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(54) Title: DISCRETE METALLIC COPPER NANOPARTICLES

(57) Abstract: Discrete copper nanoparticles, which are reversibly re-suspendible and/or re-dispersible, and which have a narrow size distribution with sigma value of less than 30 percent of their most frequent average diameter, and novel methods for preparing same are provided. Further provided are uses of the copper nanoparticles in applications such as for electronic printing.
DISCRETE METALLIC COPPER NANOPARTICLES

FIELD AKD BACKGROUND OF THE INVENTION

The present invention, in some embodiments thereof, relates to metallic nanoparticles and more particularly, but not exclusively, to discrete copper nanoparticles 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.

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. For example, U.S. Patent No. 4,600,604 by Siuta discloses a metal oxide coated copper powder. The copper powder has an average particle size of 1 to 5 μm (micron) and the oxide layer is substantially continuous with a thickness of 1 to 20 nm (nanometer). The oxide coating, which is formed from an organometallic coating deposited by solution, controls the sintering and shrinkage characteristics of the particles when used in connection with ceramic substrates.
U.S. Patent No. 4,781,980 by Yoshitake et al. discloses a coated copper powder for use in a conductive paste composition, wherein an antioxidation film of an organic acid salt is formed on the surface of the copper powder using a liquid route. This coating provides good humidity resistance and thermal resistance to the powder by reducing surface oxidation.

U.S. Patent No. 5,470,373 by Edelstein et al. discloses oxidation resistant copper nanoparticles that include an additive that is phase separated from the copper, wherein the additive can be selected from nickel, cobalt, iron, manganese, cadmium, zinc, tin, magnesium, calcium and chromium.

U.S. Patent 5,981,069 by Tani et al. describes a copper powder that has a coating made of copper phosphate at the outer surface thereof, wherein the coating is formed by chemically reacting the outer surface of the copper powder and covers the entire surface of the copper powder uniformly, thereby providing anti-oxidizing properties.

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.
SUMMARY OF THE INVENTION

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

The present inventors and devised and successfully practices a novel process for producing copper nanoparticles in an aqueous environment. The novel process produces copper nanoparticles which are characterized by a very low organic content, as opposed to other metallic nanoparticles known in the art, which are prepared in the presence of organic capping substances which impart a high organic content thereto.

The resulting copper nanoparticles are characterized by a narrow size distribution averaging between 40 nm to 140 nm, and are further characterized by a primary spherical particle of about 5-10 nm, clumped into a spherical raspberry-shaped primary nanocluster or monolithic cuboid-shaped nanoparticles. The processes disclosed herein make use of a metal displacement reaction between copper ions and metallic zinc to produce copper nanoparticles. Manipulating various parameters of the process enables to control the morphology and shape of the obtained nanoparticles.

The processes according to some embodiments of the present invention are particularly well suited for the production of particulate products of finely divided particles having a small average diameter or weight size. In addition to making nanoparticles within a desired range of average particle size, the particles may be produced with a desirably narrow size distribution, thereby providing size uniformity that is desired for many applications in nanotechnology and other fields. The present invention, in some embodiments thereof, also provides processes of producing copper nanoparticles with distinct surface chemistries, governed by certain oxides which confer stability and prevent further aggregation.

It is an inherent aspect of the present invention in some embodiments thereof to enable the use of zinc/copper cementation reactions to produce high quality copper nanoparticles in a low-cost and simple process, especially suitable for large scale production.

Hence, according to an aspect of some embodiments of the present invention there, there is provided a composition-of-matter which includes copper nanoparticles characterized by:
a) being at least 95 percent by weight reversibly re-suspendible in a liquid media as nanoparticles;

b) having a mode particle diameter (most frequent) after re-suspension that ranges from 10 nm to 200 nm; and

c) having a standard deviation (σ) of particle diameter after re-suspension that ranges from 5 nm to 50 nm.

In some embodiments the copper nanoparticles are generally shaped as spheroids.

In some embodiments, at least 95 percents of the spheroids are in a form a cluster (nanocluster) of spheroids.

In some embodiments, the cluster is generally shaped as a raspberry-like cluster (nanocluster).

In some embodiments, the cluster has a mode particle diameter that ranges from 100 nm to 190 nm.

In some embodiments, a mode particle diameter of each of the spheroids ranges from 5 nm to 50 nm.

In some embodiments, the copper nanoparticles have an exterior surface characterized as comprising an atomic concentration of phosphate that ranges from 1 % to 4 % and an atomic concentration of carbon that ranges from 20 % to 30 %.

In some embodiments, the copper nanoparticles are generally shaped as cuboids.

In some embodiments, the nanoparticles comprise single-crystalline nanoparticles.

In some embodiments, the cuboids have a mode particle diameter that ranges from 50 nm to 120 nm.

In some embodiments, the copper nanoparticles have an exterior surface characterized as comprising an atomic concentration of sulfur that ranges from 0.5 % to 2 % and an atomic concentration of carbon that ranges from 15 % to 25 %.

In some embodiments, an oxide content on the surface of the copper nanoparticles remains substantially invariable for a time period of at least one week.

In some embodiments, the copper nanoparticles have a crystalline core.

In some embodiments, the copper nanoparticles have an external oxide layer.

In some embodiments, the oxide layer comprises Cu₂O and/or Cu(OH)₂-
In some embodiments, the carbon content of the copper nanoparticles is less than 20 percent of the total weight of the copper nanoparticles.

In some embodiments, the composition-of-matter is in a form of a dispersion.

In some embodiments, the composition-of-matter is in a form of a powder.

In some embodiments, the composition-of-matter is in a form of a suspension in an aqueous medium.

According to another aspect of the present invention, there is provided a process of manufacturing a composition-of-matter which includes copper nanoparticles, the process is effected by:

mixing a copper salt with a powder of elemental zinc in an aqueous solution in the presence of a phosphorous-containing compound, thereby obtaining the composition-of-matter which comprises the copper nanoparticles,

wherein:

the concentration a copper ion in the salt ranges from 10 mM to 150 mM; and

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

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

In some embodiments, the pH of the aqueous solution ranges from 1.5 to 6.

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

In some embodiments, the powder of elemental zinc has a grit size of less than 10 microns.

In some embodiments, the obtained copper nanoparticles are generally shaped as spheroids.

a) being at least 95 percent by weight reversibly re-suspendible in a liquid media as nanoparticles,

b) having a mode particle diameter (most frequent) after re-suspension that ranges from 10 nm to 200 nm; and

c) having a standard deviation (σ) of particle diameter after re-suspension that ranges from 5 nm to 50 nm.

In some embodiments, the obtained copper nanoparticles are generally shaped as spheroids.
In some embodiments, the process further includes mixing the copper salt, the powder of elemental zinc and the phosphorous-containing compound with a thiol-containing compound.

In some embodiments, the concentration of the thiol-containing compound in the aqueous solution ranges from 0.05 mM to 10 mM.

In some embodiments, the obtained copper nanoparticles are generally shaped as cuboids.

In some embodiments, the process further includes, subsequent to mixing the copper salt with the powder of elemental zinc, filtering the copper nanoparticles.

In some embodiments, the process further includes drying the copper nanoparticles.

In some embodiments, the process further includes, subsequent to the drying of the copper nanoparticles, dispersing the copper nanoparticles.

In some embodiments, the dispersing is effected by a technique selected from the group consisting of re-suspension by ultrasound in a liquid medium, sieving, high shear mixing, and 3-roll milling.

In some embodiments, the copper salt is selected from the group consisting of CuSO₄, CuCl₂, Cu(NO₃)₂, (CH₃COO)₂Cu, Cu(C₂H₅O₂)₂, CuCO₃, Cu[C₆H₁₁(CH₂)₃CO₂]₂, copper(II) stearate complex, CuCl₂O₄, copper(II) ethylenediamine complex and Cu(OH)₂.

In some embodiments, the phosphorous-containing compound is selected from the group consisting of phosphoric acid, hypophosphite, (NH₄)₃PO₄, Ca₃(PO₄)₂, FePO₄, Fe₃(PO₄)₂, Na₃PO₄, Ca(H₂PO₄)₂ and KH₂PO₄, or stem from phosphorous acids (such as, without limitation H₃PO₂ and H₃PO₄), phosphorous oxides (such as, for example, P₄O₆ and P₄O₁₀), a phshide, a phosphinate, a phosphine oxide, a phosphine, a phosphinite, a phosphite, a phosphonate and a phosphonite.

In some embodiments, the thiol-containing compound is selected from the group consisting of β-mercaptoethanol, cysteine, methanethiol (CH₃SH), ethanethiol (C₂H₅SH), 1-propanethiol (C₃H₇SH), 2-propanethiol (CH₃CH(SH)CH₃), butanethiol (C₄H₉SH), tetrabutyl mercaptan (C(CH₃)₃SH), pentanethiols (CsH₁₁SH), coenzyme-A, lipoamide, glutathione, dithiothreitol/dithioerythritol and 2-mercaptoindole.
In some embodiments, the process further includes, prior to mixing the copper salt with the powder of elemental zinc, contacting the powder of elemental zinc with an acid.

In some embodiments, the acid is selected from the group consisting of phosphorus acid (H$_3$PO$_3$), hypophosphorous acid (HsPO$_2$), sodium hypophosphite (NaH$_2$PO$_2$), H$_2$PO(OH), HPO(OH)$_2$, phosphoric acid (H$_3$PO$_4$), PO(OH)$_3$, peroxomonophosphoric acid (H3PO5), OP(OH)$_2$OOH, hypophosphoric acid (H$_4$P$_2$O$_6$), (OH)$_2$P(O)-P(O)(OH)$_2$, pyrophosphoric acid (H$_4$P$_2$O$_7$), (OH)$_2$(O)P-O-P(O)(OH)$_2$, triphosphoric acid (H$_5$P$_3$O$_{10}$), H$_4$P$_2$O$_6$, H(OH)(O)P-O-P(O)(OH)$_2$, boric acid (H$_3$BO$_3$), chlorosulfonic acid (HClO$_3$S), chromosulfuric acid (CrO$_3$), fluoro phosphoric acid (H$_2$FO$_3$P), hexafluorophosphoric acid (HF$_6$P), hydriodic acid (HI), hydrobromic acid (HBr), hydrochloric acid (HCl), hydrofluoric acid (HF), iodic acid (HIO$_3$), magic acid (HF$_6$O$_2$Sb), nitric acid (HNO$_3$), nitrosylsulfuric acid (HNO$_5$S), silicic acid (O$_2$Si), sulfamic acid (H$_3$NO3S), sulfur dioxide (H$_2$O$_2$S), sulfuric acid (H$_2$O$_4$S), tetrafluoroboric acid (HBF$_4$) and any mixture, hydrate or complex thereof.

According to another aspect of some embodiments of the present invention, there is provided a composition of matter comprising copper nanoparticles, the composition of matter is prepared by the process presented herein.

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

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

According to still another aspect of the present invention, there is provided an inkjet ink composition which includes the composition-of-matter as presented herein.

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

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

According to still another aspect 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 the composition-of-matter as presented herein and heating the shape thereby obtaining the copper element.

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 mariners, 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:

FIGs. 1A-B are two conceptual illustrations of a cluster of spheroids, an exemplary shape of the copper nanoparticles according to some embodiments of the present invention, particularly those produced according to the procedure presented in Example 1 in the Examples section hereinbelow, wherein the small circles in FIG. 1A represent the primary spherical nanoparticles and the cluster of spheroids is the dispersible/suspendible species or discreet nanoparticle, which is well represented by the shape of a raspberry in FIG. 1B, wherein each berry is discrete and is essentially a cluster of spheroids (hence the phrase "raspberry-shaped nanoparticles");

FIGs. 2A-B present SEM micrographs of the powder obtained by reacting copper sulfate, sodium hypophosphite, and zinc dust at molar ratios of 1:4:1, showing
the raspberry-shaped copper nanoparticles at a magnification of 1:45000 (FIG. 2A) and a magnification of 1:85000 (FIG. 2B);

FIGs. 3A-B present TEM micrographs of a single primary particle which forms a part of a raspberry-shaped nanoparticle obtained as described hereinabove and shown in FIGs. 2A-B, showing that each primary particle is a single crystal covered by a layer of an amorphous matter (FIG. 3A), and that the amorphous layer covering the individual primary particle is having a thickness of about 1 nm (FIG. 3B);

FIG. 4 presents an XRD spectrum of the powder of copper nanoparticles obtained as described hereinabove and shown in FIGs. 2A-B, showing two major Cu peaks and a peak corresponding to Cu$_2$O, whereby the wide peaks corroborate the presence of nano-scaled particles;

FIG. 5 presents a high resolution XPS spectrum of Cls taken from the powder of copper nanoparticles obtained as described hereinabove and shown in FIGs. 2A-B, showing the spectrum measured in the "as received" state, and curve-fitted with 3 components, wherein the "A" line can be related to carbon bounded to hydrogen, and the higher binding energy, lines "B" and "C", can be assigned to C=O and/or C-O-C=O for the "B" line, and to C=O and/or O-C=O for the "C" line;

FIG. 6 presents a high resolution XPS spectrum of Cu2p taken from the powder of copper nanoparticles obtained as described hereinabove and shown in FIGs. 2A-B, showing the spectrum measured in the "as received" state, and curve-fitted with 2 components, wherein the lower binding energy line can be related to Cu$_2$O (based on the Cu LMM line measurements), and the higher binding energy line can be assigned to Cu(OH)$_2$;

FIG. 7 presents a high resolution XPS spectrum of P2s taken from the powder of copper nanoparticles obtained as described hereinabove and shown in FIGs. 2A-B, showing the spectrum measured in the "as received" state, and curve-fitted with 2 components, wherein the lower binding energy line "A" can be related to P in structures of the type Na$_3$PO$_4$, and the higher binding energy line "B" can be assigned to structures similar to P$_4$O$_{10}$or H$_2$PO$_4$;

FIG. 8 presents a bar and a sigmoid plot of the dynamic light scattering (DLS) data measured for the powder of copper nanoparticles, obtained as described hereinabove and shown in FIGs. 2A-B, after re-suspending (dispersing) the powder in...
an aqueous formulation containing polyethylene glycol, showing that the average particle size is about 130 nm and further demonstrating a very tight size distribution;

FIG. 9 presents a SEM micrograph of a powder comprised of cuboid-shaped copper nanoparticles obtained in the presence of mercaptoethanol and produced according to the procedure presented in Example 2 in the Examples section hereinbelow, showing that the size distribution of these copper nanoparticles is very narrowly centered around 70-80 nm, and there is no aggregation of the particles.

FIGs. 10A-B present TEM micrographs of individual cuboid-shaped copper nanoparticles obtained in the presence of mercaptoethanol and shown in FIG 9, showing that no amorphous layer can be observed around these copper nanoparticles;

FIG. 11 presents an XRD spectrum measured for the powder comprised of cuboid-shaped copper nanoparticles shown in FIG. 9, showing two major Cu peaks and a peak corresponding to Cu$_2$O$_3$ whereby the wide peaks corroborate the presence of nano-scaled particles;

FIG. 12 presents a high resolution XPS spectrum of Cls taken from the powder of cuboid copper nanoparticles shown in FIGs. 9 and 10, showing the spectrum measured in the "as received" state, and curve-fitted with 3 components, wherein the "A" line can be related to carbon bounded to hydrogen, the higher binding energy lines "B" and "C" can be assigned to C-OH and/or C-O-C=O for the "B" line, and to C=O and/or O-C-O for the "C" line;

FIG. 13 presents a high resolution XPS spectrum of Cu2p$_{3/2}$ taken from the powder of cuboid copper nanoparticles shown in FIGs. 9 and 10, showing the spectrum measured in the "as received" state, and curve-fitted with one component of Cu$_2$O;

FIG. 14 presents a high resolution XPS spectrum of S2p taken from the powder of the cuboid copper nanoparticles shown in FIGs. 9 and 10, showing the spectrum measured in the "as received" state, and curve-fitted with 2 components, wherein the lower binding energy line "A" can be related to a sulfide-like bonding state, and the higher binding energy line "B" can be assigned to a sulfate type bonding;

FIG. 15 presents a bar and a sigmoid plot of the dynamic light scattering (DLS) data measured for the powder of the cuboid copper nanoparticles shown in FIGs. 9 and 10, after re-suspending (dispersing) the powder in an aqueous formulation containing
polyethylene glycol, showing that the average particle size of about 70 nm with a very tight size distribution; and

FIG. 16 is an HRSEM micrograph of the powder of copper nanoparticles obtained using acid-treated zinc as described herein.

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 copper nanoparticles and to novel 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. As discussed hereinabove, 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.

A cementation process is an electrochemical reaction involving the precipitation of a more noble metal ion from solution by another more electropositive metal according to the overall reaction: \( mN^{n+} + nM = nM^{n+} + mN \), where \( N \) is the noble metal and \( M \) is the precipitant.

Cementation reactions are first order processes with respect to the noble metal. In addition to the pH-dependence, the rate of cementation is also a function of the depositing surface area, onto which the copper ions are reduced and precipitated. Different reaction conditions will have different effects on the evolution of the cathodic surface area of the reducing metal and hence have different effects on the rate constant of the reaction. It is accepted that the reaction rate is controlled by a boundary layer ionic diffusion mechanism at higher temperatures, and surface reactions at lower temperatures.
The mechanism by which the overall cementation reaction at the solid-liquid interface occurs is generally considered to involve a number of steps, as follows: (i) diffusion of Cu\(^{2+}\) ions to the solid surface; (ii) adsorption of the Cu\(^{2+}\) onto the surface; (iii) chemical reaction at the surface; (iv) desorption of oxidized species of the reducing metal from the solid surface; and (v) diffusion of the oxidized species of the reducing metal away from the surface.

It has been shown that the rate of copper/zinc cementation decreases with decreasing pH. The decrease in the rate constant with increasing acidity may be attributed to re-dissolution of some of the precipitated copper due to increase in the acidity of the solution, especially in the presence of molecular oxygen (from the atmosphere), or alternatively, may be attributed to Zn dissolution.

Copper/zinc cementation reactions are known to produce large dendritic copper particles. While conceiving the present invention, the present inventors have considered a method which utilizes copper/zinc cementation reactions, to produce copper nanoparticles characterized by small average sizes and narrow size distributions.

The present inventors hypothesized that well-defined and discrete nanoparticles of copper would be obtained in a dispersed solid phase if the reduced copper species would not form on the zinc particles but rather detach and form freely-dispersed nuclei which can grow concomitantly.

While reducing the present invention to practice, the present inventors have used various substances in order to drive the cementation reaction towards formation of dispersed nuclei, and have evaluated the effect of these substances on the shape and size distribution of the resulting copper nanoparticles.

As demonstrated in the Examples section that follows, the present inventors have surprisingly uncovered that by performing the copper/zinc cementation reaction in the presence of a phosphorous-containing compound, such as phosphorous-containing acid, copper nanoparticles which form discrete and uniformly sized (narrow size distribution) batch are obtained. The present inventors have further surprisingly uncovered that discrete and uniformly sized nanoparticles with various morphologies, shape and/or surface chemistry can be obtained by manipulating the nature of the substances that are added to the cementation reaction. The various shapes, morphologies and chemistries of the obtained nanoparticles, and their exceptionally
controlled size distribution, impart to the nanoparticles unique properties which render them highly suitable for use in a myriad of applications, while controlling the process parameters so as to suit the properties of the obtained nanoparticles to a desired application.

Thus, some embodiments of the present invention relate to a novel process of preparing a composition-of-matter which comprises copper nanoparticles, whereby the obtained nanoparticles are uniquely characterized as re-suspendible in a liquid media and by defined characteristics of their particle size distribution, as detailed hereinafter. Embodiments of the present invention further relate to a composition of matter that comprises copper nanoparticles with uniquely improved characteristics.

**Process of manufacturing:**

While reducing the present invention to practice, it was observed that CuSO₄ dissolved in HaO is reduced by elemental zinc in the presence of sodium hypophosphite (NaH₂PO₂) at room temperature. It was further observed that carrying out the reaction with different phosphorous-containing compounds (e.g., phosphate species) and different thiol-containing compounds leads to products with different geometries and oxygen content. For example, by using zinc as a reducing species and phosphorous acid (H₃PO₃) as an additive, dendritic structures are formed. By using H₃PO₃ as an additive together with thiol-containing species such as cysteine or β-mercaptoethanol, cuboid-shaped copper nanoparticles are formed which are characterized by higher oxygen content. By using sodium hypophosphite (NaPO₂H₂) as an additive, raspberry-shaped spheroid copper nanoparticles are formed.

The protective nature of phosphate 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.

Hence, according to an aspect of embodiments of the present invention there is provided a process of manufacturing a composition-of-matter which comprises copper
nanoparticles, the process being effected by mixing a copper salt with a powder of elemental zinc in an aqueous solution in the presence of a phosphorous-containing compound.

In some embodiments of the invention, the process of manufacturing the composition-of-matter 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 phosphorous-containing compound ranges from 1:1 to 1:5. In some embodiments the ratio is 1:4 copper ions to phosphorous-containing compounds.

For example, the concentrations of zinc, copper sulfate, and sodium hypophosphite used in an exemplary process according to embodiments of the present invention, can be 30 mM, 30 mM, and 120 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 phosphorous-containing compound is about 1:4.

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

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 contribute to the rapid reduction of the copper salt, leading to rapid nucleation which is conductive to the formation of small nanoparticles, whereby the phosphorous-containing compound (e.g., sodium hypophosphite) serves 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).

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.
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. For example, conducting the reaction at pH levels between 4-5 results in spherical, raspberry-shaped nanoclusters, while conducting the reaction at pH values below 1.5 results in the massive formation of large and undesired dendritic, leaf-like structures. The pH of the reaction can be set and controlled by the choice and concentration of the phosphorous-containing compound, and optionally by adding pH-adjusting agents (e.g., strong acids such as sulfuric acid).

Hence, according to some embodiments, the pH of the aqueous solution in which the copper nanoparticles are formed ranges from 1.5 to 6. According to some embodiments, the copper nanoparticles presented herein are formed in a pH that ranges from 2 to 6, from 3 to 6, from 4 to 6, from 4 to 5 or from 5 to 6.

For example, using a phosphorous-containing compound which is a relatively weak acid, results in a reaction mixture with a PH of 4 to 6, or 4 to 5. Lower pH values can be obtained by adding, for example, sulfuric acid.

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 (CuSO₄), copper(II) chloride (CuCl₂), copper(II) nitrate (Cu(NO₃)₂), copper(II) acetate (Cu(CH₃COO)₂), copper acetylacetonate (Cu(CsH₇O₂)₂), copper(II) carbonate (CuCO₃), Cu₆H₁₁(CH₂)₃CO₂₂, copper(II) stearate complex, CuCl₂O₄, copper(II) ethylenediamine complex, Cu(OH)₂, copper(I) bromide (CuBr), copper(I) bromide dimethyl sulfide complex (CuBr·CH₃SCH₃), copper(I) chloride (CuCl), copper(I) iodide (CuI), copper(I) tetraiodomercurate(II) (Cu₂HgI₄), copper(I) thiocyanate (CuSCN), copper(II) D-glucanate (C₁₂H₂₂CuO₁₄), copper(II) bromide (CuBr₂), copper(II) cyclohexanonytrate ([C₆H₁₁(CH₂)₃CO₂]₂Cu), copper(II) fluoride (CuF₂), copper(II) formate (HCOO)₂Cu, copper(II) hydroxide phosphate, (Cu₃(OH)PO₄), copper(II) pyrophosphate (Cu₃P₂O₇), copper(II) selenite CuSeO₃, copper(II) tartrate ([CH₃(OH)CO₂]₂Cu), copper(II) tetrafluoroborate (Cu(BF₄)₂), cupric nitrate (Cu(NO₃)₂), and tetraammininecopper(II) sulfate (Cu(NH₃)₄SO₄), as well as any hydrate, ligand complex or combination thereof.

The phrase "phosphorous-containing compound" as used herein refers to a compound which comprises one or more phosphor atoms, optionally one or more
phosphor-oxide group, and further optionally, which is a derivative of phosphoric acid. The phosphorous-containing compound, in some embodiments, is selected capable of acting as a passivating agent for copper nanoparticles in the process presented herein.

Exemplary phosphorous-containing compound may include a phosphate group (such as, for non-limiting examples, (NH₄)₂PO₄, Ca₃(PO₄)₂, FePO₄, Fe₃(PO₄)₂, Na₂PO₄, Ca(H₂PO₄)₂ and KH₂PO₄), or stem from phosphorous acids (such as, without limitation, H₃PO₂ and H₂PO₄), phosphorous oxides (such as, for example, P₄O₆ and P₄O₁₀), and other phosphides, phosphinates, phosphine oxides, phosphines, phosphinates, phosphites, phosphonites and phosphonites, as these terms are defined herein.

The term "phosphate", as used herein, refers to a OP(OH)₃ or a OP(OR)₃ compound, wherein R is an organic substituent such as alkyl, alkenyl, cycloalkyl, heteroalicyclic, aryl, heteroaryl and the likes, as these terms are defined herein below. When more than one R substituents are present in a compound, the substituents can be different substituents or identical.

The term "phosphinate", as used herein, refers to a OP(OR)₂₄ compound, wherein R is hydrogen or an organic substituent, as defined herein.

The term "phosphine oxide", as used herein, refers to a OPR₃ compound, wherein R is hydrogen or an organic substituent, as defined herein.

The term "phosphine", as used herein, refers to a PR₃ compound, wherein R is hydrogen or an organic substituent, as defined herein.

The term "phosphinite", as used herein, refers to a P(OR)₂₄ compound, wherein R is hydrogen or an organic substituent, as defined herein.

The term "phosphite", as used herein, refers to a P(OR)₃ compound, wherein R is hydrogen or an organic substituent, as defined herein.

The term "phosphonate", as used herein, refers to a OP(OR)₂₄R compound, wherein R is hydrogen or an organic substituent, as defined herein.

The term "phosphonite", as used herein, refers to a P(OR)₂₄R compound, wherein R is hydrogen or an organic substituent, as defined herein.

As used herein, the term "alkyl" describes an aliphatic hydrocarbon including straight chain and branched chain groups. According to some embodiments, the alkyl group has 1 to 20 carbon atoms, and more preferably 1-10 carbon atoms. Whenever a numerical range; e.g., "1-10", is stated herein, it implies that the group, in this case the
alkyl group, may contain 1 carbon atom, 2 carbon atoms, 3 carbon atoms, etc., up to and including 10 carbon atoms. As used herein, the term "low alkyl" refers to an alkyl having 1-3 carbon atoms in its main hydrocarbon chain, and the term "high alkyl" refers to an alkyl having 4-20 carbon atoms in its main hydrocarbon chain. The alkyl can be substituted or unsubstituted. When substituted, the substituent can be, for example, an alkyl, an alkenyl, an alkynyl, a cycloalkyl, an aryl, a heteroaryl, a halide, a hydroxyl and an alkoxy, as these terms are defined herein.

The term "alkenyl" describes an unsaturated alkyl, as defined herein, having at least two carbon atoms and at least one carbon-carbon double bond. The alkenyl may be substituted or unsubstituted by one or more substituents, as described herein.

The term "alkynyl", as defined herein, is an unsaturated alkyl having at least two carbon atoms and at least one carbon-carbon triple bond. The alkynyl may be substituted or unsubstituted by one or more substituents, as described herein.

The term "cycloalkyl" describes an all-carbon monocyclic or fused ring (i.e., rings which share an adjacent pair of carbon atoms) group where one or more of the rings does not have a completely conjugated pi-electron system. The cycloalkyl group may be substituted or unsubstituted.

The term "heteroalicyclic" describes a monocyclic or fused ring group having in the ring(s) one or more atoms such as nitrogen, oxygen and sulfur. The rings may also have one or more double bonds. However, the rings do not have a completely conjugated pi-electron system. The heteroalicyclic may be substituted or unsubstituted.

The term "aryl" describes an all-carbon monocyclic or fused-ring polycyclic (i.e., rings which share adjacent pairs of carbon atoms) groups having a completely conjugated pi-electron system. The aryl group may be substituted or unsubstituted.

The term "heteroaryl" describes a monocyclic or fused ring (i.e., rings which share an adjacent pair of atoms) group having in the ring(s) one or more atoms, such as, for example, nitrogen, oxygen and sulfur and, in addition, having a completely conjugated pi-electron system. Examples, without limitation, of heteroaryl groups include pyrrole, furane, thiophene, imidazole, oxazole, thiazole, pyrazole, pyridine, pyrimidine, quinoline, isoquinoline and purine. The heteroaryl group may be substituted or unsubstituted.
The optional presence of any given substituent at any given position in a compound or group described herein, is subject to the chemical feasibility of such substitution, hence the scope of the present embodiments is meant to span chemical substitutions based on chemical feasibility.

Substituted alkyls, alkenyls, ary ls, heteroalicyclics, heteroaryls and the likes may also have other substituents such as, for example, hydroxyl, halo, amine, sulfonate, sulfoxide, phosphonate, alkoxy, aryloxy, thiohydroxy, thiaoalkoxy, thioaryloxy, cyano, isocyanate, nitro, azo, S/N-sulfonamide, C/O-carboxylate, N/O-thiocarbamate, urea, thiourea, N/O-carbamate, C/N-amide guanyl, guanidine and hydrazine. The number of substituents in each of the groups described herein can vary from null to one, two, three, four, five, six and even more.

The term "hydroxyl" describes a -OH group.
The term "alkoxy" describes both an -O-alkyl and an -O-cycloalkyl group, as defined herein.
The term "amine" is used herein to describe a -NR'R" group, whereas R' and R" are as defined herein.
The term "halide" and "halo" describes fluorine, chlorine, bromine or iodine.
The term "sulfate" describes a -O-S(=O)₂-R', where R' is as defined hereinabove.
The term "sulfonate" describes a -S(=O)₂-R', where R' is as defined herein.
The term "sulfoxide" or "sulfinyl" describes a -S(=O)-R', where R' is as defined hereinabove.
The term "S-sulfonamide" describes a -S(=O)₂-NR'R", with R' and R" as defined herein.
The term "N-sulfonamide" describes an R'SC=O₂-NR"-, where R' and R" are as defined herein.
The term "aryloxy" describes both an -O-aryl and an -O-heteroaryl group, as defined herein.
The term "thiohydroxy" describes a -SH group.
The term "thiaoalkoxy" describes both a -S-alkyl group, and a -S-cycloalkyl group, as defined herein.
The term "thioaryloxy" describes both a -S-aryl and a -S-heteroaryl group, as defined herein.

The term "cyano" describes a -C≡N group.

The term "isocyanate" describes an -N=C=O group.

The term "nitro" describes an -NO₂ group.

The term "azo" or "diazo" describes an -N=NR', with R' as defined herein above.

The term "C-carboxylate" describes a -C(=O)-OR', where R' is as defined herein.

The term "O-carboxylate" describes a -OC(=O)R', where R' is as defined herein.

The term "C-thiocarboxylate" describes a -C(=S)-OR', where R' is as defined herein.

The term "O-thiocarboxylate" describes a -OC(=S)R', where R' is as defined herein.

The term "N-carbamate" describes an R"OC(=O)-NR'-, with R' and R" as defined herein.

The term "O-carbamate" describes an -OC(=O)-NR'R", with R' and R" as defined herein.

The term "O-thiocarbamate" describes a -OC(=S)-NR'R", with R' and R" as defined herein.

The term "N-thiocarbamate" describes a n R"OC(=S)NR'-, with R' and R" as defined herein.

The term "S-dithiocarbamate" describes a -SC(=S)-NR'R", with R' and R" as defined herein.

The term "N-dithiocarbamate" describes an R"SC(=S)NR'- with R' and R" as defined herein.

The term "urea", which is also referred to herein as "ureido", describes a -NR'C(=0)-NR"R m with R' and R" as defined herein and R" is as defined herein for R' and R".

The term "thiourea", which is also referred to herein as "thioureido", describes a -NR'-C(=S)-NR"R m, with R', R" and R" as defined herein.
The term "C-amide" describes a \(-\text{C}(=\text{O})-\text{NR'}\text{R}''\) where R' and R'' are as defined herein.

The term "N-amide" describes a \(\text{R'C}(=\text{O})-\text{NR'}\text{R}''\), where R' and R'' are as defined herein.

The term "guanyl" describes a \(\text{R'R''NC}(=\text{N})-\), where R' and R'' are as defined herein.

The term "guanidine" describes a \(-\text{R'NC}(=\text{N})-\text{R''R}'''\), where R', R'', and R'''' are as defined herein.

The term "hydrazine" describes a \(-\text{NR'}-\text{NR''R}'''\), with R', R'', and R'''' as defined herein.

An exemplary process of manufacturing the composition-of-matter according to embodiments of the present invention was carried out as described in the Examples section that follows. The reaction was found to be rather fast and lasted only several minutes to reach completion (from 2 to 10 minutes), during which the typical deep aquamarine colored copper sulfate solution turns into a lucid burgundy suspension. The suspension of copper nanoparticles obtained was filtered several times, and the filtrand was washed with water and ethanol to afford a brown compressed wet powder ("wet cake"). This brown powder responded to weak mechanical pressure by turning into pinkish copper stripes which was indicative of the ease at which these nanoparticles can be sintered.

Using the exemplary process as described hereinabove afforded an exemplary composition-of-matter (e.g., in the form of a powder of copper nanoparticles) which was further investigated and characterized by various methods. For example, scanning electron microscope (SEM) observations showed that the obtained powder consists of raspberry-shaped nanoclusters having an average size (diameter) of about 100 nm, each being comprised of a plurality of primary spheroid particles, as defined herein, each having a diameter of about 10 nm. Transmission electron microscopy (TEM) observations revealed that the primary particles are spherical, single-crystalline particles having an average diameter of about 5 nm, and having a thin amorphous coating. X-ray scattering analysis (XRD) measurements provided spectra exhibiting wide peaks corresponding to Cu and Cu\(_2\)O, with a percentage of Cu\(_2\)O in the range of 2 % to 10 %, while the width of the peaks indicated very small crystalline particles.
Furthermore, multi modal dynamic light scattering (DLS) measurements using an aqueous formulation of this exemplary powder containing PEG exhibited a narrow size distribution having an average of 130 nm. X-ray photoelectron spectroscopy (XPS) analysis of the powder revealed the presence of oxygen, carbon and phosphate groups in the outer-layer, at atomic concentrations of 37 %, 29 %, and 1.2 %, respectively. The XPS oxygen spectra indicated the presence of Cu(OH)$_2$ as the dominant surface oxide species. The XPS carbon spectra indicated the presence of alkyl chains, which most probably correspond to adsorbed ethanolic groups originating from the wash step of the filtrand.

Altogether, the XRD, XPS, and TEM data obtained with an exemplary powder of copper nanoparticles, obtained by a process according to some embodiments of the present invention, suggest that the copper nanoparticles contain crystalline Cu$_2$O and are surrounded by an amorphous Cu(OH)$_2$ layer. Furthermore, despite the excess of hypophosphite used in this exemplary process, XPS analysis revealed very little phosphate groups on the surface (typically from 0.5 % to 4 atomic %). Without being bound to any particular theory, these findings suggest that the hypophosphite plays a transient role in protecting the nanoparticles against massive aggregation and clumping, and enables the formation of a thin layer of oxides and hydroxides which confer long term stability to the copper nanoparticles.

In some embodiments of the invention, the copper nanoparticles produced by the process described herein are characterized by:

a) being at least 95 percent by weight reversibly re-suspendible in a liquid media as nanoparticles,

b) having a mode particle diameter (most frequent) after re-suspension that ranges from 10 nm to 200 nm; and

c) having a standard deviation ($\sigma$) of particle diameter after re-suspension that ranges from 5 nm to 50 nm.

As detailed herein, the copper nanoparticles produced by the process described herein can be in a form of raspberry-shaped nanoclusters.

Without being bound by any particular theory, the raspberry-shaped copper nanoparticle clusters produced according to some embodiments of the present invention, are intermediate forms between individual discrete spheroid copper nanoparticles and
uncontrolled aggregates thereof. One of the unique features of the process according to embodiments of the present invention is in its ability to allow the controlled formation of clusters of nanoparticles. Hence, by allowing a certain, well controlled clustering of discrete spheroid nanoparticles into the raspberry-shaped nanoparticles it is possible to relax the requirement for substantial organic capping using large amounts of organic substances. Control over the formation of the raspberry-shaped nanoparticles is achieved by using certain phosphorous-containing molecules, which perform a transient role in stabilizing the evolving copper nanoparticle. It is assumed that once the size of the evolving raspberry-shaped nanoparticle exceeds a few tens of nanometers, the amorphous oxide developed is sufficient to prevent further oxidation and agglomeration. The clusters formed can be as small as 50 nm and due to their structure have a higher surface area than a spherical particle of similar size. This enhanced surface area is beneficial for promoting sintering at lower temperatures, and is a highly beneficial property for many applications using copper nanoparticles.

While further reducing the present invention to practice, it was observed that the use of thiol-containing compounds as additives in the aforementioned processes, affects the shape of the resulting copper nanoparticles as well as their outer-coat (surface) chemistry. Specifically, it was observed that cuboid-shaped copper nanoparticles having an average size of about 70 nm are formed, which exhibit single-crystalline morphology, as determined by electron-microscopic analysis.

Hence, according to some embodiments of the present invention, copper ions are reduced in an aqueous environment by zinc powder in the presence of a phosphorous-containing compound and in the presence of a thiol-containing compound. Therefore, in some embodiments, the process further includes mixing the copper salt, the powder of elemental zinc and the phosphorous-containing compound with a thiol-containing compound. The resulting copper nanoparticles according to these embodiments, are generally shaped as cuboids, as defined herein.

According to some embodiments of the present invention, the concentration of the thiol-containing compound in the aqueous solution ranges from about 0.05 mM to about 10 mM.

The phrase "thiol-containing compound", as used herein, refers to a R-SH compound, wherein R can be any organic moiety, including alkyls, cycloalkyls,
alkenyls, alkynyls, aryls, heteroaryls, heteroalicylics, as defined herein, as well as amino acids, peptide backbones, and the likes, and is also known as a mercapto-containing compound. Exemplary thiol-containing compounds include, without limitation, β-mercaptoethanol, cysteine, methanethiol (CH₃SH), ethanethiol (C₂H₅SH), 1-propanethiol (C₃H₇SH), 2-propanethiol (CH₃CH(SH)CH₃), butanethiol (C₄H₉SH), tetrabutyl mercaptan (C(CH₃)₂SH), pentanethiols (C₅H₁₁SH), coenzyme-A (also a phosphate-containing compound), lipoamide, glutathione, dithiothreitol/dithioerythritol (an epimeric pair) and 2-mercaptoindole.

The present inventors have observed that despite the use of these thiol containing compounds, XPS analysis of the resulting cuboid copper nanoparticles, afforded by embodiments of the process presented herein using a thiol-containing compound, revealed very little thiol groups on the surface of those copper nanoparticles, usually less than 1 atomic percent. Without being bound by any particular theory, it is assumed that the thiol group plays a transient role in protecting the nanoparticles against massive aggregation, and enables the formation of a thin layer of oxides and which confers long term stability.

Furthermore, HRSEM evaluation of exemplary cuboid copper nanoparticles, afforded by an exemplary process according to embodiments of the present invention using a thiol-containing compound, revealed cuboid-shaped nanoparticles having an average size of about 90 nm with a very narrow size distribution. Multi modal dynamic light scattering measurements using an aqueous formulation containing PEG afforded a narrow size distribution having an average size of 70 nm, indicating that these primary particles do not undergo agglomeration or clumping. XRD measurements revealed wide peaks corresponding to Cu and Cu₂O, while the percentage of Cu₂O determined from these measurements was between 2 % to 10 %, and the width of the peaks indicates very small crystalline particles. XPS analysis of the powder of the cuboid copper nanoparticles showed the presence of carbon and sulfate groups at atomic concentrations of 25 % and 0.3 % respectively (of the total 0.3 % sulfur, 70 % correspond to sulfide-like bonding and 30 % to sulfate-like bonding), and reveals Cu₂O as the only oxide species on the surface. TEM micrographs as well as XPS analysis did not reveal an amorphous layer of hydroxides on the surface of the nanoparticles.
The present inventors have also noted that in cases where the nanoparticles were exposed to thiol-containing compounds during the reaction alone, the atomic concentration of sulfur, as detected by XPS, did not exceed 1 percent. However, when a sample of an "as-produced" powder of the cuboid copper nanoparticles, afforded by an exemplary process according to embodiments of the present invention using a thiol-containing compound, were incubated overnight in an aqueous environment containing thiols, re-filtered and washed, XPS analysis detected up to 4 % sulfur on their surface, present primarily as sulfide groups. Furthermore, when powders prepared using phosphorous-containing compounds as additives were incubated over night with thiols, the phosphate content was no longer detectable, indicating complete substitution of the phosphate groups by the thiols on the surface of the nanoparticles. However, when powders prepared using phosphorous-containing compounds as additives were incubated over night with carboxylic acids containing compounds, XPS analysis revealed that the carboxylic acids did not replace the phosphate groups.

Once the copper nanoparticles are formed in the reaction solution, the solution is optionally filtered in order to isolate the nanoparticles. Hence, according to some embodiments of the present invention, the reaction mixture is filtered using an appropriate filtering method, and the residue (filtrand) of nanoparticles is optionally washed with a solvent, such as a mixture of water and ethanol, or any other washing formulation. In some embodiments, the resulting "wet cake" is left to dry or placed in an oven set to a low temperature, such as 50 °C, to dry for several hours.

As indicated above, nanoparticles may form agglomerates as a result of their relatively high surface energies. Even in the presence of the anti-agglomeration substance the compositions-of-matter presented herein may contain a minor amount of soft agglomerates, particularly after storage for extended periods of time. However it has been shown that the compositions-of-matter obtained by the process presented herein, such soft agglomerates may be dispersed easily by minor mechanical treatments, such as shaking and stirring, exposure to ultrasound in a liquid medium, sieving, high shear mixing and 3-roll milling.

While further reducing the present invention to practice, the present inventors have found that conducting the reaction with acid-treated zinc powder in order to further decrease the size of the zinc particles, improves the results in terms of a narrower
particle size distribution and in the formation of discrete, spheroid or cuboid shaped copper nanoparticles. It is assumed that the acid-treated zinc powder affords smaller zinc particles for the cementation reaction with copper, and that this substantial reduction in zinc particle size leads to the improved formation of copper nanoparticles.

Hence, according to some embodiment of the present invention, the zinc powder used to convert the copper ions into metallic copper nanoparticles is contacted with an acid prior to its mixing with the copper ions. According to some embodiments, the acid is an inorganic acid, and according to other embodiments, the inorganic acid is a phosphorous-containing acid.

that are suitable for use in the context of these embodiments of the invention include, but are not limited to, phosphorus acid (H$_3$PO$_3$), sodium hypophosphite (NaH$_2$PO$_2$), hypophosphorous acid (H$_2$PO$_3$), H$_2$PO(OH)$_2$, phosphoric acid (H$_3$PO$_4$), PO(OH)$_2$, peroxomonophosphoric acid (H$_3$PO$_5$), OP(OH)$_2$OOH, hypophosphoric acid (H$_4$P$_2$O$_7$), (OH)$_2$P(O)-P(OH)$_2$, pyrophosphoric acid (H$_4$P$_2$O$_7$), (OH)$_2$(O)P-O-P(O)(OH)$_2$, triphosphoric acid (H$_5$P$_3$O$_{10}$), H$_4$P$_2$O$_6$ and H(OH)(O)P-O-P(O)(OH)$_2$, boric acid (H$_3$BO$_3$), chlorosulfonic acid (HClO$_3$S), chromosulfuric acid (CrO$_3$), fluorophosphoric acid (H$_2$F$_2$O$_3$P), hexafluorosphosphoric acid (HF$_6$P), hydriodic acid (HI), hydrobromic acid (HBr), hydrochloric acid (HCl), hydrofluoroc acid (HF), iodic acid (HIO$_3$), magic acid (HF$_6$O$_3$SSb), nitric acid (HNO$_3$), nitrosylsulfuric acid (HNO$_3$S), silicic acid (O$_2$Si), sulfamic acid (H$_2$NO$_3$S), sulfur dioxide (H$_2$O$_2$S), sulfuric acid (H$_2$O$_4$S), tetrafluoroboric acid (HBF$_4$) and any mixture, hydrate or complex thereof.

As discussed hereinabove, the process described herein results in a composition-of-matter that comprises copper nanoparticles that are characterized by unique physical and chemical properties, which can be manipulated by varying the process parameters. As aforementioned, the surface chemistry of the produced nanoparticles can be attenuated through controlled oxidation, adsorption of chemical species and the use of additives. According to some embodiments of the present invention, by changing the reaction parameters and by using different organic substances as capping/passivating agents, it is possible to produce nanoparticles of different shapes, morphologies and surface chemistries.
Hence, according to an aspect of embodiments of the invention, there is provided a composition-of-matter which comprises copper nanoparticles, prepared by the process described herein. Such a composition-of-matter can exhibit various characteristics, as described herein.

According to another aspect of embodiments of the invention, there is provided a composition-of-matter comprising copper nanoparticles characterized by:

a) being at least 95 percent by weight reversibly re-suspendible in a liquid media as nanoparticles,

b) having a mode particle diameter (most frequent) after re-suspension that ranges from 10 nm to 200 nm; and

c) having a standard deviation (\(\sigma\)) of particle diameter after re-suspension that ranges from 5 nm to 50 nm.

**Copper nanoparticles characterization:**

The nanoparticles in the composition-a matter, according to embodiments of the present invention, are characterized as being composed of a plurality of discrete, separate and individual copper nanoparticles, which are readily re-suspendible in a liquid media after being in a form of, for example, a compressed dry powder or as a compressed wet powder of copper nanoparticles. By "re-suspendible", it is meant that the composition-of-matter presented herein can be suspended in a liquid media and regain similar suspension properties repeatedly, each time it is being taken out from suspension and then put back into suspension, and this reversibility is applicable for at least 90 %, 95 %, 98 %, 99 % and even higher percentages of the total mass of the composition. By "regaining similar suspension properties repeatedly" it is meant that the plurality of discrete, separate and individual copper nanoparticles can be suspended in a liquid media as discrete, separate and individual copper nanoparticles having a characteristic average particle size and particle size distribution; thereafter the nanoparticles be filtered out of the suspension (and optionally dried) to afford a compressed powder thereof; and thereafter be re-suspended in a liquid media which will have similar characteristic average particle size and particle size distribution.

Attaining this attribute has been one of the most challenging goals of modern-days nanoparticle science, since nanoparticles tend to form large irreversible agglomerates of particles due to their chemical and physical properties, which limits
their use as nanoparticles. The nanoparticles presented herein can be re-suspended in a liquid media repeatedly without forming large agglomerates.

For example, the nanoparticles presented herein can be extracted from the reaction mixture in which they are prepared typically as a "wet cake" (the wet solid residue left after filtration, also known as retentate or filtrand) or a wet compressed powder which is then dried to a "dry cake" or a dry compressed powder form, and thereafter can be re-suspended in the same or a different liquid media over and over again without forming large agglomerates.

Accordingly, the composition-of-matter described herein can be in a form of, for example, a dispersion, as defined herein, a powder (wet or dry) or as a suspension in a liquid medium. The liquid medium can be, for example, an aqueous solution (e.g., water) or an organic solution.

Another attribute of the nanoparticles presented herein is their very narrow particles size distribution. As used herein and in the art, a particles size distribution, or PSD, of a powdered or particulate matter, can be represented by a list of values in a mathematical function that defines the relative amounts of particles present in the material, typically sorted according to the particles size. Hence, a PSD of a sample can be represented by the sum of the products of relative amounts, typically represented by their percentage of the whole sample, and the various particle size bins, typically represented in a particle size range which populates each bin and denoted by the upper and lower limits of particle sizes. In other words, a PSD describes the relative portion of each particle size in a plurality of particles in the powdered or particulate matter.

The size of a nanoparticle is typically expressed as the maximal projected diameter of the particles, or otherwise as stemming from the measurement technique or method.

Hence, the copper nanoparticles described herein can be characterized and defined by the specific characteristics of their PSD, namely the mean, median, mode and standard deviation, wherein the first three values are each a statistical physical property of the particles, having the units nm and representing the mean size, the median size or the most frequent size (mode) of the nanoparticles, respectively.

The meaning of the phrase "standard deviation", in the context of the present embodiments is as it is typically used, namely it is a measure of the variability in the
size of the entire population of copper nanoparticles, and is given in the same units as
the measured data, and in the case of a PSD, in particle size. As in the general case, a
low standard deviation indicates that the data points tend to be very close to the mean,
whereas high standard deviation indicates that the data are spread out over a large range
of values.

In the context of some embodiments of the present invention, the copper
nanoparticles maintain a low standard deviation of particle sizes, as can be seen in
Examples 1 and 2 in the Examples section that follows (for example, in the results of
the dynamic light scattering (DLS)).

Thus, the nanoparticles of the composition-of-matter are further characterized by
having a mode particle diameter (most frequent) after re-suspension that ranges from 10
nm to 200 nm; and having a standard deviation (σ) of particle diameter after re-
suspension that ranges from about 5 nm to about 50 nm.

These parameters which indicate the properties of a collection of particles, are
specified in their "after re-suspension" in order to signify that the copper nanoparticles
presented herein are such that allow their re-suspension from, e.g., a compressed
powder form back into their pre-compression state. This is to signify that the attributes
of the nanoparticles presented herein, which make them highly suitable for many
applications where nanoparticles are needed in general and copper nanoparticles are
required specifically, can be exhibited reproducibly even after storage and mild
compression. By mild compression it is meant settling of a precipitant or the forming of
a "cake" (the filtrand), as oppose to sintering, high-pressure compression and other
methods which are meant to harden and solidify nanoparticles in bulk.

The characteristics of the copper nanoparticles composing the composition-of-
matter described herein can be measured by any technique known in the art. Exemplary
techniques are described in the Examples section that follows. Other techniques would
be readily recognized by a person skilled in the art.

It is noted herein that the compositions-of-matter comprising copper
nanoparticles according to embodiments of the present invention, are substantially free
of micron-size particles (over about 1000 nm in diameter). According to other
embodiments, the compositions-of-matter are substantially free of particles having a
size over about 500 nm, over about 300 nm, or over about 200 nm.
By "substantially" it is meant throughout herein at least 95 %, at least 96 %, at least 97 % at least 98 %, at least 99 %, at least 99.5 %, at least 99.8 %, at least 99.9 %, at least 99.99 % and even 100 %.

Another attribute by which particles are characterized is their shape, or at least a close approximation to a descriptive out-form thereof. As delineated hereinabove, copper nanoparticles, according to some embodiments of the present invention, can be manufactured reproducibly so as to have a narrow range of shapes according to the conditions in the process of their manufacturing.

According to some embodiments of the present invention, the copper nanoparticles 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" and "spherical nanoparticles" are used herein interchangeably. These nanometric spheroids, which may represent primary particles, are estimated to have an overall diameter of from about 5 run to about 50 nm, or from 5 nm to 40 nm, or from 5 nm to 30 nm, or from 5 nm to 20 nm, or from 5 nm to 10 nm, as can be determined by SEM/TEM/HRSEM measurements (see, for example, the Examples section that follows, Example 1). As can also be deduced from electron-micrographs measurements, in some embodiments, the spheroids are crystalline, namely each sphere is substantially a single crystal, having substantially one continuous lattice.

In some embodiments, the core of the nanoparticle is crystalline while an external layer thereof is amorphous (non-crystalline).

In some embodiments, the spheroid copper nanoparticles form substantially uniform clusters.

Hence, according to some embodiment, the copper nanoparticles are discrete, individual and separable raspberry-shaped nanoclusters, each made of numerous spheroid (e.g., single-crystalline spheroid) nanoparticles.

Figures IA-B present two conceptual illustrations of clusters of spheroids, which are an exemplary shape of the copper nanoparticles according to some embodiments of the present invention. The small circles in Figure IA represent the primary single-crystalline spherical nanoparticles having an average size of 5-10 nm, and the cluster of about 10-20 spheroids is the dispersible/suspendible species or discreet nanoparticle, which is well represented by the shape of a raspberry, as presented in Figure IB,
wherein each berry is a discrete fruit which is essentially a cluster of spheroids (hence
the phrase "raspberry-shaped nanoparticles").

In that regard, the nanoparticle species in such a compositions-of-matter are the
raspberry-shaped nanoclusters. Hence, according to some embodiments, at least 95
percents of the primary spherical nanoparticles are found in a form a cluster of
spheroids.

According to some embodiments, the composition-of-matter which comprises
the aforementioned raspberry-shaped nanoclusters has a mode particle diameter (most
frequent) that ranges from about 100 run to about 190 ran. According to some
embodiments, the mode particle diameter of the raspberry-shaped nanoparticles ranges
from about 110 nm to about 180 nm, or from about 110 nm to about 140 nm. The PSD
of these compositions are characterized by a standard deviation of less than 50 % of the
mode particle diameter, less than 40 % of the mode particle diameter, less than 30 % of
the mode particle diameter, or less than 20 % of the mode particle diameter.

According to some embodiments of the present invention, the copper
nanoparticles are generally shaped as cuboids, which is a close approximation to a cube
or a box. Herein, the terms "cuboids" and cubical nanoparticles are used
interchangeably.

Unlike the raspberry-shaped cluster of spheroids nanoparticles described
hereinabove, which are held together to afford one discrete particle, the cuboid-shaped
copper nanoparticle is structured substantially as one metallic copper crystal having a
single-crystalline lattice throughout its body.

A cubical shape of the nanoparticles can be determined by SEM/TEM/HRSEM
micrographs (see, for example, the Examples section that follows below, Example 2).
As can also be estimated from electron-micrographs, these cuboids are crystalline,
namely each cuboid nanoparticle is substantially a single crystal, having substantially
one continuous lattice. In some embodiments, the core of the cubical nanoparticle is
crystalline. In some embodiments, the cubical nanoparticles are single-crystalline and
do not have a visible amorphous layer coating the core.

According to some embodiments, the cuboid copper nanoparticles have a mode
particle diameter (most frequent) that ranges from about 50 nm to about 120 nm.
According to some embodiments, the mode particle diameter of the cuboid copper
nanoparticles ranges from about 60 nm to about 110 nm, or from about 70 nm to about 100 nm, or from about 60 nm to about 100 nm. The PSD of these compositions are characterized by a standard deviation of less than 50 % of the mode particle diameter, less than 40 % of the mode particle diameter, less than 30 % of the mode particle diameter, or less than 20 % of the mode particle diameter.

The average nanoparticle sizes and nanoparticle size distribution described herein may be measured by mixing samples of their powders in a liquid medium (such as water and PEG) and exposing the resultant suspension to ultrasound using an ultrasonic bath or horn. The ultrasonic treatment provides sufficient energy to disperse the soft agglomerates of nanoparticles. The primary nanoparticle size and size distribution may also be measured by SEM or TEM analysis.

As discussed hereinabove, metallic nanoparticles are highly sensitive to external conditions due to their small size, namely the ratio of their surface area relative to their volume or mass. This sensitivity shortens the shelf-life of most commercially available nanoparticles, particularly as a result of oxidation stemming from exposure to ambient oxygen. Some commercially available nanoparticle manufacturers coat the nanoparticles with a protective layer which then becomes a nuisance and impairment for most applications. Some nanoparticles are manufactured in processes that leave a protective external chemically-passive layer, or coat over the individual nanoparticle, which then protects them from further oxidation with some minimal detrimental effect in their use. This passive layer may be a result of use of passivating agents added to the reaction mixture in which the nanoparticles are being formed, or an intrinsic result of their production.

While reducing the present invention to practice, it was found that a composition-of-matter in the form of a dry powder comprising the copper nanoparticles can be stored at ambient conditions in a simple seal container while its oxide content did not increase over a substantially long period of time, as measured by XRD, and that the HRSEM images did not show significant variations in structure, morphology and size of the stored copper nanoparticles. These findings indicate impedance of massive evolution of oxides, and explain the lack of massive aggregation and clumping, which is in many cases related to uncontrolled development of an oxide layer which reduces the
zeta potential and triggers aggregation, but which is not observed for the copper nanoparticles presented herein.

This stable oxide content at the surface of the copper nanoparticles according to embodiments of the present invention, also means that the desired qualities expected and required from high-quality metallic nanoparticles which stem from their small size and metal chemistry (such as conductivity and other properties derived from their crystallinity), can be preserved by simple means and at easily maintained conditions for an extended period of time.

Hence, according to some embodiments of the present invention, the copper nanoparticles presented herein are resistant to oxidation by atmospheric oxygen for a time period of at least one year. According to some embodiments, the oxide content on the surface of the copper nanoparticles remains substantially invariable for a time period of at least 2 weeks, 3 weeks, 1 month, 2 months, 3 months, 6 months, 10 months and even 12 months and more. By "remains substantially invariable" it is meant that a result of an experiment that evaluates or determines the oxide content on the surface of the stored nanoparticles does not exceed about 120 % of the oxide content of the freshly-produced but otherwise similar nanoparticles, or alternatively does not exceed 110 %, 105 %, 103 %, 102 %, 101 % and even less.

This capacity to resist oxidation for extended period of time is afforded also by the presence of a passive outer-coat, which is assumed to be the oxide layer visible as an amorphous layer in the electron-microscopy of the spheroid particles, and in the chemical analysis measurements, such as XPS and XRD in all nanoparticles presented and discussed in the Examples section that follows.

In general, the external passivating layer which protects the metallic nano-crystalline particles from further oxidation and loss of crystallinity is assumed to be an oxide layer. Thus, according to some embodiments of the present invention, the copper nanoparticles presented herein are further characterized by having an external oxide layer. This oxide layer can be assayed by spectroscopic methods and its content are identified. In some embodiments, the oxide layer comprises Cu₂O (copper oxide) and/or Cu(OH)₂ (copper hydroxide). Without being bound by any particular theory, it is assumed that the copper oxide is mostly in a crystalline form which mediates the
transition from the crystalline morphology of the metallic copper core to the amorphous morphology of the out-most layer of copper hydroxide, when present/visible.

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 nanoparticles 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.

In some embodiments, the raspberry-shaped copper nanoparticles described herein have an exterior surface characterized as comprising an atomic concentration (content) of phosphate that ranges from about 1 % to about 4 % and an atomic concentration of carbon that ranges from about 20 % to about 30 %. In some embodiments, the cuboid-shaped copper nanoparticles have an exterior surface characterized as comprising an atomic concentration of sulfur that ranges from about 0.5 % to about 2 % and an atomic concentration of carbon that ranges from about 15 % to about 25 %.
All the properties and characteristics presented hereinabove and in the Examples section that follows below, render the compositions-of-matter comprising of the copper nanoparticles presented herein highly suitable for many applications, by being capable of maintaining their capacity to disperse and re-disperse as metallic nanoparticle.

The terms "disperse" and "dispersive", as used herein, refer to the tendency of a particulate matter not to become or stay as agglomerates, clumps or chunks of mass, but rather become and/or regain a state of discrete, non-aggregated free particles. It is well known in the art that the small mass and large surface area of metallic nanoparticles not only give them their desired properties but also render them susceptible to clumping and agglomeration, however the copper nanoparticles presented herein do not tend to clump and can regain their disperse form reversibly and reproducibly.

As used herein, the term "dispersing", refers to the act of crumbling, breaking apart or otherwise separating particles which have formed clumps, soft agglomerates and soft aggregates back into the un-clumped particle. The difference between dispersible and non-dispersible particles is the ability to disperse the clumped particles using simple techniques for treating large masses of matter in the form of soft agglomerates or soft aggregates, while hard agglomerates and hard aggregates are non-dispersible using similar techniques.

The term "suspension", as used herein, refers to a heterogeneous mixture of a solid in 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 both 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-of-matter is being in a form of a dispersion, or in other words, the copper nanoparticles comprising the composition are dispersed, be it as a dry powder or as a suspension of copper nanoparticles in liquid media, such as a suspension in an aqueous medium.

The compositions-of-matter 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 the composition-of-matter presented herein.

For example, the raspberry-shaped clusters of copper nanoparticles presented herein have been found to function well in certain ink formulations and processes in the field of printable electronics. Hence, an exemplary article-of-manufacturing which includes the composition-of-matter presented herein is 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-of-matter as provided herein, and heating this shape thereby obtaining the copper element.

Accordingly, there is provided an inkjet ink composition which includes a composition-of-matter 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, heating the substrate having the inkjet ink
composition applied thereon 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 power 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 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 highly useful 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 comprising the composition-of-matter 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.

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 "discrete metallic nanoparticles" is intended to include all such new technologies apriori.

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
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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 Methods

CuSO$_4$·SH$_2$O was purchased from Gadot Chemicals. NaH$_2$PO$_2$ was purchased from Riedel-de Haen.

H$_3$PO$_3$ was purchased from Aldrich.

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

Mercaptoethanol (HOCH$_2$CH$_2$SH) was purchased from Alfa Aesar.

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

SEM/HRSEM micrographs were afforded using a Zeiss Gemini Ultraplus.

TEM micrographs were afforded using an instrument.

DLS measurements were afforded using a Brookhaven instrument and the 90-Plus Particle Sizing Software Ver.3.44.

XRD measurements were afforded using a Phillips 3710 diffractometer.

XPS measurements were afforded using a VG Scientific Sigma Probe.

EXAMPLE 1

Raspberry-shaped copper nanoparticles

46.8 grams of CuSO$_4$·5H$_2$O were added to 6 liters of H$_2$O (31.24 mM Cu$^{2+}$), pre-bubbled with N$_2$ for at least 10 minutes, and the resulting solution was stirred using a homogenizer until the copper salt was completely dissolved. Thereafter, 71 grams of
NaH$_2$PO$_2$ (111.64 mM hypophosphate) were added and the mixture was stirred until all the hypophosphate has been dissolved. Thereafter, 12 grams of zinc (equivalent to 30.58 mM of Zn ions) in a powder form having grit size of less than 10 micron were added and the suspension was stirred vigorously using a homogenizer for another 8 minutes. Upon addition of the zinc powder the solution turned from clear blue to a blackish/burgundy lucid suspension.

The resulting suspension was filtered using Whatman Grade No. 42 quantitative ashless filter paper (Whatman cat. No. 1442-090), and washed with H$_2$O and ethanol. The filter paper carrying the slurry was placed in a convection oven heated to 50 °C for a few minutes. The resulting cake was removed from the filter and reintroduced into the oven and heated at 50 °C for 7 hours.

This zinc/copper displacement reaction, conducted in the presence of sodium hypophosphate, afforded copper powder comprised of raspberry-shaped nano-clusters or primary cluster (see, Figure 1) having an average size of about 100 nm, each comprised of numerous primary spheroid nanoparticles, and each having a diameter of around 10 nm.

Figures 2A-B present SEM micrographs of the powder obtained by reacting copper sulfate, sodium hypophosphate, and zinc dust at molar ratios of 1:4:1, showing the raspberry-shaped copper nanoparticles at a magnification of 1:45000 (Figure 2A) and a magnification of 1:85000 (Figure 2B).

Figures 3A-B present TEM micrographs of a single primary particle which forms a part of a raspberry-shaped nanoparticle obtained as described hereinabove and shown in Figures 2A-B, showing that each primary particle is a single crystal covered by a layer of an amorphous matter. As can be seen in Figure 3B, the amorphous layer covering the individual primary particle is having a thickness of about 1 nm.

Figure 4 presents an XRD spectrum of the powder of copper nanoparticles obtained as described hereinabove and shown in Figures 2A-B, showing two major Cu peaks and a peak corresponding to Cu$_2$O. As can be seen in Figure 4, the wide peaks corroborate the presence of nano-scaled particles.

Figure 5 is a high resolution XPS spectrum of CI$_5$ taken from the powder of copper nanoparticles obtained as described hereinabove and shown in Figures 2A-B, showing the spectrum measured in the "as received" state, and curve-fitted with 3
components, wherein the "A" line can be related to carbon bounded to hydrogen, the higher binding energy, lines "B" and "C" can be assigned to C-OH and/or C-O-C=O for the "B" line, and to C=O and/or O-C=O for the "C" line.

Figure 6 is a high resolution XPS spectrum of Cu2p taken from the powder of copper nanoparticles obtained as described hereinabove and shown in Figures 2A-B, showing the spectrum measured in the "as received" state, and curve-fitted with 2 components, wherein the lower binding energy line can be related to Cu2O (based on the Cu LMM line measurements), and the higher binding energy line can be assigned to Cu(OH)₂.

Figure 7 is a high resolution XPS spectrum of P2s taken from the powder of copper nanoparticles obtained as described hereinabove and shown in Figures 2A-B, showing the spectrum measured in the "as received" state, and curve-fitted with 2 components, wherein the lower binding energy line "A" can be related to P in structures of the type Na₃PO₄, and the higher binding energy line "B" can be assigned to structures similar to P₄O₁₀ or H₃PO₄.

As can be seen in Figures 5, 6 and 7, these results indicate the presence of an amorphous layer comprised primarily of Cu₂O and Cu(OH)₂. Typically, the atomic concentration of phosphate and carbon on the surface of the copper nanoparticles, obtained as described hereinabove, was found to be between 1-4 %, and 20-30 % respectively. This suggests that during the nucleation and growth the phosphate groups are weakly attached to the copper surface, yet provide protection against massive aggregation, as is typically the case in classical copper/zinc cementation reactions. These results may indicate that the unique oxide layer formed around the primary nanoparticles provides a kinetic barrier towards further oxidation.

Figure 8 is a bar and sigmoid plot of the dynamic light scattering (DLS) data measured for the powder of copper nanoparticles, obtained as described hereinabove and shown in Figures 2A-B, after re-suspending (dispersing) the powder in an aqueous formulation containing polyethylene glycol, showing that the average particle size is about 130 nm and a very tight size distribution.

Table 1 presents the numerical results of the DLS measurements presented in Figure 8, wherein d(nm) is the estimated diameter of the particles in nanometer, G(d) is the Gaussian distribution value, and C(d) is the cumulative distribution value.
Table 1

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As can be seen in Figure 8 and Table 1, the re-suspended raspberry-shaped copper nanoparticles are characterized by a mode particle diameter of 133 nm, and a standard deviation (σ) of particle diameter of about 30 nm.

EXAMPLE 2

Cuboid-shaped copper nanoparticles

For the production of cube-shaped copper nanoparticles, 10 grams of zinc powder (grit size less than 10 micron) and 30 µl of mercaptoethanol were added to 1 liter of degassed H₂O (equivalent to 152.9 nm of Zn ions and ) and stirred very briefly using a homogenizer. Thereafter, 38 grams of CuSO₄·SH₂O were added and the reactants were stirred for 10 seconds, followed by the addition of 10 grams of H₃PO₃, and the reaction mixture was stirred vigorously for another 5 minutes. Upon the addition of the copper salt, a clear lucid black suspension was formed, and the addition of phosphorus acid was accompanied by the evolution of bubbles, probably of hydrogen. After mixing the suspension was filtered using Whatman Grade No. 42 filter paper. Since some of the suspension seeped through the filter paper, the filtrate was passed through the loaded filter several times until the filter paper became sufficiently blocked with nanoparticles, thus allowing for effective filtration and purification of the nanoparticles. The nanoparticles were washed with H₂O and ethanol, and the filter paper carrying the black, fine slurry was put in an oven and heated at 50 °C for a few minutes. The dried cake was removed from the filter paper and the cake was
reintroduced into the oven and dried at 50 °C for 30 minutes. The resulting powder was then re-suspended in ethanol using a sonicator, filtered and dried as described previously.

Figure 9 is a SEM micrograph of a powder comprised of cuboid-shaped copper nanoparticles obtained in the presence of mercaptoethanol as described hereinabove. As can be seen in Figure 9, the size distribution of these copper nanoparticles is very narrowly centered around 70-80 nm, and there is no aggregation of the particles.

Figures 10A-B are TEM micrographs of individual cuboid-shaped copper nanoparticles obtained in the presence of mercaptoethanol as described hereinabove. As can be seen in Figures 10A-B, no amorphous layer can be observed around the copper nanoparticles.

Figure 11 presents an XRD spectrum measured for the powder comprised of cuboid-shaped copper nanoparticles obtained as described hereinabove, showing two major Cu peaks and a peak corresponding to Cu2O. As can be seen in Figure 11, the peaks are wide, corroborating the presence of nano-scaled particles.

Figure 12 is a high resolution XPS spectrum of C1s taken from the powder of copper nanoparticles obtained as described hereinabove and shown in Figures 9 and 10, showing the spectrum measured in the "as received" state, and curve-fitted with 3 components, wherein the "A" line can be related to carbon bounded to hydrogen, the higher binding energy lines "B" and "C" can be assigned to C-OH and/or C-O-C=O for the "B" line, and to C=O and/or O-C=O for the "C" line.

Figure 13 is a high resolution XPS spectrum of Cu2p3/2 taken from the powder of copper nanoparticles obtained as described hereinabove and shown in Figures 9 and 10, showing the spectrum measured in the "as received" state, and curve-fitted with one component of Cu2O.

Figure 14 is a high resolution XPS spectrum of S2p taken from the powder of copper nanoparticles obtained as described hereinabove and shown in Figures 9 and 10, showing the spectrum measured in the "as received" state, and curve-fitted with 2 components, wherein the lower binding energy line "A" can be related to a sulfide-like bonding state, and the higher binding energy line "B" can be assigned to a sulfate type bonding.
As can be seen in Figures 9-14, the cuboid-shaped copper nanoparticles do not possess an amorphous oxide layer, and the sole oxide species detected by both XRD and XPS is Cu₂O. These results are in contrast to the results obtained for the raspberry-shaped nanoparticles obtained as presented in Example 1 hereinabove.

Typically, the atomic concentration of sulfur and carbon on the surface of the cuboid-shaped copper nanoparticles was found to be between 0.5-2 %, and 15-25 % respectively, which suggests that during the nucleation and growth the thiol groups are weakly attached to the copper surface (perhaps only through hydrogen bonding), yet provide protection against massive aggregation, as is typically the case in classical copper/zinc cementation reactions. It is also suggested that the unique oxide layer formed provides a kinetic barrier towards further oxidation.

Figure 15 is a bar and sigmoid plot of the dynamic light scattering (DLS) data measured for the powder of copper nanoparticles, obtained as described hereinabove and shown in Figures 9 and 10, after re-suspending (dispersing) the powder in an aqueous formulation containing polyethyleneglycol, showing that the average particle size of about 70 nm with a very tight size distribution.

Table 2 presents the numerical results of the DLS measurements presented in Figure 18, wherein d(nm) is the estimated diameter of the particles in nanometer, G(d) is the Gaussian distribution value, and C(d) is the cumulative distribution value.

<table>
<thead>
<tr>
<th>d (nm)</th>
<th>G (d)</th>
<th>C (d)</th>
<th>d (nm)</th>
<th>G (d)</th>
<th>C (d)</th>
<th>d (nm)</th>
<th>G (d)</th>
<th>C (d)</th>
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<tr>
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<td>0</td>
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<tr>
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<tr>
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</table>
As can be seen in Figure 15 and Table 2, the re-suspended cuboid-shaped copper nanoparticles are characterized by a mode particle diameter of 70 run, and a standard deviation (\(\sigma\)) of particle diameter of about 10 nm.

The results obtained from DLS are in excellent agreement with the SEM observations, indicating lack of aggregation.

**EXAMPLE 3**

*Acid-treatment for zinc in the production of copper nanoparticles*

The following procedure was used to treat the zinc powder prior to the introduction of copper therewith. 60 grams of zinc powder (grit size less than 10 micron) and 30 grams phosphorus acid (\(\text{H}_3\text{PO}_4\)) were added to 600 ml \(\text{H}_2\text{O}\), and the mixture was mechanically agitated for 5 minutes, during which a substantial evolution of hydrogen was observed. The remaining zinc was washed with water and dried.

12 grams of the acid treated zinc were used according to the procedure presented in Example 1 hereinabove together with 46.8 grams of \(\text{CuSO}_4\cdot\text{SH}_2\text{O}\) and 71 grams of \(\text{NaH}_2\text{PO}_4\) in 6 liters of \(\text{H}_2\text{O}\).

The resulting copper nanoparticles were characterized as having a higher content of well formed and discrete copper nanoparticles using HRSEM.

Figure 16 is an HRSEM micrograph of the powder of copper nanoparticles obtained using acid treated zinc as described hereinabove.

As can be seen in Figure 16, acid treatment of the zinc powder with phosphorus acid, which is assumed to be a side reaction of the zinc/copper cementation reaction in the presence of acidic phosphate-containing compounds, afforded superb results in obtaining copper nanoparticles. It is further assumed that the improved results is linked to the reduction in size of the zinc particles which lead to the decrease in the amount of aggregation and dendrification considerably.

It was noted that when using acid treated zinc, whose particle size is a few tens of nanometers versus the ten microns grit samples used in Examples 1 and 2 hereinabove, one can obtain a powder that contains considerably higher amounts of discrete copper nanoparticles, free of aggregation or dendrification.
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-of-matter comprising copper nanoparticles characterized by:
   a) being at least 95 percent by weight reversibly re-suspendible in a liquid media as nanoparticles,
   b) having a mode particle diameter (most frequent) after re-suspension that ranges from 10 nm to 200 nm; and
   c) having a standard deviation (σ) of particle diameter after re-suspension that ranges from 5 nm to 50 nm.

2. The composition-of-matter of claim 1, wherein the copper nanoparticles are generally shaped as spheroids.

3. The composition-of-matter of claim 2, wherein at least 95% of said spheroids are in a form a cluster of spheroids.

4. The composition-of-matter of claim 3, wherein said cluster is generally shaped as a raspberry-like cluster.

5. The composition-of-matter of any of claims 3 and 4, wherein said cluster has a mode particle diameter that ranges from 100 nm to 190 nm.

6. The composition-of-matter of any of claims 2-5, wherein a mode particle diameter of each of said spheroids ranges from 5 nm to 50 nm.

7. The composition-of-matter of any of claims 2-6, wherein the copper nanoparticles have an exterior surface characterized as comprising an atomic concentration of phosphate that ranges from 1 percent to 4 percent and an atomic concentration of carbon that ranges from 20 percent to 30 percent.

8. The composition-of-matter of claim 1, wherein the copper nanoparticles are generally shaped as cuboids.
9. The composition-of-matter of claim 8, wherein the nanoparticles comprise single-crystalline nanoparticles.

10. The composition-of-matter of any of claims 8 and 9, wherein said cuboids have a mode particle diameter that ranges from 50 nm to 120 nm.

11. The composition-of-matter of any of claims 8-10, wherein the copper nanoparticles have an exterior surface characterized as comprising an atomic concentration of sulfur that ranges from 0.5 percent to 2 percent and an atomic concentration of carbon that ranges from 15 percent to 25 percent.

12. The composition-of-matter of any of claims 1-11, wherein an oxide content on the surface of the copper nanoparticles remains substantially invariable for a time period of at least one week.

13. The composition-of-matter of any of claims 1-11, wherein the copper nanoparticles have a crystalline core.

14. The composition-of-matter of any of claims 1-13, wherein the copper nanoparticles have an external oxide layer.

15. The composition-of-matter of claim 14, wherein said oxide layer comprises Cu$_2$O and Cu(OH)$_2$.

16. The composition-of-matter of any of claims 1-15, wherein a carbon content of the copper nanoparticles is less than 20 percent of the total weight of the copper nanoparticles.

17. The composition-of-matter of any of claims 1-16, being in a form of a dispersion.
18. The composition-of-matter of any of claims 1-16, being in a form of a powder.

19. The composition-of-matter of any of claims 1-16, being in a form of a suspension in an aqueous medium.

20. A process of manufacturing a composition-of-matter which comprises copper nanoparticles, the process comprising:
   mixing a copper salt with a powder of elemental zinc in an aqueous solution in the presence of a phosphorous-containing compound, thereby obtaining the composition-of-matter which comprises the copper nanoparticles,
   wherein:
   a concentration a copper ion in said salt ranges from 10 mM M to 150 mM; and
   a molar ratio between said copper ion and said elemental zinc ranges from 2:1 to 1:2.

21. The process of claim 20, wherein a molar ratio between said copper ion and said phosphorous-containing compound ranges from 1:1 to 1:5.

22. The process of any of claims 20-21, a pH of said aqueous solution ranges from 1.5 to 6.

23. The process of claim 20, wherein said powder of elemental zinc has a grit size of less than 20 microns.

24. The process of claim 20, wherein said powder of elemental zinc has a grit size of less than 10 microns.

25. The process of any of claims 20-24, wherein said copper nanoparticles are characterized by:
   a) being at least 95 percent by weight reversibly re-suspendible in a liquid media as nanoparticles,
   b) having a mode particle diameter (most frequent) after re-suspension that ranges from 10 nm to 200 nm; and
c) having a standard deviation (σ) of particle diameter after re-suspension that ranges from 5 nm to 50 nm.

26. The process of any of claims 20-25, wherein the copper nanoparticles are generally shaped as spheroids.

27. The process of any of claims 20-25, further comprising mixing said copper salt, said powder of elemental zinc and said phosphorous-containing compound with a thiol-containing compound.

28. The process of claim 27, wherein a concentration of said thiol-containing compound in said aqueous solution ranges from 0.05 mM to 10 mM.

29. The process of any of claims 27 and 28, wherein the copper nanoparticles are generally shaped as cuboids.

30. The process of any of claims 20-29, further comprising, subsequent to said mixing, filtering the copper nanoparticles.

31. The process of claim 30, further comprising drying said copper nanoparticles.

32. The process of claim 31, further comprising, subsequent to said drying, dispersing the copper nanoparticles.

33. The process of claim 32, wherein said dispersing is effected by a technique selected from the group consisting of re-suspension by ultrasound in a liquid medium, sieving, high shear mixing, and 3-roll milling.

34. The process of any of claims 20-33, wherein said copper salt is selected from the group consisting of CuSO₄, CuCl₂, Cu(NO₃)₂, (CH₃COO)₂Cu, Cu(C₅H₇O₂)₂, CuCO₃, Cu[C₆H₇(CH₂)₃CO₂]₂, copper(II) stearate complex, CuCl₂O₄, copper(II) ethylenediamine complex and Cu(OH)₂.
35. The process of any of claims 20-33, wherein said phosphorous-containing compound is selected from the group consisting of phosphoric acid, hypophosphite, (NH₄)SPO₄, Ca₃(PO₄)₂, FePO₄, Fe₃(PO₄)₂, Na₃PO₄, Ca(H₂PO₄)₂ and KH₂PO₄, or stem from phosphorous acids (such as, without limitation H₃PO₂ and H₃PO₄), phosphorous oxides (such as, for example, P₄O₆ and P₄O₁₀), a phosphide, a phosphinate, a phophine oxide, a phosphine, a phosphinite, a phosphite, a phosphonate and a phosphonite.

36. The process of claim 27, wherein said thiol-containing compound is selected from the group consisting of ß-mercaptoethanol, cysteine, methanethiol (CH₃SH), ethanethiol (C₂H₅SH), 1-propanethiol (C₃H₇SH), 2-propanethiol (CH₃CH(SH)CH₃), butanethiol (C₄H₉SH), tetrabutyl mercaptan (C(CH₃)₃SH), pentanethiols (C₅H₁₁SH), coenzyme-A, lipoamide, glutathione, dithiothreitol/dithioerythritol and 2-mercaptoindole.

37. The process of any of claims 20-36, further comprising, prior to said mixing, contacting said power of elemental zinc with an acid.

38. The process of claim 37, wherein said acid is selected from the group consisting of phosphorus acid (H₃PO₃), hypophosphorous acid (H₃PO₂), sodium hypophosphite (NaH₂PO₂), H₂PO(OH), HPO(OH)₂, phosphoric acid (H₃PO₄), PO(OH)₃, peroxomonosphorous acid (H₃PO₅), OP(OH)₂OOH, hypophosphoric acid (H₄P₂O₈), (OH)₂P(O)-P(O)(OH)₂, pyrophosphoric acid (H₄P₂O₇), (OH)₂(O)P-O-P(O)(OH)₂, triphosphoric acid (H₅P₃O₁₀), H₄P₂O₆, H(OH)(O)P-O-P(O)(OH)₂, boric acid (H₃BO₃), chlorosulfonic acid (HClO₃S), chromosulfuric acid (CrO₃), fluorophosphoric acid (H₂FO₃P), hexafluorophosphoric acid (HF₆P), hydriodic acid (HI), hydrobromic acid (HBr), hydrochloric acid (HCl), hydrofluoric acid (HF), iodic acid (HIO₃), magic acid (HF₆O₃SSb), nitric acid (HNO₃), nitrosylsulfuric acid (HNO₅S), silicic acid (O₂Si), sulfamic acid (H₃NO₃S), sulfur dioxide (H₂O₃S), sulfuric acid (H₂O₄S), tetrafluoroboric acid (HBF₄) and any mixture, hydrate or complex thereof.
39. A composition of matter comprising copper nanoparticles, the composition of matter being prepared by the process of any of claims 20-38.


41. The article-of-manufacturing of claim 40, being selected from the group consisting of an inkjet ink, a solid macro-scaled object, an electronic component and an electronic circuit.

42. An inkjet ink composition, comprising the composition-of-matter of any of claims 1-19 and 39.

43. A method of inkjet printing a substantially electrically conducting element on a substantially electrically isolating substrate, the method comprising applying the inkjet ink composition of claim 42 on the substrate.

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

45. A method of preparing a substantially electrically conducting copper element, comprising forming a shape of the element from the composition-of-matter of any of claims 1-19 and 39 and heating said shape thereby obtaining the copper element.
FIG. 5
C1s

Counts / s

Binding Energy (eV)

FIG. 6
Cu 2p standard

Counts / s

Residuals

Binding Energy (eV)
FIG. 12
C1s

FIG. 13
Cu 2p standard