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(54) Title: METHOD AND SYSTEM FOR ONLINE USER FEEDBACK ON WEBSITES AND SOFTWARE

(57) Abstract: A system for collecting and analyzing structured user feedback on websites, the system including website user structured feedback form generation functionality operative to generate structured feedback forms for providing website user feedback on website user interaction with a website-based process and website user feedback analyzing functionality operative to automatically collect and analyze website user feedback entered in the structured feedback forms and to provide at least one analysis report based on feedback from a multiplicity of website users.

METALLIC COPPER NANOPARTICLES AND MICROPARTICLES AND ARTICLES CONTAINING SAME

FIELD AND BACKGROUND OF THE INVENTION

The present invention, in some embodiments thereof, relates to metallic nanoparticles and more particularly, but not exclusively, to discrete and sintered copper nano- and micro-particles and to novel methods of producing same.

Metal nanoparticles are finding their way into a myriad of applications in fields such as mechanical, optical, magnetic, thermal, electronic and sensory devices, as well as in the field of catalysis, due to their unique properties. For example, metallic nanocrystals have considerably reduced melting temperatures as compared with the bulk. The depression in melting and annealing temperature is evident throughout the nanocrystal size regime, with the most dramatic effects observed in nanocrystals having a diameter from 2 to 6 nm. This attribute can be harnessed for a wide variety of applications that require low temperature sintering, such as electronic printing, novel adhesion techniques and composite metallic casting.

One of the major technological challenges in nano-science and nanotechnology today involves the self-assembly of nano-building blocks into larger organized conformations and geometrical architectures for device fabrication.

Low-temperature self-assembly driven processes have the potential to improve the reliability, and reduce the cost of fabrication of electronic and memory devices. To-date, most of the morphological organization schemes of nano-materials utilize organic surfactant assisted self-assembly. Large-scale organization of inorganic metal nanostructures in a controlled and predetermined manner, excluding the use of organic scaffolds is highly desirable as it avoids organic-content related problems such as decreased conductivity.

Low-temperature sintering is another form of high-order transformation, which is particularly appealing when considering printed electronics applications. This fast growing area enables printing conductive patterns as well as active components on substrates which cannot endure classical photolithographic processes. Printing of nanoparticle based inks may be achieved using several printing processes such as ink-jet, screen printing, flexography, gravure, and off-set printing. Lowering the

temperature at which these inks are cured and sintered enables the application of these processes to substrates that cannot tolerate high temperatures.

Electronic printing using screen printing (e.g., silk-printing) or ink-jet printing is one of the examples wherein discrete and uniform copper nanoparticles are in great demand. Noncontact direct writing technologies, such as inkjet printing, are advantageous not only in terms of materials cost but also in manufacturing time, since they allow precise ejection at high positioning accuracy and at controllable quantities.

Metallic inkjet inks are typically required to exhibit significant electrical conductivity and are often characterized by complex formulations involving solvents, surfactants and dispersants in addition to the appropriate electrically conductive materials. These materials are typically nanoparticles of conducting elements which are dispersed in the ink. The small particle size of the nanoparticles in electronic inks enables sintering at rather low temperatures, which allows fabrication on plastic and other heat-sensitive substrates.

Since nanoparticles are characterized by high surface areas, they are prone to surface oxidation, clustering and aggregation, and often suffer from irreversible agglomeration. Metallic nanoparticles react easily with ambient atmospheric oxygen even at room temperature and form an oxide phase on their surface, which has an undesirable effect on their function and utilization. Apart from forming an electrically resistive layer, that might be detrimental for electronic applications, the oxide layer might reduce the zeta potential of the nanoparticles and thus induce agglomeration and flocculation. While oxides of silver or gold nanoparticles, for example, are known to be electrically conductive and hence their oxidation does not have a detrimental effect on their performance, other metallic nanoparticles, such as, for example, copper nanoparticles, often become dysfunctional upon oxidation.

Copper has a lower tendency for ion migration, as compared with silver and gold, which is advantageous in terms of reducing short circuits between wires and reducing the defect rate of microelectronic circuitry. Copper has an electrical conductivity similar to that of silver and is currently much cheaper than silver or gold, making it a particularly interesting candidate for electronic printing applications. However, since copper nanoparticles exhibit rapid rate of oxidation, utilizing copper

nanoparticles has so far necessitated using inks containing a copper metal precursor in electronic printing applications, rather than copper nanoparticles.

Various methods have been disclosed for the production of copper metal powder. In general, the most common methods employed for the preparation of metallic nanoparticles involve the reduction of metal ions in solution, usually in the presence of particle-stabilizers. The copper salts usually used for such methods include, for example, CuCl2, Cu(NO3)2, CuSO4, (CH3COO)2Cu, copper(II) acetylacetonate, copper(II) carbonate, copper(II) cyclohexane butyrate, copper(II) stearate, copper(II) perchlorate, copper(II) ethylenediamine and Cu(OH)2. These salts are used with reducing agents which include, for example, NaHPO2, N2H4, and NaBH4.

There are few general methods available for achieving some extent of size control, size distribution and shape control. These methods usually use either a capping agent or a template for the restricted growth of the particles.

Numerous methodologies are known for stabilizing the nanoparticles against oxidation and agglomeration. Dispersing agents (dispersants) are typically used in the production process of copper nanoparticles. Examples of such dispersing agents include PVP (polyvinylpyrrolidone), CTAB (cetyltrimethylammonium bromide), SDS (sodium dodecyl sulfate) and Na-CMC (sodium carboxymethyl cellulose).

Nanoparticles produced according to various strategies, usually possess a passivating agent to confer solubility and stability against aggregation. The passivating agent also serves to arrest the growth of the particles at a pre-determined and uniform size. One of the requirements from passivating agents, especially when considering nanoparticles for electronic applications, is volatility upon heating. The process of thermally removing the passivating agent is sometimes referred to as thermolysis.

Usually, copper nanoparticles produced using a wet chemical approach, which requires considerable amount of organic material, will have a high organic content, mostly on the surface of the nanoparticles. The organic coating is further required for avoiding aggregation yet must be volatile at rather low temperatures in cases where the nanoparticles are to be used in electronic printing applications.

WO 2010/035258 by the present inventors, teaches a reversibly re-suspendible powder of copper nanoparticles having a raspberry-like shape and a particular particle

size distribution characterized by a mean diameter of 10-200 nm and a standard deviation of 5-50 nm.

SUMMARY OF THE INVENTION

The present invention, in some embodiments thereof, relates to metallic nanoparticles and more particularly, but not exclusively, to discrete and sintered copper nanoparticles and to novel methods of producing same.

The present invention teaches spherical copper nanoparticles and hollow spheroidal micro-particles with distinct surface topology and chemistry, governed by certain carboxyl-containing compounds, possessing self-similarity architecture. According to embodiments the invention, the unique topology and chemistry of the copper nanoparticles and microparticles promote room temperature sintering, as well as promote contact between individual structures.

It was surprisingly found that performing a typical copper/zinc cementation reaction in the presence of a carboxyl-containing compound, affords spherical copper nano- and micro-particles which are characterized by having a bosselated surface topology, as if they were formed from smaller spherical elements which themselves appear to compose even smaller spherical sub-level structural elements. Such a morphology was termed by the present inventors as fractal structuralism or self-similarity.

It was surprisingly found that when a sulfur-containing compound is reacted with pre-formed spherical copper nano- and micro-particles having a bosselated outer-surface topology (highly curved features) described herein, a fibrous network of copper is formed which covers the surface of the copper particles. These fibers are presumed to further promote tethering between different regions on the surface of each copper particle and even tethering between different neighboring particles.

It was further surprisingly found that in cases when the copper/zinc cementation reaction is carried out in the presence of both a carboxyl-containing compound and a sulfur-containing compound, copper spheres whose surfaces are completely smooth are obtained, wherein individual nanoparticles or aggregates of nanoparticles cannot be resolved. In these compositions the copper particles have undergone complete fusing at temperatures not exceeding 50 °C or even room temperature.

It was further found that all these compositions, which may be characterized as having a bosselated surface topology and able to grow copper filaments or be fused due to the charge-density effect imparted by sulfur, can be sintered at very low temperatures or by applying very mild mechanical pressure thereon, to form micron-sized copper structures. Without being bound by any particular theory, it is suggested that the bosselated surface topology obtained when performing a zinc/copper cementation reaction in the presence of a carboxyl-containing compound, advantageously enables sintering the formed particles under mild conditions.

Hence, according to an aspect of embodiments of the present invention, there is provided a composition which includes a plurality of copper nanoparticles and/or microparticles generally shaped as spheroids and characterized by a bosselated surface topology.

In some embodiments, the copper microparticles are hollow spheroidal copper microparticles.

In some embodiments, the hollow spheroidal copper microparticles are characterized by an average particle size that ranges from 0.5 μm to 20 μm.

In some embodiments, the hollow spheroidal copper microparticles are characterized by an average wall thickness that ranges from 50 nm to 200 nm.

In some embodiments, the exterior surface of the hollow spheroidal copper microparticles exhibits an atomic concentration of oxygen that ranges from 20 percent to 40 percent.

In some embodiments, the exterior surface of the hollow spheroidal copper microparticles exhibits an atomic concentration of carbon that ranges from 20 percent to 35 percent.

In some embodiments, the exterior surface of the hollow spheroidal copper microparticles exhibits an atomic concentration of phosphorous that ranges from 0 percent to 5 percent.

In some embodiments, the walls of the hollow spheroidal copper microparticles are composed of copper nanoparticles which have an average particle size that ranges from 20 nm to 200 nm.

In some embodiments, the copper nanoparticles are characterized by an average diameter that ranges from 50 nm to 500 nm.

In some embodiments, the curvature of each boss in the bosselated surface topology of the copper nanoparticles and/or microparticles is characterized by a mean curvature that ranges from 0.02 nm^{-1} to 0.5 nm^{-1}.

In some embodiments, the surface of the copper microparticles and/or nanoparticles is coated with fibrous copper.

In some embodiments, the fibrous copper has an average fiber length that ranges from 10 nm to 100 nm, and an average thickness of 5 nm to 10 nm.

In some embodiments, at least a portion of the copper microparticles and/or nanoparticles of the composition of copper particles are fused to one another.

In some embodiments, the exterior surface of the fibrous-coated copper particles and/or the fused copper particles is characterized by an atomic concentration of oxygen that ranges from 20 percent to 40 percent.

In some embodiments, the exterior surface of the fibrous-coated copper particles and/or the fused copper particles is characterized by an atomic concentration of carbon that ranges from 20 percent to 30 percent

In some embodiments, the exterior surface of the fibrous-coated copper particles and/or the fused copper particles is characterized by an atomic concentration of nitrogen that ranges from 10 to 15 percent.

In some embodiments, the exterior surface of the fibrous-coated copper particles and/or the fused copper particles is characterized by an atomic concentration of sulfur that ranges from 0.1 to 5 percent.

In some embodiments, the compositions presented herein are capable of being sintered upon an application of mild mechanical pressure thereon at a temperature lower than 100 °C or lower than 50 °C.

In some embodiments, the compositions presented herein are capable of sintering upon an application of mild mechanical pressure thereon at a temperature lower than 50 °C.

According to another aspect of embodiments of the present invention, there is provided a composition which includes a plurality of copper microparticles and/or microparticles, wherein at least a portion of the particles being fused to one another.

According to another aspect of embodiments of the present invention, there is provided a composition which includes a plurality of copper microparticles and/or

nanoparticles, the composition being capable of sintering upon an application of mild mechanical pressure thereon at a temperature lower than 100 °C or lower than 50 °C.

According to another aspect of embodiments of the present invention, there is provided a process of manufacturing the compositions presented herein, which is effected by:

mixing a copper salt with a powder of elemental zinc in an aqueous solution in the presence of a carboxyl-containing compound at room temperature to thereby obtain a powder which constitute the composition.

In some embodiments, the process further includes filtering and drying the powder.

In some embodiments, the molar ratio between the elemental zinc and the copper ion ranges from 2:1 to 1:2.

In some embodiments, the molar ratio between the carboxyl-containing compound and the copper ion ranges from 5:1 to 1:1, from 4:1 to 1:1 or from 2:1 to 1:1.

In some embodiments, the pH of the aqueous solution ranges from 1.5 to 5, from 3 to 5 or from 4 to 5.

In some embodiments, the powder of elemental zinc has a grit size of less than 20 microns.

In some embodiments, when the surface of at least a portion of the copper nanoparticles and/or microparticles is coated with fibrous copper, the process further includes:

filtering and drying the powder; and

suspending the powder in an aqueous solution in the presence of a sulfur-containing compound.

In some embodiments, the process is effected by mixing the copper salt with a powder of elemental zinc in an aqueous solution is effected in the presence of a sulfur-containing compound.

In some embodiments, when the copper salt, the elemental zinc, the carboxyl-containing compound and the sulfur-containing compound are mixed together, at least a portion of the resulting copper microparticles and/or nanoparticles are fused to one another.

In some embodiments, the concentration of the sulfur-containing compound ranges from 0.05 mM to 10 mM.

In some embodiments, the sulfur-containing compound is selected from the group consisting of thiourea, β-mercaptoethanol, thiosemicarbazide, methyl chlorothiolformate, dithiooxamide, thioacetamide, dimethyl trithiocarbonate, ammonium diethyldithiocarbamate, 2-methyl-3-thiosemicarbazide, 4-methyl-3-thiosemicarbazide, ethylene trithiocarbonate, vinylene trithiocarbonate, 2-cyanothioacetamide, cysteine, methanethiol (CH_3SH), ethanethiol (C_2H_5SH), 1-propanethiol (C_3H_7SH), 2-propanethiol ($CH_3CH(SH)CH_3$), butanethiol ($C4H_9SH$), tetrabutyl mercaptan ($C(CH_3)_3SH$), pentanethiols ($C_5H_{11}SH$), coenzyme-A, lipoamide, glutathione, dithiothreitol/dithioerythritol and 2-mercaptoindole.

In some embodiments, the copper salt is selected from the group consisting of $CuSO_4$, $CuCl_2$, $Cu(NO_3)_2$, $(CH_3COO)_2Cu$, $Cu(C_5H_yO_2)_2$, $CuCO_3$, $Cu[C_6H_{11}(CH_2)_3CO_2]_2$, copper(II) stearate complex, $CuCl_2O_4$, copper(II) ethylenediamine complex and $Cu(OH)_2$.

In some embodiments, the carboxyl-containing compound is selected from the group consisting of citric acid, oxalic acid, ethylenediamine tetraacetic acid (EDTA), a monocarboxylic acid (formic acid, acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid and capric acid), a dicarboxylic acid (malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, isophthalic acid and terephthalic acid), a tricarboxylic acid (isocitric acid, aconitic acid, tricarballylic acid, trimesic acid and mellitic acid) and a tetracarboxylic acid (1,1,2,2-ethanetetracarboxylic acid, 1,1,4,4-butanetetracarboxylic acid, 1,1,2,3-propanetetracarboxylic acid, 1,2,3,4-tetracarboxybenzene and pyromellitic acid).

According to another aspect of embodiments of the present invention, there is provided a composition which includes copper nanoparticles which are being prepared by the processes presented herein.

In some embodiments, the compositions are capable of sintering upon an application of mild mechanical pressure thereon at a temperature lower than 100 °C or lower than 50 °C.

According to another aspect of embodiments of the present invention, there is provided an article-of-manufacturing which includes any of the compositions presented herein.

In some embodiments, the article-of-manufacturing is formed upon an application of mild mechanical pressure on the composition at a temperature lower than 100 °C or lower than 50 °C.

In some embodiments, the article-of-manufacturing is selected from the group consisting of an inkjet ink, a dry toner, a solid macro-scaled object, an electronic component and an electronic circuit.

According to another aspect of embodiments of the present invention, there is provided an inkjet ink composition, which includes any of the compositions presented herein.

According to another aspect of embodiments of the present invention, there is provided a toner composition, which includes any of the compositions presented herein.

In some embodiments, the inkjet ink composition or the toner composition is being curable upon an application of mild mechanical pressure thereon at a temperature lower than 100 °C or lower than 50 °C.

According to another aspect of embodiments of the present invention, there is provided a method of printing a substantially electrically conducting element on a substantially electrically isolating substrate, the method is effected by applying the inkjet ink composition or the toner composition on the substrate.

In some embodiments, the method further includes, subsequent to applying the composition, pressing the substrate having the composition applied thereon to thereby form the electrically conducting element on the substantially electrically isolating substrate.

In some embodiments, the method further includes, subsequent to applying the composition, heating the substrate having the composition applied thereon to thereby form the electrically conducting element on the substantially electrically isolating substrate.

According to another aspect of embodiments of the present invention, there is provided a method of preparing a substantially electrically conducting copper element, the method is effected by forming a shape of the element from any of the compositions

presented herein and applying mild pressure on the shape at a temperature lower than 100 °C or lower than 50 °C, thereby obtaining the copper element.

According to another aspect of embodiments of the present invention, there is provided a method of preparing a substantially electrically conducting copper element, the method is effected by forming a shape of the element from any of the compositions presented herein and heating the shape, thereby obtaining the copper element.

According to another aspect of embodiments of the present invention, there is provided a method of preparing a substantially electrically conducting copper layer on at least a portion of a surface of a substrate, the method is effected by spraying a suspension of the composition containing fused copper particles onto the surface.

As used herein the term "about" refers to ± 10 %.

The terms "comprises", "comprising", "includes", "including", "having" and their conjugates mean "including but not limited to". The term "consisting of" means "including and limited to".

The term "consisting essentially of" means that the composition, method or structure may include additional ingredients, steps and/or parts, but only if the additional ingredients, steps and/or parts do not materially alter the basic and novel characteristics of the claimed composition, method or structure.

As used herein, the singular form "a", "an" and "the" include plural references unless the context clearly dictates otherwise. For example, the term "a compound" or "at least one compound" may include a plurality of compounds, including mixtures thereof.

Throughout this application, various embodiments of this invention may be presented in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the invention. Accordingly, the description of a range should be considered to have specifically disclosed all the possible subranges as well as individual numerical values within that range.

Whenever a numerical range is indicated herein, it is meant to include any cited numeral (fractional or integral) within the indicated range. The phrases "ranging/ranges between" a first indicate number and a second indicate number and "ranging/ranges from" a first indicate number "to" a second indicate number are used herein

interchangeably and are meant to include the first and second indicated numbers and all the fractional and integral numerals therebetween.

As used herein the term "method" refers to manners, means, techniques and procedures for accomplishing a given task including, but not limited to, those manners, means, techniques and procedures either known to, or readily developed from known manners, means, techniques and procedures by practitioners of the chemical, pharmacological, biological, biochemical and medical arts.

Unless otherwise defined, all technical and/or scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which the invention pertains. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of embodiments of the invention, exemplary methods and/or materials are described below. In case of conflict, the patent specification, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and are not intended to be necessarily limiting.

BRIEF DESCRIPTION OF THE DRAWINGS

The patent or application file contains at least one drawing executed in color. Copies of this patent or patent application publication with color drawing(s) will be provided by the Office upon request and payment of the necessary fee. Some embodiments of the invention are herein described, by way of example only, with reference to the accompanying drawings and images. With specific reference now to the drawings and images in detail, it is stressed that the particulars shown are by way of example and for purposes of illustrative discussion of embodiments of the invention. In this regard, the description taken with the drawings and images makes apparent to those skilled in the art how embodiments of the invention may be practiced.

In the drawings:

FIG. 1 is an HRSEM electromicrograph at a magnification of 37,000X, showing an exemplary hollow spheroidal micro-particles according to some embodiments of the present invention, of about 1.5 μm in size, which seem to be composed of sub-micron sized spherical copper nanoparticles of about 20 nm to 50 nm in diameter

FIGs. 2A-B are HRSEM electromicrographs at a magnification of 10,000X (FIG. 2A) and 40,000X (FIG. 2B), showing in the center exemplary hollow spheroidal

micro-particles according to some embodiments of the present invention, having a diameter of about 4 μm and exhibiting a bosselated surface topology;

FIGs. 3A-C are HRSEM electromicrographs of exemplary hollow spheroidal micro-particles according to some embodiments of the present invention, composed of smaller spherical copper nanoparticles, cantering on a hollow spheroidal micro-particle of about 15 μm at a magnification of 10,000X (FIG. 3A), 50,000X (FIG. 3B) and 200,000X (FIG. 3C), demonstrating the self-similarity (fractal) nature of the copper particles;

FIGs. 4A-C are HRSEM electromicrographs of exemplary hollow spheroidal micro-particles according to some embodiments of the present invention, composed of smaller spherical copper nanoparticles, cantering on a hollow spheroidal micro-particle of about 5 μm at a magnification of 10,000X (FIG. 4A), 50,000X (FIG. 4B) and 200,000X (FIG. 4C), demonstrating the self-similarity (fractal) nature of the copper particles;

FIG. 5 is a HRSEM electromicrograph of copper particles sintered into flat structures by applying weak manual pressure on a powder comprising hollow spheroidal micro-particles according to some embodiments of the present invention;

FIG. 6 presents a high resolution XPS spectrum of C1s obtained for a powder of exemplary hollow spheroidal copper micro-particles according to some embodiments of the present invention, prepared using citric acid as an acid and hypophosphite as an additive;

FIG. 7 presents a high resolution XPS spectrum of Cu2p obtained for a powder of exemplary hollow spheroidal copper micro-particles according to some embodiments of the present invention, prepared using citric acid as an acid and hypophosphite as an additive;

FIG. 8 is a HRSEM electromicrograph at a magnification of 100,000X of the surface of a hollow spheroidal copper micro-particle treated with a sulfur-containing compound according to some embodiments of the present invention, showing a fibrous network of copper coating the surface;

FIG. 9 is a HRSEM electromicrograph at a magnification of 200,000X of the surface of a hollow spheroidal copper micro-particle treated with a sulfur-containing

compound according to some embodiments of the present invention, showing a fibrous network of copper coating the surface;

FIG. 10 is a HRSEM electromicrograph at a magnification of 200,000X of the spherical copper nanoparticles tethered by the fibrous network of copper coating their surface to the surface of a spheroidal copper micro-particle after being treated with a sulfur-containing compound according to some embodiments of the present invention;

FIG. 11 is a TEM electromicrograph showing the fibrous copper network appearing on the surface of copper particles treated with a sulfur-containing compound according to some embodiments of the present invention;

FIG. 12 presents the C1 XPS spectrum of C1s obtained for a powder of exemplary spherical copper nanoparticles, after being treated with a sulfur-containing compound according to some embodiments of the present invention;

FIG. 13 presents a high resolution XPS spectrum of Cu2p obtained for a powder of exemplary spherical copper nanoparticles, after being treated with a sulfur-containing compound according to some embodiments of the present invention;

FIG. 14 presents a high resolution XPS spectrum of N1s obtained for a powder of exemplary spherical copper nanoparticles, after being treated with a sulfur-containing compound according to some embodiments of the present invention;

FIG. 15 presents XPS spectrum of S2p obtained for a powder of exemplary spherical copper nanoparticles, after being treated with a sulfur-containing compound according to some embodiments of the present invention;

FIG. 16 is a HRSEM electromicrograph of a copper nanostructure prepared with citric acid and thiourea, according to some embodiments of the present invention, showing the initial stage of surface sintering;

FIG. 17 is a HRSEM electromicrograph of a copper nanostructure prepared with citric acid and thiourea, according to some embodiments of the present invention, showing an intermediate stage of surface sintering; and

FIG. 18 is a HRSEM electromicrograph of a copper nanostructure prepared with citric acid and thiourea, according to some embodiments of the present invention, showing full surface sintering.

DESCRIPTION OF EMBODIMENTS OF THE INVENTION

The present invention, in some embodiments thereof, relates to metallic nanoparticles and more particularly, but not exclusively, to discrete and sintered copper nano- and micro-particles and to methods of producing same.

Before explaining at least one embodiment of the invention in detail, it is to be understood that the invention is not necessarily limited in its application to the details set forth in the following description or exemplified by the Examples. The invention is capable of other embodiments or of being practiced or carried out in various ways.

Cementation is a well-known chemical reaction in hydrometallurgical processes, which is used, for example, to recover copper from acid leach solutions and gold from cyanide leach solutions. Metal displacement reaction between copper ions and metallic zinc are used for decades to produce metallic copper, and in modern days to produce copper nanoparticles. Since this reaction involves solid zinc particles, this reaction can be regarded as a modified copper/zinc cementation process. Copper/zinc cementation reactions are known to produce large dendritic copper particles rather than discrete nano- or micro-particles.

WO 2010/035258, by the present inventors, discloses a process in which copper salts such as $CuSO_4$ dissolved in H_2O are reduced by elemental zinc in the presence of a phosphate containing compound such as phosphoric acid, H_3PO_3, and other phosphate containing compounds, such as hypophosphite, to yield copper nanoparticles. The surface chemistry of the produced nanoparticles can be attenuated through controlled oxidation, adsorption of chemical species and the use of surfactants. According to the teaching of WO 2010/035258, by changing the reaction parameters and by using different organic capping layers it is possible to produce nanoparticles of different morphologies, and surface chemistries. It was shown, for example, that carrying out the reaction with different phosphate species and different thiol containing molecules, leads to products with different geometries and oxygen-content; by using H_3PO_3 as additive and thiol containing species such as cysteine or β-mercaptoethanol, cubic structures are formed which are characterized by a higher oxygen content; and by using sodium hypophosphite as additive, raspberry shaped spherical particles are formed.

While further exploring the effect of the reaction parameters on the copper particles formed upon reacting copper salt with zinc in an aqueous solution, the present

inventors have surprisingly uncovered that by using carboxylic acids in the zinc/copper cementation reaction, copper nanoparticles which self-assemble into various unique architectures are formed.

Using this newly discovered process, the present inventors have constructed successfully nano-scale copper building blocks that self-assemble to form or curved copper structures with a high level of predictability, depending on the composition of the building blocks. The resulting particles can be used in a process which enables room temperature sintering of copper nanoparticles and microparticles. The process makes use of a metal displacement reaction between copper ions and metallic zinc to produce intermediate primary copper nanoparticles, which can thereafter form spherical copper nanoparticles which then self-assemble to form hollow microstructures and/or nanostructures with unique bosselated surface morphology. The invention also teaches how to promote tethering and sintering at room temperature between adjacent copper structures.

Hence, as presented hereinbelow, embodiments of the present invention involve utilizing a chemical reduction scheme carried out in an aqueous environment to produce copper nanoparticles and nanostructures which spontaneously assemble (self-assemble) into super-molecular micro-structures. According to some embodiments of the present invention, copper salts such as $CuSO_4$ dissolved in H_2O are reduced by elemental zinc in the presence of a carboxylic acid to yield copper nanoparticles and nanostructures that self-assemble into hierarchical micro-structures.

Depending on various parameters of the process, various hierarchical hollow spheroidal micro-structures, according to some embodiments of the present invention, are micro-scale super-structures characterized by a mean diameter that ranges from 500 nm to 2000 nm (2 μm) and composed of sub-level copper nanoparticles of 50 nm to 200 nm in diameter, which have a bumpy exterior shell, suggesting that these sub-level copper nanoparticles are themselves composed of sub-sub-level copper nanoparticles of 5 nm to 20 nm in diameter.

While reducing the present invention to practice, it was further surprisingly found that certain sulfur containing molecules can give rise to new phenomena on the surface of these copper nanoparticles and micro-structures, expressed primarily by the growth of copper filaments (fibers) thereon. Experimental results obtained by the

present inventors were in agreement with the phenomenological model developed thereby, using the Helfrich-Canham Hamiltonian, involving extrinsic and intrinsic surface curvature at nanoscopic scales, which governs the formation of copper filaments on bumpy, and hence curved, exterior of copper particles.

Based on the filament-growth phenomenon, the present inventors have developed a process aimed at initiating chemically triggered tethering of nanoparticles into nano- and micro-structures. Without being bound by a particular theory, it is suggested that the mechanism of the process involves a correlation between charge density and surface flow phenomena, and maintains that singularities in charge density generate elastic stresses on the highly curved surface of the nanoparticle and thus induce curvature flow (curvature flow is a geometric flow of surfaces induced from elastic stresses whose source is curvature).

Thus, some embodiments of the present invention relate to a novel process of preparing a composition which comprises copper micro-particles, whereby the obtained micro-particles are uniquely characterized by their unique hollow spheroidal structure, as detailed hereinafter. Embodiments of the present invention further relate to a composition that comprises copper nano- and micro-particles with unique low temperature sintering and spontaneous tethering characteristics.

Process of manufacturing:

While reducing the present invention to practice, it was observed that $CuSO_4$ dissolved in H_2O is reduced by elemental zinc in the presence of a carboxylic acid at room temperature, and it was further observed that carrying out the zinc/copper cementation reaction with a carboxylic acid such as, for example, citric acid, leads to the formation of copper microstructures which appear and presumed to be formed from small spherical copper nanoparticles of an average size of 5 nm – 20 nm, which self-assemble into larger spherical clusters of an average size of 20 nm – 200 nm, which self-assemble into hollowed spheroidal micro-structures of 0.5 μm to 5 μm in size and even larger up to 10 μm or up to 20 μm.

These micro-scales structures of self-similarity (fractal) character exhibit a characteristic chemical content and surface topology. The surface chemistry was found to be relatively low in organic content, a feature which allows facile sintering into larger macroscopic structures. The surface exhibited regular and dense bumpy or blistered

topology, which can be described as bullous or bosselated, namely having small round lumps of high curvature.

It was further surprisingly found that adding different sulfur-containing compounds such as, for example, thiourea, alters the exterior surface of the spherical copper particles so as to be covered with what looked like copper "hair", or a network of filament-like growths emanating from the surface of the nanoparticles; a phenomenon which is believed to be related to the bosselated topology of the surface.

Hence, according to an aspect of embodiments of the present invention there is provided a process of manufacturing a composition which comprises copper particles having a bosselated surface topography, as is further described and defined hereinbelow. The process, according to this aspect, is effected by mixing a copper salt with a powder of elemental zinc in an aqueous solution in the presence of a carboxyl-containing compound (e.g., a carboxylic acid as defined herein) at room temperature.

In some embodiments, mixing the solution is effected by stirring it. In some embodiments, stirring is effected vigorously for several minutes, typically 5-15 minutes.

The reaction results in obtaining a powder of copper particles with desired architecture. In some embodiments, the powder is in a form of suspension in the aqueous solution.

According to some embodiments obtaining the composition is effected by consecutively subjecting the obtained suspension to filtration and washing with water and ethanol, so as to afford a brown compressed wet powder ("wet cake").

In some embodiments, the process continues by drying the wet cake into a dry powder.

According to some embodiments of the present invention, the molar ratio between the zinc and the copper ion ranges from 2:1 to 1:2, or the ratio is 1:1.

According to some embodiments of the present invention, the molar ratio between the carboxyl-containing compound and the copper ion ranges from 4:1 to 1:4, and according to some embodiments of the present invention, the molar ratio between the carboxyl-containing compound and the copper ion is 1:1.

Without being bound by any particular theory, it is suggested that the chemical conditions (e.g., concentration and nature of the reactants) used in the process described herein contributes to the rapid reduction of the copper salt, leading to rapid nucleation

which is conductive to the formation of small nanoparticles, whereby the carboxyl-containing compound (e.g., citric acid) may serve as a passivating agent which further contributes to the retardation of aggregation and agglomeration (clumping of the resulting copper nanoparticles into an inseparable non-dispersible mass).

The phrase "carboxyl-containing compound", as used herein, refers to an organic compound having at least one carboxyl group (-COOH), hence, in the context of the present embodiments, a carboxyl-containing compound is a carboxylic acid.

Exemplary carboxyl-containing compounds which are suitable for use in the context of embodiments of the invention include, but are not limited to, monocarboxylic acids such as, for example, formic acid, acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid and capric acid; dicarboxylic acids such as, for example, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, isophthalic acid and terephthalic acid; tricarboxylic acids, such as, for example, citric acid, isocitric acid, aconitic acid, tricarballylic acid, trimesic acid and mellitic acid; and tetracarboxylic acids such as ethylenediamine tetraacetic acid (EDTA), 1,1,2,2-ethanetetracarboxylic acid, 1,1,4,4-butanetetracarboxylic acid, 1,1,2,3-propanetetracarboxylic acid, 1,2,3,4-tetracarboxybenzene and pyromellitic acid.

According to some embodiments of the present invention, the carboxyl-containing compound is citric acid.

Unlike many electro-plating or otherwise other metallization techniques which are intended to form a metallic layer on a surface of a substrate, the process presented herein is intended to form metallic copper without a substrate, namely for metallic copper in the form of a suspension of copper particles, hence the process is effected while the solution wherein the process is performed is stirred throughout the cementation reaction between the zinc and the copper salt, as well as kept at room temperature.

Another factor which is assumed to contribute to the rapid formation of discrete copper nuclei is the physical form of the elemental zinc. Without being bound by any particular theory, it has been found empirically that a very fine powder of zinc will tend to result in more dispersible copper nanoparticles. Therefore, according to some

embodiments, the powder of elemental zinc has a grit size of less than 20 microns, and according to other embodiments, the zinc powder has a grit size of less than 10 microns.

Copper salts which are usable in the context of embodiments of this aspect of the invention include, but are not limited to, copper(II) sulfate ($CuSO_4$), copper(II) chloride ($CuCl_2$), copper(II) nitrate ($Cu(NO_3)_2$), copper(II) acetate ($Cu(CH_3COO)_2$), copper acetylacetonate ($Cu(C_5H_7O_2)_2$), copper(II) carbonate ($CuCO_3$), $Cu[C_6H_{11}(CH_2)_3CO_2]_2$, copper(II) stearate complex, $CuCl_2O_4$, copper(II) ethylenediamine complex, $Cu(OH)_2$, copper(I) bromide (CuBr), copper(I) bromide dimethyl sulfide complex ($CuBr{\cdot}CH_3SCH_3$), copper(I) chloride (CuCl), copper(I) iodide (CuI), copper(I) tetraiodomercurate(II) (Cu_2HgI_4), copper(I) thiocyanate (CuSCN), copper(II) D-gluconate ($C_{12}H_{22}CuO_{14}$), copper(II) bromide ($CuBr_2$), copper(II) cyclohexanebutyrate ($[C_6H_{11}(CH_2)_3CO_2]_2Cu$), copper(II) fluoride ($CuF_2$), copper(II) formate $(HCO_2)_2Cu$, copper(II) hydroxide phosphate, ($Cu_2(OH)PO_4$), copper(II) pyrophosphate ($Cu_2P_2O_7$), copper(II) selenite $CuSeO_3$, copper(II) tartrate ($[-CH(OH)CO_2]_2Cu$), copper(II) tetrafluoroborate ($Cu(BF_4)_2$), cupric nitrate ($Cu(NO_3)_2$), and tetraamminecopper(II) sulfate ($Cu(NH_3)_4SO_4$), as well as any hydrate, ligand complex or combination thereof.

In some embodiments of the invention, the process of manufacturing the composition which comprises copper nanoparticles is effected such that the concentration the copper ions ranges from about 10 mM to about 150 mM; and the molar ratio between the copper ions and the elemental zinc ranges from 2:1 to 1:2. In some embodiments, the molar ratio between the copper and the zinc is 1:1.

According to other embodiments, the molar ratio between the copper ions and the carboxyl-containing compound ranges from 1:1 to 1:5. In some embodiments the ratio is 1:4 copper ions to carboxyl-containing compounds.

For example, the concentrations of zinc, copper sulfate, and citric acid used in an exemplary process according to embodiments of the present invention, can be 30 mM, 30 mM, and 60 mM respectively. According to this embodiment, the ratio of zinc to copper salt is 1:1, and the ratio of zinc or copper salt to the carboxyl-containing compound is about 1:2.

However, other ratios are also contemplated, as long as the desired discrete, re-suspendible and uniformly sized nanoparticles, as defined herein, are obtained.

While further reducing the present invention to practice, it was found that the pH of the reaction has the ability to determine the rate of particle formation and thus the shape of the obtained primary particles, which are an intermediate form or a transition state of copper nanoparticles, which is typically not isolated or observed as discrete particles in the final composition. It was found that conducting the reaction at pH levels between 5 to 1.5 results in discrete copper particles rather than dendritic structures. The pH of the reaction can be set and controlled by the choice and concentration of the carboxyl-containing compound, and optionally by adding pH-adjusting agents, such as sodium hydroxide.

Hence, according to some embodiments, the pH of the aqueous solution ranges from 1.5 to 5. According to some embodiments, the copper nano- and micro- presented herein are formed in a pH that ranges from 2 to 4, from 3 to 4 or from 3.5 to 4.

For example, using a carboxyl-containing compound which is a relatively strong acid, optimal pH values can be obtained by adding, for example, a base such as sodium hydroxide.

It was found that using the above process, composition comprising a plurality of particles was obtained, wherein at least a portion of which are hollow spheroidal particles with particle size at the micron range, hence hollow spheroidal micro-particles.

As exemplified in Figures 1, 2A, 2B, 3A, 4A and 4B, an exemplary process according to embodiments of the invention results in copper micro-particles which are hollow spheroidal particles.

In some embodiments, the particles are characterized by an average particle size that ranges from 0.5 μm to 20 μm, and a wall thickness that ranges from 50 nm to 200 nm.

As further exemplified in Figures 3A-C and 4A-C and discussed in the Examples section that follows, the copper particles produced by the process according to some embodiments of the present invention, seem to be formed by semi-ordered aggregation of smaller spherical copper nanoparticles having an average particle size that ranges from 20 nm to 200 nm, which themselves are composed from smaller copper nanoparticles, in what can be described as a fractal structuralism or self-similarity architecture.

As can further be seen in these figures, the surface of the copper particles is characterized by a bosselated surface topology. The phrase "bosselated surface topology", as used herein throughout, refers to a bullous, blistered or bubbled surface texture having round bumps or blisters arranged densely thereon.

Being covered with roundish bumps, the surface of the copper particles produced according to some embodiments of the present invention, is further characterized by a curvature stemming from the roundness of the bumps, which can be measured as inverse of the mean radius of each boss, or bump.

Thus, according to some embodiments of the present invention, the curvature of each boss in the bosselated surface of the copper particles is characterized by a mean curvature that ranges from 0.02 nm^{-1} (the inverse of a radius of 50 nm) to 0.5 nm^{-1} (the inverse of a radius of 2 nm).

The inventors have surprisingly found that contacting the obtained composition with a sulfur-containing compound further affects the architecture of the obtained particles in the composition. It was surprisingly uncovered that the step at which such a sulfur-containing compound is added also affects the resulting product. Thus, it was found that when it is added after a powder that comprises the particles is formed, filament-coated composition of copper nano- and micro-particles is obtained, and when a sulfur-containing compound is added to the reaction solution, together with the zinc and the acid, a composition of fused nano- and micro-particles is obtained.

Hence, according to some embodiments of the present invention, the process of manufacturing copper particles is effected by:

re-suspending the dried powder of the bosselated copper nanoparticles and/or microparticles obtained so far in an aqueous solution (such as water) in the presence of a sulfur-containing compound, as described herein.

In some embodiments, the dried powder is re-suspended in an aqueous solution to thereby obtain an aqueous suspension thereof;

and a sulfur-containing compound is then added, and optionally dissolved in this aqueous suspension.

In some embodiments, the suspension is stirred at room temperature for several (2-8) hours.

In some embodiments, once the suspension is contacted with the sulfur-containing compound and optionally stirred, the formed powder is filtered and dried.

The resulting composition of this two-steps process (two filtering and drying steps) according to some embodiments of the present invention, comprises spherical copper particles characterized by a surface coated with fibrous metallic copper, as exemplified in Figures 8-10.

As exemplified in Figures 8-10 and more so in Figure 11, this fibrous metallic copper is characterized by fibers having a length of about 10 nm to 100 nm and a thickness of about 5 nm to 10 nm.

The phrase "sulfur-containing compound", as used herein, described a compound which comprises one or more sulfur atoms, optionally one or more thiocarbonyl group, and further optionally, one or more thiol group, as these are defined hereinbelow.

The terms "thiocarbonyl" or "thioketone" refer interchangeably to a –(C=S)– group, which is basically a carbonyl with a sulfur atom in stead of an oxygen atom.

The terms "thiol" or "thiohydroxy" refer interchangeably to a –SH group.

Exemplary sulfur-containing compounds in clued, without limitation, thiourea, thiosemicarbazide, methyl chlorothiolformate, dithiooxamide, thioacetamide, dimethyl trithiocarbonate, ammonium diethyldithiocarbamate, 2-methyl-3-thiosemicarbazide, 4-methyl-3-thiosemicarbazide, ethylene trithiocarbonate, vinylene trithiocarbonate, 2-cyanothioacetamide, β-mercaptoethanol, cysteine, methanethiol (CH_3SH), ethanethiol (C_2H_5SH), 1-propanethiol (C_3H_7SH), 2-propanethiol ($CH_3CH(SH)CH_3$), butanethiol ($C4H_9SH$), tetrabutyl mercaptan ($C(CH_3)_3SH$), pentanethiols ($C_5H_{11}SH$), coenzyme-A, lipoamide, glutathione, dithiothreitol/dithioerythritol and 2-mercaptoindole.

The concentration of the sulfur-containing compound ranges from 0.05 mM to 10 mM according to some embodiments of the present invention.

Without being bound by any particular theory, the sulfur-containing compound, in some embodiments, is selected capable of acting as a localized charge density modifier on the surface of highly curved metallic copper particles, produced according to the process presented herein.

As presented hereinabove, the present inventors have surprisingly uncovered that this curvature is possibly the underlying factor for the growth of metallic copper

filaments on the surface of the copper particles produced according to some embodiments of the present invention.

Without being bound by any particular theory, it has been shown in the art that the surface bonding between a foreign atom and the metallic surface depends on the electronegativity of the foreign atom. For a uni-banded (valence electron energy states), one dimensional surface (chain of metallic atoms) a localized state (chemical bond), exists if the bond energy is below the valence band. Studies of the polarization currents in a hydrochloric or hydrosulfuric solution, containing iron or nickel electrodes with and without corrosion inhibitors, have shown a profound effect on corrosion inhibitors such substances as urea, thiourea and acetone. Compared to non-inhibited and inhibited solution, thiourea had the most intense effect on the polarization current density around the Nernst potential.

It is known that due to the high electronegative nature of the sulfur group in thiourea, localized charge density peaks occur on the surface of metal surfaces onto which thiourea is adsorbed. Hence, according to some embodiments of the present invention, organic molecules such as thiourea, when reacted with highly curved structures, such as the surfaces of the copper particles produced according to some embodiments of the present invention, can induce high curvature stresses which result in surface flow. Without being bound by this theory, it is assumed that this surface flow can be manifested in the formation of metallic copper filaments emanating from the bosselated surface of nanostructures.

It should be noted that both nanoparticles and hollow microparticles in the obtained composition are coated with the fibrous copper, and that these metallic copper filaments may lead, according to some embodiments of the present invention, to tethering between copper nano- and/or micro-particles, leading to mechanical and electrical contact between them even when produced at room temperature.

The present inventors have further surprisingly uncovered that when the spherical copper particles are produced in the presence of a sulfur-containing compound, their surface seems as if it was sintered and the composition obtained from such a process seems to comprise fused metallic copper particles.

To disambiguate the terms "sintered", "tethered" and "fused", it is noted that in the context of the present embodiments, sintering is effected by applying heat and/or

pressure on pre-fabricated compositions of copper nano- and/or microparticles according to some embodiments of the present invention, tethering is observed when the filamentous coating on neighboring copper particles intertwines, and fused copper particles are observed in copper particle compositions which were prepared in the presence of a sulfur-containing compound without heat and/or pressure.

Hence, as used herein, the term "sintered" refers to a morphological solid state of a particulate matter which has been transformed so as to fuse its particles into a substantially continuous non-particulate dense matter. In the context of the present embodiments, the term "sintered" refers to a morphological solid state wherein heat is not necessarily involved, or where no application of external of heat is involved. In the context of the present embodiments sintering may occur as a result of the application of mild mechanical pressure or the application of heat.

The term "fused", as used herein, refers to a morphological solid state of a particulate matter which has been transformed so as to fuse its particles into a substantially continuous non-particulate loose matter. In the context of the present embodiments, the term "fused" refers to a morphological solid state wherein neither heat nor pressure is necessarily involved, but it is rather as a result of specific chemical conditions during a chemical reaction, which forms connected particles rather than discrete particles.

The term "tethered", as used herein, refers to a morphological solid state of a particulate matter which has been transformed so as to have its particles entangled in a network of fibrous matter. In the context of the present embodiments, the term "tethered" refers to a morphological solid state which is a result of specific chemical conditions during a chemical reaction, which forms fiber-entangled particles rather than discrete particles.

Hence, according to some embodiments of the present invention, the process of manufacturing a composition as described herein, is effected by performing the mixing of the copper salt, the zinc and the carboxyl-containing compound, in the presence of a sulfur-containing compound as described herein. Thus, the addition of the sulfur-containing compound is performed prior to the copper/zinc cementation reaction and thus prior to filtering and drying the powder.

In some embodiments, the process is effected by adding a sulfur-containing compound to the aqueous solution containing the copper salt, the elemental zinc grit and the carbonyl-containing compound;

stirring the solution vigorously at room temperature using a homogenizer for several (5-15) minutes; and

filtering and drying the obtained powder.

As exemplified in Figures 16-18, the composition obtained according to these embodiments of the invention differs from the composition obtained according to embodiments where the sulfur-containing compound is added after a powder of copper particles is formed, in that the filaments, which were clearly observable in the two-steps process, seem to be fused or sintered to the surface of the spherical copper particles in such a way so as to fuse the copper particles to one another. Hence, this composition prepared with a sulfur-containing compound is characterized by fused spherical copper particles having an average particle size that ranges from 50 nm to 20 μm.

The composition obtained by these embodiments of the invention presents a unique possibility to obtain a continuous layer of conductive metallic copper on the surface of any substrate, at room temperature and without any additional chemical, physical or mechanical step, by simply spraying an aqueous solution containing a copper salt, fine elemental zinc powder, a carboxyl-containing compound and a sulfur-containing compound onto the surface. The resulting copper particles which will form in the solution would be fused to one another and therefore constitute a sintered layer on the surface of the substrate.

Exemplary processes of manufacturing the compositions described herein were carried out as described in the Examples section that follows. The typical reaction was found to be rather fast and lasted only several minutes to reach completion (from 2 to 10 minutes) at room temperature, during which the typical deep aquamarine colored copper sulfate solution turns into a lucid burgundy-suspension, or lucid blackish suspension in cases where a sulfur-containing compound is involved.

The reactions may be performed with or without the presence of a phosphorous-containing compound. Exemplary suitable phosphate compounds are as described in WO 2010/035258.

According to some embodiments of the present invention, the processes of manufacturing the compositions presented herein involve reaction with are devoid of a phosphorous-containing compound.

It is noted herein that the powders obtained by any of the processes described hereinabove, responded to weak mechanical pressure by turning into pinkish copper stripes which was indicative of the ease at which these nanoparticles can be sintered.

Copper nanoparticles characterization:

Using the exemplary process as described hereinabove afforded several exemplary compositions (e.g., in the form of a powder of copper nano- and micro-particles) which were further investigated and characterized by various methods, and were found to posses different architectures, influenced by the reaction parameters.

For example, high-resolution scanning electron microscope (HRSEM) observations showed that the obtained powder comprises hollow spheroidal copper micro-particles having an average size of about 0.5 μm to 20 μm, a wall of 50 nm to 200 nm in thickness and a bosselated surface topology. Each of these copper particles seems to be comprised of a plurality of spherical copper nanoparticles. X-ray photoelectron spectroscopy (XPS) spectra analyses provided the chemical composition of the resulting copper particles.

Hence, according to an aspect of embodiments of the present invention there is provided a composition which includes a plurality of copper nanoparticles and/or microparticles generally shaped as spheroids and characterized by a bosselated surface topology.

According to some embodiments of the present invention, the copper nano- and micro-particles have an overall spherical shape. Accordingly, in some embodiments, the copper nanoparticles are generally shaped as spheroids, which is a close approximation to a sphere. The phrases "spheroids", "spheroidal particles " and "spherical particles" are used herein interchangeably. These nano- and micrometric spheroids, which may represent higher self-similar (fractal) structures of the transition state primary nanoparticles, are characterized by having an average particle size as can be determined by SEM/TEM/HRSEM measurements.

According to some embodiments of the present invention, the compositions presented herein include a plurality of particles, a portion of which are hollow spheroidal microparticles and a portion of which are spherical nanoparticles.

The phrase "a portion of", as used herein, refers to a part of a physical quantity, such as surface area or weight. In the context of the plurality of particles comprising a composition, a portion of the composition describes 1 weight percent, 10 weight percents, 50 weight percents, 70 weight percents, 80 weight percents, 90 weight percents and even 100 weight percents (meaning that the composition consists of that species), and any value therebetween, including 0 for absent (and consisting the other type of particle species).

According to some embodiments of the present invention, the composition consists of hollow spheroidal copper microparticles.

In some embodiments, the hollow spheroidal copper micro-particles are characterized by an average particle size that ranges from about 0.5 μm to about 20 μm.

In some embodiments, the hollow spheroidal copper micro-particles are characterized by a wall thickness that ranges from about 50 nm to about 200 nm.

Alternatively, according to some embodiments of the present invention, the composition consists of copper nanoparticles having a bosselated surface topology.

Alternatively, according to some embodiments of the present invention, a portion of the composition includes copper nanoparticles and another portion thereof includes hollow spheroidal copper microparticles, all of which exhibit a bosselated surface topology.

The protective nature of certain organic and inorganic groups in terms of conferring stability to metallic nanoparticles has been described in the art. The ability of certain oxides to confer this stability has also been suggested. Most procedures for nanoparticle production aim at obtaining discrete nanoparticles and rely on the presence of considerable amounts of organic capping layers, however, the presence of organic capping agents reduces the quality of the nanoparticles and should be minimized. This non-trivial challenge of reducing an organic content in copper nanoparticles was achieved by the processes presented herein, as can be discerned clearly from the facile room temperature mild pressure-driven sintering thereof.

As discussed hereinabove, other known metallic nanoparticles are produced in the presence of passivating agents, which are in most cases organic substances. The existence of a considerable amount of organic molecules in or on metallic nanoparticles, takes away some if not all their desired properties, and hence these passivating substances are required to "disappear" when they are no longer needed. This is mostly afforded in currently known methodologies by selecting volatile passivating agents. However, volatility of the undesired passivating agents infer exposure to elevated temperatures, and even in those conditions, not all of the organic content of the passivated nanoparticles can be rid of, not to mention application wherein elevated temperature is not possible.

The copper nano- and micro-particles presented herein therefore enjoy another beneficial property, which can be referred to as a "low organic content", namely a very low percentage by weight/mass of organic molecules versus copper. A quantitative measure for the content of organic molecules can be the carbon content. Metallic nanoparticles having a carbon-content above a certain threshold would be considered useless for certain applications. Hence, according to embodiments of the present invention, the carbon content of the copper nanoparticles presented herein is less than 20 percent of the total weight of the copper nanoparticles (their total mass).

According to some embodiments of the present invention, the copper nanoparticles presented herein have a carbon content of less than 10 percents of their total mass, or less than 5 percents of their total mass.

XPS analysis of powders produced using a carboxyl-containing compound such as citric acid, detect relatively low presence of organic elements (O and C, and P and S when used) on the surface of the copper particle. Considering that the chemical content is relevant to the exterior of the particle, and that the core of the particle consists essentially of pure copper, values of 40 % and even 50 % of carbon measured by XPS are indicative of very low carbon content of the entire mass of the particle.

Thus, according to some embodiments of the present invention, the micro-particles have an exterior surface which is characterized as comprising an atomic concentration of oxygen that ranges from 20 percent to 40 percent; an atomic concentration of carbon that ranges from 20 percent to 35 percent; and when used, an atomic concentration of phosphorous that ranges from 0 percent to 5 percent.

It is noted herein that the figures present examples of the compositions according to some embodiments of the present invention, and serve as to demonstrate exemplary embodiments.

As discussed hereinabove and seen in the figures, the wall of the hollow spheroidal copper micro-particles seems to comprise spherical copper nanoparticles having an average particle size that ranges from 20 nm to 200 nm.

It can be stated that in general, the outcome of the process presented hereinabove, is a composition comprising spherical copper nanoparticles which may undergo some process of self-assembly into larger hollow spheroidal micro-particles, and/or or become coated with filamentous copper and thereafter, optionally tether to one another.

According to some embodiments of the present invention, the spherical copper nanoparticles of the composition are characterized by an average particle size that ranges from 50 nm to 500 nm, and a bosselated surface topology, as this term is defined hereinabove.

In general, the surface topology of the nanoparticles and microparticles of the compositions according to the present embodiments, is characterized by round bumps or bosses, wherein the curvature of each of these bosses in the bosselated surface topology is having a mean curvature that ranges from 0.02 nm^{-1} to 0.5 nm^{-1}.

As discussed hereinabove, when treated with a sulfur-containing compound, at least a portion of the plurality of pre-formed copper nanoparticles and/or microparticles, having a bosselated surface topology, may become coated with fibrous copper.

For example, hollow spheroidal copper microparticles as described herein may become coated with a network of fibrous copper. Alternatively, spherical copper nanoparticles as described herein may become coated with a network of fibrous copper. Further alternatively, when both types of particles are present in the composition, both types of copper particles may become coated with a network of fibrous copper.

According to some embodiments of the present invention, the fibrous copper is characterized by fibers having a length of about 10 nm to about 100 nm and a thickness of about 5 nm to about 10 nm. This fibrous copper may be formed in such a way so as to tether neighboring particles to one another.

Tethering of particles as a result of the formation of fibrous copper may occur between various types of particles, thereby forming entangled complex structures which comprise large and small particles, depending of their relative presence in the composition. Hence, spherical nanoparticles may be tethered to other spherical nanoparticles; hollow microparticles may be tethered to other hollow microparticles; and spherical nanoparticles may be tethered to hollow microparticles.

As further discussed hereinabove, when a sulfur-containing compound is introduced into the copper/zinc cementation reaction mixture as well as a carboxyl-containing compound, the surface on the copper nanoparticles and/or microparticles having a bosselated surface topology, become fused.

According to some embodiments of the present invention, at least a portion of the copper microparticles and/or nanoparticles become fused to one another.

As can be seen in Figures 16-18, the surface of the copper particles in the exemplary composition shown therein appears smooth, and the boundary between features on the surface of a particle or even the boundary between individual particles becomes less discernable.

The chemical composition of the compositions which comprise a sulfur-containing compound, either the composition wherein pre-formed copper particles are treated with a sulfur-containing compound or the composition wherein the copper particles are formed in the presence of a sulfur-containing compound, was examined as exemplified in the Examples section below.

Hence, according to some embodiments of the present invention, the exterior surface of the copper microparticles and/or nanoparticles obtained by introducing a sulfur-containing compound into the reaction mixture, or by post-treating the same with a sulfur-containing compound, is characterized as comprising an atomic concentration of oxygen that ranges from 20 percent to 40 percent.

According to some embodiments of the present invention, the exterior surface is characterized as comprising an atomic concentration of carbon that ranges from 20 percent to 30 percent.

According to some embodiments of the present invention, the exterior surface is characterized as comprising an atomic concentration of nitrogen that ranges from 10 to

15 percent (when nitrogen is present in the sulfur-containing compound such as thiourea).

According to some embodiments of the present invention, the exterior surface is characterized as comprising an atomic concentration of sulfur that ranges from 0.1 to 5 percent.

As presented in the Examples section that follows below, XPS analysis of an exemplary composition prepared by exposing pre-formed copper particles to thiourea according to some embodiments of the present invention, reveals the presence of nitrogen at a content of 11 % and sulfur at an amount of 0.5 %, indicating that the sulfur group is essentially eliminated from the surface of the copper particles.

The unique surface chemistry and overall morphology of the compositions presented herein, afforded either with or without a sulfur-containing compound, affords a unique capacity to sinter into macroscopic structures upon an application of mild mechanical pressure thereon at a temperature lower than 100 °C, and even lower than 50 °C (e.g., at room temperature). In the compositions afforded by treating with a sulfur-containing compound, HRSEM evaluation suggests that that this fibrous network facilitates physical contact between copper nano- and micro-particles and can promote sintering at room temperature.

As demonstrated in the Examples section that follows and illustrated in Figure 5, sub-micron and micron sized copper particles, which are produced as powders according to some embodiments of the present invention, can be sintered at room temperature by manually applying very weak pressure, to yield metallic copper lines.

Thus, according to some embodiments of the invention, sintering of dry powders of the compositions presented herein can be afforded by applying mechanical pressure at room temperature thereon.

The compositions presented herein are highly suitable for many applications where nanoparticles are used in general, and in particular to those applications where the nanoparticles are discrete, do not tend to form agglomerate irreversibly, and have a low carbon (organic) content. The fact that these compositions are formed in a very cost effective and easily up-scaled processes, make them highly desirable for many industrial applications.

Hence, according to yet another aspect of the present invention there is provided an article-of-manufacturing consisting of or comprising any of the compositions presented herein.

Such article-of-manufacturing may be formed, according to some embodiments of the present invention, by applying a mild mechanical pressure on the composition at a temperature lower than 100 °C, lower than 50 °C or at room temperature.

By "mild mechanical pressure" it is meant that the mechanical pressure can be applied, for example, directly by hand mediated by a small tool, or otherwise by a mechanical pressure which is less than 100 MPa, less than 10 MPa or less than 1 MPa, which is applied for less than 1 minute on a sample of 1 gram of any of the compositions presented herein.

Alternatively, since the compositions presented herein are meant also for forming fine micro-scale conductive copper objects which are substantially two-dimensional, the mild mechanical pressure required for sintering would be on thinly spread patterns of the compositions. For example, a powder of any of the compositions is formed, applied as a thin layer of about 0.5 micron to 50 microns on a substrate, and then pressed mildly (with less than 10 MPa or less than 1 MPa) to sinter the composition into a continuous metallic copper layer.

Such mechanical pressure can be applied by a roll-to-roll printing mechanism and since heating to temperatures higher than 100 °C is not necessary, such techniques can be suitable for substrates which do not tolerate high temperatures. The ability to transform copper powder (copper particles) into copper sheets or lines by applying moderate mechanical pressure can enable, for example, applications such as roll-to-roll printing of conducting patterns such as RFID antennas.

The article-of-manufacturing, according to some embodiments of the present invention can be, for example, an inkjet ink, a dry toner, a solid macro-scaled object, an electronic component and an electronic circuit.

The application of the composition presented herein can be afforded by means of applying a suspension of the composition onto a substrate, and thereafter effecting sintering thereof by mild heat, mild pressure without heat, or a combination thereof, according to the substrate and the desired results.

The term "suspension", as used herein, refers to a heterogeneous mixture of a solid in the form of fine solute-like particles dispersed in a liquid or solvent-like phase. Typically, a suspension will have a tendency to settle, namely the fine particles of the solid matter may have the tendency to precipitate after a period of time. This period of time depends on many factors, such as the substances of the particles and the liquid, the temperature and other physical parameters like stirring and shaking, and the presence of other substances, such as dispersing agents, emulsifiers, surface-active agents, thickeners and the likes. The term "suspension" as used herein, is similar to the term dispersion, with the proviso that the media is a condense medium, typically a liquid. Thus, a suspension is a collection of discrete and separated particles dispersed in a liquid medium. The capacity to re-disperse is applicable also in liquid media, namely the capacity to re-suspend, or go from a precipitant to a suspension reversibly and reproducibly.

Thus, according to some embodiments of the present invention, the composition is being in a form of a dispersion, or in other words, the copper nano- and/or micro-particles comprising the composition are dispersed, be it as a dry powder or as a suspension of copper particles in liquid media, such as a suspension in an aqueous medium.

For example, any of the compositions presented herein can function well in certain ink formulations and processes in the field of printable electronics. Hence, an exemplary article-of-manufacturing which includes the composition presented herein formulated into an inkjet ink composition. Such inkjet inks are used, for example, to form electronic circuits, electronic components, electronic elements and devices by inkjet printing.

Correspondingly, there is provided a method of preparing a substantially electrically conducting copper element. This method includes forming a shape of the element from a composition as provided herein, and applying either heat or pressure, or both, onto this shape to thereby obtain the copper element.

Accordingly, there is provided an inkjet ink composition which includes a composition as presented herein.

Correspondingly, there is provided a method of inkjet printing a substantially electrically conducting element on a substantially electrically isolating substrate. Such a

method includes applying the inkjet ink composition provided herein on the substrate. According to some embodiments of the present invention, the method of printing further includes, subsequent to applying the ink, curing the substrate having the inkjet ink composition applied thereon by mild heat to thereby form the electrically conducting element on the substantially electrically isolating substrate.

Another field where fine metal powders are highly in demand is the field of powder metallurgy, mainly for molding and casting metal objects. Powder metallurgy uses sintering process for making various parts out of metal powders. The metal powder is compacted by placing it in a closed metal cavity (the die, matrix or mold) under pressure. This compacted material is placed in an oven and sintered in a controlled atmosphere at moderate temperatures (relative to the temperature needed to melt the metal) and the metal powders coalesce and form a solid. A second pressing operation, repressing, can be done prior to sintering to improve the compaction and the material properties. Metallic nanoparticles are therefore typically used for these applications since the cleaner (organic-free) the nanoparticles and the smaller they are, the better the end-result of a metal object will be.

Hence, according to other embodiments of the present invention, the article-of-manufacturing described herein is a metal object of any shape and size, which is made by any powder metallurgy process and which comprises the composition according to embodiments of the present invention.

Exemplary objects include, but are not limited to, objects of complex structures such that are not feasible by conventional machining and other material removal methods, molten-metal casting methods or molten-metal extrusion methods, as well as simple objects, shafts, bearings, blades, pistons, housing, casing, tubing, and any object that combines the latter.

Compositions according to some embodiments of the present invention are assumed to possess an electrostatic charge which can be used to direct them to predetermined locations on given substrates. Charged copper micro-particles capable of undergoing sintering by mild mechanical pressure may enable fabrication of conductive patterns using electrophotography.

Hence, according to some embodiments of the present invention, an exemplary article-of-manufacturing can be a dry toner, useful for example in a roll-to-roll printing technique.

As used herein, the term "toner" refers to a powder of charged particles which are positioned photoelectronically according to a predetermined patter onto a platform, which can then transfer the pattered particles onto a final substrate. Toners are used in printing technique such as in laser printers and photocopiers to form the printed text and images on the paper.

According to some embodiments of the present invention, the toner is curable upon application of mild mechanical pressure thereon at a temperature lower than 100 °C, or lower than 50 °C.

The toner can therefore be used in a method of printing a substantially electrically conducting element on a substantially electrically isolating substrate, by applying the toner on the substrate and pressing the substrate having the toner applied thereon to thereby form the electrically conducting element on the substantially electrically isolating substrate.

Alternatively, according to some embodiment of the invention, any of the compositions presented herein can be fed through a rolling machine to produce conductive copper sheets not supported by a substrate.

One feature of suspensions of the sintered copper particles presented hereinabove is their excellent coating abilities of a variety of substrates. The phenomenon of tethering between copper particles, mediated by the nano-filaments, as described and demonstrated herein, can be used to build high-surface area structures for catalysis and may also be used to facilitate re-joining of cracks formed in copper structures.

According to some embodiments of the invention, nano- and micro-sized sintered copper particles can be obtained by performing a zinc/copper cementation reaction in the presence of a carboxyl-containing compound such as citric acid and a sulfur-containing compound such as thiourea. The resulting suspension of the composition obtained by the aforementioned process can be used to wet-spray a surface of a substrate so as to afford a layer of sintered metallic copper thereon.

The present inventors postulated a mechanism according to which fine filament-coated copper nanoparticles first pack into a micelle like structures, leading to spherical structures held together by virtue of weak forces; thereafter, increased surface charge density brought about by the adsorption of sulfur leads to surface flow which transforms the discrete spherical nanoparticles into a sintered body.

Hence, according to yet another aspect of embodiments of the present invention, there is provided a method of preparing a substantially electrically conducting copper layer on at least a portion of a surface of a substrate, which is effected by spraying a suspension of the sintered copper particles described hereinabove onto the surface. It is noted that by using the composition which is prepared by combining zinc, copper salt, a carboxyl-containing compound and a sulfur-containing compound, the intrinsic tendency of the copper particles in such compositions to sinter may render heat curing and/or pressure setting unnecessary.

It is expected that during the life of a patent maturing from this application many relevant metallic nanoparticles will be developed and the scope of the phrase "copper particles" is intended to include all such new technologies *a priori*.

It is appreciated that certain features of the invention, which are, for clarity, described in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features of the invention, which are, for brevity, described in the context of a single embodiment, may also be provided separately or in any suitable subcombination or as suitable in any other described embodiment of the invention. Certain features described in the context of various embodiments are not to be considered essential features of those embodiments, unless the embodiment is inoperative without those elements.

Various embodiments and aspects of the present invention as delineated hereinabove and as claimed in the claims section below find experimental support in the following examples.

EXAMPLES

Reference is now made to the following examples, which together with the above descriptions, illustrate some embodiments of the invention in a non limiting fashion.

MATERIALS AND INSTRUMENTAL METHODS

$CuSO_4 \cdot 5H_2O$ was purchased from Gadot Chemicals.

Zinc powder, grit size less than 10 micron, was purchased from Sigma-Aldrich.

Citric acid was purchased from Sigma-Aldrich.

Thiourea was purchased from Sigma-Aldrich.

All commercial reagents and materials were used without further purification or treatment unless mentioned otherwise.

High-Resolution Scanning Electron Microscope (HRSEM) micrographs were afforded using a Zeiss Gemini Ultruplus.

X-ray photoelectron spectroscopy (XPS) measurements were afforded using a VG Scientific Sigma Probe.

EXAMPLE 1

Hollow spheroidal copper micro-particles

General Procedure A:

Copper salt is dissolved in degassed water to thereby obtain a copper salt solution. A carboxyl-containing compound is added to the solution at a ratio that ranges from 5:1 to 1:1 with respect to the copper, and stirred until fully dissolved. The pH of the solution is adjusted with a hydroxyl salt to range from 1.5 to 5. Thereafter, zinc dust (grit size 10-20 micron) is added to form a suspension which is stirred vigorously using a homogenizer for several minutes at room temperature. Optionally, a phosphorous-containing compound is added to the copper salt solution prior to the addition of zinc.

The suspension of metallic copper particles is filtered on paper to form a cake which is washed with water and alcohol, dried in room temperature and in an oven at 50 °C for several hours.

Copper cementation with zinc, citric acid and sodium hypophosphite:

In an exemplary procedure, 46.8 grams of $CuSO_4 \cdot 5H_2O$ were added to 6 liters of H_2O, pre-bubbled with N_2 for at least 10 minutes, and stirred using a homogenizer until completely dissolved. Thereafter, 71 grams of sodium hypophosphite and 60 grams of citric acid monohydrate were added and the mixture was stirred until all the citrate has dissolved. The pH of the solution was adjusted to 5 using sodium-hydroxide. Thereafter, 12 grams of zinc dust (grit size 10 micron) were added and the suspension was stirred vigorously using a homogenizer for another 8 minutes at room temperature.

With the addition of the zinc powder the solution turns from clear green-blue to a reddish/brown lucid suspension. The resulting suspension was filtered through a #42 filter paper and washed with H_2O and ethanol. The filter paper carrying the red slurry was put in a convection oven heated to 50 °C for a few minutes, taken out, and the dried slurry, now in the form of cake, was removed from the filter paper.

The cake was reintroduced into the oven and heated at 50 °C for 7 hours. This procedure results in copper nanostructures which self-assemble to form spherical copper nanoparticles and hollow spheroidal copper micro-particles.

Analysis of the Resulting Composition:

When citric acid (or another carboxyl-containing compound such as, for example, EDTA or oxalic acid) was included in the copper/zinc cementation reaction, discrete spherical nanoparticles and microparticles were obtained. These nanostructures pack together to yield hollow spheroidal micro-particles having a self-similarity architecture and a final average particle size that ranges from 0.5 micron to 20 microns.

The hollow spheroidal copper micro-particles were obtained when the molar ration between citric acid and copper sulfate is greater than 1:1. In cases where this molar ratio is smaller than 1:1 (less citric acid), heavily aggregated dendritic structures were formed rather than spheres of any size.

The following electromicrographic analysis refers to the composition obtained as described hereinabove using 6 liters H_2O bubbled with N_2, 46.8 grams of $CuSO_4$, 71 grams of NaH_2PO_2 71, 60 grams of citric acid and 12 grams of powdered zinc, at pH 5.

Surface composition of the above composition, as determined by XPS, revealed a composition of 34.87 % oxygen, 29.37 % carbon, 30.11 % copper, 3.15 % zinc and 2.53 % phosphorous.

Similar compositions, in terms of visual appearance, were obtained when the cementation reaction was performed in a solution devoid of a phosphorous-containing compound, and/or using various ingredient ratios and various carboxyl-containing compounds.

Figure 1 and Figures 2A-B are HRSEM electromicrographs of hollow spheroidal micro-particles, prepared as described above with citric acid and hypophosphite. As shown in the electromicrographs, the obtained particles have an average particle size of from 0.5 μm to 20 μm, and are comprised of sub-micron spherical nanoparticles each having dimensions of from 20 nm to 200 nm.

Without being bound to any particular theory, it is assumed that these hollow spheroidal copper micro-particles of various microscopic sizes are the result of an incremental self-assembly of spherical copper nanoparticles in the size range of from 5 nm to 20 nm, which pack together to form a larger spherical copper nanoparticles of from 50 nm to 200 nm, which then pack together to form the hollow spheroidal copper micro-particles being from 0.5 to 20 micron in size. Such self-similarity architecture or fractal structuralism is a characteristic of the hollow spheroidal copper micro-particles described herein.

Figures 3 and 4 present two series of HRSEM electromicrographs in increasing magnification levels of exemplary hollow spheroidal copper micro-particles having self-similarity architecture, based on incremental packing of smaller spherical copper nanoparticles.

When mild mechanical pressure was applied at room temperature on a composition comprising the hollow spheroidal copper micro-particles described herein, these powers tend to sinter into larger metallic copper structures.

Figure 5 is a HRSEM electromicrograph of a streak of powder of exemplary hollow spheroidal copper micro-particles, which was pressed manually using a spatula at room temperature. Upon pressure-effected sintering at room temperature, the color of the substance changed from typical saddle-brown of the powder to metallic red luster.

Figure 6 presents a high resolution XPS spectrum of C1s measured for a sample of hollow spheroidal copper micro-particles obtained with citric acid as described hereinabove. The C1s spectrum was curve-fitted with 3 components. While the A line

is related to carbon bound to hydrogen, the higher binding energy line B is assigned to C-OH and/or C-O-C=O. The C line is related to C=O and/or O-C-O.

Figure 7 presents a high resolution XPS spectrum of Cu2p measured for a sample of hollow spheroidal copper micro-particles obtained with citric acid and with hypophosphite as an additive. The Cu2p3/2 spectrum was curve-fitted with 3 components. While the lower binding energy line is related to Cu_2O and metallic Cu (based on the Cu LMM line measurements), the higher binding energy lines can be assigned as CuO and $Cu(OH)_2$. The presence of a metallic Cu line is due to the fact that the surface oxide is thin enough to allow the photoelectrons from the metal to escape through the oxide layer. The Cu oxide layer (estimated from the experimental Cu oxide and Cu metal peak ratio) is a few nm thick.

EXAMPLE 2

Spherical copper nanoparticles coated with fibrous copper

General Procedure B:

A powder of copper nano- and micro-particles is prepared according to General Procedure A presented hereinabove, and is thereafter suspended using a homogenizer in degassed water at room temperature. A sulfur-containing compound is added to the suspension and the obtained mixture is stirred for several hours. The resulting suspension is filtered and dried.

Copper particles treated with thiourea:

in an exemplary procedure, copper particles powder was prepared as follows: 234 grams of $CuSO_4 \cdot 5H_2O$ were added to 6 liters of H_2O, pre-bubbled with N_2 for at least 10 minutes, and stirred using a homogenizer until completely dissolution was achieved. Thereafter, 345 grams of citric acid monohydrate were added and the mixture was stirred until all the citrate has dissolved. The pH of the solution was adjusted to 3.6 using sodium-hydroxide. Thereafter, 60 grams of zinc dust (grit size 10 micron) were added and the suspension was stirred vigorously using a homogenizer for another 8 minutes at room temperature. With the addition of the zinc powder the solution turns from clear green-blue to a reddish/brown lucid suspension. The resulting suspension was filtered through a #42 filter paper and washed with H_2O and ethanol. The filter paper carrying the red slurry was put in a convection oven heated to 50 °C for a few

minutes, taken out, and the dried slurry, now in the form of cake, was removed from the filter paper. The cake was reintroduced into the oven and heated at 50 °C for 7 hours. This procedure resulted in a powder of spherical copper nanoparticles and hollow spheroidal copper micro-particles.

7 grams of the powder were dispersed at room temperature in 2.5 liters H_2O using a homogenizer. Thereafter, 0.6 grams of thiourea (7 mmol) were added and the suspension was mixed for a few hours. During the mixing a golden color developed in the suspension, and a black/golden colored coating developed on the glassware.

The resulting suspension was filtered using #42 filter paper and washed with H_2O and ethanol. The filter paper carrying the slurry was put in a convection oven heated to 50 °C for a few minutes, taken out, and the dried slurry, now in the form of cake, was removed from the filter. The cake was then reintroduced into the oven and heated at 50 °C for 7 hours.

Analysis of the Resulting Composition:

The addition of a sulfur-containing compound such as thiourea, to aqueous suspensions of copper nano- and micro-particles, produced as described hereinabove, resulted in the appearance of extremely fine fibrous structures over the surface and in-between the copper particles. In many cases these nano-fibers appear to tether copper particles as if the network of fiber joins of the particles.

Similar compositions, in terms of visual appearance, were obtained when the cementation reaction was performed in a solution devoid of a phosphorous-containing compound, and/or using various ingredient ratios and various carboxyl-containing compounds and sulfur-containing compounds.

As can be seen in the electromicrographs presented below, the above procedure resulted in a dense network of fibrous matter, covering the copper particles.

Figure 8 is a HRSEM electromicrograph of the surface of a spheroidal copper micro-particle, obtained as described hereinabove and treated with thiourea, being completely covered with fibrous copper.

Figures 9 and 10 are HRSEM electromicrographs showing a surface of a hollow spheroidal copper micro-particle prepared as described hereinabove, having spherical copper nanoparticles tethered thereto by fibrous copper.

Figure 11 is a TEM electromicrograph showing the fibrous copper network formed on the surface of spherical copper nanoparticles and hollow spheroidal copper micro-particles, prepared as described hereinabove, due to the treatment thereof with thiourea, wherein the TEM evaluation suggests that the copper comprising these fibers is semi-crystalline.

As can be seen in the HRSEM and TEM electromicrographs presented in Figures 8-10, the fibrous network facilitates physical contact between copper nano- and micro-particles and can promote room temperature sintering of copper nano- and micro-particles. The width of the nano-filaments cannot be resolved using HRSEM even at magnifications of 200,000X, indicating that their diameter is less than 10 nm. TEM evaluation of these nano-filaments suggests that the copper therein is amorphous or semi-crystalline.

The following XPS analysis pertains to a sample prepared as described hereinabove and according to General Procedure B presented hereinabove, with 7 grams of copper particles powder, prepared according to General Procedure A as presented hereinabove, from 6 liters of H_2O, 234 grams of $CuSO_4 \cdot 5H_2O$, 345 grams of citric acid, 60 grams of zinc dust, and treated with 0.6 grams of thiourea.

Figure 12 presents a high resolution XPS C1s spectrum of a sample of copper particles, obtained and treated with thiourea as described hereinabove. The spectrum was curve-fitted with 5 components. While the A line can be related to carbon bound to hydrogen, the higher binding energy lines can be assigned to carbon atoms bonded to O and N in various chemical configurations.

Figure 13 presents a high resolution XPS Cu2p spectrum of a sample of copper particles, obtained and treated with thiourea as described hereinabove. The spectrum was curve-fitted with 6 components. While the lower binding energy line can be related to Cu_2O (based on the Cu LMM line measurements), the higher binding energy lines can be assigned as CuO and $Cu(OH)_2$. The E, G and F lines are typical shake-up lines typical for Cu bonded as Cu_2O.

Figure 14 presents a high resolution XPS N1s spectrum of a sample of copper particles, obtained and treated with thiourea as described hereinabove. The spectrum was curve-fitted with 2 components. While the A line can be related to nitrogen

bounded to copper, the higher binding energy line B can be assigned to the nitrogen atoms bonded in a N-C=O configuration.

Figure 15 presents a high resolution XPS S2p spectrum of a sample of copper particles, obtained and treated with thiourea as described hereinabove. The spectrum obtained is typical for a sulfide-like bonding state.

As can be seen in the spectra presented in Figures 12-15, the atomic concentrations of nitrogen and sulfur on the surface of the nanoparticles are 11.5 % and 0.5 % respectively, with oxygen (oxide) at 36 % and carbon at 26 %. The marked differences and the low detection levels of sulfur suggest that the sulfur group undergoes hydrolysis.

EXAMPLE 3

Spherical copper nanoparticles coated with fused copper fibers

General Procedure C:

A carboxyl-containing compound and a sulfur-containing compound are dissolved in degassed water, and the pH of the solution is adjusted using a hydroxyl salt to range from 1.5 to 5. A copper salt is dissolved in the solution, and thereafter zinc dust (grit size 10-20 micron) is added to the solution to form a suspension which is stirred vigorously using a homogenizer for several minutes at room temperature.

The suspension of metallic copper particles is filtered on paper to form a cake which is washed with water and alcohol, dried in room temperature and in an oven at 50 °C for several hours.

Fused copper particles prepared in the presence of thiourea:

In an exemplary procedure, 12 grams of citric acid, and 2.3 grams of thiourea were dissolved in 6 liters of H_2O, pre-bubbled with N_2 for at least 10 minutes, and the pH of the solution adjusted to 4 using sodium-hydroxide. Thereafter, 46.8 grams of $CuSO_4 \cdot 5H_2O$ were added, and the pH of the solution drops to 2.8. Thereafter, 12 grams of zinc dust (grit size 10 micron) were added and the suspension was stirred vigorously at room temperature using a homogenizer for additional 8 minutes. With the addition of the zinc powder a blackish lucid suspension was formed.

The resulting suspension was filtered using #42 filter paper and washed with H_2O and ethanol. The filter paper carrying the red slurry was put in a convection oven

heated to 50 °C for a few minutes, taken out, and the dried slurry, now in the form of cake, was removed from the filter. The cake was then reintroduced into the oven and heated at 50 °C for 7 hours.

Analysis of the Resulting Composition:

The above procedure resulted in copper particles which are fused together to form continuous copper structures. Hence, conducting the zinc/copper cementation reaction in the presence of citric acid and thiourea afforded fused copper particles which appeared as if were sintered.

It should be noted here that at no time during the entire process did the temperature rise above 50 °C; the cementation reaction was conducted at room temperature and the compositions were drying at 50 °C, indicating that the observed particle fusing occurred at low temperatures relative to typical copper-sintering temperatures.

The HRSEM analyses of various copper particles, grown in the presence of thiourea according to the procedure presented hereinabove, revealed fused copper particle surface, as if sintered. Figures 16 to 18 reveal some of the intermediate stages in the formation of fused copper particles.

Figure 16 is a HRSEM electromicrograph showing a micelle-like packing of linear chains of copper nanoparticles, which is assumed to be the first step in the process of obtaining fused copper particles.

Figure 17 is a HRSEM electromicrograph showing a copper nanoparticles prepared by the procedure presented hereinabove, exhibiting a surface area in an intermediate stage in the transformation into a smooth fused morphology. As can be seen in Figure 17, most of the sub-level spherical features have sintered to form a smooth surface.

Figure 18 is a HRSEM electromicrograph showing copper particles prepared in the presence of thiourea as presented hereinabove, exhibiting a surface which seems to be completely fused.

Although the invention has been described in conjunction with specific embodiments thereof, it is evident that many alternatives, modifications and variations will be apparent to those skilled in the art. Accordingly, it is intended to embrace all

such alternatives, modifications and variations that fall within the spirit and broad scope of the appended claims.

All publications, patents and patent applications mentioned in this specification are herein incorporated in their entirety by reference into the specification, to the same extent as if each individual publication, patent or patent application was specifically and individually indicated to be incorporated herein by reference. In addition, citation or identification of any reference in this application shall not be construed as an admission that such reference is available as prior art to the present invention. To the extent that section headings are used, they should not be construed as necessarily limiting.

WHAT IS CLAIMED IS:

1. A composition comprising a plurality of copper nanoparticles and/or microparticles, said nanoparticles and/or microparticles being generally shaped as spheroids and characterized by a bosselated surface topology.

2. The composition of claim 1, wherein said copper microparticles are hollow spheroidal copper microparticles.

3. The composition of claim 2, wherein said hollow spheroidal copper microparticles are characterized by an average particle size that ranges from 0.5 μm to 20 μm.

4. The composition of any of claims 2 and 3, wherein said hollow spheroidal copper microparticles are characterized by an average wall thickness that ranges from 50 nm to 200 nm.

5. The composition of any of claims 2 to 3, wherein an exterior surface of said hollow spheroidal copper microparticles comprises an atomic concentration of oxygen that ranges from 20 percent to 40 percent.

6. The composition of any of claims 2 to 5, wherein an exterior surface of said hollow spheroidal copper microparticles comprises an atomic concentration of carbon that ranges from 20 percent to 35 percent.

7. The composition of any of claims 2 to 6, wherein an exterior surface of said hollow spheroidal copper microparticles comprises an atomic concentration of phosphorous that ranges from 0 percent to 5 percent.

8. The composition of any of claims 2 to 7, wherein a wall of said hollow spheroidal copper microparticles comprises spherical copper nanoparticles having an average particle size that ranges from 20 nm to 200 nm.

9. The composition of claim 1, wherein said copper nanoparticles are characterized by an average diameter that ranges from 50 nm to 500 nm.

10. The composition of any of claims 1 to 9, wherein a curvature of each boss in said bosselated surface topology is characterized by a mean curvature that ranges from 0.02 nm^{-1} to 0.5 nm^{-1}.

11. The composition of any of claims 1 to 10, wherein a surface of said copper microparticles and/or nanoparticles is coated with fibrous copper.

12. The composition of claim 11, wherein said fibrous copper comprises copper fibers having an average length that ranges from 10 nm to 100 nm.

13. The composition of any of claims 11 and 12, wherein said fibrous copper comprises fibers having an average thickness of 5 nm to 10 nm.

14. The composition of any of claims 1 to 13, wherein at least a portion of said copper microparticles and/or nanoparticles are fused to one another.

15. The composition of any of claims 11 to 14, wherein an exterior surface of said copper microparticles and/or nanoparticles is characterized as comprising an atomic concentration of oxygen that ranges from 20 percent to 40 percent.

16. The composition of any of claims 11 to 14, wherein an exterior surface of said copper microparticles and/or nanoparticles is characterized as comprising an atomic concentration of carbon that ranges from 20 percent to 30 percent.

17. The composition of any of claims 11 to 14, wherein an exterior surface of said copper microparticles and/or nanoparticles is characterized as comprising an atomic concentration of nitrogen that ranges from 10 to 15 percent.

18. The composition of any of claims 11 to 14, wherein an exterior surface of said copper microparticles and/or nanoparticles is characterized as comprising and an atomic concentration of sulfur that ranges from 0.1 to 5 percent.

19. The composition of any of claims 1 to 18, capable of being sintered upon an application of mild mechanical pressure thereon at a temperature lower than 100 °C.

20. A composition comprising a plurality of copper microparticles and/or microparticles, at least a portion of said particles being fused to one another.

21. A composition comprising a plurality of copper microparticles and/or nanoparticles, the composition being capable of sintering upon an application of mild mechanical pressure thereon at a temperature lower than 100 °C.

22. A process of manufacturing the composition of any of claims 1 to 19, the process comprising

mixing a copper salt with a powder of elemental zinc in an aqueous solution in the presence of a carboxyl-containing compound at room temperature to thereby obtain a powder which comprises the plurality of copper nanoparticles and/or microparticles, thereby obtaining the composition.

23. The process of claim 22, further comprising filtering and drying said powder.

24. The process of any of claims 22 and 23, wherein a molar ratio between said elemental zinc and said copper ion ranges from 2:1 to 1:2.

25. The process of any of claims 22 to 24, wherein a molar ratio between said carboxyl-containing compound and said copper ion ranges from 5:1 to 1:1.

26. The process of any of claims 22 to 25, wherein a pH of said aqueous solution ranges from 1.5 to 5.

27. The process of any of claims 22 to 26, wherein said powder comprises hollow spheroidal copper microparticles.

28. The process of any of claims 22 to 26, wherein a surface of at least a portion of said copper nanoparticles and/or microparticles is coated with fibrous copper, the process further comprising:

filtering and drying said powder; and

suspending said powder in an aqueous solution in the presence of a sulfur-containing compound.

29. The process of claim 28, wherein said fibrous copper comprises copper fibers having an average length that ranges from 10 nm to 100 nm.

30. The process of claim 28, wherein said fibrous copper comprises copper fibers having an average thickness that ranges from 5 nm to 10 nm.

31. The process of any of claims 22 to 26, wherein mixing a copper salt with a powder of elemental zinc in an aqueous-solution is effected in the presence of a sulfur-containing compound.

32. The process of claim 31, wherein at least a portion of said copper microparticles and/or nanoparticles are fused to one another.

33. The process of any of claims 28 to 32, wherein said sulfur-containing compound is thiourea.

34. The process of any of claims 22 to 33, wherein said carboxyl-containing compound is citric acid.

35. A composition comprising copper nanoparticles, the composition being prepared by the process of any of claims 22 to 34.

36. The composition of claim 35, capable of sintering upon an application of mild mechanical pressure thereon at a temperature lower than 100 °C.

37. An article-of-manufacturing comprising the composition of any of claims 1 to 19.

38. The article-of-manufacturing of claim 37, formed upon an application of mild mechanical pressure on said composition at a temperature lower than 100 °C.

39. The article-of-manufacturing of any of claims 37 and 38, being selected from the group consisting of an inkjet ink, a dry toner, a solid macro-scaled object, an electronic component and an electronic circuit.

40. An inkjet ink composition, comprising the composition of any of claims 1 to 19.

41. A toner composition, comprising the composition of any of claims 1 to 19.

42. The inkjet ink composition of claim 40 or the toner composition of claim 41, being curable upon an application of mild mechanical pressure thereon at a temperature lower than 100 °C.

43. A method of printing a substantially electrically conducting element on a substantially electrically isolating substrate, the method comprising applying the inkjet ink composition of claim 40 or the toner composition of claim 41 on the substrate.

44. The method of claim 43, further comprising, subsequent to said applying, pressing the substrate having said composition applied thereon to thereby form the electrically conducting element on the substantially electrically isolating substrate.

45. The method of claim 43, further comprising, subsequent to said applying, heating the substrate having said composition applied thereon to thereby form the electrically conducting element on the substantially electrically isolating substrate.

46. A method of preparing a substantially electrically conducting copper element, the method comprising forming a shape of the element from the composition of any of claims 1 to 19 and applying mild pressure on said shape at a temperature lower than 100 °C, thereby obtaining the copper element.

47. A method of preparing a substantially electrically conducting copper element, the method comprising forming a shape of the element from the composition of any of claims 1 to 19 and heating said shape, thereby obtaining the copper element.

48. A method of preparing a substantially electrically conducting copper layer on at least a portion of a surface of a substrate, the method comprising spraying a suspension of the composition of claim 14 onto said surface.

FIG. 1

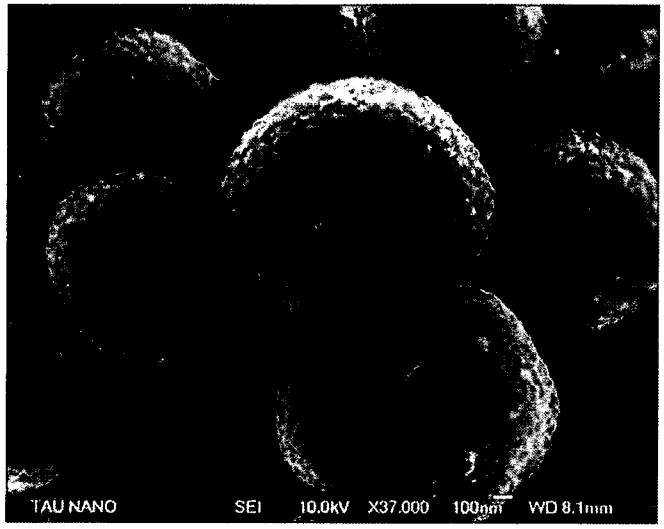


FIG. 2A

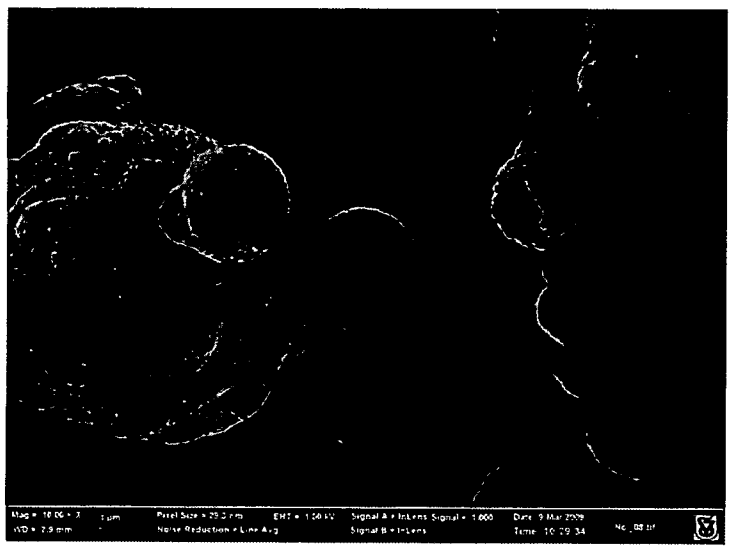


FIG. 2B

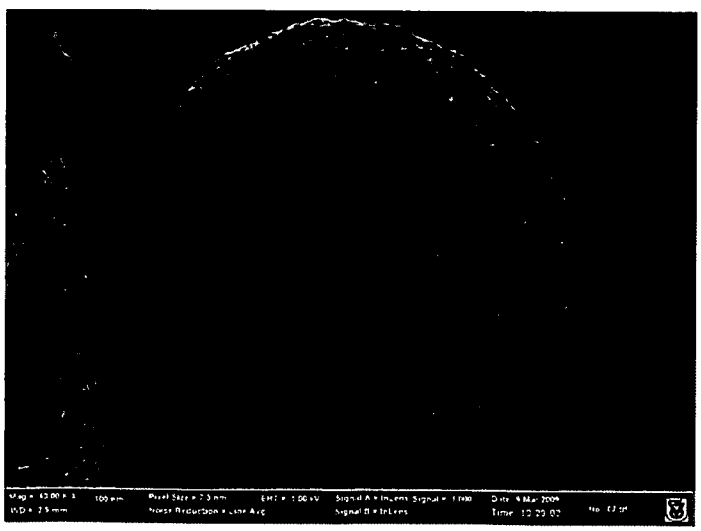


FIG. 3A

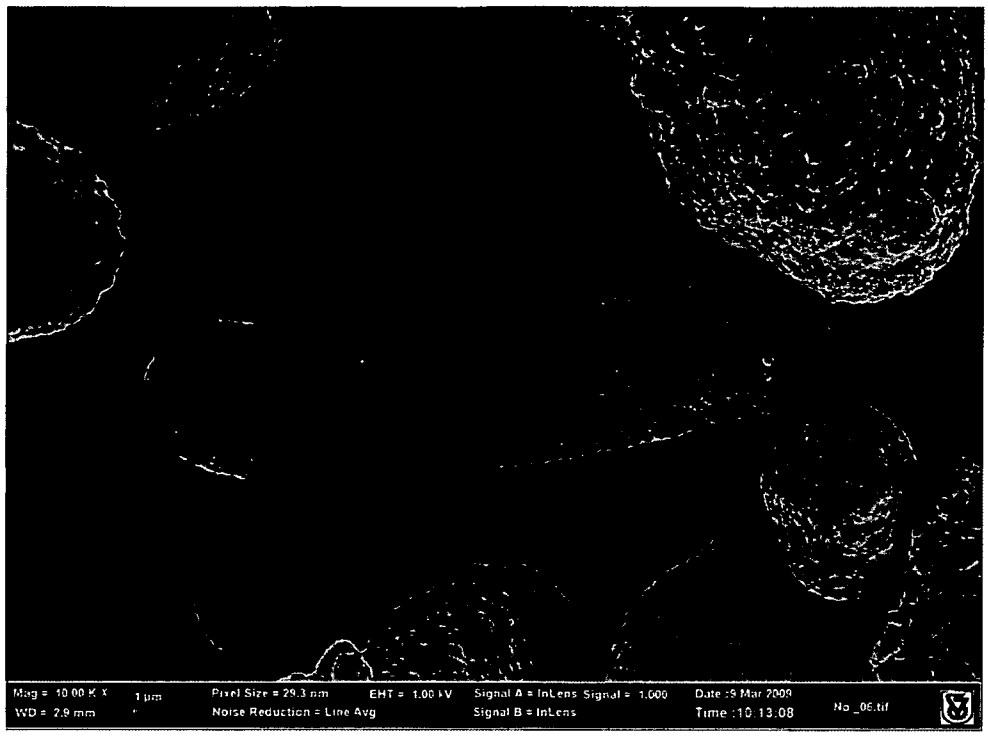

Mag = 10.00 K X
1 µm
Pixel Size = 29.3 nm
EHT = 1.00 kV
Signal A = InLens Signal = 1.000
Date :9 Mar 2009
WD = 2.9 mm
Noise Reduction = Line Avg
Signal B = InLens
Time :10:13:08
No_06.tif

FIG. 3B

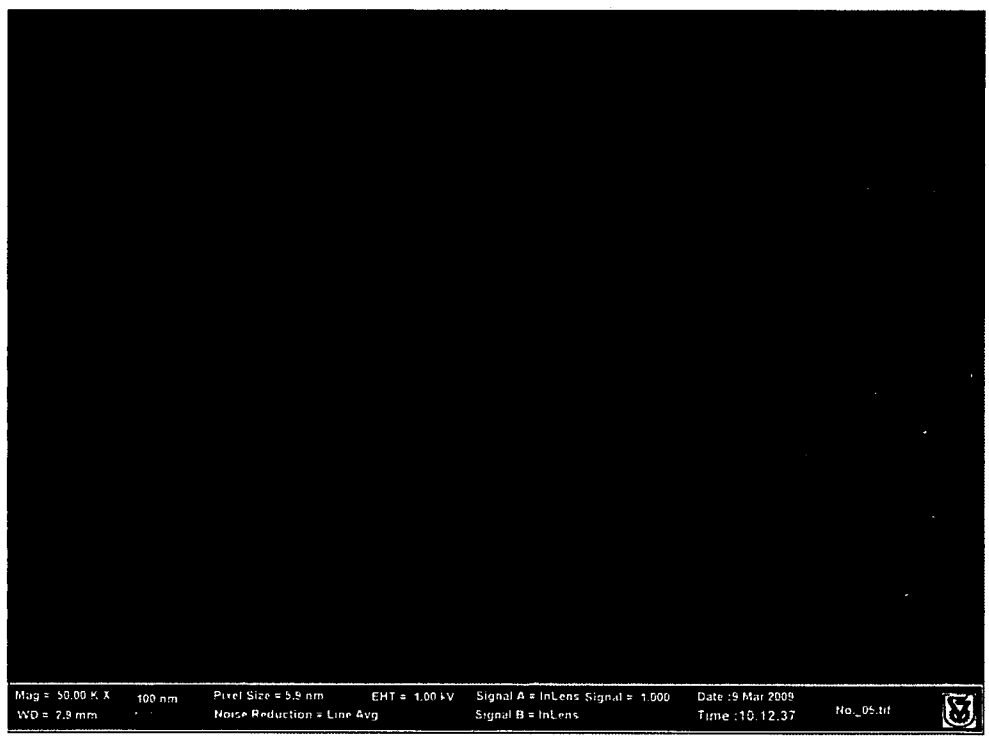

Mag = 50.00 K X
100 nm
Pixel Size = 5.9 nm
EHT = 1.00 kV
Signal A = InLens Signal = 1.000
Date :9 Mar 2009
WD = 2.9 mm
Noise Reduction = Line Avg
Signal B = InLens
Time :10:12:37
No_05.tif

FIG. 3C

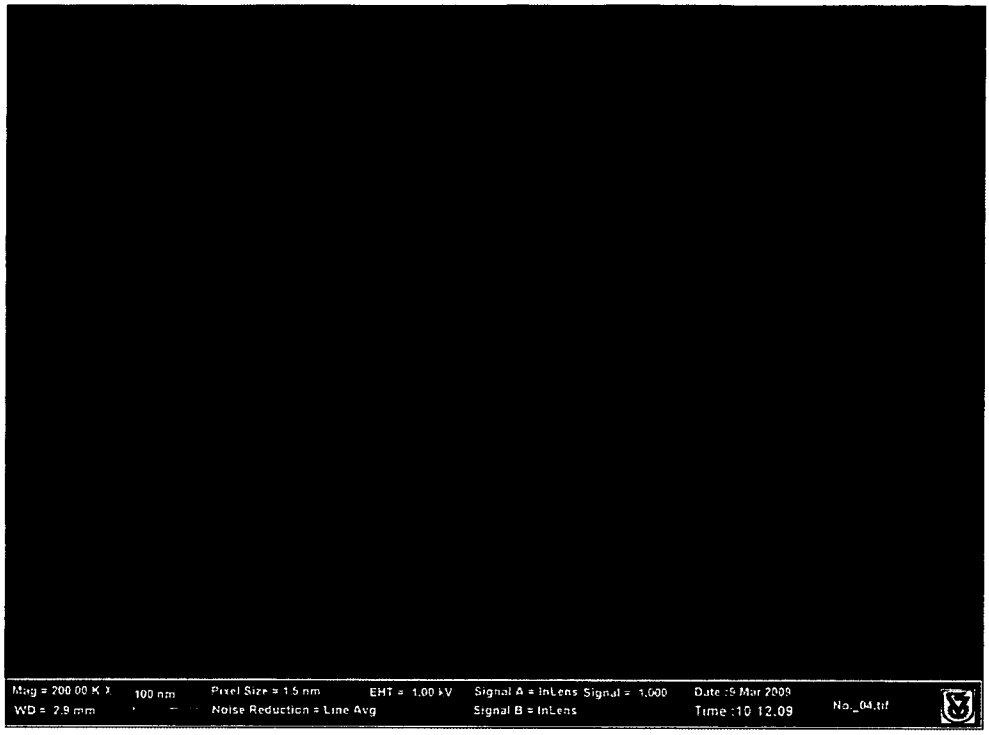

Mag = 200.00 K X
100 nm
Pixel Size = 1.5 nm
EHT = 1.00 kV
Signal A = InLens Signal = 1.000
Date :9 Mar 2009
WD = 2.9 mm
Noise Reduction = Line Avg
Signal B = InLens
Time :10 12.09
No._04.tif

FIG. 4A

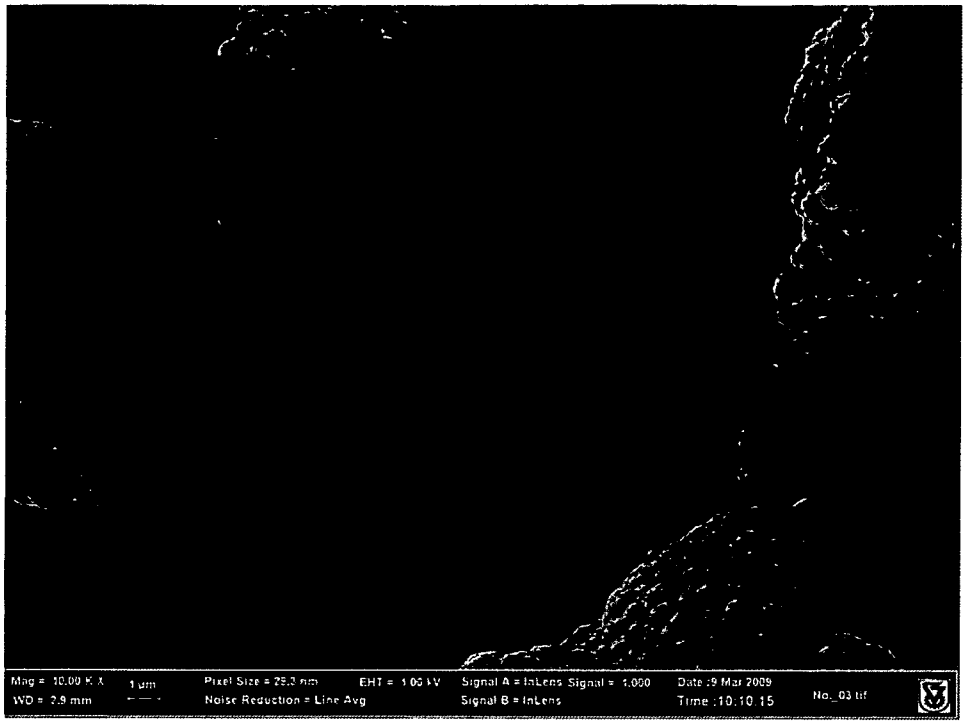

Mag = 10.00 K X
1 um
Pixel Size = 25.3 nm
EHT = 1.00 kV
Signal A = InLens Signal = 1.000
Date :9 Mar 2009
WD = 2.9 mm
Noise Reduction = Line Avg
Signal B = InLens
Time :10:10:15
No_03.tif

FIG. 4B

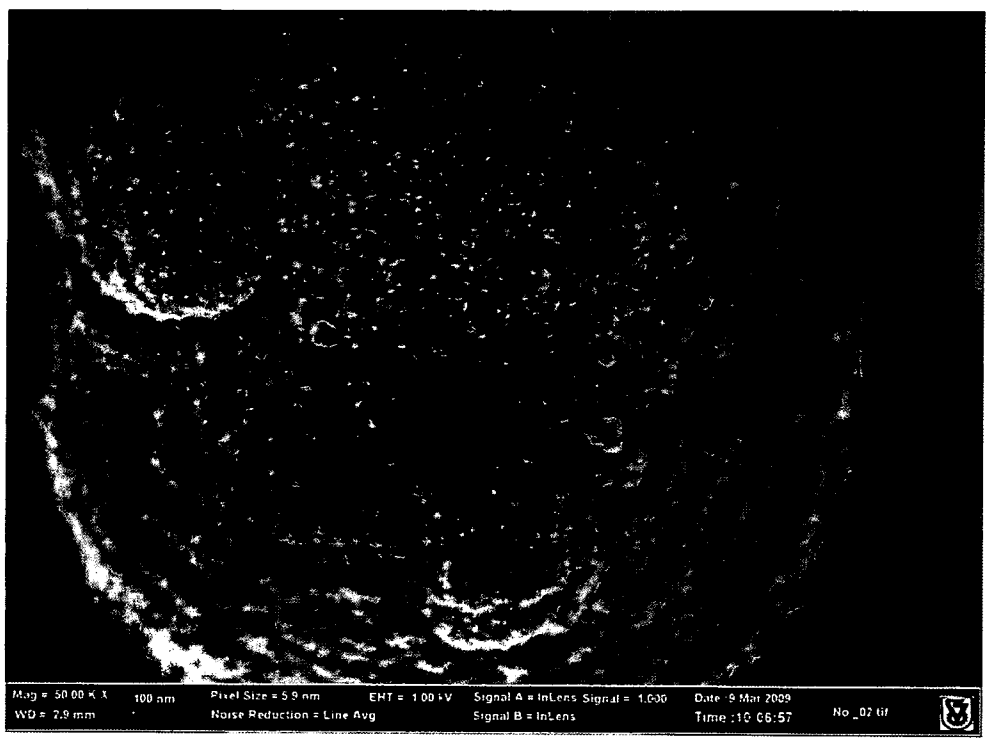

Mag = 50.00 K X
100 nm
Pixel Size = 5.9 nm
EHT = 1.00 kV
Signal A = InLens Signal = 1.000
Date :9 Mar 2009
WD = 2.9 mm
Noise Reduction = Line Avg
Signal B = InLens
Time :10:06:57
No_02.tif

FIG. 4C

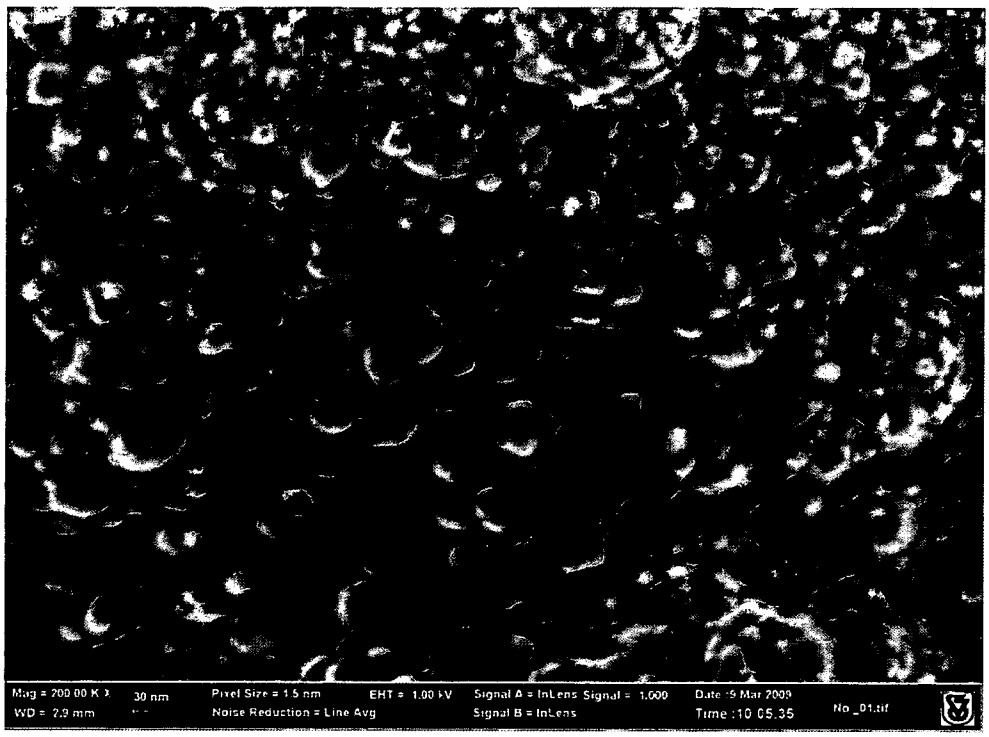
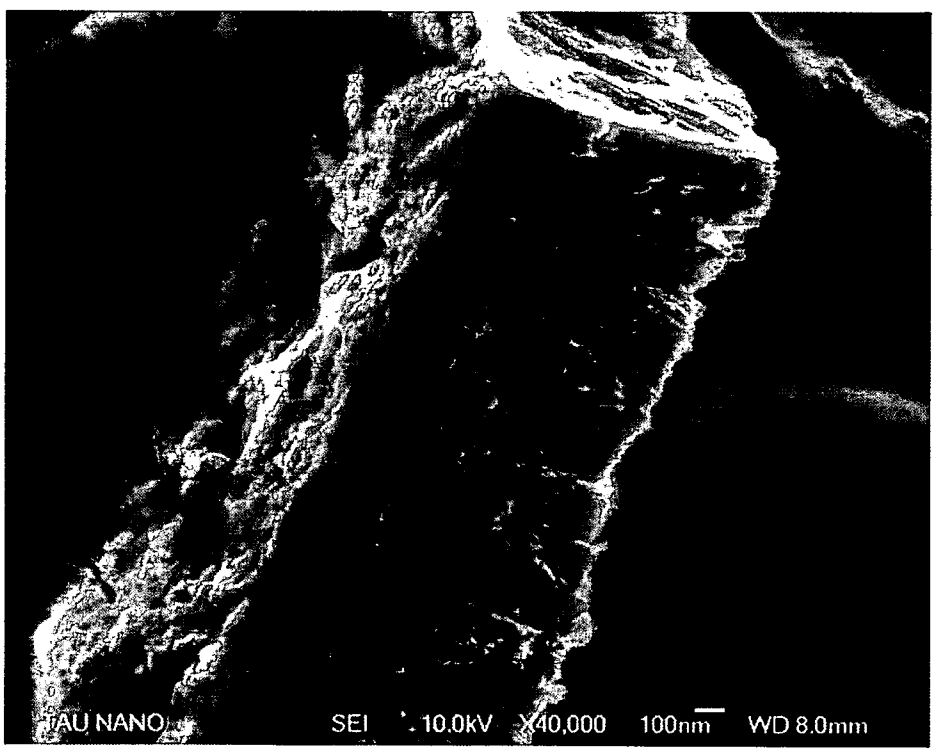

Mag = 200.00 K X
30 nm
Pixel Size = 1.5 nm
EHT = 1.00 kV
Signal A = InLens Signal = 1.000
Date :5 Mar 2009
WD = 2.9 mm
Noise Reduction = Line Avg
Signal B = InLens
Time :10 05.35
No_01.tif

FIG. 5


TAU NANO
SEI
10.0kV
X40,000
100nm
WD 8.0mm

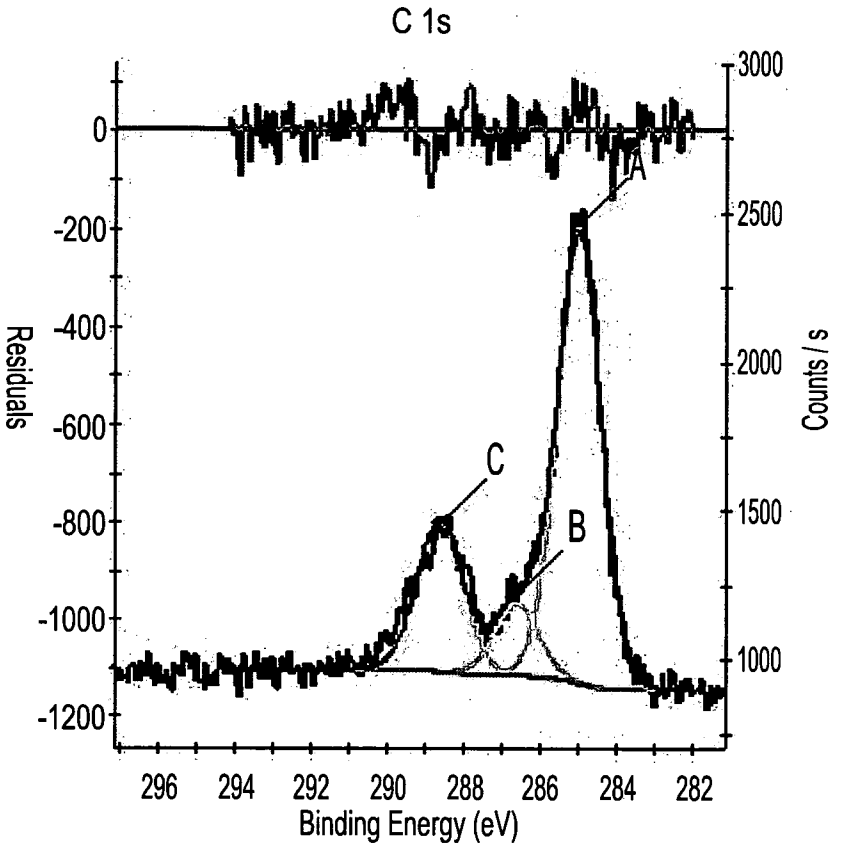

C 1s
3000
0
2500
-200
-400
2000
-600
1500
-800
-1000
1000
-1200
Residuals
Counts / s
A
B
C
296
294
292
290
288
286
284
282
Binding Energy (eV)

FIG. 6

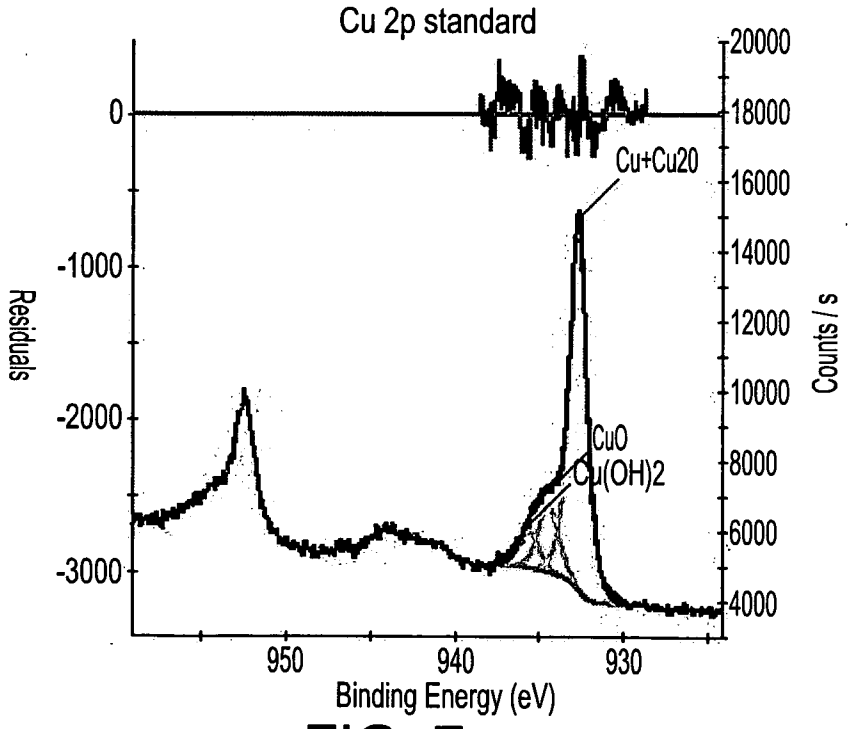

Cu 2p standard
20000
0
18000
Cu+Cu20
16000
14000
-1000
12000
Residuals
Counts / s
10000
-2000
CuO
8000
Cu(OH)2
6000
-3000
4000
950
940
930
Binding Energy (eV)

FIG. 7

FIG. 8

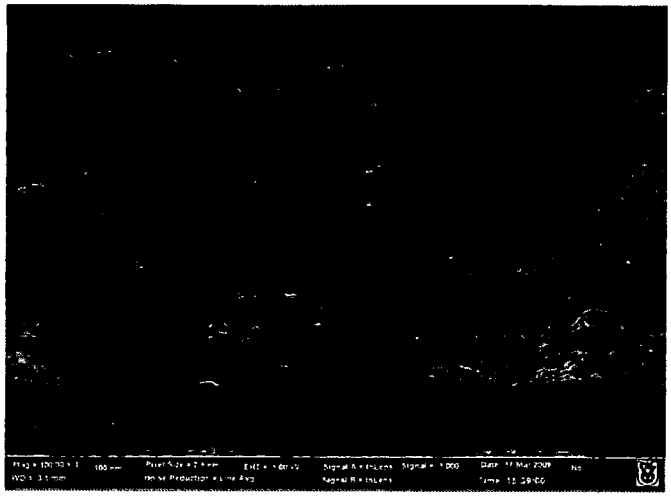


FIG. 9

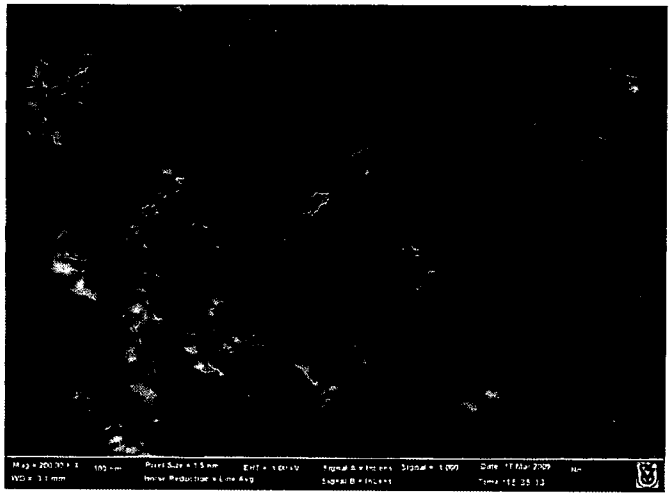


FIG. 10

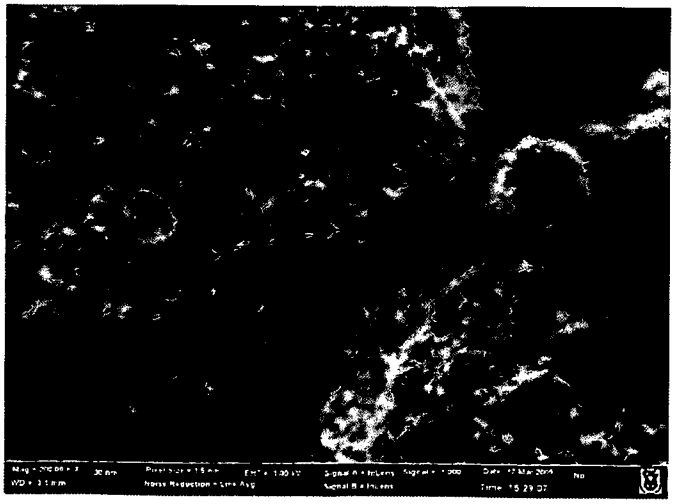


FIG. 11

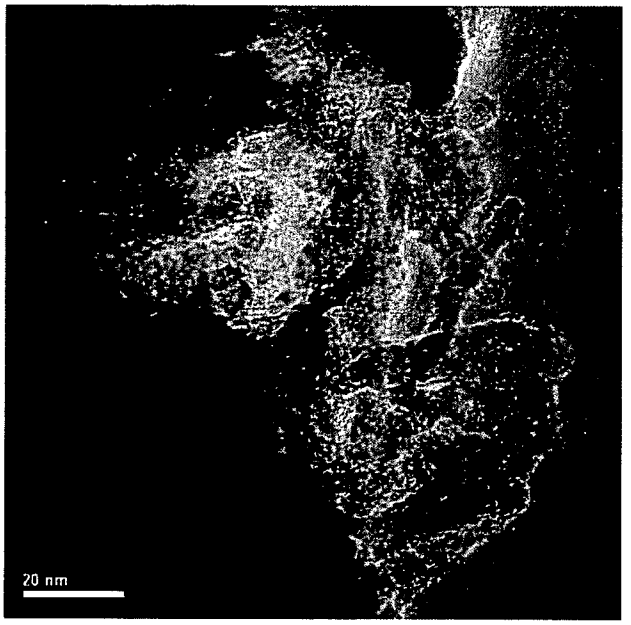


FIG. 12

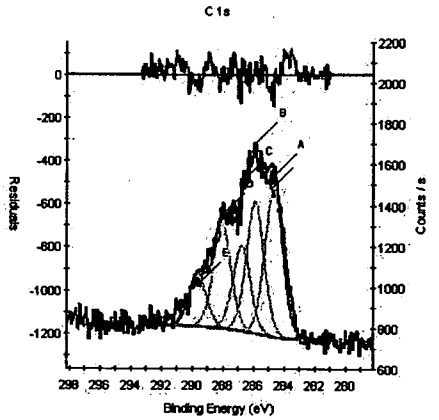
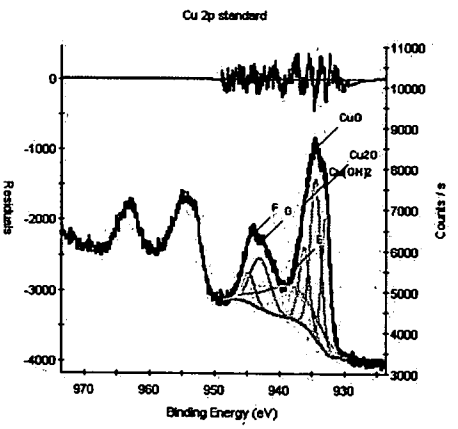


FIG. 13



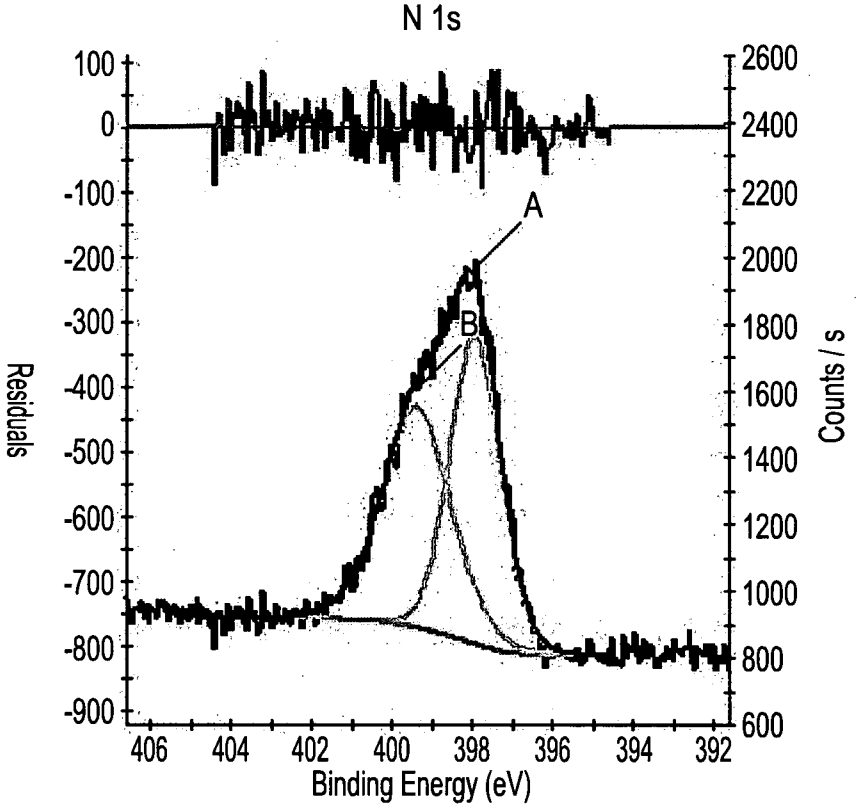

N 1s
Residuals
Counts / s
A
B
100
0
-100
-200
-300
-400
-500
-600
-700
-800
-900
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
406
404
402
400
398
396
394
392
Binding Energy (eV)

FIG. 14

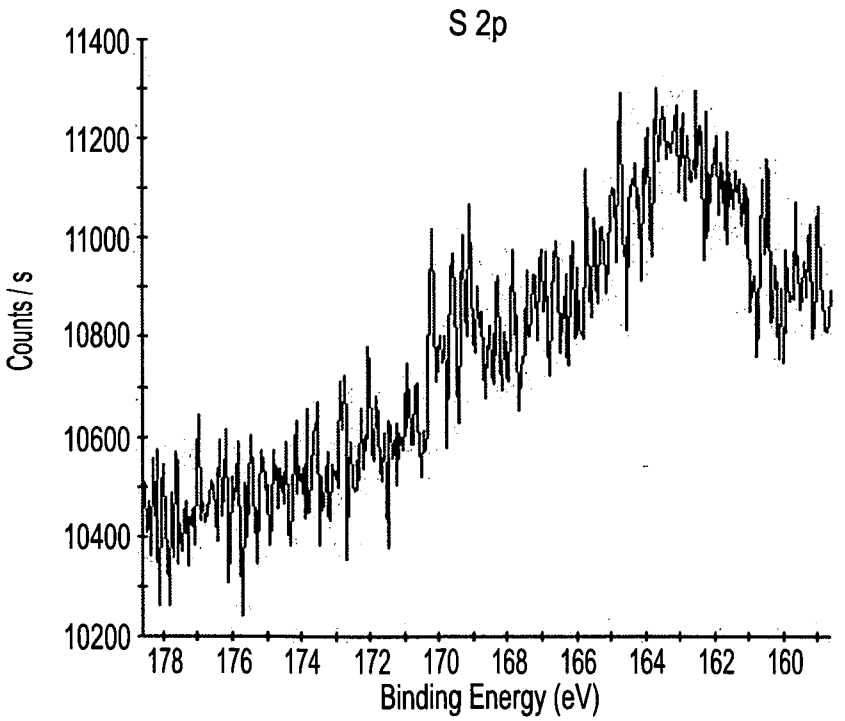

S 2p
Counts / s
11400
11200
11000
10800
10600
10400
10200
178
176
174
172
170
168
166
164
162
160
Binding Energy (eV)

FIG. 15

FIG. 16

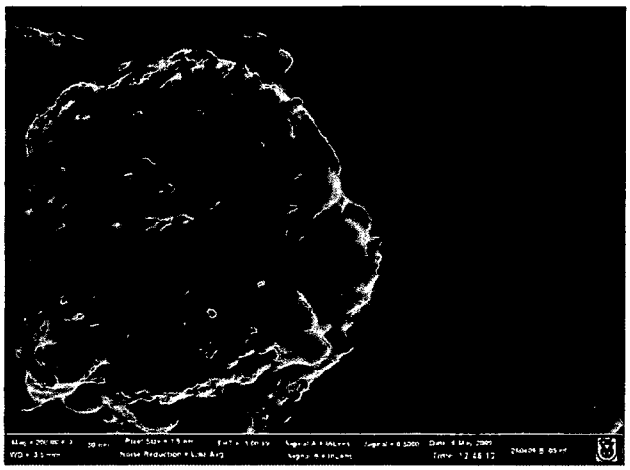


FIG. 17

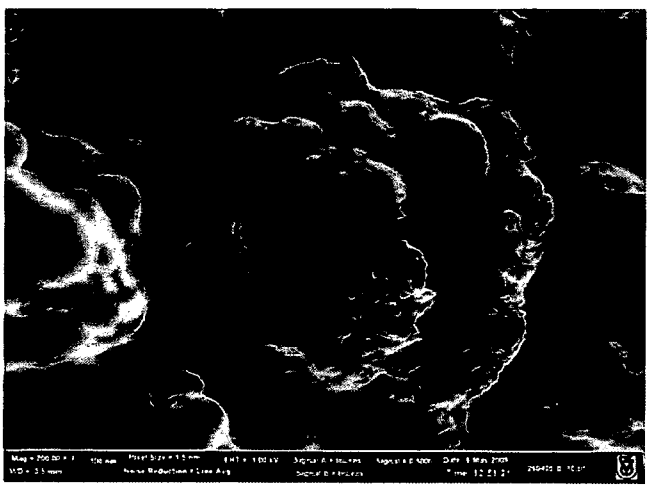


FIG. 18