate further comprises paper, synthetic engineered paper, cardboard, a coated corrugated cardboard, an uncoated corrugated cardboard, or any combination thereof.

75. The method of claim 72, wherein at least a portion of a surface of the substrate is capable of being modified to give rise to a surface capable of adhering to the deposited composition.

76. The method of claim 57, wherein the composition further comprises metallic particles.

77. The method of claim 76, wherein the metallic particles have a width in the range of from about 200 nm to about 20000 nm.

78. The method of claim 76, wherein a metallic particle comprises silver, copper, gold, zinc, cadmium, palladium, iridium, ruthenium, osmium, rhodium, platinum, iron, nickel, cobalt, indium, silver oxide, copper oxide, gold oxide, zinc oxide, cadmium oxide, palladium oxide, iridium oxide, ruthenium oxide, osmium oxide, rhodium oxide, platinum oxide, iron oxide, nickel oxide, cobalt oxide, indium oxide, or any combination thereof.

79. The method of claim 57, wherein curing comprises exposing the deposited composition to a temperature of less than about 140°C for less than about 90 seconds.

80. The method of claim 57, wherein the structure has a thickness of less than about 20 μm.

81. A method for forming a conductive structure, comprising:

depositing a metallic nanoparticle composition comprising at least one metallic nanoparticle onto the substrate, wherein the composition is capable of forming after curing at a temperature of less than about 140°C for less than about 90 seconds a cohesive and conductive structure having a resistivity in the range of from about 2 times to about 15 times the bulk resistivity of the corresponding metal and having a thickness of less than about 20 μm; and,

curing the deposited composition.

82 The method of claim 81, wherein depositing comprises a printing method.

83. The method of claim 82, wherein the printing method comprises flexographic printing, rotogravure printing, lithographic printing, intaglio printing, relief printing, screen printing, inkjet printing, laser printing, or any combination thereof.

84. The method of claim 81, wherein the composition comprises a population of metallic nanoparticles, a ligand, a medium, or any combination thereof.

85. The method of claim 81, wherein the nanoparticle population comprises individual nanoparticles, nanoparticle agglomerate, nanoparticle floc, or any combination thereof.

86. The method of claim 85, wherein individual metallic nanoparticles have an average cross-sectional dimension in the range of from about 1 nm to about 100 nm.

87. The method of claim 85, wherein nanoparticle flocs have an average cross-sectional dimension in the range of from about 100 to about 10000 nm.

88. The method of claim 84, wherein an individual metallic nanoparticle comprises silver, copper, gold, zinc, cadmium, palladium, iridium, ruthenium, osmium, rhodium, platinum, iron, nickel, cobalt, indium, silver oxide, copper oxide, gold oxide, zinc oxide, cadmium oxide,

palladium oxide, iridium oxide, ruthenium oxide, osmium oxide, rhodium oxide, platinum oxide, iron oxide, nickel oxide, cobalt oxide, indium oxide, or any combination thereof.

89. The method of claim 84, wherein one or more ligands are characterized as bound to a surface of one or more metallic nanoparticles so as to give rise to one or more metallic nanoparticles stabilized against irreversible aggregation.

90. The method of claim 84, wherein the nanoparticles are present in the range of from about 0.5 to about 70 wt %.

91. The method of claim 84, wherein the ligand is present in the range of from about 0.5 to about 75 wt %.

92. The method of claim 84, wherein the medium is present in the range of from about 30 to about 98 wt %.

93. The method of claim 84, wherein the composition further comprises a rheology modifier.

94. The method of claim 93, wherein the rheology modifier comprises an associative thickener.

95. The method of claim 93, wherein the rheology modifier is present in the range of from about 0 wt% to about 15 wt%.

96. The method of claim 84, wherein the composition further comprises a binder.

97. The method of claim 96, wherein the binder comprises a latex, a polymer latex, an emulsion polymer, polyimide, a silicone, a fluorocarbon, a polyamic acid, a polyurethane, a polyester, an epoxy, or any combination thereof.

98. The method of claim 96, wherein the binder is present in the range of from about 0 wt% to about 20 wt%.

99. The method of claim 81, wherein the substrate comprises a glass, a ceramic, a polymer, a silicon, a nitride, a carbide, a ceramic precursor, fabric, or any combination thereof.

100. The method of claim 99, wherein the polymer comprises a polyester, a polyolefin, a polycarbonate, an acrylic polymer, polyethylene naphthalate, polyimide, polyamideimide, polyvinyl chloride, polypropylene, a liquid crystal polymer, polycarbonate, or any combination thereof.

101. The method of claim 99, substrate further comprises paper, synthetic engineered paper, cardboard, a coated corrugated cardboard, an uncoated corrugated cardboard, or any combination thereof.

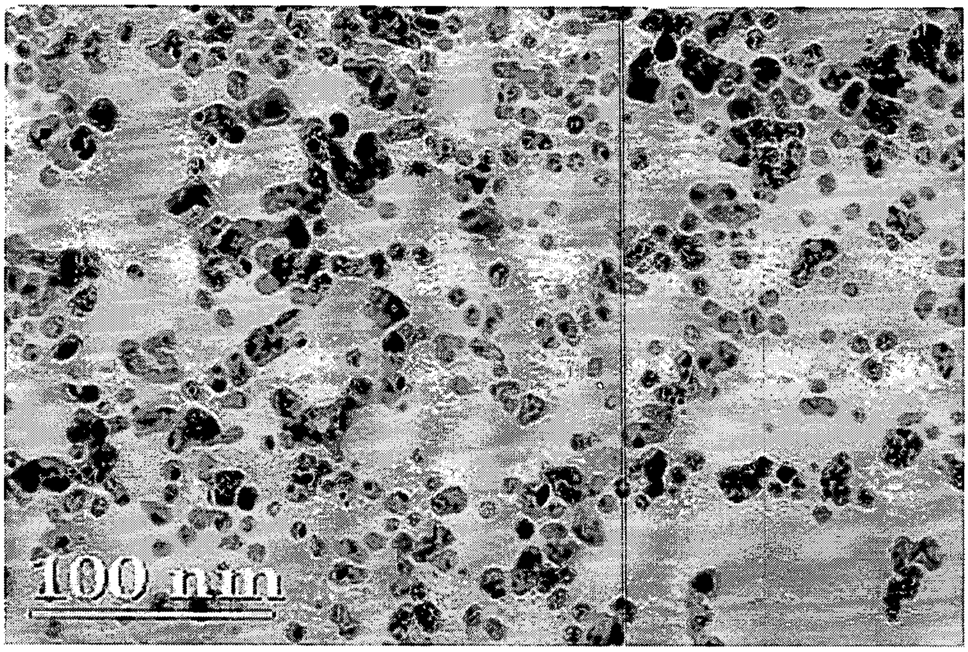
102. The method of claim 99, wherein at least a portion of a surface of the substrate is capable of being modified to give rise to a surface capable of adhering to the deposited composition.

103. The method of claim 84, wherein the composition further comprises metallic particles.

104. The method of claim 103, wherein the metallic particles have a width in the range of from about 200 nm to about 20000 nm.

105. The method of claim 103, wherein a metallic particle comprises silver, copper, gold, zinc, cadmium, palladium, iridium, ruthenium, osmium, rhodium, platinum, iron, nickel, cobalt, indium, silver oxide, copper oxide, gold oxide, zinc oxide, cadmium oxide, palladium oxide, iridium oxide, ruthenium oxide, osmium oxide, rhodium oxide, platinum oxide, iron oxide, nickel oxide, cobalt oxide, indium oxide, or any combination thereof.

Figure 1(A)



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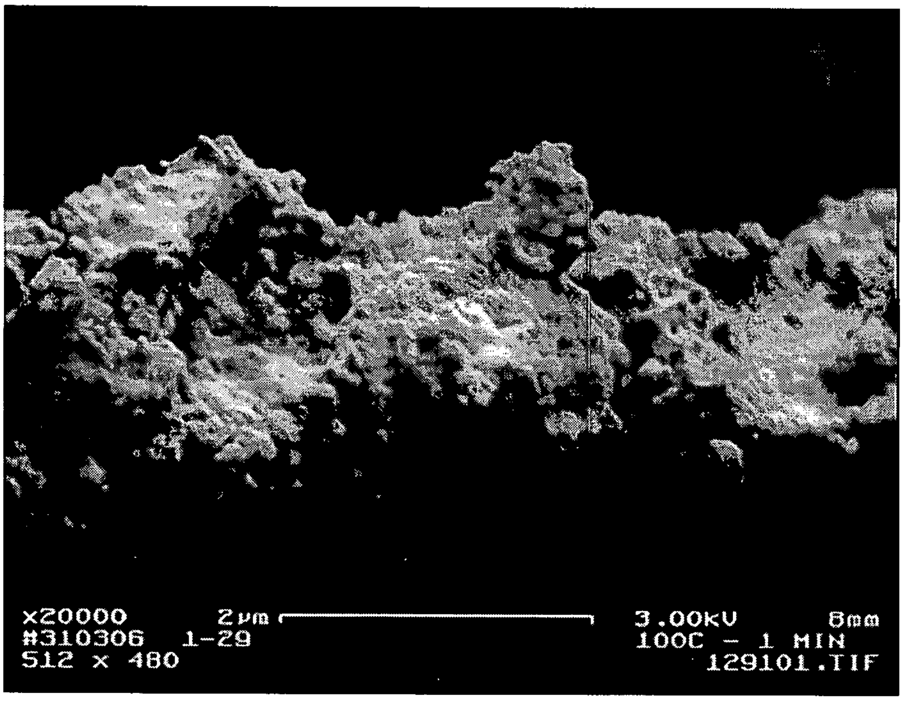
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Figure 1(C)

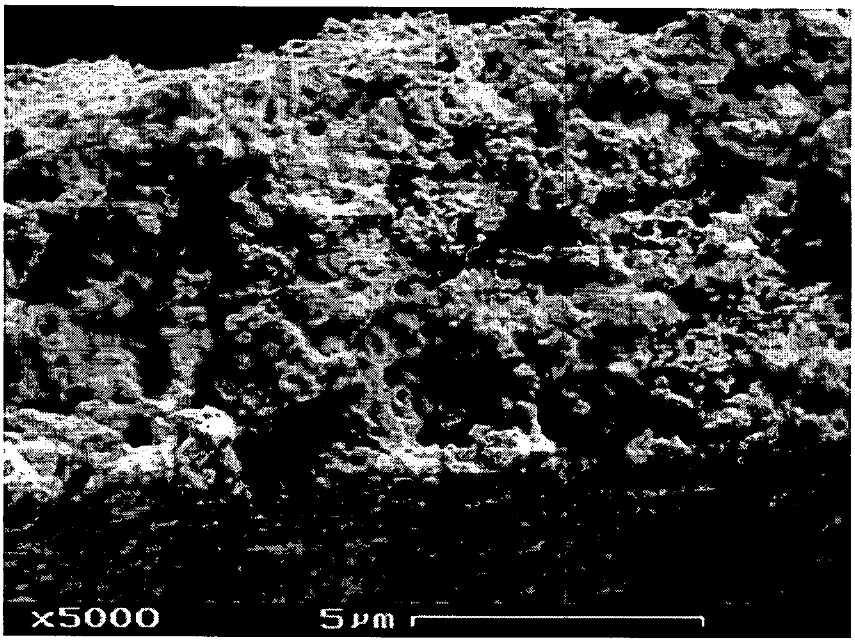
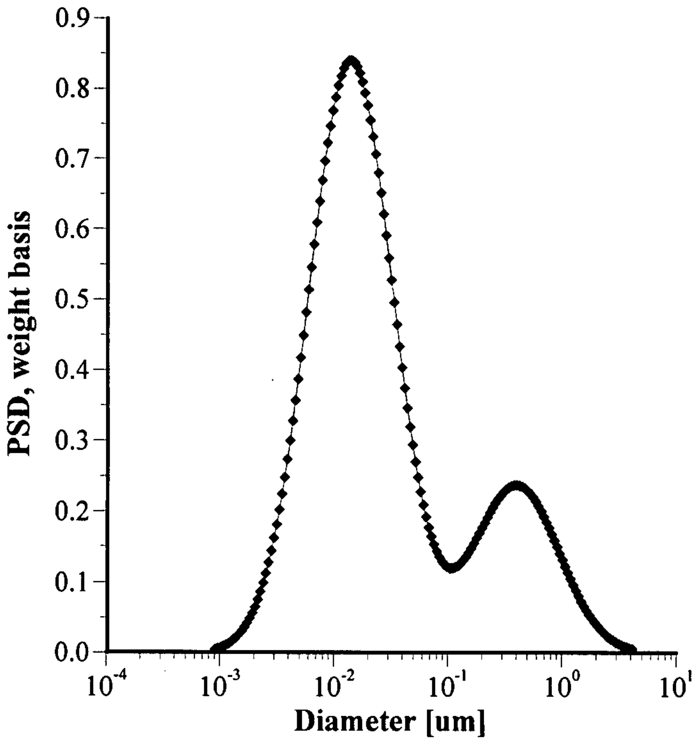


Figure 2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0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
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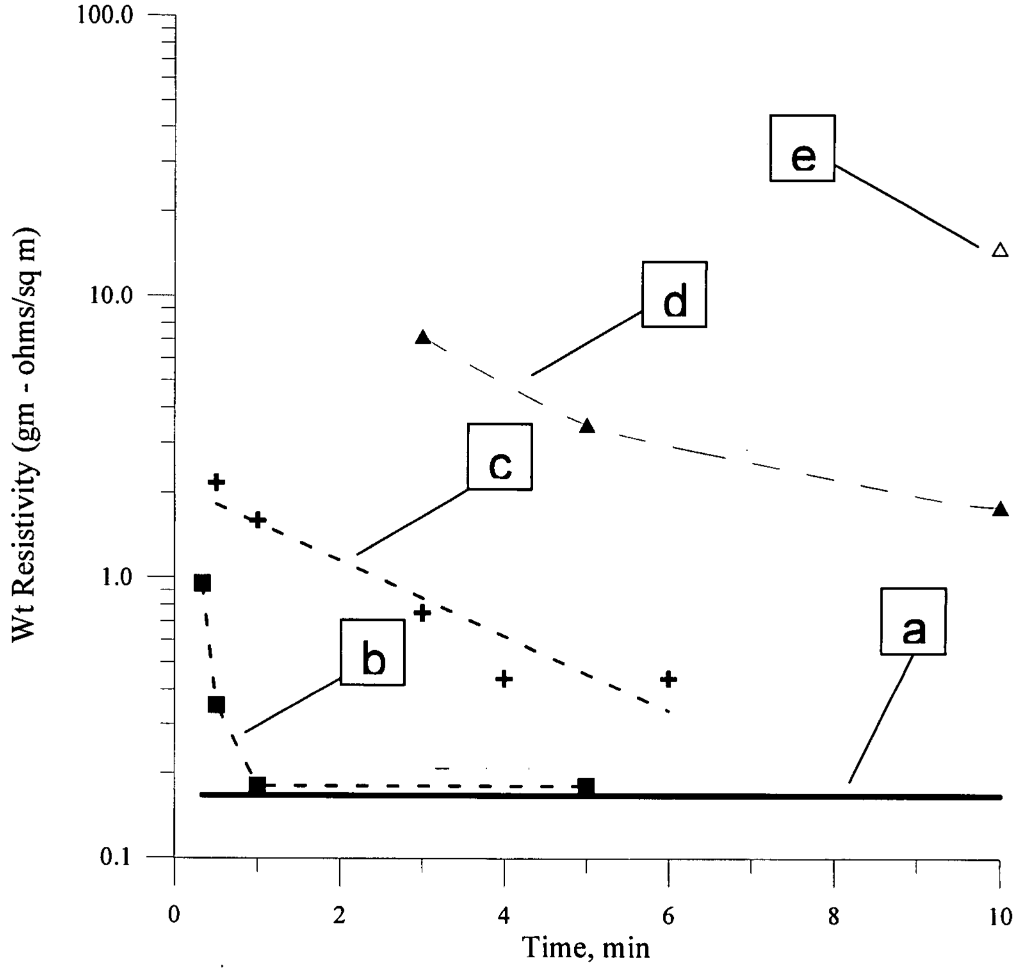
10^{-2}
10^{-1}
10^{0}
10^{1}
Diameter [um]

Figure 3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1.0
0.1
Wt Resistivity (gm - ohms/sq m)
0
2
4
6
8
10
Time, min
a
b
c
d
e