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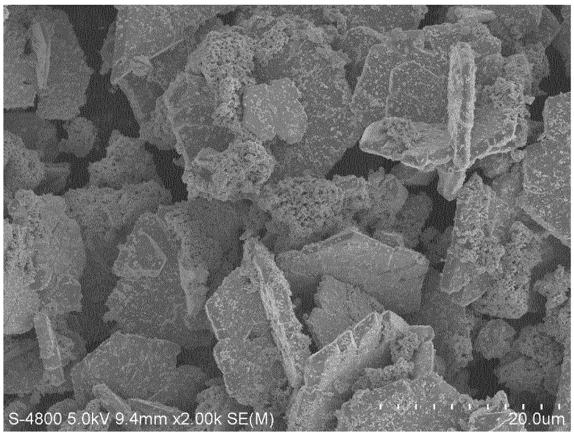
(54) METALLIC COPPER PARTICLES, AND PRODUCTION METHOD THEREFOR

(57) Provided are: metallic copper particles exhibiting excellent low-temperature sintering properties at temperatures equal to or lower than 300°C; and a production method therefor. In these metallic copper particles, metallic copper fine particles are adhered to the surfaces of large-diameter metallic copper particles. With regard to the metallic copper particles to be produced, copper oxide and hypophosphoric acid and/or a salt thereof are mixed and reduced, preferably in the presence of 1-500 mass% of gelatin and/or collagen peptide. The reduction reaction temperature is preferably in the range of 20-100°C. The produced metallic copper particles have a volume resistivity value when heated to a temperature of 300°C under a nitrogen atmosphere of 1×10^{-2} Ω·cm or less.

FIG.2



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Description

Technical Field

[0001] The present invention relates to a metallic copper particle and a process for producing the metallic copper particle. The present invention also relates to a dispersion in which the metallic copper particle is blended and a process for producing the dispersion. The present invention further relates to an electrode, a wiring pattern, and a film coating formed by using the metallic copper dispersion, and still further relates to a decorative article with the film coating formed thereon, an antimicrobial article with the film coating formed thereon, and a process for producing a metallic copper-containing film for use in them.

Background Art

[0002] Metallic copper particle is an inexpensive material having a good electrical conductivity, and has been widely used as a material for securing electrical conduction, such as a member for forming a circuit of a printed wiring board, various electrical contact members, an external electrode member for a capacitor or the like, and the metallic copper particle has been also used in an internal electrode for a multilayer ceramic capacitor in recent years.

[0003] Dispersion blending metallic copper particles is a general term that usually includes compositions, such as coating materials, paints, pastes, and inks, which is obtained by dispersing a metallic copper particle in a solvent, and further blending one or more additives such as a binder, a dispersant, and a viscosity modifier therein when necessary. Such a dispersion is used, by taking advantage of characteristics of the metallic copper particles, in various uses such as uses to secure electrical conduction, antistatic uses, uses to shield electromagnetic waves, and uses to give metallic luster or antibacterial properties. Specifically, the metallic copper particles are used, by taking advantage of characteristics thereof, for shielding electromagnetic wave in transparent members of a liquid crystal display or the like. Moreover, the technique for forming a fine electrode or a fine circuit-wiring pattern has been proposed. This technique is as follows: a dispersion blending metallic copper particles is applied on a substrate to form an electrode pattern or circuit-wiring pattern by a coating method such as screen printing or inkjet printing, and thereafter the metallic copper particles are fused by heating at a relatively low temperature. This has been being applied particularly to the production of printed wiring boards. Furthermore, the fusion between the metallic copper particles easily progresses even under a mild heating condition to exhibit metallic luster, and thus such a simple technique for preparing a mirror surface has been attracting attention in design and decoration uses. In recent years, its applications as a joining material in a device that is used at high temperatures, such as a power semiconductor, has been also studied.

[0004] As for metallic copper particle and dispersion dispersing the metallic copper particles, for example, Patent Literature 1 discloses that a metallic copper particle is generated by mixing a divalent copper oxide and a reducing agent in a solvent in the presence of a complexing agent and protective colloid to reduce the divalent copper oxide, and that the metallic copper particles obtained there are dispersed in a dispersion medium to prepare a fluid composition. Further, in Patent Literature 1, as the protective colloid, a gelatin is illustrated, and as the reducing agent, hydrazine reducing agents such as hydrazine and hydrazine compounds like hydrazine hydrochloride, hydrazine sulfate, and hydrazine hydrate; sodium borohydride, sodium sulfite, sodium hydrogen sulfite, sodium thiosulfate, sodium nitrite, and sodium hyponitrite; phosphorous acid and salts thereof such as sodium phosphite; and hypophosphorous acid and salts thereof such as sodium hypophosphite are listed.

[0005] Moreover, Patent Literature 2 discloses a dispersion including: a metallic copper particle having a gelatin on the surface of the particle; a polymeric dispersant; and an organic solvent in which the gelatin has a difference between an amine value and an acid value (amine value - acid value) of 0 or less, and the polymeric dispersant has a difference between an amine value and an acid value (amine value - acid value) of 0 to 50.

[0006] Furthermore, Patent Literature 3 discloses that a nano size metallic particle is mixed with a micron size metallic particle while performing the treatment to adsorb it on the surface of the micron size metallic particle, thereby forming a fine particle adsorbed mixed body in which the nano size metallic particle is adsorbed on the surface of the micron size metallic particle.

Citation List

Patent Literature

[0007]

Patent Literature 1: WO 2006/019144 A1
Patent Literature 2: WO 2010/024385 A1

Patent Literature 3: JP 4848674 B

Summary of Invention

Technical Problem

[0008] Patent Literatures 1 and 2 disclose the following: the metallic copper particle is obtained by reducing copper oxide with hydrazine in the presence of a gelatin are excellent in the dispersion stability and are heat-meltable at a relatively low temperature, and thus the metallic copper particles are fired under a reducing atmosphere and are suitably used in various uses such as uses to secure electrical conduction, antistatic uses, uses to shield electromagnetic waves, and uses to give metallic luster or antibacterial properties. However, in the methods disclosed in these Patent Literatures, there is the problem that the metallic copper particle cannot be easily produced for the reasons such as that a closed firing facility is required to perform a firing under a reducing atmosphere. Moreover, Patent Literature 3 discloses that a high electrical conductivity is exhibited through the heat treatment at a low temperature. In this case, however, it is considered to be difficult to sufficiently reduce the resistance of an easily oxidized metal like copper. Therefore, a metallic copper particle which can be fired under a nonreducing atmosphere such as nitrogen and which can provide an excellent sinterability at a lower temperature and a sufficiently low volume resistance value has been desired.

Solution Problem

[0009] In order to solve the above problems, the present inventors have searched for a metallic copper particle having a volume resistance value of 1×10^{-2} Ω·cm or less after heating the metallic copper particle at a temperature of 300°C under a nitrogen atmosphere. As a result, the inventors have found, for example, that the above problems can be solved by a metallic copper particle in which at least one fine metallic copper particle is adhered on the surface of a large diameter metallic copper particle, and that when copper oxide and hypophosphorous acid and/or a salt thereof are mixed in a solvent in the presence of a gelatin and/or a collagen peptide to reduce the copper oxide, the desired metallic copper particle having a volume resistance value of 1×10^{-2} Ω·cm or less after the metallic copper particle is heated at a temperature of 300°C under a nitrogen atmosphere can be unexpectedly obtained, and thus have completed the present invention. In the present invention, the "metallic copper particle" is a superordinate concept including a large diameter metallic copper particle; at least one fine metallic copper particle and an aggregate thereof; and further includes the case where a small metallic copper particle is mixed therewith.

[0010] Namely, one embodiment according to the present invention relates to (1) a metallic copper particle including at least one fine metallic copper particle and a large diameter metallic copper particle wherein the at least one fine metallic copper particle are adhered on the surface of the large diameter metallic copper particle, and another embodiment according to the present invention relates to (2) a process for producing a metallic copper particle having a volume resistance value of 1×10^{-2} Ω·cm or less after heating the metallic copper particle at a temperature of 300°C under a nitrogen atmosphere, the process comprising mixing copper oxide and hypophosphorous acid and/or a salt thereof in a solvent in the presence of a gelatin and/or a collagen peptide, thereby reducing the copper oxide.

[0011] Specifically, the present invention is as follows.

(1) A metallic copper particle including at least one fine metallic copper particle and a large diameter metallic copper particle wherein the at least one fine metallic copper particle is adhered on a surface of the large diameter metallic copper particle.

(2) The metallic copper particle according to (1), wherein an aggregate of the fine metallic copper particles is adhered on the surface of the large diameter metallic copper particle. (Hereinafter, the metallic copper particle defined in each of (1) and (2) is sometimes referred to as a "composite particle".)

(3) The metallic copper particle according to (1) or (2), further including a small metallic copper particle in a mixed state. (Hereinafter, the metallic copper particle defined in (3) is sometimes referred to as a "mixed particle" in contrast with the "composite particle".)

(4) The metallic copper particle according to (1) or (2), wherein a gelatin and/or a collagen peptide exist on at least one selected from the group consisting of the metallic copper particle, the large diameter metallic copper particle, and the at least one fine metallic copper particle.

(5) The metallic copper particle according to (3), wherein a gelatin and/or a collagen peptide exist on at least one selected from the group consisting of the metallic copper particle, the large diameter metallic copper particle, the at least one fine metallic copper particle, and the small metallic copper particle.

(6) The metallic copper particle according to (1), (2), or (4), wherein at least one selected from the group consisting of the metallic copper particle, the large diameter metallic copper particle, and the at least one fine metallic copper particle includes an organic acid and/or a salt thereof.

(7) The metallic copper particle according to (3) or (5), wherein at least one selected from the group consisting of the metallic copper particle, the large diameter metallic copper particle, the at least one fine metallic copper particle, and the small metallic copper particle includes an organic acid and/or a salt thereof.

(8) The metallic copper particle according to any one of (1) to (7), having a specific surface area of 0.1 to 10 m^2/g.

(9) A process for producing a metallic copper particle having a volume resistance value of 1×10^{-2} Ω·cm or less after heating the metallic copper particle at a temperature of 300°C under a nitrogen atmosphere, the process comprising mixing a copper oxide and hypophosphorous acid and/or a salt thereof in a solvent in the presence of a gelatin and/or a collagen peptide, thereby reducing the copper oxide.

(10) The process for producing a metallic copper particle according to (9), wherein the gelatin and/or the collagen peptide exist in 1 to 500 parts by mass with regard to 100 parts by mass of the metallic copper particle.

(11) The process for producing a metallic copper particle according to (9) or (10), wherein the reduction reaction is performed in a temperature range of 40 to 95°C.

(12) The process for producing a metallic copper particle according to any one of (9) to (11) comprising mixing the copper oxide and the hypophosphorous acid and/or the salt thereof in the solvent in the presence of the gelatin and/or the collagen peptide, and an amine complexing agent, thereby reducing the copper oxide.

(13) The process for producing a metallic copper particle according to any one of (9) to (12) comprising mixing the copper oxide and the hypophosphorous acid and/or the salt thereof in the solvent in the presence of the gelatin and/or the collagen peptide, and an organic acid, thereby reducing the copper oxide.

(14) The process for producing a metallic copper particle according to any one of (9) to (13) comprising mixing the copper oxide and the hypophosphorous acid and/or the salt thereof in the solvent in the presence of the gelatin and/or the collagen peptide, an amine complexing agent, and an organic acid, thereby reducing the copper oxide.

(15) The process for producing a metallic copper particle according to any one of (9) to (14), wherein the reduction reaction is performed at a pH of 3 or lower.

(16) A metallic copper dispersion including the metallic copper particle according to any one of (1) to (8).

Advantageous Effects of Invention

[0012] The metallic copper particle according to the present invention can be fired under a nonreducing atmosphere such as nitrogen, is excellent in sinterability at lower temperatures, and exhibits a sufficiently low volume resistance value even in the case of a low temperature heating. Moreover, by using the process for producing a metallic copper particle according to the present invention, the metallic copper particle that is excellent in sinterability at low temperatures and that exhibits a sufficiently low volume resistance value even when heated under a nonreducing atmosphere can simply be produced. Therefore, the metallic copper-containing film that is excellent in electrical conductivity and metallic color tone can be simply produced by applying a dispersion including the metallic copper particles according to the present invention on the surface of a base material or by heating the dispersion under a nonreducing atmosphere after the application. Moreover, the dispersion can be also used for joining members. Furthermore, the metallic copper-containing film can be also produced by performing heating, light irradiation, plasma irradiation, or the like under a reducing atmosphere in place of or together with heating under a nonreducing atmosphere.

[0013] For these reasons, in the present invention, metallic copper particle(s) and the dispersion including them can be used in materials for securing electrical conduction, materials for antistatic, materials for shielding electromagnetic waves, materials for giving metallic luster or antibacterial properties, and the like, and can be used particularly in uses for forming a fine electrode and a fine circuit-wiring pattern, such as a print wiring board making use of the electrical conductivity of the metallic copper-containing film, in uses for joining chips and substrates, in design and decoration uses making use of metallic color tone of the metallic copper-containing film, and the like.

Brief Description of Drawings

[0014]

[Fig. 1] Fig. 1 shows an X-ray diffraction chart for sample A produced in Example 1.
[Fig. 2] Fig. 2 shows an electron micrograph for sample A produced in Example 1.
[Fig. 3] Fig. 3 shows an electron micrograph (enlarged photograph) for sample A produced in Example 1.
[Fig. 4] Fig. 4 shows an electron micrograph for sample B produced in Example 2.
[Fig. 5] Fig. 5 shows an electron micrograph (enlarged photograph) for sample B produced in Example 2.
[Fig. 6] Fig. 6 shows an electron micrograph for sample C produced in Example 3.
[Fig. 7] Fig. 7 shows an electron micrograph (enlarged photograph) for sample C produced in Example 3.
[Fig. 8] Fig. 8 shows an electron micrograph for sample D produced in Example 4.
[Fig. 9] Fig. 9 shows an electron micrograph (enlarged photograph) for sample D produced in Example 4.

[Fig. 10] Fig. 10 shows an electron micrograph for sample E produced in Example 5.
[Fig. 11] Fig. 11 shows an electron micrograph (enlarged photograph) for sample E produced in Example 5.
[Fig. 12] Fig. 12 shows an electron micrograph for sample F produced in Example 6.
[Fig. 13] Fig. 13 shows an electron micrograph (enlarged photograph) for sample F produced in Example 6.
[Fig. 14] Fig. 14 shows an electron micrograph for sample G produced in Example 7.
[Fig. 15] Fig. 15 shows an electron micrograph (enlarged photograph) for sample G produced in Example 7.
[Fig. 16] Fig. 16 shows an electron micrograph for sample H produced in Example 8.
[Fig. 17] Fig. 17 shows an electron micrograph (enlarged photograph) for sample H produced in Example 8.
[Fig. 18] Fig. 18 shows an electron micrograph for sample I produced in Example 9.
[Fig. 19] Fig. 19 shows an electron micrograph (enlarged photograph) for sample I produced in Example 9.
[Fig. 20] Fig. 20 shows an electron micrograph for sample J produced in Example 10.
[Fig. 21] Fig. 21 shows an electron micrograph (enlarged photograph) for sample J produced in Example 10.
[Fig. 22] Fig. 22 shows an electron micrograph for sample K produced in Example 11.
[Fig. 23] Fig. 23 shows an electron micrograph (enlarged photograph) for sample K produced in Example 11.
[Fig. 24] Fig. 24 shows an electron micrograph for sample L produced in Example 12.
[Fig. 25] Fig. 25 shows an electron micrograph (enlarged photograph) for sample L produced in Example 12.
[Fig. 26] Fig. 26 shows an electron micrograph for sample M produced in Example 13.
[Fig. 27] Fig. 27 shows an electron micrograph (enlarged photograph) for sample M produced in Example 13.
[Fig. 28] Fig. 28 shows an electron micrograph for sample Z produced in Example 26.
[Fig. 29] Fig. 29 shows an electron micrograph (enlarged photograph) for sample Z produced in Example 26.
[Fig. 30] Fig. 30 shows an electron micrograph for sample AE produced in Comparative Example 1.
[Fig. 31] Fig. 31 shows an electron micrograph (enlarged photograph) for sample AE produced in Comparative Example 1.
[Fig. 32] Fig. 32 shows an electron micrograph for sample AF produced in Comparative Example 2.
[Fig. 33] Fig. 33 shows an electron micrograph (enlarged photograph) for sample AF produced in Comparative Example 2.
[Fig. 34] Fig. 34 shows an electron micrograph for sample AG produced in Comparative Example 3.
[Fig. 35] Fig. 35 shows an electron micrograph (enlarged photograph) for sample AG produced in Comparative Example 3.
[Fig. 36] Fig. 36 shows an electron micrograph of a cross section of a metallic copper-containing film produced by heating, at 120°C in the air, sample Q produced in Example 17.
[Fig. 37] Fig. 37 shows an electron micrograph (enlarged photograph) of a cross section of a metallic copper-containing film produced by heating, at 120°C in the air, sample Q produced in Example 17.

Description of Embodiments

[0015] In the present invention, the "metallic copper particle" is a composite particle in which two kinds of particles each having a relatively different particle diameter are composited. Herein, the particle having a larger particle diameter is referred to as the "large diameter metallic copper particle", and the particle having a smaller particle diameter are referred to as the "fine metallic copper particle". The "particle diameter" does not necessarily mean the average primary particle diameter, and is appropriately defined in consideration of the shape, distribution, and the like. Specifically, the metallic copper particle according to the present invention is a metallic copper particle which includes a large diameter metallic copper particle and at least one fine metallic copper particle adhered on the surface of the large diameter metallic copper particle, and is a particle in which the at least one fine metallic copper particle and the large diameter metallic copper particle are composited and not merely mixed. It is preferable that an aggregate of the fine metallic copper particles is adhered on the surface of the large diameter metallic copper particle. The metallic copper particle according to the present invention also includes one in which a "small metallic copper particle" of a different type from the above composite particle is mixed in addition to the above composite particle.

[0016] The "metallic copper" in the present invention is a substance having metallic property, the substance including at least metal copper, metal copper alloy, or copper hydride, and the "metallic copper" may be metal copper or an alloy including metal copper as the main component, such as a copper-tin, copper-zinc, copper-bismuth, copper-nickel, copper-lead, or copper-phosphorus alloy. Copper hydride is classified as a copper compound, but is converted to metal copper by heating, and thus is defined herein as included in the metallic copper. Moreover, the metallic copper particle may be a particle of which the surface is coated with a metal such as silver or tin, a metallic copper alloy, or a metal oxide such as silica or alumina, and may also include an impurity, a copper compound, a copper alloy, a stabilizer against oxidation, or the like on the surface or inside of the metallic copper particle as long as the inclusion of them does not affect its uses. For example, phosphorus of a component of a reducing agent is liable to remain in the metallic copper particle. The content of phosphorus can be adjusted by the amount of phosphorus to be used during the reduction reaction, washing after the reduction reaction, or the like, and is preferably about 0 to about 5 parts by mass with regard to 100 parts by mass of the metallic copper particle, more preferably 0 to 2 parts by mass, still more preferably 0 to 1 part by mass. The gelatin and/or the collagen peptide which act as a protective colloid also remain on the surface or the like of the metallic copper particle, but the content thereof can be adjusted by the amount of the gelatin and/or the collagen peptide to be used or by removing the gelatin and/or the collagen peptide after the reduction reaction. Moreover, in the case where a complexing agent is used, the complexing agent is included in the metallic copper particle according to the amount of the complexing agent to be used.

[0017] In the present invention, the "large diameter metallic copper particle" refers to a coarser particle compared with the fine metallic copper particle described below. The shape of the large diameter metallic copper particle is not particularly limited, and the large diameter metallic copper particle having an arbitrary shape can be used. For example, a particle having a shape constituted by a curved surface such as a spherical shape or an elliptical shape, a particle having a shape constituted by a polyhedron such as a flat shape, a granular shape, a rectangular parallelepiped shape, a cubic shape, a rod shape, a needle-shaped particle, or a wire shape, a particle having such a shape as flat plates are combined, and a particle having an irregular shape which cannot be specified in shape can be used, and these particles may be mixed. With respect to the particle having such a shape as flat plates are combined, it can be confirmed that such a particle partially exists in the electron micrographs shown in, for example, Figs. 2, 4, and 6. In the present invention, the shape of the metallic copper particle, the large diameter metallic copper particle, the fine metallic copper particles and an aggregate thereof can be observed with a scanning electron microscope (which is sometimes written as "SEM" hereinafter). The particle having a flat shape refers to a particle of which the thickness is thinner with regard to the flat surfaces of the particle. It is preferable that in view of the volume resistivity after heating, the large diameter metallic copper particle is a particle having such a shape as flat plates are combined, a particle having a flat shape, or a particle having a granular shape, or the like.

[0018] The particle diameter of the large diameter metallic copper particle can be appropriately selected according to its uses (e.g. film thickness, film width, and the like). In the case where the particle diameter can be specified by the average primary particle diameter, it is preferable that the average primary particle diameter is generally 0.1 to 100 μm, and the range of 1.0 to 30 μm is more preferable. The average primary particle diameter is preferably at least 5 times as large as that of the fine metallic copper particles described below. The average primary particle diameter is determined by measuring the particle diameters of 100 or more particles that are randomly selected from an SEM image and calculating the number average of the measured particle diameters. In the case of a highly anisotropic particle, the maximum diameter of the particle is defined as a particle diameter of the particle. For example, in the case of particles having a flat shape, the average width of the flat surfaces of the particles (specifically, average value of maximum diameters of the flat surfaces of the particles) is defined as the average primary particle diameter, and the average primary particle diameter thereof is preferably in a range of 0.1 to 100 μm, more preferably in a range of 0.5 to 50 μm, and still more preferably in a range of 1.0 to 30 μm. The average thickness of the particles having a flat shape can be appropriately set, and the average thickness thereof is preferably 0.005 to 10 μm, more preferably 0.01 to 10 μm, and still more preferably 0.05 to 5 μm. In the case of particles having a granular shape or the like, the average primary particle diameter of the particles (specifically, average value of maximum diameters of the particles) is preferably in a range of 0.1 to 100 μm, more preferably in a range of 0.5 to 50 μm, and still more preferably in a range of 1.0 to 30 μm.

[0019] The "fine metallic copper particle" in the present invention refer to a finer particle than the large diameter metallic copper particle (, namely, a particle having smaller particle diameter than the large diameter metallic copper particle), and the component composition thereof may be the above metallic copper having the same quality as the large diameter metallic copper particle, or may be the above metallic copper having the different quality from the large diameter metallic copper particle. The shape of the fine metallic copper particle is not particularly limited, and the fine metallic copper particle having an arbitrary shape can be used. In the case where the particle diameter is specified by the average primary particle diameter, the average primary particle diameter of the fine metallic copper particles is preferably in a range of 2 to 500 nm, more preferably 5 to 300 nm, and still more preferably in a range of 10 to 250 nm. The average primary particle diameter of the fine metallic copper particles is also determined by measuring each maximum particle diameter of the 100 or more fine metallic copper particles that are randomly selected from an SEM image and calculating the number average of the measured maximum particle diameters. In the case where the particle shape in the aggregated interface between the adjacent particles may be unclear because at least part of the fine metallic copper particles in the present invention form an aggregate as described below. In this case, however, the particle shape may be estimated from its outline.

[0020] In the case where the particle diameter can be specified by the average primary particle diameter, when the average primary particle diameter of the fine metallic copper particles is, for example, 400 nm within the preferable range of 2 to 500 nm described above, the range of 0.1 to 100 μm which is described above as a generally preferable range of the average primary particle diameter of the large diameter metallic copper particle means a range larger than 0.4 μm to 100 μm or smaller (a range of 2 μm to 100 μm when it is further required considering that the average primary particle diameter of the large diameter metallic copper particles is preferably at least 5 times as large as that of the fine metallic copper particles) within the range. When the average primary particle diameter of the fine metallic copper particles is, for example, 10 nm, it is meant that the range of 0.1 to 100 μm which is described above as a generally preferable range of the average primary particle diameter of the large diameter metallic copper particles is preferable. The average primary particle diameter of the fine metallic copper particles is preferably 1/5 or smaller of the average particle diameter of the large diameter metallic copper particles, more preferably 1/7 or smaller, and still more preferably 1/10 or smaller.

[0021] Regarding the fine metallic copper particle, it is preferable that an aggregate is formed by the aggregation of a plurality of the fine metallic copper particles. The "aggregation" herein is distinguished from "agglomeration" referring to a state where adjacent particles are in contact with each other at a point(s), and refers to a state where adjacent particles are bound each other through necking or fusion or a state where adjacent particles share a face(s) each other. It can be confirmed through the observation of a SEM image whether the aggregate is formed by the aggregation of a plurality of the fine metallic copper particles. In the case where the particles share a face(s) each other even when an interface is observed between the particles, the particles are considered as forming an aggregate. A plurality of the fine metallic copper particles may aggregate to form a particle having an irregular shape. The aggregate is formed by the aggregation of the two or more fine metallic copper particles, preferably the three or more fine metallic copper particles, and more preferably the four or more fine metallic copper particles.

[0022] The metallic copper particle of the present invention is a composite particle in which at least one fine metallic copper particle is adhered on the surface of the large diameter metallic copper particle, and preferably, an aggregate formed by the aggregation of the fine metallic copper particles are adhered on the surface of the large diameter metallic copper particle. The adhesion may be performed by aggregation, adsorption, or combination thereof. It can be confirmed through the observation of a SEM image whether at least one fine metallic copper particle and/or the aggregate of the fine metallic copper particles is adhered on the surface of the large diameter metallic copper particle. When the large diameter metallic copper particle and at least one fine metallic copper particle are merely mixed, the adhesion state of them cannot be obtained, and the state where a plurality of the fine metallic copper particles aggregate cannot be also obtained. Additionally, in this case, the large diameter metallic copper particle and the fine metallic copper particle(s) exist individually. Thus, the large diameter metallic copper particle and the fine metallic copper particle(s) can be clearly distinguished from the metallic copper particle according to the present invention. Also, all of the fine metallic copper particles do not necessarily form the aggregate, and some of the fine metallic copper particles may be adhered as an agglomerate or single particle on the surface of the large diameter metallic copper particle. It is preferable that the aggregation between the large diameter metallic copper particles less frequently occurs. As described below, the particle which constitutes the above metallic copper particle, namely, the particle having a flat shape; the particle having a granular shape or the like; the particle having such a shape as flat plates are combined; or the particle having an irregular shape can be produced by adjusting the amount of the gelatin and/or the collagen peptide, or the complexing agent to be used at the time of the reduction reaction and the condition of the reduction reaction, and further the metallic copper particles in the states where these particles are mixed can be also produced thereby.

[0023] It is preferable that one embodiment of the metallic copper particle according to the present invention is a mixed particle including the above metallic copper particle (i.e. composite particle) in a mixed state with a small metallic copper particle of a different type from it. The "the small metallic copper particle" refer to, in the state of being mixed with the above metallic copper particle (i.e. the composite particle in which the at least one fine metallic copper particle and/or an aggregate thereof are adhered on the surface of the large diameter metallic copper particle), a particle(s) other than the above composite particle. In this case, the component composition thereof may be the above metallic copper having the same quality as the composite particle or may be the above metallic copper having the different quality from it. It is preferable that the particle diameter of the small metallic copper particle is smaller than that of the above large diameter metallic copper particle (in other words, the particle diameter of the above large diameter metallic copper particle is larger than that of the small metallic copper particle). In the case where the particle diameter can be specified by the average primary particle diameter, the average primary particle diameter of the small metallic copper particles is, for example, preferably in a range of 2 to 1000 nm, more preferably in a range of 5 to 500 nm, and still more preferably 10 to 400 nm. The average primary particle diameter of the small metallic copper particles is also determined by measuring the maximum particle diameter of each of 100 or more particles that are randomly selected from an SEM image and calculating the number average of the measured maximum particle diameters. The shape of the small metallic copper particle is not particularly limited, and the small metallic copper particle having an arbitrary shape can be used.

[0024] The state where the composite particle and the small metallic copper particle are mixed is obtained by simultaneously producing the composite particle and the small metallic copper particle as well as by separately adding the small metallic copper particle to the produced composite particle. By employing such a state, sinterability thereof at a further lower temperature becomes excellent, and a much lower volume resistance value is provided even in the case of a low temperature heating, compared with the case where the metallic copper particle (i.e. composite particle) is singularly used. The reason is not necessarily clear, but it is considered that a large number of the small metallic copper particles exist in spaces between the metallic copper particles (i.e. composite particles) during the film formation, thereby enhancing the conduction among the metallic copper particles. It is favorable that the small metallic copper particle exists independently from the metallic copper particle, namely, a state where the small metallic copper particle is not adhered on the surface of the large diameter metallic copper particle but exist individually from the metallic copper particle is preferable. The state of the small metallic copper particle is not particularly limited, and the small metallic copper particle may exist in the state of a single particle, may exist in the state of an agglomerate formed by gathering a plurality of the small metallic copper particles, may exist in the state of an aggregate of the small metallic copper particles as in the case of the fine metallic copper particles, or may exist in the state of the mixture of them. The mixing ratio of the metallic copper particle (i.e. composite particle) and the small metallic copper particle can be appropriately set, but the amount of the small metallic copper particle is preferably in a range of 1 to 50% by mass with regard to the metallic copper particle (i.e. composite particle), more preferably in a range of 2 to 30% by mass, and still more preferably in a range of 3 to 20% by mass.

[0025] As an index of the volume resistance value of the metallic copper particle according to the present invention, the volume resistance value of a metallic copper-containing film prepared by heating and firing the metallic copper particles at a temperature of 300°C under a nitrogen atmosphere is used. Specifically, the volume resistance value measured according to the "< Method 1 for Measuring Volume Resistance Value >" described below is $1 \times 10^{-2}\ \Omega\cdot\text{cm}$ or less, preferably $1 \times 10^{-3}\ \Omega\cdot\text{cm}$ or less, and more preferably $1 \times 10^{-4}\ \Omega\cdot\text{cm}$ or less. In this way, when using the metallic copper particle according to the present invention, its sintering occurs even when being heated at a temperature of 300°C under a nitrogen atmosphere, and thus has a low volume resistance value and a high electrical conductivity.

< Method 1 for Measuring Volume Resistance Value >

[0026] A copper paste is prepared by: mixing 10 g of a metallic copper powder, 3.5 g of a vehicle (resin: 20% by mass of ethyl cellulose N200 and solvent: terpineol), and 6.5 g of terpineol; and then kneading the mixture with a three-roll mill. The prepared copper paste is applied to an alumina substrate and fired, using an atmosphere tube furnace, at 300°C for one hour under a nitrogen atmosphere to prepare a metallic copper-containing film. The specific resistance value of the prepared metallic copper-containing film is measured using MCP-T610 Loresta GP manufactured by Mitsubishi Chemical Analytech Co., Ltd. by a direct current four-terminal method. Thereafter, the cross section is observed with a scanning electron microscope to measure the film thickness, and the volume resistance value is calculated with regard to the specific resistance value.

[0027] The metallic copper particle according to the present invention has a low volume resistance value after heating it at a temperature of 300°C under a nitrogen atmosphere. Therefore, a copper-containing film or joined body having a low volume resistance value can be produced even at a temperature of 300°C or lower under a nonreducing atmosphere (namely, under an inert atmosphere) such as nitrogen or argon, and a copper-containing film or joined body having a low volume resistance value can be also produced even at a temperature of 300°C or lower under a reducing atmosphere such as hydrogen. It is preferable that the heating temperature of the metallic copper particle according to the present invention is a lower temperature in the case where plastic is used as a base material. For example, a temperature of 200°C or lower is more preferable, and a temperature of 150°C or lower is still more preferable. Furthermore, a copper-containing film having a low volume resistance value can be also produced by performing light irradiation, plasma irradiation, or the like in place of or together with the heating under the above non-reducing atmosphere (i.e. under an inert atmosphere) or under the above reducing atmosphere.

[0028] In this way, the metallic copper particle according to the present invention can be fired under a nonreducing atmosphere such as nitrogen, is excellent in sinterability at a lower temperature, and exhibits a sufficiently low volume resistance value even in the case of a low temperature heating. The reason is not necessarily clear, but it is considered that the sinterablity at a low temperature and the reduction in the volume resistivity are provided, for example, by the following: the melting point of the fine metallic copper particle is dominantly low; the increase in the melting point due to aggregation when the fine metallic copper particles form an aggregate thereof is unexpectedly small; it is presumed that the contact area with the air outside becomes small to suppress the oxidation of the fine metallic copper particles by forming the aggregate; and further, the gaps between the large diameter metallic copper particles having a volume resistance value comparable to that of the bulk are efficiently connected by the fine metallic copper particle(s) (and/or an aggregate thereof) or the small metallic copper particle mixed therewith during heating.

[0029] The metallic copper particle according to the present invention is, as described above, the following: a composite particle in which at least one fine metallic copper particle and/or an aggregate thereof are adhered on the surface of a large diameter metallic copper particle; or a mixed particle including the composite particle in which the at least one fine metallic copper particle and/or the aggregate thereof are adhered on the surface of the large diameter metallic copper particle, in a mixed state with a small metallic copper particle.

[0030] In the metallic copper particle according to the present invention, it is preferable that at least one selected from the group consisting of the metallic copper particle, the large diameter metallic copper particle, the at least one fine metallic copper particle, and the small metallic copper particle has a gelatin and/or a collagen peptide, and it is more preferable that the surface of the metallic copper particle and/or the surface of the at least one fine metallic copper particle have a gelatin and/or a collagen peptide. In addition, the meaning of "the at least one fine metallic copper particle has a gelatin and/or a collagen peptide" is not only that non-aggregated fine metallic copper particles have the gelatin or the like but also that at least one fine metallic copper particle constituting an aggregate has the gelatin or the like.

[0031] Namely, in the metallic copper particle according to the present invention, it is preferable that the gelatin and/or the collagen peptide exist on at least one selected from the group consisting of the metallic copper particle (i.e. the composite particle in which the at least one fine metallic copper particle and/or an aggregate thereof are adhered on the surface of the large diameter metallic copper particle), the large diameter metallic copper particle and the at least one fine metallic copper particle which constitute the above composite particle. In the case of the mixed particle in which the small metallic copper particle is mixed with the above composite particle, it is preferable that the gelatin and/or the collagen peptide exist on at least one selected from the group consisting of the metallic copper particle (i.e. composite particle), the large diameter metallic copper particle, the at least one fine metallic copper particle, and the small metallic copper particle. Among others, it is more preferable that the gelatin and/or the collagen peptide exist on the surface of the composite particle and/or the surface of the at least one fine metallic copper particle constituting the composite particle. As a result, the oxidation of the metallic copper particle in the presence of oxygen can be suppressed, and thus the volume resistivity after heating can be further reduced. Moreover, the gelatin and the collagen peptide serve as protective colloid, and can suppress the agglomeration of the metallic copper particles in an aqueous solvent. It is preferable that the gelatin and/or the collagen peptide exist in a range of about 0.1 to about 15 parts by mass with regard to 100 parts by mass of the metallic copper particle and the like (namely, at least one particle selected from the above group wherein the at least one particle has the gelatin and/or the collagen peptide) because desired effects are obtained, and the more preferable range is about 0.1 to about 10 parts by mass. The details about the gelatin and/or the collagen peptide that can be used will be described in the paragraphs related to the production process. The content of the gelatin is determined by performing CHN analysis of the metallic copper particle based on the assumption that the total amounts of C, H, and N in % by mass satisfying the ratio of C, H, and N in the used gelatin originates in the gelatin.

[0032] In the metallic copper particle according to the present invention, it is preferable that at least one selected from the group consisting of the metallic copper particle, the large diameter metallic copper particle, the at least one fine metallic copper particle, and the small metallic copper particle includes an organic acid and/or a salt thereof. In addition, the meaning of "the at least one fine metallic copper particle includes an organic acid and/or a salt thereof" is not only that non-aggregated fine metallic copper particles include an organic acid or the like but also that the at least one fine metallic copper particle constituting an aggregate includes an organic acid or the like.

[0033] Namely, in the metallic copper particle according to the present invention, it is preferable that the organic acid and/or a salt thereof exist on at least one selected from the group consisting of the metallic copper particle (i.e. the composite particle in which the at least one fine metallic copper particle and/or an aggregate thereof are adhered on the surface of the large diameter metallic copper particle), the large diameter metallic copper particle and the at least one fine metallic copper particle which constitute the above composite particle. In the case of the mixed particle in which the small metallic copper particle is mixed with the above composite particle, it is preferable that the organic acid and/or a salt thereof exist on at least one selected from the group consisting of the metallic copper particle (i.e. composite particle), the large diameter metallic copper particle, the at least one fine metallic copper particle, and the small metallic copper particle. The organic acid and/or a salt thereof may exist in a mixed state with the metallic copper particle, or may be adsorbed on the surface of the metallic copper particle. In particular, it is preferable that the organic acid and/or a salt thereof are adsorbed on the surface of the metallic copper particle. It is considered that the organic acid and/or a salt thereof facilitate the sintering between the metallic copper particles at a low temperature during heating, and the volume resistivity after heating the metallic copper particle at a low temperature can be much more reduced. Specifically, the volume resistance value of a metallic copper-containing film prepared by heating and firing the metallic copper particles at a temperature of 120°C under an air atmosphere is used as an index, and a volume resistance value of 1×10^{-1} $\Omega \cdot$cm or less can be achieved in terms of the volume resistance value measured according to the "< Method 2 for Measuring Volume Resistance Value >" described below, and further a metallic copper-containing film having a volume resistance value in the order of 1×10^{-3} $\Omega \cdot$cm can be also obtained. Examples of the organic acid and/or a salt thereof include carboxylic acids, amino acids, aminocarboxylic acids and salts thereof. Among them, carboxylic acids are preferable, and formic acid is more preferable. In the case where the metallic copper particle and the like include the organic acid and/or a salt thereof, the content thereof can be appropriately set, but is preferably set to 0.01 to 1% by mass in the metallic copper particle and the like.

[0034] The specific surface area of the metallic copper particle according to the present invention, which is measured by a nitrogen adsorption BET method is preferably about 0.1 to about 10 m^2/g, more preferably about 0.2 to about 8 m^2/g, still more preferably about 0.3 to about 7 m^2/g, and much more preferably about 1 to about 6 m^2/g. It is considered that the specific surface area of the metallic copper particle reflects an abundance ratio of the large diameter metallic copper particle and the at least one fine metallic copper particle (In this regard, in the case where the small metallic copper particle is mixed therewith, the above abundance ratio further includes them.). In the case where the BET specific surface area is within the above range, the metallic copper particle is excellent in sinterability at a further lower temperature and exhibits a much lower volume resistance value even in the case of a low temperature heating.

[0035] Among others, the metallic copper particle having a specific surface area in a range of 1 to 5 m^2/g provides a metallic copper-containing film exhibiting electrical conductivity when being heated at a temperature of 120°C under an air atmosphere. Specifically, the volume resistance value is used as an index, and a volume resistance value in the order of $1 \times 10^{+1}$ $\Omega\cdot$cm can be achieved in terms of the volume resistance value measured according to the "< Method 2 for Measuring Volume Resistance Value >" described below, and further a metallic copper-containing film that exhibits a volume resistance value of 1×10^{-1} $\Omega\cdot$cm or less is obtained. In this way, the metallic copper particle according to the present invention has a low volume resistance value and a high electrical conductivity because the sinterability or the contact property between the particles are improved even when heating the metallic copper particle at a temperature of 120°C under an air atmosphere. Therefore, the metallic copper particle according to the present invention can be used with a base material having a low heat resistance temperature, and can be employed in a wide range of uses. Moreover, the firing in the air can be performed, and thus constraints on facilities such as control of an atmosphere can be avoided.

< Method 2 for Measuring Volume Resistance Value >

[0036] A copper paste is prepared by: mixing 5 g of a metallic copper powder, a phenol resin (0.62 g of Resitop: PL-5208 (containing 59% by weight of phenol resin as active ingredient)), and 0.26 g of ethylene glycol monobutyl ether acetate using a deaerating stirrer; and then kneading the mixture with a three-roll mill. The prepared copper paste is applied to an alumina substrate and fired at 120°C for 10 minutes in a natural convection type drier to prepare a metallic copper-containing film. The specific resistance value of the obtained metallic copper-containing film is measured using MCP-T610 Loresta GP manufactured by Mitsubishi Chemical Analytech Co., Ltd. by a direct current four-terminal method. Thereafter, the cross section is observed with a scanning electron microscope to measure the film thickness, and the volume resistance value is calculated based on the above specific resistance value.

[0037] The metallic copper particle according to the present invention, when being blended with a solvent, a resin, and the like to prepare a dispersion, exhibits a high fluidity even in the case where the concentration is high. Dispersion including metallic particles in a nano order is generally liable to lose fluidity when the concentration thereof becomes high. Micronization of a metallic copper particle, which is a general method for improving the sinterability at a low temperature, is in a trade-off relation with fluidity of the dispersion, and thus it is difficult to make the concentration of the dispersion high. To the contrary, when using the metallic copper particle according to the present invention, the dispersion which has such an excellent sinterability at a low temperature that the sintering can be performed even by heating at 120°C in the air and which maintains a sufficient fluidity even when the concentration of the metallic copper particle is made to be 50% by mass or more can be prepared. The reason is not clear, but it is considered that the capture of a solvent and the like can be reduced because the at least one fine metallic copper particle is adhered on the large diameter metallic copper particle or because the fine metallic copper particles in a state of aggregation thereof are adhered on the large diameter metallic copper particle. Due to this characteristic, the metallic copper dispersion according to the present invention can be suitably used in joining materials and the like for which a high concentration dispersion is required.

[0038] The metallic copper particle according to the present invention can be applied to various kinds of dispersions (coating materials, paints, metallic pastes, inks, and the like), and is suitable for the application in metallic pastes among others. The metallic paste herein is a paste including a metallic copper particle, a binder resin, a solvent, and the like as main components, in which a surfactant, a crosslinking agent, a polymeric dispersant, or the like are appropriately blended, thereby providing suitable fluidity and viscosity. The metallic paste can be used for various kinds of printing, and can be suitably used for printing by a platemaking, particularly. Examples of the printing by a platemaking include screen printing, offset printing, and gravure printing, and the screen printing is preferable in view of thick-film formation. The screen printing is a method of placing a paste on a screen in which holes corresponding to a wiring or electrode pattern are formed, followed by rubbing off the paste with a squeegee to print the wiring or electrode pattern on a substrate. By the screen printing, printing to form a thick film having a thickness of several μm to several tens μm can be easily performed, and thus the screen printing is often utilized in a production process of printed wiring boards, electronic parts, or flat panel displays. It is desirable that the metallic paste has a certain degree of viscosity in view of thick-film formation, and a metallic paste having a viscosity of 2000 mPa·s or higher is generally used.

[0039] The metallic copper particle according to the present invention has a characteristic that the thixotropy index value is relatively high when a metallic paste is prepared by blending the metallic copper particle with a solvent, a resin, and the like. The thixotropy index (which is referred to as TI value, hereinafter) herein is a value calculated from a viscosity ratio of the viscosity (ηa) of the metallic paste when the metallic paste is stirred at a predetermined low shear rate to the viscosity (ηb) of the metallic paste when the metallic paste is stirred at a predetermined high shear rate, and is specifically calculated from the following expression.

$$\mathrm{TI} = \eta a/\eta b$$

[0040] The measurement of the viscosity ηa and the viscosity ηb that are needed for calculation of the TI value is performed under the following condition.

<Method for Preparing Metallic Paste>

[0041] A metallic paste (Cu solid content of 75% by mass) is prepared by: mixing 9 g of a metallic copper powder, 1 g of a vehicle (resin: 20% by mass of ethyl cellulose N200, and solvent: terpineol), and 2 g of terpineol; and kneading the mixture with a three-roll mill.

<Method for Measuring Viscosity of Metallic Paste>

[0042] The viscosity of the metallic paste is measured using a B type viscometer (model HB DV-I+) manufactured by Brookfield AMETEK. The measurement temperature is set at 20°C, and CPE-52 is used as a corn spindle. The viscosity (ηa) at a shear rate of 10 [1/sec] and the viscosity (ηb) at a shear rate of 100 [1/sec] are measured, and the TI value is calculated by applying the measured ηa and ηb to the above expression.

[0043] The fact that the TI value is high means that although the viscosity of a paste is suitably maintained in a normal state, when a high shear force is applied to the paste, the viscosity thereof is easily lowered. In a metallic paste using the metallic copper particle according to the present invention, the TI value can be set to be dominantly high value, and specifically, the TI value can be set to be 3.0 or more, preferably 3.5 or more, and more preferably 4.0 or more. Therefore, for example, in the screen printing, the fluidity of the metallic paste during continuous printing becomes favorable, and a thick film can be obtained after completion of patterning on a substrate. Moreover, cracks, disconnection, short-circuits, bleeding, and the like are suppressed, and thus the thick film can be reproducibly obtained during continuous printing. Furthermore, in printing such as inkjet printing in which a high shear force is applied to the metallic paste, ejection of the metallic paste from holes can be made smooth, and fixing of the metallic paste to a printing medium can be made favorable.

[0044] The reason that the TI value of the metallic copper dispersion (i.e. metallic paste) as an embodiment according to the present invention is high is not necessarily clear, but it is considered that the at least one fine metallic copper particle (and/or an aggregate of the fine metallic copper particles) adhered on the large diameter metallic copper particle or (in the case where the small metallic copper particle is mixed therewith,) the small metallic copper particle serves such a function as a lubricant so as to contribute to the improvement of the TI value.

[0045] Next, the present invention relates to a method for producing the metallic copper particle, and in the method, a copper compound and hypophosphorous acid and/or a salt thereof are mixed in a solvent in the presence of a gelatin and/or a collagen peptide to reduce the copper compound, thereby producing the metallic copper particle. In the present invention, it is preferable to use a gelatin and/or a collagen peptide, copper oxide, and hypophosphorous acid and/or a salt thereof. By using these three compounds, the metallic copper particle having a volume resistance value of 1×10^{-2} Ω·cm or less after the metallic copper particle is heated at a temperature of 300°C under a nitrogen atmosphere can be easily produced. Particularly, according to this method, the large diameter metallic copper particle and the at least one fine metallic copper particle each of which has a different average particle diameter can be produced by a single reduction operation, and thus there is no need to perform a complicated treatment that powders each of which has a different average particle diameter are mixed. Moreover, a metallic copper particle including a large diameter metallic copper particle and at least one fine metallic copper particle wherein the at least one fine metallic copper particle is adhered on the surface of the large diameter metallic copper particle can be also prepared. Further, the metallic copper particle in which an aggregate of a plurality of the fine metallic copper particles is adhered on the surface of the large diameter metallic copper particle can be also prepared. Furthermore, when a mixed particle in which the small metallic copper particle is mixed with the composite particle adhering the at least one fine metallic copper particle and/or an aggregate thereof on the surface of the large diameter metallic copper particle, the metallic copper particle (i.e. composite particle) and the small metallic copper particle each of which has a different shape and particle diameter can be easily produced by a single reduction operation.

[0046] The gelatin includes the following: a gelatin in a state as extracted; a gelatin obtained by hydrolyzing the above gelatin in a state as extracted so as to become lower the molecular weight (, which is sometimes referred to as a "collagen peptide", hereinafter); and a gelatin obtained by chemically modifying these gelatins (, which is sometimes referred to as a "modified gelatin", hereinafter). In general, a gelatin is an animal protein obtained from a collagen as a parental material. In the production process of a gelatin, a pretreatment of raw materials is performed with an inorganic acid such as hydrochloric acid or sulfuric acid, or lime in order to efficiently extract a high-quality gelatin from raw materials such as cattle bones, cattle hides, and pig hides. The gelatin obtained through the pretreatment with the inorganic acid is called an "acid-treated gelatin" and the gelatin obtained from the pretreatment with the lime is called an "alkali-treated gelatin" (or "lime-treated gelatin"). During the process of extracting a gelatin, an acid amide in a collagen is hydrolyzed, and releases ammonia to change into a carboxyl group, and thus the isoionic point of the gelatin is lowered. Because particularly the alkali-treated gelatin is deamidized to nearly 100% in a liming process, the isoionic point is in an acidic region, and the pH thereof is nearly 5. On the other hand, the acid-treated gelatin has a low deamidization ratio because of a short raw material treatment period, and thus has an isoionic point in an alkaline region, and the pH thereof is about 8 to about 9 near the isoionic point of a collagen. For these reasons, a gelatin has an amine value because of having a basic group and a hydroxy group, and further has an acid value because of having an acidic group. In the present invention, it is preferable that the gelatin exists on the surface of the metallic copper. More preferably, the gelatin is the alkali-treated gelatin. Also, the gelatin having a difference between the amine value and the acid value measured according to the method described below, namely "(amine value - acid value)", of 0 or less is preferable. More preferably, the difference between the amine value and the acid value is in a range of -50 to 0. Compared with the acid-treated gelatin, the alkali-treated gelatin exhibits excellent effects as a protective colloid of the metallic copper particle, and thus is preferable.

[0047] Moreover, the collagen peptide (i.e. hydrolyzed gelatin) is, directly or through a gelatin, obtained by hydrolyzing a collagen (specifically, collagen protein) included in animal bones and hides by means of an enzyme, acid, alkali, or the like. As a hydrolysis method for obtaining the collagen peptide (i.e. hydrolyzed gelatin), conventionally known methods can be used. For example, the hydrolysis can be performed according to a method of using an enzyme, a method of using chemical treatment with an acid or alkali, or the like. As the enzyme, any enzyme may be used as long as the enzyme has a function of cleaving a peptide bond of a gelatin. The enzyme is usually called a proteolytic enzyme or protease. Specific examples of the enzyme include a collagenase, a thiol protease, a serine protease, an acidic protease, an alkaline protease, a metal protease, or the like, and one of them may be singularly used, or two or more thereof may be used in combination. Examples of the thiol protease include plant-derived thiol proteases such as a chymopapain, papain, a promelain, and a ficin and animal-derived thiol proteases such as a cathepsin, and calcium-dependent proteases. Examples of the serine proteases include trypsin, cathepsin D, or the like. Examples of the acid protease include hepsin, chymosin, or the like. When the enzyme is used, it is preferable to use 0.01 to 5 parts by mass of the enzyme with regard to 100 parts by mass of the gelatin before the hydrolysis treatment, and it is preferable that the temperature condition of the hydrolysis is 30 to 70°C and the treatment time is 0.5 to 24 hours. When the hydrolysis is performed using the enzyme, deactivation of the enzyme is performed after the treatment. The deactivation of enzyme is performed by heating, and the heating temperature is, for example, 70 to 100°C.

[0048] When the acid or alkali is used, it is preferable to set the pH of the gelatin solution to be 3 or less, or 10 or more, and it is preferable that the temperature condition of the hydrolysis is 50 to 90°C and the treatment time is 1 to 8 hours. Examples of the acid include hydrochloric acid, sulfuric acid, and nitric acid. Examples of the alkali include sodium hydroxide and calcium hydroxide. When the hydrolysis is performed with the acid or alkali, desalting is performed by neutralization with a neutralizing agent or by an ion exchange resin. At the time when the hydrolysis treatment is completed, the hydrolyzed gelatin is dissolved or dispersed in the hydrolysis treatment liquid. Various purification treatments which are usually used can be applied to this solution. The purification treatment is not particularly limited. For example, activated carbon can be added to improve tone of color or textures, or remove impurities, or conventionally known solid-liquid separation treatment such as filtration or centrifugal separation can be applied to remove impurities.

[0049] The modified gelatin may be obtained by chemically modifying gelatin, namely, by chemically modifying a side chain of each amino acid residue, a terminal amino group, a terminal carboxyl group, or the like, included in a gelatin. For example, by chemically modifying the side chain of amino acid residues included in the gelatin to introduce the following: a functional group including a nitrogen element, such as an amino group, an imino group, a cyano group, an azo group, an azi group, a nitrile group an isonitrile group, a diimide group, a cyano group, an isocyanate group, and a nitro group; a functional group including a sulfur element, such as a thiol group, sulfone group, a sulfide group, and a disulfide group; and a functional group including both the nitrogen element and the sulfur element, such as a thioisocyanate group and a thioamide group, the average particle diameter of the metallic copper particle to be obtained can be controlled to various levels according to the kind and amount of the above functional groups.

[0050] As a general chemical modification method, for example, the method having the steps of: adding a water-soluble carbodiimide to a gelatin solution so as to activate a carboxyl group included in a gelatin; and then reacting an arbitrary amino compound with the activated carboxyl group to amidate the gelatin can be used. According to this method, for example, an amino acid such as methionine, which includes a sulfur element or an amino acid such as lysine, which includes a nitrogen element can be simply introduced. Examples of the water-soluble carbodiimide include 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC), 1-cyclohexyl-3-(2-morpholinyl-4-ethyl)carbodiimide ·p-toluenesulfonic acid salt (CMC), N,N'-dicyclohexylcarbodiimide (DCC), and the like. The gelatin that is applicable to the present invention may be gelatin obtained by performing the hydrolysis treatment and the chemical modification. In this case, the chemical modification may be performed after the hydrolysis treatment, or the hydrolysis treatment may be performed after the chemical modification.

[0051] In the present invention, the average particle diameter of the metallic copper particle can be controlled by selecting whether the size of the average molecular weight of the gelatin is large or small. In this case, regardless of the measurement methods of the average molecular weight such as the mass average molecular weight and the number average molecular weight, any measurement methods can be used as the judgment standard on whether the size of the average molecular weight of the gelatin is large or small. Specifically, taking the mass average molecular weight as an example, the mass average molecular weight of the gelatin to be used is preferably 2000 to 300000. Moreover, it is preferable that the number average molecular weight of the gelatin is 200 to 60000. When the average molecular weight is too small, there is a risk that the gelatin does not sufficiently function as protective colloid. Also, when the average molecular weight is too large, there is a risk that it becomes difficult to control the average particle diameter, and there is also a risk that the content of organic components in the protective colloid becomes too large. The mass average molecular weight of the gelatin is more preferably 250000 or less, still more preferably 200000 or less, and particularly preferably 2000 to 200000. Moreover, the number average molecular weight of the gelatin is more preferably 50000 or less, still more preferably 30000 or less, and particularly preferably 500 to 20000. In this way, the reason why the hydrolyzed gelatin of which the molecular weight is lowered by the hydrolysis is preferable is because by using such a gelatin, the variation of the particle diameter distribution of the metallic copper particles to be obtained becomes small, and is also because the sintering at a lower temperature in preparing a metallic copper-containing film becomes possible.

(Measurement of Molecular Weight of Gelatin)

[0052] The "average molecular weight" in the present invention is a value measured by a "PAGI method". The "PAGI method" herein is a method for estimating the molecular weight distribution by determining a chromatogram of a sample solution by a gel filtration technique using a high-performance liquid chromatography. Specifically, the average molecular weight was measured according to the following method. In a 100 mL measuring flask, 2.0 g of a sample was placed, an eluent consisting of an equal amount mixed solution of 0.1 mol/L potassium dihydrogen phosphate, and 0.1 mol/L disodium hydrogen phosphate was added thereto, and then the sample was expanded for 1 hour, the resultant was heated at 40°C for 60 minutes to dissolve the sample, then the resulting eluent was diluted accurately 10 times after cooling to room temperature, and the resultant solution was used as a test liquid. The chromatogram of the test liquid was determined by the following gel filtration method. Columns: Shodex Asahipak GS 620 7G installed in tandem with another one was used. By using flow rate: 1.0 mL/min, column temperature: 50° C., measurement wavelength: 230 nm, and pullulan (P-82, manufactured by SHOWA DENKO K.K.) of which the molecular weight is known, the elution time was determined, and thereby a calibration curve was made. Thereafter, the gelatin was analyzed, and the mass average molecular weight and number average molecular weight of this specimen were determined using the following equation. In the following equation, Si represents absorbance at each point, and Mi represents a molecular weight at elution time Ti.

$$\text{Mass average molecular weight} = (\Sigma \mathrm{Si} \times \mathrm{Mi}) / \Sigma \mathrm{Si}$$

$$\text{Number average molecular weight} = \Sigma \mathrm{Si} / (\Sigma \mathrm{Si} / \mathrm{Mi})$$

[0053] It is preferable that the amount of the gelatin and/or the collagen peptide to be used is 1 to 500 parts by mass with regard to 100 parts by mass of the metallic copper particle to be produced, more preferably 5 to 500 parts by mass, still more preferably 5 to 300 parts by mass, most preferably 5 to 200 parts by mass. The reason why the above range is preferable is because in the case where the amount of the gelatin and/or the collagen peptide to be used is in the above range, a metallic copper particle having a desired volume resistance value after the metallic copper particle is heated at a temperature of 300°C under a nitrogen atmosphere can be produced. The other protective colloids may be used in addition to the gelatin and/or the collagen peptide as long as the volume resistance value of the metallic copper particle is not impaired. The degree of aggregation of the fine metallic copper particles can be controlled according to the amount of the gelatin and/or the collagen peptide to be used, and the fine metallic copper particles more easily aggregate when the amount of the gelatin and/or the collagen peptide to be used is smaller.

[0054] Next, a copper compound is used as a raw material for a metallic copper particle. As the copper compound, the following: hardly soluble (or insoluble) copper compounds such as copper oxides; water soluble copper compounds such as copper sulfate, copper nitrate, copper formate, copper acetate, copper chloride, copper bromide, and copper iodide; and one or more copper compounds selected from these compounds can be used. Particularly, copper oxides, copper sulfate, copper nitrate, and copper formate are preferable, and copper oxides are more preferable among them. With respect to copper oxides, when a divalent copper oxide such as copper oxide (copper (II) oxide) or copper hydroxide (copper (II) hydroxide) or a monovalent copper oxide such as cuprous oxide (copper (I) oxide) or copper hydroxide (copper (I) hydroxide) is used, a metallic copper particle having a desired volume resistance value can be produced. Among them, the "divalent copper oxides" are more preferable than the "monovalent copper oxides". In the "divalent copper oxide", the atomic valence of the copper oxide is divalent (Cu^{2+}), and includes copper (II) oxide, copper (II) hydroxide, and a mixture thereof. The divalent copper oxide may appropriately include an impurity such as another metal, a metal compound, or a nonmetallic compound, but it is preferable that the monovalent copper oxide is substantially free of impurities except for those in an inevitable amount. Moreover, a divalent copper oxide having X-ray diffraction peaks assigned to copper (II) oxide is preferably used. It is preferable to use the copper (II) oxide having an average crystallite diameter in a range of 20 to 500 nm, the average crystallite diameter calculated from the following expression 1 based on an X-ray diffraction peak of (110) plane of the copper (II) oxide, and a range of 50 to 200 nm is still more preferable. When the average crystallite diameter of the divalent copper oxide is at least in the range, a desired metallic copper particle can be produced. When the average crystallite diameter is smaller than the above range, the copper (II) oxide has a small particle diameter and low crystallinity. As a result, a dissolution rate of the copper (II) oxide accelerates, and thus the reduction reaction rate is difficult to be controlled unless a large amount of a complexing agent is used. On the other hand, when the average crystallite diameter is larger than the above range, the particle diameter is large and its crystallinity is favorable. As a result, a dissolution rate decelerates, and thus unreacted copper (II) oxide is liable to remain in the metallic copper particle unless the reduction reaction time is long. Therefore, the above range is preferable. The process for producing the copper oxide is not limited, and a copper oxide industrially produced, for example, through an electrolytic process, a chemical conversion process, an oxidation-by-heating process, a thermal decomposition process, an indirect wet process, or the like can be used. Another copper compound may be used in addition to the copper oxide as long as the volume resistance value of the metallic copper particle is not impaired.

$$\text{Expression 1: } DHKL = K^{*}\lambda/\beta\cos\theta$$

DHKL: average crystallite diameter (Å)
λ: wavelength of X-ray
β: half-width value of diffraction peak
θ: Bragg's angle
K: constant (= 0.9)

[0055] Next, when hypophosphorous acid (i.e. phosphinic acid) and/or a salt thereof are used as a reducing agent, a metallic copper particle having a desired volume resistance value after the metallic copper particle is heated at a temperature of 300°C under a nitrogen atmosphere can be produced compared with the case where a reducing agent such as hydrazine is used. Examples of the hypophosphite include salts such as a sodium salt and a potassium salt, and when the hypophosphite is used, the reaction easily progresses by adjusting on an acidic side the pH in the reduction reaction. The amount of the reducing agent to be used can be appropriately set as long as it is an amount capable of reducing a copper compound to a metallic copper particle, and the range of 0.33 to 5 mol with regard to 1 mol of copper included in the copper compound is preferable. When the amount of the reducing agent is smaller than the above range, the reaction is hard to progress, so that the metallic copper particle is not sufficiently produced. Also, when the amount of the reducing agent is larger than the above range, the reaction excessively progresses, so that the desired metallic copper particle is hard to obtain. Therefore, the above range is preferable. The amount of the reducing agent to be used is more preferably in a range of 0.4 to 4 mol, and still more preferably 0.5 to 4 mol. Also, another reducing agent may be used in addition hypophosphorous acid and/or a salt thereof in a range where there is no problem in terms of the volume resistance value of the metallic copper particle.

[0056] It is preferable that the reduction reaction is performed at a pH of 3 or lower. The above reduction reaction performed at a pH of 3 or lower does not mean that the reaction is constantly performed at a pH of 3 or lower but that the reduction reaction has only to pass through a state where the pH is 3 or lower. In particular, it is preferable that aging at the time of and after the completion of the reduction reaction is performed at a pH of 3 or lower. It is considered that a balance among the elution of a copper ion, the nuclear generation rate of copper, and the nuclear growth rate of copper can be kept by using, as a raw material, a copper compound including at least copper oxide which is hardly soluble and reducing it in a liquid medium having a pH of 3 or lower by using hypophosphorous acid and/or a salt thereof as a reducing agent in the presence of gelatin and/or a collagen peptide. Therefore, a metallic copper particle including a large diameter metallic copper particle and at least one fine metallic copper particle wherein the at least one fine metallic copper particle is adhered on the large diameter metallic copper particle can be produced, and further the metallic copper particle specifically characterized as one embodiment of the present invention, in which an aggregate of a plurality of the fine metallic copper particles are adhered on the surface of the large diameter metallic copper particle can be also produced. Moreover, a mixed particle in which the metallic copper particle (i.e. composite particle) and a small metallic copper particle are mixed can be also produced by selecting a reduction condition.

[0057] Next, in the present invention, a complexing agent may be added at the time of the reduction reaction when necessary, and it is preferable to use the amine complexing agent such as the amines or the alkanol amines, described below. It is considered that the "complexing agent" in the present invention acts in a process eluting copper ions from the copper compound or in a process reducing the copper compound to produce metallic copper. The "complexing agent" in the present invention means a compound capable of forming a copper complex compound by binding of donor atoms in a ligand included in the complexing agent with copper ions or metallic copper, and examples of the donor atom include nitrogen, oxygen, and sulfur. Specifically, as examples thereof, the complexing agents described in the following (1) to (5) are included.

(1) The complexing agents having nitrogen as the donor atom include, for example, (a) amines (for example, primary amines such as butylamine, ethylamine, propylamine, and ethylenediamine; secondary amines such as dibutylamine, diethylamine, dipropylamine and imines such as piperidine and pyrrolidine; tertiary amines such as tributylamine, triethylamine, and tripropylamine; and those having two or more kinds of the primary to tertiary amines in one molecule of diethylenetriamine or triethylenetetramine), (b) nitrogen-containing heterocyclic compounds (for example, imidazole, pyridine, and bipyridine), (c) nitriles (for example, acetonitrile, and benzonitrile) and cyanides, (d) ammonia and ammonium compounds (for example, ammonium chloride, and ammonium sulfate), and (e) oximes.

(2) The complexing agents having oxygen as the donor atom include, for example, (a) carboxylic acids (for example, oxycarboxylic acids such as citric acid, malic acid, tartaric acid, and lactic acid; monocarboxylic acids such as acetic acid and formic acid; dicarboxylic acids such as oxalic acid and malonic acid; aromatic carboxylic acids such as benzoic acid), (b) ketones (for example, monoketones such as acetone, and diketones such as acetylacetone and benzoylacetone), (c) aldehydes, (d) alcohols (for example, monohydric alcohols, glycols, and glycerols), (e) quinones, (f) ethers, (g) phosphoric acid (for example, orthophosphoric acid) and phosphoric acid compounds (for example, hexametaphosphoric acid, pyrophosphoric acid, and phosphorous acid), and (h) sulfonic acid or sulfonic acid compounds.

(3) The complexing agents having sulfur as the donor atom include, for example, (a) aliphatic thiols (for example, methyl mercaptan, ethyl mercaptan, propyl mercaptan, isopropyl mercaptan, n-butyl mercaptan, allyl mercaptan, and dimethyl mercaptan), (b) alicyclic thiols (such as cyclohexyl thiol), (c) aromatic thiols (for example, thiophenol), (d) thioketones, (e) thioethers, (f) polythiols, (g) thiocarbonic acids (for example, trithiocarbonic acids), (h) sulfur-containing heterocyclic compounds (for example, dithiol, thiophene, and thiopyran), (i) thiocyanates and isothiocyanates, and (j) inorganic sulfur compounds (for example, sodium sulfide, potassium sulfide, and hydrogen sulfide).

(4) The complexing agents having two or more kinds of donor atoms include, for example, (a) amino acids (where the donor atoms are nitrogen and oxygen: for example, neutral amino acids such as glycine and alanine; basic amino acids such as histidine and arginine; and acidic amino acids such as aspartic acid and glutamic acid), (b) amino polycarboxylic acids (where the donor atoms are nitrogen and oxygen: for example, ethylenediaminetetraacetate (EDTA), nitrilotriacetate (NTA), iminodiacetate (IDA), ethylenediaminediacetate (EDDA), ethyleneglycoldiethyletherdiaminetetraacetate (GEDA)), (c) alkanolamines (where the donor atoms are nitrogen and oxygen: for example, ethanolamine, diethanolamine, and triethanolamine), (d) nitroso compounds and nitrosyl compounds (where donor atoms are nitrogen and oxygen), (e) mercaptocarboxylic acids (where donors are sulfur and oxygen: for example, mercaptopropionic acid, mercaptoacetic acid, thiodipropionic acid, mercaptosuccinic acid, dimercaptosuccinic acid, thioacetic acid, and thiodiglycolic acid), (f) thioglycols (donors are sulfur and oxygen: for example, mercaptoethanol, and thiodiethylene glycol), (g) thionic acids (where the donors are sulfur and oxygen), (h) thiocarbonic acids (where the donor atoms are sulfur and oxygen: for example, monothiocarbonic acid, dithiocarbonic acid, and thione carbonic acid), (i) aminothiols (where the donors are sulfur and nitrogen: for example, aminoethylmercaptan and thiodiethylamine), (j) thioamides (where the donor atoms are sulfur and nitrogen: for example, thioformamide), (k) thioureas (where the donor atoms are sulfur and nitrogen), (1) thiazoles (where the donor atoms are sulfur and nitrogen: for example, thiazole, and benzothiazole), (m) sulfur-containing amino acids (where the donors are sulfur, nitrogen and oxygen: for example, cysteine, methionine).

(5) Examples of salts of the above compounds and derivatives thereof include alkali metal salts such as trisodium citrate, potassium sodium tartrate, sodium hypophosphite, and disodium ethylenediaminetetraacetate; and esters of carboxylic acid, phosphoric acid, and sulfonic acid.

[0058] Among these complexing agents, at least one thereof can be used. The amount of the complexing agent to be used can be appropriately set, but it is preferable to set the amount of the complexing agent to be used in a range of 0.01 to 500 parts by mass with regard to 1000 parts by mass of the copper compound because the effects of the present invention are easily obtained. By reducing the amount of the complexing agent to be used within the above range, primary particles of the metallic copper particle can be made smaller, and by increasing the amount of the complexing agent to be used, primary particles thereof can be made larger. The amount of the complexing agent to be used is preferably in a range of 0.1 to 500 parts by mass, still more preferably in a range of 0.5 to 250 parts by mass.

[0059] In the present invention, the complexing agent including at least one selected from nitrogen and oxygen as the donor atom is preferable because the effects of the present invention are easily obtained. Specifically, at least one complexing agent selected from amines, nitrogen-containing heterocyclic compounds, nitriles, cyanides, carboxylic acids, ketones, phosphoric acid and phosphoric acid compounds, amino acids, aminopolycarboxylic acids, alkanolamines, salts thereof, or derivatives thereof is more preferable. Among the carboxylic acids, oxycarboxylic acids are preferable; among the ketones, diketones are preferable; and among the amino acids, basic or acidic amino acids are preferable. Further, it is preferable that the complexing agent is at least one complexing agent selected from butylamine, ethylamine, propylamine, dibutylamine, diethylamine, dipropylamine, tributylamine, triethylamine, tripropylamine, imidazole, citric acid or alkali metal salts thereof, acetylacetone, hypophosphorous acid or alkali metal salts thereof, histidine, arginine, ethylenediaminetetraacetate or alkali metal salts thereof, ethanolamine, and acetonitrile. As described above, the amount of the oxygen or nitrogen complexing agent to be used is preferably in a range of 0.01 to 500 parts by mass with regard to 1000 parts by mass of the copper compound, more preferably in a range of 0.1 to 500 parts by mass, and still more preferably in a range of 0.5 to 250 parts by mass.

[0060] In the present invention, it is preferable to use the complexing agent including oxygen as the donor atom, and among others, it is more preferable to use the complexing agent corresponding to an organic acid. As described above, it is preferable to perform the reduction reaction in a region of a pH of 3 or lower. In this regard, it is considered that the use of the organic acid as the complexing agent can be lower the initial pH of the reaction liquid and have, in the reduction reaction, some effect on the elution of copper ions and the nuclear generation and nuclear growth rate of copper. Therefore, the metallic copper particle including a large diameter metallic copper particle and at least one fine metallic copper particle wherein the at least one fine metallic copper particle is adhered on the large diameter metallic copper particle can be produced more effectively, and the metallic copper particle specifically characterized as one embodiment of the present invention, in which an aggregate of a plurality of the fine metallic copper particles is adhered on the surface of the large diameter metallic copper particle can be also produced more effectively. Moreover, by selecting a reduction condition, the mixed particle in which the composite particle and the small metallic copper particle are mixed can be also produced, and thus a mixture (i.e. mixed particle) of the large diameter metallic copper particle on which the partially aggregated fine metallic copper particles are adhered and the small metallic copper particle is easily obtained. Further, in the state where the metallic copper particle (i.e. composite particle) and the small metallic copper particle are mixed, the specific surface area easily falls within the range of 1 to 6 m^2/g, and in this case, the ratio of both particles (the metallic copper particle (i.e. composite particle) and the small metallic copper particle) is a ratio in the case of exhibiting particularly excellent sinterability at low temperature. Furthermore, it is presumed that an organic acid remains adsorbed on the surface of the produced metallic copper particle, and the organic acid disappears even at a relatively low temperature during heating to make it easy to sinter the metallic copper particles, so that the volume resistance value at the time of a low temperature heating can remarkably be reduced. Examples of the organic acid include carboxylic acids, amino acids, and aminocarboxylic acids. Among these organic acids, carboxylic acids are more preferable, and formic acid is most preferable therein.

[0061] In the production methods according to the present invention, in the case of using the complexing agent corresponding to the organic acid, the volume resistance value of a metallic copper-containing film prepared by performing heating and firing at a temperature of 120°C under an air atmosphere is used as an index, and a volume resistance value of 1×10^{-1} $\Omega \cdot m$ or less can be achieved in terms of the volume resistance value measured according to the < Method 2 for Measuring Volume Resistance Value > described above, and further a metallic copper-containing film that exhibits a volume resistance value of 1×10^{-2} $\Omega \cdot cm$ or less can be obtained. In this way, the metallic copper particle according to the present invention has a low volume resistance value and a high electrical conductivity because the sinterability or the contact property between the particles are improved even when heating the metallic copper particle at a temperature of 120°C under an air atmosphere. Therefore, the metallic copper particle according to the present invention can be used with a base material having a low heat resistance temperature, and can be employed in a wide range of uses. Moreover, the firing in the air can be performed, and thus constraints on facilities such as control of an atmosphere can be avoided.

[0062] In the present invention, in the case where the gelatin and/or the collagen peptide and, when necessary, the complexing agent exist at the time of mixing the copper oxide and the reducing agent, the order to add each raw material is not limited. Examples of adding each raw material include (1) a method for performing the concurrent addition of the copper oxide and the reducing agent to a solvent including the gelatin and/or the collagen peptide, and, when necessary, the complexing agent, (2) a method for adding the reducing agent to a solvent including the gelatin and/or the collagen peptide, the copper compound, and, when necessary, the complexing agent, (3) a method for performing the concurrent addition of the reducing agent and the complexing agent to a solvent including the gelatin and/or the collagen peptide, and the copper compound, and (4) a method for adding a mixed solution of the reducing agent and the complexing agent to a solvent including the gelatin and/or the collagen peptide, and the copper compound. Among these, methods (3) and (4) are preferable because the reaction is easily controlled, and method (4) is particularly preferable. The copper compound, the reducing agent, the complexing agent, and the gelatin and/or the collagen peptide may be suspended or dissolved in a solvent in advance before these are used in the reduction reaction. In addition, the "concurrent addition" means a method for separately adding the copper compound and the reducing agent, or the complexing agent and the reducing agent at the same time during the reaction or at the same time period during the reaction, and includes not only continuous addition of both materials during the reaction but also intermittent addition of one or both materials.

[0063] As a solvent, for example, an aqueous solvent or an organic solvent such as an alcohol is used, and the aqueous solvent is preferably used. It is preferable that the reaction temperature is in a range of 10°C to a boiling point of the used solvent because the reaction easily progresses, more preferably in a range of 20 to 100°C because a fine metallic copper particle is obtained, still more preferably in a range of 30 to 95°C, particularly preferably 40 to 95°C. As described above, the pH of the reaction liquid may be 3 or less during the reduction reaction. In the case where hypophosphorous acid is used as a reducing agent, the initial pH of the reaction liquid is not particularly limited and may be appropriately set because the pH can be lowered by the addition of hypophosphorous acid. In the case where the hypophosphite is used as a reducing agent, it is preferable to adjust the initial pH of the reaction liquid to 3 or lower by adding an arbitrary acid in advance. It is preferable to add an organic acid to the reaction liquid in advance as described above irrespective of whichever reducing agent is used. In addition, the pH may be lowered with only an organic acid, and the pH may be also set at 3 or lower using an organic acid in combination with hypophosphorous acid as a reducing agent. An inorganic acid other than hypophosphorous acid, such as phosphoric acid, a phosphate, pyrophosphoric acid, or pyrophosphate, may be used for the pH adjustment. In particular, by the use of pyrophosphoric acid for the pH adjustment, the reduction reaction of copper oxide using hypophosphorous acid (i.e. phosphinic acid) and/or a salt thereof can be softly progressed, and thus the heat generation at the time of the reaction can be suppressed. Furthermore, by making it easy to control the reaction rate, the adjustment of the particle size becomes easy. Moreover, a defoaming agent may be used in order to suppress foaming during reaction. The reaction time can be controlled and set by the time for adding raw materials such as a reducing agent, and about 10 minutes to six hours is appropriate, for example. After the completion of adding raw materials such as a reducing agent, the reaction liquid may be subjected to aging as it is. The aging temperature or time can be appropriately set. The aging temperature at the same level as the above reaction temperature is appropriate, and the aging time of about 10 minutes to about six hours is appropriate.

[0064] The production of a particle having a flat shape becomes easy by adding 10% by mass or more of polymer gelatin with regard to the produced metallic copper particle. Also, the above production becomes easy when the temperature of the reduction reaction is 50°C or higher. The production of a particle having a granular shape or the like becomes easy by adding 10% by mass or more of the collagen peptide with regard to the produced metallic copper particle. Moreover, the production of a particle having a granular shape or the like becomes easy when the temperature of the reduction reaction is set at 20 to 90°C in the presence of the gelatin and/or the collagen peptide. The production of the particle having an irregular shape becomes easy when the temperature of the reduction reaction is set at 90°C or higher. The average particle diameter of the large diameter metallic copper particle and the abundance ratio of the large diameter metallic copper particle and the at least one fine metallic copper particle can be adjusted according to the reaction temperature or aging temperature, and the average particle diameter and the abundance ratio of the large diameter metallic copper particle become larger as the temperature becomes higher. The average particle diameter and shape of the large diameter metallic copper particle and the abundance ratio of the large diameter metallic copper particle and the at least one fine metallic copper particle can be also adjusted according to the reaction time or aging time. Moreover, the average particle diameter and shape of the small metallic copper particle, and the abundance ratio of the metallic copper particle (i.e. composite particle) and the small metallic copper particle can be also adjusted according to the reaction time or aging time.

[0065] In the present invention, the mixed particle including the metallic copper particle (specifically, the composite particle in which the at least one fine metallic copper particle and/or an aggregate thereof are adhered on the surface of the large diameter metallic copper particle) in a mixed state with the small metallic copper particle can be produced at once without undergoing a mixing process of particles, according to the above production methods. According to the above production methods, the metallic copper particle in which the size or particle shape of the large diameter metallic copper particle, the size or particle shape of the at least one fine metallic copper particle, or the size or particle shape of the small metallic copper particle is different, and the metallic copper particle in which the abundance ratio of them is different can be produced. Moreover, the above mixed particle including the small metallic copper particle in the mixed state can be also obtained by mixing the above metallic copper particle (specifically, the composite particle in which the at least one fine metallic copper particle and/or an aggregate thereof are adhered on the surface of the large diameter metallic copper particle) and the small metallic copper particle separately prepared.

[0066] According to the above methods, the metallic copper particles, in the presence of the gelatin and/or the collagen peptide and the complexing agent when necessary, are produced, and then fractionation and washing are performed when necessary. Moreover, the gelatin and/or the collagen peptide, adhered on the surface of the metallic copper particles are decomposed by adding a protective colloid remover to the solvent after the reaction, thereby agglomerating the metallic copper particles, and subsequently, the resultant can be fractionated. The "protective colloid remover" is a compound that decomposes or dissolves protective colloid to suppress the action of the protective colloid, and when part, if not all, of the protective colloid can be removed from the solvent, the effects according to the present invention are obtained. The kind of protective colloid remover is appropriately selected according to the protective colloid to be used. Specifically, for removing the protein protective colloid, proteases such as serine proteases (for example, trypsin and chymotrypsin), thiol proteases (for example, papain), acid proteases (for example, pepsin), and metalloproteases can be used. The additive amount of the protective colloid remover may be an amount which protective colloid can be removed to such an extent that the metallic copper particles can be agglomerated and fractionated. Although the additive amount of the protective colloid remover is different depending on the kind thereof, in the case of a protease, with regard to 1000 parts by mass of protein protective colloid, a range of 0.001 to 1000 parts by mass is preferable, 0.01 to 200 parts by mass is more preferable, and 0.01 to 100 parts by mass is still more preferable. The temperature of the solvent at the time of adding the protective colloid remover can be appropriately set, and may be in the state where the temperature of the reduction reaction is retained, or a range of 10°C to the boiling point of the used solvent is preferable because the removal of the protective colloid easily progresses, and a range of 40 to 95°C is more preferable. When the protective colloid remover is added and then the resultant state is appropriately retained, the protective colloid can be decomposed, and for example, about 10 minutes to about 10 hours of the retention time is appropriate. After removing the protective colloid to agglomerate the metallic copper particles, fractionation is performed by an ordinary method. The method for performing the fractionation is not particularly limited, and methods such as gravity filtration, pressure filtration, vacuum filtration, suction filtration, centrifugal filtration, and natural sedimentation can be used. However, from the industrial viewpoint, the pressure filtration, the vacuum filtration, and the suction filtration are preferable, and it is preferable to use a filter machine such as a filter press and a roll press because the dehydration ability is high and the treatment of a large amount is possible.

[0067] As an embodiment of the above method, it is preferable to further add a flocculant agent after adding the protective colloid remover because the yield is much more improved. The publicly known flocculants can be used, and specific examples thereof include anionic flocculants (for example, partially hydrolyzed products of polyacrylamide, acrylamide-sodium acrylate copolymers, and sodium alginate), cationic flocculants (for example, polyacrylamide, dimethylaminoethyl methacrylate, dimethylaminoethyl acrylate, polyamidine, and chitosan), and amphoteric flocculants (for example, acrylamide-dimethylaminoethyl acrylate-acrylic acid copolymers). The additive amount of the flocculants can be appropriately set according to a required amount, and is preferably in a range of 0.5 to 100 parts by mass with regard to 1000 parts by mass of the metallic copper particle, and more preferably in a range of 1 to 50 parts by mass.

[0068] Alternatively, a similar effect of improving the yield is also obtained by adding a protective colloid remover after adjusting the pH of the solvent in a range of 1 to 8 using an alkali in place of the use of the flocculant. When the pH is lower than 1, the metallic copper particle corrodes or dissolves, and thus a range of 1 to 7 is a preferable pH region. It is more preferable that the pH be in a range of 1 to 6 because the amount of the alkali to be used is reduced.

[0069] After the metallic copper particles are subjected to a solid-liquid separation and washed when necessary, the solid of the metallic copper particles obtained thereby can be used by dispersing it in an aqueous solvent or an organic solvent such as an alcohol, preferably in the aqueous solvent. Alternatively, the solid of the metallic copper particles may be dried by an ordinary method, and further the solid can be used by dispersing it in an aqueous solvent or an organic solvent such as an alcohol, preferably in the aqueous solvent after drying. The metallic copper particle is easily oxidized, and thus it is preferable that drying is performed under an atmosphere of an inert gas such as nitrogen or argon in order to suppress oxidization. After drying, grinding may be performed when necessary.

[0070] Next, the present invention relates to a metallic copper dispersion including the above metallic copper particle. Any aqueous solvent and/or any organic solvent can be used as a dispersion medium, and a polymeric dispersant may be used when necessary. Moreover, another metallic particle such as a silver, nickel, copper, or tin particle or an alloy particle such as a copper-tin alloy particle may be mixed with the metallic copper particle when necessary. The mixing ratio of the metallic particle or the alloy particle can be appropriately set.

[0071] In the present invention, the gelatin and/or the collagen peptide suitably exist on the surface of the metallic copper particle. However, the gelatin and/or the collagen peptide have a high acid value, and thus the metallic copper particle having the gelatin and/or the collagen peptide on the surface thereof dissociates in a solvent to be electrically negative and is easy to agglomerate in an organic solvent. Thus, it is preferable to mix a polymeric dispersant in order to neutralize acid sites which are the cause of an acid value of the gelatin and/or the collagen peptide. The polymeric dispersant as well as the gelatin and/or the collagen peptide includes a hydroxyl group, an acidic group, a basic group, and the like, and thus has an amine value and an acid value, and the polymeric dispersant having an amine value of 10 to 150 mgKOH/g is preferable, more preferably 10 to 130 mgKOH/g, still more preferably 10 to 90 mgKOH/g, particularly preferably 15 to 80 mgKOH/g, and most preferably 15 to 50 mgKOH/g. The amine value in the above range can contribute to the dispersion stability of the metallic copper particle in an organic solvent, and thus is preferable. Moreover, with respect to the amine value and acid value of the polymeric compound, it is preferable that the polymeric compound has an amine value (i.e. base site) and an acid value (i.e. acid site) in an amount which is almost equal to or more than the amount to compensate (i.e. neutralize) the amine value and acid value of the gelatin and/or the collagen peptide that exist on the surface of the metallic copper particle, and it is preferable that the difference between the amine value and the acid value, namely (i.e. "(amine value - acid value)") is in a range of 0 to 50, and more preferably in a range of 1 to 30. The polymeric dispersant may be electrostatically bound to the acid sites or base sites of the gelatin and/or the collagen peptide through the base sites or acid sites thereof. For these reasons, it is considered that (amine value of polymeric dispersant × mass of polymeric dispersant) - (acid value of gelatin × mass of gelatin) is preferably 0 or more.

[0072] It is preferable that the polymeric dispersant has a specific heat capacity of 1.0 to 2.0 J/(g·K) at the glass transition point. This is because the heat accumulation amount of the polymeric dispersant is so small that the heat amount necessary for raising a temperature by 1 K can be small and the heat amount added for the purpose of decomposition can be small. The specific heat capacity is more preferably in a range of 1.2 to 1.9 J/(g·K), and still more preferably in a range of 1.3 to 1.8 J/(g·K). Moreover, it is preferable that the polymeric dispersant has a glass transition point in a range of -70 to 10 °C because the glass transition occurs at a low temperature to make the heat amount added for the purpose of decomposition small. The glass transition point is preferably in a range of -70 to 7°C, still more preferably in a range of -70 to 5°C, and still more preferably in a range of -70 to 0°C. For these reasons, in the present invention, a more preferable polymeric dispersant has an amine value of 10 to 90 mgKOH/g and a glass transition point in a range of -70 to 10°C, and a still more preferable polymeric dispersant has an amine value of 10 to 90 mgKOH/g, a glass transition point in a range of -70 to 10°C, and a specific heat capacity of 1.0 to 2.0 J/(g·K) at the glass transition point.

(Measurement of Specific Heat Capacity at Glass Transition Point)

[0073] According to JIS K 7123-1987 "Testing Methods for Specific Heat Capacity of Plastics", the specific heat capacity was measured with DSC Q 100 Type manufactured by TA Instruments. With respect to a temperature-raising pattern, the temperature was held at -90°C for 5 minutes, then raised to 40°C at 5°C/min, and held at 40°C for 5 minutes. As analytical software, option software "Thermal Specialty Library" manufactured by TA Instruments was used.

(Measurement of Glass Transition Point)

[0074] According to JIS K 7121-1987 "Testing Methods for Transition Temperatures of Plastics", the glass transition point was measured with DSC Q 100 Type manufactured by TA Instruments. With respect to a temperature-raising pattern, the temperature was held at -90°C for 5 minutes, then raised to 40°C at 5°C/min, and held at 40°C for 5 minutes.

[0075] The polymeric dispersant is, for example, a polymer or copolymer having a tertiary amino group, quaternary ammonium group, heterocyclic group having a basic nitrogen atom, or a basic group such as a hydroxyl group, and may have an acidic group such as a carboxyl group, and thus the amine value and acid value of the polymeric dispersant are compensated, so that (amine value - acid value) may be 0. The polymeric dispersant having an amine value higher than the acid value is preferable, and (amine value - acid value) is in a range of 0 to 50, and more preferably in a range of 1 to 30. Because the basic group or acidic group of the polymeric dispersant is a functional group affinitive to the metallic copper particle covered with the gelatin, the polymeric dispersant having one or more basic or acidic groups in the main chain and/or the side chain is preferable, and the polymeric dispersant having several basic or acidic groups in the main chain and/or the side chain is more preferable. The basic or acidic groups may be included at one terminal of the main chain of the polymer and/or one terminal of the side chain of the polymer. The straight-chain polymers such as A-B block type polymers; polymers having a comb-shaped structure with a plurality of side chains; and the like can be used as the polymeric dispersant. The mass average molecular weight of the polymeric dispersant is not limited, but it is preferable that the mass average molecular weight measured by a gel permeation chromatography method is in a range of 2000 to 1000000 g/mol. When the mass average molecular weight is less than 2000 g/mol, the dispersion stability is not sufficient, and when the mass average molecular weight exceeds 1000000 g/mol, the viscosity is too high and the handling is likely to be difficult. Thus, the mass average molecular weight is more preferably in a range of 4000 to 1000000 g/mol, still more preferably in a range of 10000 to 1000000 g/mol, and further more preferably in a range of 1000 to 100000 g/mol. Moreover, the polymeric dispersant including a small amount of elements of phosphorus, sodium, and potassium is preferable, and the polymeric dispersant not including these elements is more preferable. When the elements of phosphorus, sodium, and potassium are included in the polymeric dispersant, the elements remain as ash in producing an electrode, a wiring pattern, or the like by heating and firing, and thus the polymeric dispersant not including these elements is preferable. One or more of such polymeric dispersants can be appropriately selected and used.

[0076] Specifically, the polymeric dispersant includes polymers having a basic group such as salts of long-chain polyaminoamides and polar acid esters, unsaturated polycarboxylic acid polyaminoamides, polycarboxylic acid salts of polyaminoamides, and salts of long-chain polyaminoamides and acid polymers. Moreover, the polymeric dispersant includes alkylammonium salts, amine salts, and amide amine salts of polymers such as acrylic polymers, acrylic copolymers, modified polyester acids, polyether ester acids, polyether carboxylic acids, and polycarboxylic acids, and straight-chain type acrylic polymers or straight-chain type acrylic copolymers are preferable. Commercially available polymeric dispersants can be also used as such a polymeric dispersant. Examples of the commercially available polymeric dispersant include DISPERBYK (which is a registered trade-mark)-106, DISPERBYK-109, DISPERBYK-110, DISPERBYK-111, DISPERBYK-130, DISPERBYK-161, DISPERBYK-162, DISPERBYK-163, DISPERBYK-167, DISPERBYK-168, DISPERBYK-180, DISPERBYK-182, DISPERBYK-183, DISPERBYK-184, DISPERBYK-185, DISPERBYK-2000, DISPERBYK-2001, DISPERBYK-2013, DISPERBYK-2163, DISPERBYK-2164, BYK-4512, BYK-P105, LPN-21854, and LPC-22124 (, all of which are manufactured by BYK-Chemie GmbH), FLOWLEN DOPA-15B, FLOWLEN DOPA-15BHFS, FLOWLEN 17HF, FLOWLEN DOPA-22, FLOWLEN DOPA-33, and FLOWLEN DOPA-44 (, all of which are manufactured by Kyoeisha Chemical Co., Ltd.), and ED-212 and ED-213 (, all of which are manufactured by Kusumoto Chemicals, Ltd.).

[0077] The amine values of the gelatin and/or the collagen peptide, and the polymeric dispersant denote the total amount of free bases and bases, and expressed by an equivalent amount of potassium hydroxide in mg to the amount of hydrochloric acid needed to neutralize 1 g of a sample. Moreover, the acid value denotes the total amount of free fatty acids and fatty acids, and expressed by an amount of potassium hydroxide in mg needed to neutralize 1 g of a sample. Specifically, the amine value and the acid value are measured by the following method according to JIS K7700 or ASTM D2074 below.

(Method for Measuring Amine Value)

[0078] In 300 mL of a mixed solvent of ethanol and pure water, 5 g of the gelatin and/or the collagen peptide, or the polymeric dispersant, and several drops of a bromocresol green ethanol solution are dissolved. Then, to the resultant mixed solution a 0.1 M HCl ethanol solution whose factor (correction coefficient) has been calculated is added, and the amine value is calculated from the titer of the 0.1M HCl ethanol solution when yellow of a bromocresol green indicator continues for 30 seconds.

(Method for Measuring Acid Value)

[0079] In 300 mL of pure water, 5 g of the gelatin and/or the collagen peptide, or the polymeric dispersant, and several drops of a phenolphthalein solution are dissolved. Then, to the resultant mixed solution a 0.1M KOH ethanol solution whose factor (correction coefficient) has been calculated is added. The acid value is calculated from the titer of the 0.1M KOH ethanol solution when light red of a phenolphthalein indicator continues for 30 seconds.

[0080] The organic solvent can appropriately be selected, and specifically, at least one selected from hydrocarbon solvents such as toluene, xylene, solvent naphtha, normal hexane, isohexane, cyclohexane, methylcyclohexane, normal heptane, tridecane, tetradecane, and pentadecane; alcoholic solvents such as methanol, ethanol, butanol, IPA (isopropyl alcohol), normal propyl alcohol, 2-butanol, TBA (tertiary butanol), butanediol, ethylhexanol, benzyl alcohol, and terpineol; ketone solvents such as acetone, methyl ethyl ketone, methyl isobutyl ketone, DIBK (diisobutyl ketone), cyclohexanone, and DAA (diacetone alcohol); ester solvents such as ethyl acetate, butyl acetate, methoxybutyl acetate, cellosolve acetate, amyl acetate, normal propyl acetate, isopropyl acetate, methyl lactate, ethyl lactate, and butyl lactate; ether solvents such as methyl cellosolve, cellosolve, butyl cellosolve, dioxane, MTBE (methyl tertiary butyl ether), and butyl carbitol; glycol solvents such as ethylene glycol, diethylene glycol, triethylene glycol, and propylene glycol; glycol ether solvents such as diethylene glycol monomethyl ether, triethylene glycol monomethyl ether, propylene glycol monomethyl ether, and 3-methoxy-3-methyl-1-butanol; and glycol ester solvents such as ethylene glycol monomethyl ether acetate, PMA (propylene glycol monomethyl ether acetate), diethylene glycol monobutyl ether acetate, and diethylene glycol monoethyl ether acetate can be used for the organic solvent. The organic solvent having a low viscosity is preferable for adaptation reduction in viscosity of the metallic copper dispersion, and the organic solvent having a viscosity in a range of 1 to 20 mPa·s is preferable. As such an organic solvent, toluene, butyl carbitol, butanol, propylene glycol-1-monomethyl ether-2-acetate, butyl cellosolve, tetradecane, and the like are suitably used. Also, the aqueous solvent can be appropriately selected, and specifically, water, and water and water-soluble solvents can be used.

[0081] It is preferable that the gelatin and/or the collagen peptide exist in an amount within a range of about 0.1 to about 15 parts by mass with regard to 100 parts by mass of the metallic copper particle because a desired effect is obtained. The more preferable range is about 0.1 to about 10 parts by mass. It is preferable that the polymeric dispersant be in a range of 0.1 to 20 parts by mass with regard to 100 parts by mass of the metallic copper particle because a desired effect is obtained. The above range is preferable because when the amount of the polymeric dispersant is too much smaller than the above range, it is difficult to obtain the effects of the present invention, and when the amount of the polymeric dispersant is too much larger than the above range, the electrical conductivity may be obstructed in electrode material uses and cloudiness or the like may occur to deteriorate an appearance in decorative article uses. The more preferable range is 0.1 to 10 parts by mass. The concentration of the metallic copper particle in the dispersion can be appropriately adjusted, and specifically, the concentration of the metallic copper particle can be adjusted to 10 % by mass or more, preferably 10 to 99% by mass, and more preferably about 20 to about 95% by mass.

[0082] The metallic copper dispersion according to the present invention can maintain a sufficient fluidity even when the concentration of the metallic copper particle is made 50% by mass or more. Therefore, the metallic copper dispersion according to the present invention can be suitably used for joining materials and the like for which a high-concentration paste is required. Moreover, in the metallic copper dispersion according to the present invention, the metallic copper particle is sufficiently dispersed, and thus even if the metallic copper particle is in a high concentration, viscosity of the dispersion can be adjusted to be relatively low. For example, the viscosity of the dispersion can be set to preferably 100 mPa·s or less, more preferably 1 to 30 mPa·s, and still more preferably 1 to 20 mPa·s. Furthermore, the dispersion according to the present invention can be suitably used for ink jet printing, spray coating, and the like by setting the concentration of the metallic copper particle to an appropriate concentration of 15% by mass or more.

[0083] In the metallic copper dispersion according to the present invention, in addition to the above metallic copper particle, the above aqueous solvent and/or the above organic solvent, and the above polymeric dispersant when necessary, a curable resin, a thickener, a plasticizer, an antifungal agent, a surfactant, a non-surfactant type dispersant, a surface control agent (leveling agent), and the like can be appropriately blended when necessary. The curable resin can further improve adhesion of a coating product to a base material. As the curable resin, resins of a dissolved type in a low-polar and non-aqueous solvent, an emulsion type, a colloidal dispersion type, and the like can be used without limitation. Moreover, as for the kind of the curable resin, known resins such as protein polymers, acrylic resins, polyester resins, urethane resins, phenol resins, epoxy resins, and cellulose can be used without limitation. It is preferable that the blending amount of the curable resin component is 10 parts by mass or less with regard to 100 parts by mass of the metallic copper particle, the more preferable range is 8 parts by mass or less, and a range of 5 parts by mass or less is still more preferable. As the surfactant, a cationic surfactant is preferable, and is a compound having surface activity in a portion showing positive electric charge by the dissociation in an aqueous solvent. Examples thereof include (1) quaternary ammonium salts ((a) aliphatic quaternary ammonium salts (such as $[RN(CH_3)_3]^+X^-$, $[RR'N(CH_3)_2]^+X^-$, $[RR'R''N(CH_3)]^+X^-$, and $[RR'R''R'''N]^+X^-$ wherein R, R', R", and R'" represent a same or different alkyl group and X represents a halogen atom such as Cl, Br, and I, and the same shall apply hereinafter), and (b) aromatic quaternary ammonium salts (such as $[R_3N(CH_2Ar)]^+X^-$ and $[RR'N(CH_2Ar)_2]^+X^-$ wherein Ar represents an aryl group), and (c) heterocyclic quaternary ammonium salts (such as pyridinium salts ($[C_6H_5N\text{-}R]^+X^-$) and imidazolinium salts ($[R\text{-}CN(CNR'R'')C_2H_4]^+X^-$)), and (2) alkylamine salts (such as RH_2NY, $RR'HNY$, and $RR'R''NY$ wherein Y represents an organic acid, an inorganic acid, or the like), and one of these may be used, or two or more thereof may be used. Specifically, the aliphatic quaternary ammonium salts include octyltrimethylammonium chloride, stearyltrimethylammonium chloride, cetyltrimethylammonium chloride, cetyltrimethylammonium bromide, lauryltrimethylammonium chloride, dioctyldimethylammonium chloride, distearyldimethylammonium chloride, trioctylmethylammonium chloride, tristearylmethylammonium chloride, tetraoctylammonium chloride, and the like. The aromatic quaternary ammonium salts include decyldimethylbenzylammonium chloride, lauryldimethylbenzylammonium chloride, stearyldimethylbenzylammonium chloride, benzethonium chloride, and the like. The heterocyclic quaternary ammonium salts include cetylpyridinium chloride, an alkyl isoquinolinium bromide, and the like. The alkylamine salts include neutralized products of octylamine, decylamine, laurylamine, stearylamine, coconut oil amine, dioctylamine, distearylamine, trioctylamine, tristearylamine, and dioctylmethylamine neutralized with an inorganic acid such as hydrochloric acid, nitric acid, and sulfuric acid, or a carboxylic acid such as acetic acid. Alternatively, a neutralized product obtained by reacting a mercapto carboxylic acid on the surface of the metallic copper particle and/or a salt thereof with alkylamine may be used as the alkylamine salt. Among the quaternary ammonium salts, those having at least one alkyl group with a number of carbon atoms of 8 or more or benzyl group are particularly preferable, and such quaternary ammonium salts include stearyltrimethylammonium chloride (number of carbon atoms of alkyl group: 18), octyltrimethylammonium chloride (number of carbon atoms of alkyl group: 8), lauryltrimethylammonium chloride (number of carbon atoms of alkyl group: 12), cetyltrimethylammonium chloride (number of carbon atoms of alkyl group: 16), cetyltrimethylammonium bromide (number of carbon atoms of alkyl group: 16), tetraoctylammonium bromide (number of carbon atoms of alkyl group: 8), dimethyltetradecylbenzylammonium chloride (number of carbon atoms of alkyl group: 14), distearyldimethylbenzylammonium chloride (number of carbon atoms of alkyl group: 18), stearyldimethylbenzylammonium chloride (number of carbon atoms of alkyl group: 18), and benzalkonium chloride (number of carbon atoms of alkyl group: 12 to 18). Moreover, among the alkylamines of the alkylamine salts, those having at least one alkyl group with a number of carbon atoms of 8 or more are preferable, and such alkylamines include octylamine (number of carbon atoms of alkyl group: 8), laurylamine (number of carbon atoms of alkyl group: 12), stearylamine (number of carbon atoms of alkyl group: 18), dioctylamine (number of carbon atoms of alkyl group: 8), dilaurylamine (number of carbon atoms of alkyl group: 12), distearylamine (number of carbon atoms of alkyl group: 18), trioctylamine (number of carbon atoms of alkyl group: 8), and trilaurylamine (number of carbon atoms of alkyl group: 12). Moreover, the surface control agent controls surface tension of an organic solvent dispersion prevent defects such as cissing and craters, and the surface control agents include acrylic surface control agents, vinyl surface control agents, silicone surface control agents, fluorine surface control agents, and the like. The additive amounts of the surfactant and the surface control agent can be appropriately adjusted, and it is preferable that the amount is, for example, 2.0 parts by mass or less with regard to 100 parts by mass of the metallic copper particle, and more preferably 0.2 parts by mass or less.

[0084] Furthermore, in the metallic copper dispersion according to the present invention, a fine metal particle other than the metallic copper may be appropriately blended according to the purpose of use in a range where the characteristics of the metallic copper of the present invention are not obstructed. For example, a fine metal particle such as gold, silver, nickel, or tin may be blended in the metallic copper dispersion.

[0085] The metallic paste according to the present invention includes a metallic copper particle, a binder resin, a solvent, and the like as main components, and appropriately including a surfactant, a crosslinking agent, a polymer dispersant, and the like blended therein. The metallic paste has a characteristic of having a relatively high thixotropy index (TI) value measured by the method described above, and specifically, the TI value can be set to 3.0 or more, preferably 3.5 or more, and more preferably 4.0 or more. The metallic paste actually used is prepared by appropriately blending the metallic copper particle and the like, and is desirable to have a certain degree of viscosity in view of a thick film formation, and generally, a metallic paste having a viscosity of 2000 mPa·s or higher is preferable.

[0086] Next, one embodiment according to the present invention is a process for producing a metallic copper dispersion including: mixing a copper compound and hypophosphorous acid and/or a salt thereof in a solvent in the presence of gelatin and/or a collagen peptide to reduce the copper compound; thereafter performing solid-liquid separation; and subsequently mixing and dispersing an obtained metallic copper particle in an aqueous solvent and/or an organic solvent. Moreover, preferably, one embodiment according to the present invention is a process for producing a metallic copper dispersion including: reducing a copper compound in the presence of gelatin and/or a collagen peptide in an aqueous solvent; thereafter performing solid-liquid separation; and subsequently mixing and dispersing: an obtained metallic copper particle having the gelatin and/or the collagen peptide on a surface of the particle; and a polymeric dispersant in an organic solvent.

[0087] A wet mixer is used for mixing the metallic copper particle and the aqueous solvent and/or the organic solvent, and, for example, fixed mixers such as stirrers, spiral mixers, ribbon mixers, and fluidizing mixers, rotary mixers such as cylindrical mixers and twin cylindrical mixers, wet grinding mills such as sand mills, ball mills, bead mills, colloid mills, and sand grinder mills, shakers such as paint shakers, and dispersion machines such as ultrasonic dispersion machines can be used. After appropriately selecting the mixer and the like from among those described above, mixing conditions thereof, mixing time thereof, and a dispersion media thereof are appropriately set. In this way, a metallic copper dispersion including the metallic copper particle dispersed in the organic solvent is obtained. Moreover, the metallic copper particle may be ground before mixing when necessary using a grinding mill such as a compression grinding type mill, an impact compression grinding type mill, a shearing grinding type mill, and a friction grinding type mill. Also, the metallic copper particle may be mixed at the same time when the metallic copper particle is ground.

[0088] Next, a metallic copper-containing film for an electrode, a wiring pattern, a design or decorative film coating, and the like, which use the metallic copper dispersion as one embodiment according to the present invention will be described. The metallic copper-containing film is a film in which a metallic copper is fixed on a base material. In addition, a metallic copper-containing film in which the metallic copper particle is more firmly fixed can be obtained by adding a curable resin to the dispersion. Moreover, by applying heat to the film coating or irradiating the film coating with light or plasma, the metallic copper particle is molten and bonded, and can be fixed still more firmly. In such a metallic copper-containing film, the thickness, size, shape, and the like are not limited, the film thickness may be thin or thick, and the whole surface of the base material or part thereof may be covered with the metallic copper-containing film. Alternatively, the metallic copper-containing film may have a fine line shape formed on part of the base material, a broad line shape, or a fine dot shape. As to the specific uses, the metallic copper-containing film can be used for an electrode and a wiring pattern by making use of conductivity of metallic copper, and can be also used for decoration uses and antimicrobial uses by making use of tone of color and antimicrobial action of metallic copper. Moreover, the metallic dispersion can be used for joining uses.

[0089] A decorative article or an antimicrobial article which are one embodiment according to the present invention is obtained by forming the metallic copper-containing film on at least part of the surface of a base material, and a metal color tone or antibacterial properties of the metallic copper particle are given on the surface of the base material of the decorative article or the antimicrobial article. The whole surface of the base material can be colored to give a metal color tone or antibacterial properties, and additionally, design, a mark, and a logo mark can be formed on part of the surface of the base material, or other characters, figures, and symbols can be also formed. As the base material, an inorganic material such as metal, glass, ceramics, rock, and concrete, an organic material such as rubber, plastics, paper, wood, leather, fabric, and fiber, and a material in which the inorganic material and the organic material are used in combination or are compounded can be used. The metallic copper-containing film can be formed on a raw material before processing the base material having such a material quality into an article to be used to give a decoration or antibacterial properties, or in all articles after processing the base material, a decoration or antibacterial properties can be given. In this case, the case where a decoration or antibacterial properties is given on the surfaces of articles coated in advance on the surfaces of these base materials is also included.

[0090] Specific examples of articles giving the decoration or antibacterial properties include the following:

(1) exterior and interior of transportation such as automobiles, tracks, and buses, a bumper, a doorknob, a rearview mirror, a front grille, a reflecting plate of a lamp, a display instrument, and the like;
(2) exterior of electric appliances such as a television set, a refrigerator, a microwave oven, a personal computer, a mobile phone, and a camera, a remote control, a touch panel, a front panel, and the like;
(3) exterior of buildings such as houses, buildings, department stores, stores, shopping malls, pachinko parlors, wedding halls, funeral halls, shrines, and temples, window glass, an entrance, a doorplate, a gate, a door, a doorknob, a show window, interior, and the like;
(4) house facilities such as lighting equipment, furniture, furnishings, toilet equipment, Buddhist altars and fittings, a Buddha statue, and the like;
(5) utensils such as hardware and tableware;
(6) vending machines of beverage, tobacco, and the like;
(7) containers for synthetic detergents, skin care products, soft drinks, alcoholic beverages, confectionery, food products, tobacco, and pharmaceuticals;
(8) packing materials such as wrapping paper and a carton box;
(9) outfits and accessories such as clothes, shoes, bags, glasses, artificial nails, artificial hair, and jewels;
(10) sporting goods such as a baseball bat, and a golf club, and products for hobbies such as fishing tools;
(11) stationery such as pencils, colored paper, notebooks, and postcards for New Year's greetings, and business equipment such as desks and chairs; and
(12) covers and bands for books, toys such as dolls and small toy cars, cards such as a commuter pass, and recording media such as CDs and DVDs. Moreover, human nails, skin, eyebrows, hair, and the like can be used as a base material.

[0091] Next, one embodiment according to the present invention is a process for producing a metallic copper-containing film wherein the above metallic copper dispersion is used. A step (a) in the production process according to the present invention is a step of adhering the metallic copper dispersion on the surface of the base material. A step (b) is a step of heating the metallic copper-containing film produced in the above step (a) under a nonreducing gas atmosphere or under a reducing gas atmosphere. A step (c) is a step of irradiating the whole or partial region of the metallic copper-containing film with light after the above step (a). Moreover, a step (d) is a step of irradiating the whole or partial region of the metallic copper-containing film with plasma after the step (a). Further, a step (e) is a step of removing the metallic copper-containing film in the region not irradiated after the above step (c) or (d). Furthermore, a step (f) is a step of transferring the metallic copper-containing film obtained through the above steps (a) to (d) on another base material. The metallic copper-containing film can be also produced in the above step (a), and the subsequent steps (b) to (f) are a step performed when necessary. A firm metallic copper-containing film can be produced by performing any one of the steps (b) to (e), and moreover, by performing the step (f), a metallic copper-containing film can be simply produced on a base material which is difficult to directly form the metallic copper-containing film. Moreover, when an electrode and a wiring pattern are produced, it is also possible to perform any combination of steps (b) to (f) after the step (a).

Step (a)

[0092] The metallic copper dispersion according to the present invention is adhered (which is typically expressed by "applied" hereinafter) on the base material. As for application of the metallic copper dispersion, a general printing method or transfer method, such as screen printing, gravure printing, flexographic printing, ink jet printing, or offset printing, or a general application method using a spray, a slit coater, a curtain coater, a bar coater, a brush, a pen brush, or a spin coater can be used. The thickness of the coated layer is not particularly limited, and can be appropriately selected according to the purpose of use and uses, however, a thickness of 0.001 to 100 μm is preferable, and a thickness of 0.005 to 70 μm is more preferable. An application pattern at this time can be applied on the whole surface of the base material, and can be also applied in pattern or figuratus form. According to the application method, the purpose of use, and uses, the particle diameter of the metallic copper particle, the kind of the polymeric dispersant, the organic solvent, and other compounds can be appropriately selected. Similarly, viscosity of the dispersion and the concentration of metallic copper can be appropriately selected.

[0093] As the base material, glasses such as alkali-free glass, quartz glass, crystallized transparent glass, Pyrex (which is a registered trade-mark) glass, and sapphire glass; inorganic materials such as Al_2O_3, MgO, BeO, ZrO_2, Y_2O_3, CaO, and GGG (gadolinium-gallium-garnet); acrylic resins such as PET (polyethylene terephthalate), PEN (polyethylene naphthalate), polypropylene, polycarbonate, and polymethyl methacrylate; vinyl chloride resins such as polyvinyl chloride and vinyl chloride copolymers; organic materials such as epoxy resins, polyarylates, polysulfones, polyethersulfones, polyimides, fluororesins, phenoxy resins, polyolefin resins, nylons, styrene resins, and ABS resins; and a substrate formed by using a composite material in which inorganic particles having a diameter of several nanometers are dispersed in the organic material; a silicon wafer; and a metal plate, and the like can be used. The base material can be appropriately selected from these materials according to uses, and used as a flexible base material in a film form and the like or a rigid base material. In addition, the size of the base material is not limited, the shape of the base material may be any shape such as a disc shape, a card shape, and a sheet-like shape, and the surface of the base material does not need to be planar, and may have depressions and projections, or may have a curved surface.

[0094] On the base material, a foundation layer may be provided in order to improve planarity of the surface of the base material and adhesive strength and in order to prevent deterioration of the metallic copper-containing film. Examples of materials for the foundation layer include polymer materials such as polymethyl methacrylate, acrylic acid-methacrylic acid copolymers, styrene-maleic anhydride copolymers, polyvinyl alcohols, N-methylolacrylamide, styrene-vinyltoluene copolymers, chlorosulfonated polyethylenes, nitrocellulose, polyvinyl chloride, polyvinylidene chloride, chlorinated polyolefins, polyesters, polyimides, vinyl acetate-vinyl chloride copolymers, ethylene-vinyl acetate copolymers, polyethylenes, polypropylenes, and polycarbonates; thermosetting resins, photocurable or electron beam curable resins; and surface modifiers such as coupling agents. As the material of the foundation layer, materials having high adhesion between the base material and the metallic copper-containing film are preferable. Specifically, thermosetting, photocurable or electron beam curable resins, and surface modifiers such as coupling agents (for example, silane coupling agents, titanate coupling agents, germanium coupling agents, and aluminum coupling agents), colloidal silica, and the like are preferable.

[0095] The foundation layer can be formed by dissolving or dispersing the above material in an appropriate solvent to prepare a coating liquid, applying the coating liquid on the surface of the base material using a coating method such as spin coating, dip coating, extrusion coating, and bar coating. It is preferable that the layer thickness (at the drying) of the foundation layer is generally 0.001 to 20 μm, and more preferably 0.005 to 10 μm.

[0096] When necessary, a film after the metallic copper dispersion is applied thereon may be heated at an appropriate temperature to evaporate and remove (which is described as "drying by heating" hereinafter) the organic solvent or the aqueous solvent (in this case, depending on the kind thereof, other compounds having low-boiling point are included) in the metallic copper-containing film. The temperature for drying by heating can be appropriately set, but in order to suppress oxidization of metallic copper, the temperature of 150°C or less is preferable, and the temperature of 120°C or less is more preferable. The heating time can also be set appropriately. Also, an atmosphere can be appropriately set, and further, heating can be performed under a nonreducing gas atmosphere (i.e. inert gas atmosphere (for example, nitrogen or argon) or oxygen gas-containing atmosphere (for example, in the air)) or a reducing gas atmosphere. Nitrogen gas, argon gas, helium gas, and the like can be used as an inert gas. In addition, evaporation and removal of the organic solvent or the like is not limited to drying by heating, and a natural drying method or a reduced pressure drying method may be used. In the case of reduced pressure drying, it is performed under pressure lower than atmospheric pressure, and specifically, the reduced pressure drying may be performed under vacuum pressure and ultra-vacuum pressure.

Step (Preliminary Step for Step (b))

[0097] After the step (a), it is preferable to heat the metallic copper-containing film at an appropriate temperature when necessary. By heating, organic compounds included in the metallic copper-containing film, such as the gelatin and/or the collagen peptide, and the polymeric dispersant can be decomposed and/or vaporized (which is described as "oxidization firing by heating" hereinafter). It is preferable that the heating is performed under an oxygen-containing atmosphere in order to accelerate decomposition and/or vaporization of the organic compounds, and more preferably in an oxygen-containing gas stream. It is preferable that the concentration of oxygen in the atmosphere is 10 to 10000 ppm because oxidization of the metallic copper particle does not progress so fast. The temperature for oxidization firing by heating can be appropriately set according to the kind of the base material or the like, and the temperature of 100 to 500°C is preferable, and the temperature of 120 to 300°C is more preferable. The heating time can be also set appropriately, and can be set to, for example, about one minute to about 48 hours, and the heating time of about 10 minutes to about 48 hours is preferable.

Step (b)

[0098] A copper-containing film is heated at an appropriate temperature under a nonreducing gas atmosphere (i.e. under inert gas atmosphere or oxygen gas-containing atmosphere (for example, in the air)) or under a reducing gas atmosphere (which is described as "firing by heating" hereinafter). The inert gas atmosphere is preferable, and nitrogen gas, argon gas, helium gas, and the like can be used as an inert gas. In the present step, fusion between the metallic copper particles formed in the previous step such as "Preliminary Step for Step (b)" is made to occur, and, when necessary, a reduction reaction of the copper compound or the like to metallic copper is made to occur. This is because the melting point of the nano-size particle (i.e. the fine metallic copper particle or the small metallic copper particle) included in the metallic copper particle according to the present invention becomes lower than that of a bulk due to a size effect thereof, and thus this nano size particle is molten even in a relatively low temperature range. As a result, electric resistance can be remarkably reduced and a metal color tone can be improved through the step in a short time. For example, hydrogen gas, carbon monoxide gas, and the like can be used as a reducing gas, and the nitrogen gas including about 0.1 to about 5% of hydrogen gas is preferable in view of safety and availability. The heating temperature can be appropriately set according to the kind of the base material or the like, and the heating temperature of 50 to 500°C is preferable, the heating temperature of 80 to 300°C is more preferable, and a temperature from the heating temperature in the step (i.e. "Preliminary Step for Step (b)") to 300°C is still more preferable. The heating time can be also set appropriately, and can be set to, for example, about one minute to about 48 hours, and the heating time of about 10 minutes to about 48 hours is preferable. By this heating step, a volume resistance value of the obtained metallic copper-containing film can be made at 1×10^{-2} Ω·cm or less, preferably 1×10^{-3} Ω·cm or less, more preferably 1×10^{-4} Ω·cm or less, and still more preferably 1×10^{-5} Ω·cm or less.

[0099] The step for evaporation and removal of the organic solvent, which is performed when necessary, the step for the oxidization firing by heating (i.e. "Preliminary Step for Step (b)"), and the step for the firing by heating (i.e. "Step (b)") may be performed separately, or may be performed continuously. Moreover, these steps are not limited to the case of performing the step for the oxidization firing by heating after the drying by heating, and the step for the oxidization firing by heating can be performed after a natural drying or reduced pressure drying is performed without performing the drying by heating, or the organic solvent can be evaporated and removed in the step for the oxidization firing by heating, which also serves as the step for the drying by heating, and these steps do not need to be clearly distinguished.

Step (c)

[0100] The whole or partial region of the metallic copper-containing film produced in the step (a) is irradiated with light. The light may be infrared rays, visible rays, ultraviolet rays, X-rays (soft X-rays to hard X-rays), a laser beam that radiates by amplifying light, or sunlight. A pattern is drawn on the base material by moving a light source or the base material while irradiating the metallic copper-containing film with the light. A pattern can be also drawn on the base material by converging a laser beam oscillated with a laser oscillator, setting a diameter of irradiation appropriately, and moving a laser mount section or the base material while irradiating the metallic copper-containing film with the laser beam. The light is absorbed by the metallic copper-containing film, and along with the decomposition and/or vaporization of the organic compounds such as the gelatin and/or the collagen peptide and the polymeric dispersant by the heat generated thereby, the fusion between the metallic copper particles occurs, and thus the reduction of electric resistance of an irradiated portion of the metallic copper-containing film and the improvement of a metal color tone thereof can be provided. The nano size particle (the fine metallic copper particle or the small metallic copper particle) according to the present invention has the melting point lower than the melting point of a bulk due to a size effect thereof, and thus the pattern can be drawn with a relatively low energy and at a high speed.

[0101] According to kinds and blending amounts of the gelatin and/or the collagen peptide, the polymeric dispersant, the complexing agent and the like which are used, a wavelength of the light can be arbitrarily selected in a range where the metallic copper-containing film can absorb the light, and the light with a wavelength in an ultraviolet region, a visible light region, an infrared region, or the like is preferable because it is easy to use. Light sources that emit incandescent light, discharge light, electroluminescence, or the like can be used as the light source, and an incandescent lamp, light sources that make use of luminescence by discharge such as an infrared lamp, a visible light lamp, an ultraviolet lamp, a mercury lamp, and xenon lamp, semiconductor devices (e.g. light emitting diodes) and the like that emit light when a voltage is applied, such as LED can be used as the light source. Typical lasers include: semiconductor lasers using GaN, GaAsAl, InGaAsP, or the like; excimer lasers using ArF, KrF, XeCl, or the like; dye lasers using rhodamine, or the like; gas lasers using He-Ne, He-Cd, CO_2, Ar ion, or the like; free electron lasers; solid state lasers such as ruby lasers and Nd: YAG lasers; and so on. Moreover, a higher order harmonic wave such as a second harmonic wave and third harmonic wave of these lasers may be also used, and a laser beam at any wavelength in the ultraviolet region, the visible light region, and the infrared region can be used. Further, irradiation of a continuous wave or irradiation of a pulse wave may be used. Conditions on applied energy such as a diameter of irradiation of the light, a scan speed, and an output can be appropriately set in a range in which oxidization of metallic copper, and ablation and peening of the metallic copper-containing film do not occur. The diameter of irradiation can be appropriately set in accordance with a pattern or figure to be drawn, and the diameter of irradiation of 10 μm to 5 mm is suitable. The scan speed can be also set appropriately according to other parameters, required accuracy, manufacturing capacity, and the like.

[0102] An atmosphere performing light irradiation such as an inert gas atmosphere, a reducing gas atmosphere, and an oxygen gas-containing atmosphere (e.g. air atmosphere) can be appropriately set. By using the metallic copper dispersion according to the present invention, a metallic copper-containing film having a low resistance and a good metal color tone can be formed without causing the oxidation of copper in the metallic copper-containing film even under the oxygen gas-containing atmosphere (e.g. air atmosphere), which is expected to be attributed to the presence of the gelatin. Specifically, this can be achieved by irradiation with a continuous wave laser beam having a wavelength in the infrared region at a scan speed of 1 to 500 mm/s and at an output range of 1 to 140 W under the oxygen gas-containing atmosphere

[0103] (e.g. air atmosphere). At this time, conditions on laser irradiation are adjusted so that main peak strength in a Cu_2O (111) plane may be 20 or less when main peak strength in a metallic copper (111) plane is assumed to be 100 in X-ray diffraction of the metallic copper-containing film at a portion irradiated with the laser beam. It is more preferable to set an output of the laser beam to be 10 to 100 W, and an output of the laser beam in a range of 20 to 50W is still more preferable. The semiconductor lasers are preferable because the semiconductor lasers are generally suitable for irradiation with a continuous laser beam having a wavelength in the infrared region.

Step (d)

[0104] Next, the whole or partial region of the metallic copper-containing film produced in the step (a) is irradiated with plasma to produce a metallic copper-containing film. In this step, organic compounds included in the metallic copper-containing film, such as the gelatin and/or the collagen peptide, and the polymeric dispersant are decomposed or vaporized, and fusion of metallic copper particles is made to occur. Plasma irradiation can be appropriately selected from among publicly known methods. For example, a metallic copper-containing film is placed in a plasma treatment apparatus, a gas is introduced, and energy is applied to ionize the gas to be in a plasma state. Excitation energy that is supplied to the gas is, for example, electric discharge, direct current, radio frequency, microwave, or electromagnetic radiation. Moreover, in general, plasma can be also generated by applying voltage between two electrodes to form an electric field. Gases suitable for plasma treatment include helium, argon, hydrogen, nitrogen, air, nitrous oxide, ammonia, carbon dioxide, oxygen, and the like, and the oxygen gas, the hydrogen gas, a mixed gas of oxygen and helium or argon, and a mixed gas of hydrogen and helium or argon are more preferable. The plasma treatment can be performed under atmospheric conditions, or the plasma treatment may be performed in an apparatus capable of retaining plasma under a reduced pressure or a vacuum condition. It is preferable that the pressure is in a range of about 10 mTorr to about 760 Torr (about 1.333 to about 101325 Pa).

[0105] Specifically, the plasma treatment can be performed as described in the following example. First of all, the metallic copper-containing film is placed in a plasma treatment apparatus, and the base material is heated in the atmospheric air when necessary. The heating temperature can be set according to the material quality of the base material, and the heating temperature is preferably 180°C or less when a plastic having a low heat resistance is used, and more preferably 120°C or less. As the lower limit value of the heating temperature, a temperature of about 20°C is practical. Next, it is preferable that heating be performed under a reduced pressure or a vacuum condition, and the heating temperature is preferably 180°C or less, and still more preferably 120°C or less. The heating time can be appropriately set. And a gas is introduced in the plasma treatment apparatus to generate plasma while heating is continuously performed, and the whole or partial region of the metallic copper-containing film is irradiated with its plasma. It is preferable that microwave energy having a frequency of 2450 MHz is supplied to generate microwave surface wave plasma. When a partial region is irradiated with plasma, the other region can be protected so as not to be irradiated with plasma by putting a mask pattern on the metallic copper-containing film. The plasma irradiation time can be appropriately set, and is, for example, about 0.01 to about 30 minutes, and a plasma irradiation time of about 0.01 to about 10 minutes is suitable. The plasma irradiation can be also performed in two stages. In the first step thereof, the metallic copper-containing film is irradiated with plasma in the presence of oxygen gas to decompose an organic compound such as the gelatin, and thereafter in the second step thereof, the metallic copper-containing film is irradiated in the presence of a reducing gas, thereby making it possible to sinter the metallic copper particle.

Step (e)

[0106] Further, an unnecessary portion of the metallic copper-containing film, a portion of the metallic copper-containing film, not irradiated with the light in the above step (c), or a portion of the metallic copper-containing film, not irradiated with the plasma in the above step (d) may be removed using an appropriate solvent when necessary. As the solvent, various solvents such as alcohol solvents, glycol ether solvents, and aromatic solvents can be used. The unnecessary portion or the like can be removed by immersing the base material in such a solvent or wiping off the portion with fabric or paper dipped in the solvent.

Step (f)

[0107] Next, the whole or partial region of the metallic copper-containing film produced on the base material can be also transferred on another base material after the step (a), the step (b), the step (c), the step (d), or the step (e).

[0108] In addition, the steps (b) to (e) after the step (a) can be arbitrarily combined and performed. For example, the step (b) can be performed after the step (a), and the step (c) can further be performed. Also, the step (c), the step (d), or the step (e) can be performed after the step (a), and the step (b) can further be performed. Moreover, in the step (b), only the "Preliminary Step for Step (b)" of the step (b) or only the step (b) can be combined and performed. For example, the step (c) can be performed after the step (a), and the step (b) can further be performed.

[0109] It is preferable that the whole of the metallic copper-containing film produced by any one of (a) to (f) in the present invention is sintered because the resistance value is low. Thus, it is preferable to perform heating, light irradiation, or plasma irradiation with sufficient time and strength for sintering the whole of the metallic copper-containing film. However, only the surface portion of the metallic copper-containing film may be sintered and the inside thereof may not be sintered, and there is no problem even when only part of the surface is sintered, as long as the performance of the resistance value or the like, necessary for uses can be obtained. The volume resistance value of the metallic copper-containing film is preferably 50 $\mu\Omega\cdot$cm or less, more preferably 20 $\mu\Omega\cdot$cm or less, and still more preferably 10 $\mu\Omega\cdot$cm or less. The thickness, size, shape, and the like of such a metallic copper-containing film are not limited, and the metallic copper-containing film may be a thin film or a thick film, and the film may cover the whole or part of the base material. Alternatively, the metallic copper-containing film may have a fine wire-like shape or wide wire-like shape formed on part of the base material, or may have a fine dotted shape. It is preferable that the thickness be, for example, 1 μm or less, more preferably 0.5 μm or less. As specific uses, the metallic copper-containing film can be used for an electrode and a wiring pattern, for joining chips and substrates, and for other uses making use of the electrical conductivity of metallic copper, and can be also used for decoration uses and antibacterial uses making use of color tone or antibacterial properties of metallic copper.

Examples

[0110] Hereinafter, the present invention will be described in more detail giving Examples, however the present invention is not limited to these Examples.

Example 1

[0111] To 150 ml of pure water, 24 g of industrial copper(II) oxide (N-120 manufactured by NC-Tech Co., Ltd.) and 9.55 g of gelatin (amine value of 23, acid value of 29, amine value - acid value = -6, and mass average molecular weight of 200000) as protective colloid were added and mixed, and the temperature of the mixed solution was raised to 80°C. After the temperature was raised, a solution prepared by mixing 1.2 g of aminoethanol as a complexing agent and 99 g of 50% hypophosphorous acid in 150 ml of pure water was added to the mixed solution under stirring, the resultant mixture was reacted with copper oxide for one hour, and then the reaction solution was subjected to aging for two hours to produce a copper particle coated with the gelatin. Thereafter, the copper particle was subjected to filtration and washing until a specific conductivity of a filtrate reached 100 μS/cm or less, and dried for 10 hours at a temperature of 60°C under an atmosphere of nitrogen gas to obtain a metallic copper particle coated with the gelatin (sample A).

Examples 2 to 5

[0112] Metallic copper particles (samples B to E) according to the present invention were obtained in the same manner as in Example 1 except that the amount of the gelatin in Example 1 was changed to the amounts described in Table 1.

Examples 6 to 7

[0113] Metallic copper particles (samples F to G) according to the present invention were obtained in the same manner as in Example 1 except that the reaction temperature set at 80°C in Example 1 was changed to 60°C or 70°C.

Example 8

[0114] A metallic copper particle (sample H) according to the present invention was obtained in the same manner as in Example 1 except that the aminoethanol in Example 1 was not added.

Example 9

[0115] A metallic copper particle (sample I) according to the present invention was obtained in the same manner as in Example 1 except that the aminoethanol in Example 1 was added in an amount of 4.86 g.

Example 10

[0116] A metallic copper particle (sample J) according to the present invention was obtained in the same manner as in Example 1 except that the gelatin in Example 1 had a mass average molecular weight of 10000.

Example 11

[0117] A metallic copper particle (sample K) according to the present invention was obtained in the same manner as in Example 1 except that the gelatin in Example 1 was 19.11 g of gelatin having a mass average molecular weight of 10000.

Example 12

[0118] A metallic copper particle (sample L) according to the present invention was obtained in the same manner as in Example 1 except that a collagen peptide having a mass average molecular weight of 5000 was further used.

Example 13

[0119] A metallic copper particle (sample M) according to the present invention was obtained in the same manner as in Example 1 except that 19.11 g of a collagen peptide having a mass average molecular weight of 5000 was further used.

Examples 14 to 15

[0120] Metallic copper particles (samples N to O) according to the present invention were obtained in the same manner as in Example 7 except that the aging time in Example 7 was changed to one hour or three hours.

Examples 16 to 18

[0121] Metallic copper particles (samples P to R) according to the present invention were obtained in the same manner as in Example 7 except that to the mixed solution of industrial copper (II) oxide, gelatin, and pure water in Example 7, citric acid, formic acid, or lactic acid was further added as an organic acid.

Examples 19 to 20

[0122] Metallic copper particles (sample S to T) according to the present invention were obtained in the same manner as in Example 1 except that the time for adding hypophosphorous acid in Example 1 was changed to two hours or three hours.

Examples 21 to 24

[0123] Metallic copper particles (samples U to X) according to the present invention were obtained in the same manner as in Example 17 except that the amount of the gelatin in Example 17 was changed.

Examples 25 to 27

[0124] Metallic copper particles (samples Y to AA) according to the present invention were obtained in the same manner as in Example 17 except that the amount of the organic acid in Example 17 was changed to the amounts described in Table 1.

Example 28

[0125] A metallic copper particle (sample AB) according to the present invention was obtained in the same manner as in Example 17 except that the reaction temperature in Example 17 was changed to 40°C .

Example 29

[0126] A metallic copper particle (sample AC) according to the present invention was obtained in the same manner as in Example 17 except that the aminoethanol in Example 17 was not added.

Example 30

[0127] A metallic copper particle (sample AD) according to the present invention was obtained in the same manner as in Example 29 except that 9.62 g of pyrophosphoric acid was added as a pH-adjusting agent to the mixed solution of industrial copper (II) oxide, gelatin, and pure water in Example 29.

Comparative Example 1

[0128] A metallic copper particle (sample AE) was obtained in the same manner as in Example 1 except that the gelatin in Example 1 was not used.

Comparative Example 2

[0129] To 350 ml of pure water, 24 g of industrial copper (II) oxide (N-120: manufactured by NC-Tech Co., Ltd.) and 9.55 g of gelatin (amine value of 23, acid value of 29, amine value - acid value = -6, and mass average molecular weight of 200,000) as protective colloid were added and mixed, and after the pH of the mixed solution was adjusted at 9 using 15% ammonia water, the temperature of the mixed solution was raised from room temperature to 90°C in 30 minutes. After the temperature was raised, a solution prepared by mixing 1.2 g of an aminoethanol solution and 38 g of 80% hydrazine monohydrate to 15 ml of pure water was added to the mixed solution in 60 minutes under stirring, and the resultant mixture was reacted with the copper (II) oxide for one hour to produce a copper particle. After producing the fine copper particle, 5 mL of a serine protease (Ptoteinase K: manufactured by Worthington Biochemical Corporation) was added as a protective colloid remover, and the resultant mixture was held for one hour. Thereafter, the mixture was subjected to filtration and washing until a specific conductivity of a filtrate reached 100 μS/cm or less, and dried for 10 hours at a temperature of 60°C under an atmosphere of nitrogen gas to obtain a metallic copper particle (sample AF).

Comparative Example 3

[0130] A metallic copper particle having a flat shape (sample AG) was obtained by mixing and suspending 10 g of the copper particle which is coated with the gelatin and which has an average particle diameter of 500 nm, synthesized in Comparative Example 2, 30 g of ethanol, and 50 g of zircon beads; shaking the suspension with a paint shaker for three hours; subsequently separating and removing the beads; and then filtrating the resultant.

Comparative Example 4

[0131] A metallic copper particle (sample AH) was obtained in the same manner as in Example 1 except that the copper oxide in Example 1 was changed to copper sulfate.

[0132] Production conditions described above are listed together in Table 1. Moreover, the pH before adding a reducing agent and the pH after aging are shown in Table 2 for some samples.

[Table 1]

	Sample	Mass average molecular weight of gelatin	Amount of gelatin	Kind of complexing agent	Amount of complexing agent (g)	Kind of organic acid	Amount of organicacid (g)	Amount of reducing agent (g)	Reaction temperature [°C]
			(g)					(50 wt% Hypophosphorous acid)	
Example 1	A	200000	9.55	Aminoethanol	1.2	Not added	0	99	80
Example 2	B	200000	4.78	Aminoethanol	1.2	Not added	0	99	80
Example 3	C	200000	5.73	Aminoethanol	1.2	Not added	0	99	80
Example 4	D	200000	14.33	Aminoethanol	1.2	Not added	0	99	80
Example 5	E	200000	19.11	Aminoethanol	1.2	Not added	0	99	80
Example 6	F	200000	9.55	Aminoethanol	1.2	Not added	0	99	60
Example 7	G	200000	9.55	Aminoethanol	1.2	Not added	0	99	70
Example 8	H	200000	9.55	Not added	0	Not added	0	99	80
Example 9	I	200000	9.55	Aminoethanol	4.86	Not added	0	99	80
Example 10	J	10000	9.55	Aminoethanol	1.2	Not added	0	99	80
Example 11	K	10000	19.11	Aminoethanol	1.2	Not added	0	99	80
Example 12	L	5000	9.55	Aminoethanol	1.2	Not added	0	99	80
Example 13	M	5000	19.11	Aminoethanol	1.2	Not added	0	99	80
Example 14	N	200000	9.55	Aminoethanol	1.2	Not added	0	99	70
Example 15	O	200000	9.55	Aminoethanol	1.2	Not added	0	99	70
Example 16	P	200000	9.55	Aminoethanol	1.2	Citric acid	11.5	99	70
Example 17	Q	200000	9.55	Aminoethanol	1.2	Formic acid	3.1	99	70
Example 18	R	200000	9.55	Aminoethanol	1.2	Lactic acid	5.4	99	70
Example 19	S	200000	9.55	Aminoethanol	1.2	Not added	0	99	80
Example 20	T	200000	9.55	Aminoethanol	1.2	Not added	0	99	80

(continued)

	Sample	Mass average molecular weight of gelatin	Amount of gelatin	Kind of complexing agent	Amount of complexing agent (g)	Kind of organic acid	Amount of organicacid (g)	Amount of reducing agent (g)	Reaction temperature [°C]
			(g)					(50 wt% Hypophosphorous acid)	
Example 21	U	200000	1.91	Aminoethanol	1.2	Formic acid	3.1	99	70
Example 22	V	200000	3.82	Aminoethanol	1.2	Formic acid	3.1	99	70
Example 23	W	200000	5.73	Aminoethanol	1.2	Formic acid	3.1	99	70
Example 24	X	200000	7.64	Aminoethanol	1.2	Formic acid	3.1	99	70
Example 25	Y	200000	9.55	Aminoethanol	1.2	Formic acid	1.6	99	70
Example 26	Z	200000	9.55	Aminoethanol	1.2	Formic acid	4.8	99	70
Example 27	AA	200000	9.55	Aminoethanol	1.2	Formic acid	6.2	99	70
Example 28	AB	200000	9.55	Aminoethanol	1.2	Formic acid	3.1	99	40
Example 29	AC	200000	9.55	Not added	0	Formic acid	3.1	99	70
Example 30	AD	200000	9.55	Not added	0	Formic acid	3.1	99	70
Comparative Example 1	AE	-	0	Aminoethanol	1.2	Not added	0	99	80
Comparative Example 2	AF	200000	9.55	Aminoethanol	1.2	Not added	0	38g of Hydrazine	90

(continued)

	Sample	Mass average molecular weight of gelatin	Amount of gelatin	Kind of complexing agent	Amount of complexing agent (g)	Kind of organic acid	Amount of organicacid (g)	Amount of reducing agent (g)	Reaction temperature [°C]
			(g)					(50 wt% Hypophosphorous acid)	
Comparative Example 4	AH	200000	9.55	Aminoethanol	1.2	Not added	0	99	80

[Table 2]

	Sample	Initial pH	pH after aging
Example 1	A	8.4	0.8
Example 16	P	3.5	0.7
Example 17	Q	3.4	0.7
Example 18	R	3.5	0.7
Example 25	Y	3.7	0.7
Example 26	Z	3.0	0.6
Example 27	AA	2.8	0.6
Example 30	AD	1.4	0.6
Comparative Example 1	AE	8.6	0.8
Comparative Example 2	AF	9.0	9.8

[0133] As a result of X-ray diffraction of the samples (A to AH) obtained in the Examples and the Comparative Examples, peaks of metallic copper were confirmed for all the samples, and thus it was found that all the samples were metallic copper. Fig. 1 shows an X-ray diffraction chart of sample A. Moreover, the specific surface areas (according to nitrogen adsorption BET method) and the amounts of phosphorus (according to XRF analysis) included in these samples are shown in Table 3. It was found that the samples of the Examples include phosphorus in an amount of about 0.2 to about 0.4% by mass. Further, it was found from these electron micrographs that in the samples of the Examples, fine metallic copper particles were adhered on the surface of a large diameter metallic copper particle, and partially aggregated fine metallic copper particles were adhered on the surface of the large diameter metallic copper particle. Furthermore, it was also found that the metallic copper particles (i.e. composite particles) and the small metallic copper particles coexisted. On the other hand, it was found that in the samples of the Comparative Examples, particles having one kind of shape and almost uniform size existed. As one example, in Fig. 2 to Fig. 35, electron micrograph (SEM photograph) of each of the samples (A to M, Z, AE, AF, AND AG) is shown. Moreover, the primary particle diameters of the samples (A to AH) are shown in Table 3.

[Table 3]

	Sample	Specific surface area [m^2/g]	Amount of P	Average primary particle diameter of fine particles [nm]	Average primary particle diameter of large diameter particles [μm]
			[% by mass]		
Example 1	A	1.9	0.26	128	15.9
Example 2	B	1.9	0.27	47	13.2
Example 3	C	1.1	0.26	103	13.5
Example 4	D	1.7	0.25	154	15.1
Example 5	E	1.9	0.26	70	12.3
Example 6	F	5.3	0.32	88	4.1
Example 7	G	2.7	0.26	114	9.8
Example 8	H	1.8	0.24	111	9.8
Example 9	I	1.8	0.25	121	9.8
Example 10	J	1.5	0.25	123	2.3
Example 11	K	1.5	0.25	148	2.3
Example 12	L	1.2	0.25	161	6.3
Example 13	M	2.0	0.25	93	12.1

(continued)

	Sample	Specific surface area [m²/g]	Amount of P	Average primary particle diameter of fine particles [nm]	Average primary particle diameter of large diameter particles [μm]
			[% by mass]		
Example 14	N	4.2	0.21	179	6.26
Example 15	O	3.8	0.21	134	11.02
Example 16	P	3.2	0.25	45	3.7
Example 17	Q	3.3	0.24	186	4.5
Example 18	R	3.4	0.23	134	5.5
Example 19	S	3.2	0.25	125	5.5
Example 20	T	3.1	0.25	143	6.2
Example 21	U	2.9	0.21	164	16.9
Example 22	V	2.7	0.25	173	14.5
Example 23	W	3.8	0.25	202	9.1
Example 24	X	3.7	0.26	211	10.4
Example 25	Y	3.1	0.28	173	10.0
Example 26	Z	3.0	0.26	203	9.4
Example 27	AA	3.2	0.24	155	18.2
Example 28	AB	5.9	0.25	149	2.2
Example 29	AC	3.5	0.25	140	15.2
Example 30	AD	3.5	0.30	60	10.2
Comparative Example 1	AE	0.5	0.24	Not exist	3.8
Comparative Example 2	AF	1.5	-	Not exist	0.5
Comparative Example 3	AG	2.5	-	Not exist	2.4
Comparative Example 4	AH	3.1	0.25	129	Not exist

[0134] The CHN analysis was performed for the metallic copper powders of samples N and Q to estimate the amounts of gelatin and of formic acid. Specifically, the amount of gelatin was calculated from the ratio of CHN components in the gelatin, and the residual organic content was estimated as the amount of formic acid and the like. The results are shown in Table 4. In the sample Q in which formic acid was added, the organic content originating in formic acid and the like was large, and it is suggested that formic acid is adsorbed on the surface. The CHN analysis was performed using Vario III CHN Elemental Analyzer manufactured by Elementar Analysensysteme GmbH, capable of analyzing the amount of C, H, and N with a TCD (Thermal conductivity detector) by burning and gasifying an organic component on the surface of each powder and separating the gas with a column.

[Table 4]

Sample	Gelatin [wt%]			Formic acid and the like [wt%]			Total amount of CHN [wt%]		
	C	H	N	C	H	N	C	H	N
N	0.50	0.08	0.18	0.01	0.00	0.00	0.51	0.08	0.18

(continued)

Sample	Gelatin [wt%]			Formic acid and the like [wt%]			Total amount of CHN [wt%]		
	C	H	N	C	H	N	C	H	N
Q	0.37	0.06	0.13	0.14	0.02	0.00	0.51	0.08	0.13

Production 1 of Metallic Copper-Containing Film (Heating at 300°C under Nitrogen Atmosphere)

[0135] Copper pastes were prepared by mixing 10 g of each of the samples (A to AG) obtained in the Examples and the Comparative Examples, 3.5 g of a vehicle (resin: 20% by mass of ethyl cellulose N200 and solvent: terpineol), and 6.5 g of terpineol, and then kneading the resultant mixture with a three-roll mill. Each of the prepared copper pastes was applied on an alumina substrate with an applicator and fired using an atmosphere tube furnace at 300°C for one hour under a nitrogen atmosphere to prepare metallic copper-containing films. The specific resistance values of the obtained metallic copper-containing films were measured using MCP-T610 Loresta GP manufactured by Mitsubishi Chemical Analytech Co., Ltd. by a direct current four-terminal method. Thereafter, the cross sections were observed with a scanning electron microscope to measure the film thicknesses, and the volume resistance values were calculated. The results are shown in Table 5. The volume resistance values are 1×10^{-2} $\Omega\cdot$cm or less in all the samples of the Examples. And, it is presumed that the existence state, the ratio, the particle diameter, the aggregation state, and the like of the fine metallic copper particles and the large diameter metallic copper particle give an influence on the results. Moreover, it is presumed that the existence state, the ratio, the particle diameter, the aggregation state, and the like of the metallic copper particle (i.e. composite particle) and the small metallic copper particles give an influence on the results. Alternatively, it is presumed that because formic acid existing on the surface is easy to disappear at low temperatures, the sintering was facilitated. On the other hand, in all the samples of the Comparative Examples, the volume resistance values were 1×10^{2} $\Omega\cdot$cm or more.

[Table 5]

	Sample	Volume resistance value	Film thickness
		[$\Omega\cdot$cm]	[μm]
Example 1	A	9.20E-05	10.1
Example 2	B	2.40E-03	11.7
Example 3	C	5.70E-04	11.1
Example 4	D	4.40E-04	17.1
Example 5	E	1.00E-04	7.4
Example 6	F	2.10E-04	11.8
Example 7	G	1.50E-04	9.5
Example 8	H	6.60E-03	10.1
Example 9	I	1.60E-03	15.5
Example 10	J	6.10E-03	9.9
Example 11	K	7.40E-03	10.5
Example 12	L	3.70E-03	12.4
Example 13	M	3.90E-03	11.2
Example 14	N	4.50E-05	12.0
Example 15	O	6.52E-05	11.1
Example 16	P	1.10E-04	10.5
Example 17	Q	5.00E-05	11.3
Example 18	R	5.80E-05	11.8

(continued)

	Sample	Volume resistance value [$\Omega\cdot$cm]	Film thickness [μm]
Example 19	S	1.90E-03	10.5
Example 20	T	1.10E-04	8.5
Example 21	U	2.20E-05	9.8
Example 22	V	3.50E-05	11.6
Example 23	W	4.20E-05	11.4
Example 24	X	2.30E-05	11.5
Example 25	Y	1.10E-04	10.8
Example 26	Z	3.60E-05	10.2
Example 27	AA	5.10E-05	11.2
Example 28	AB	1.20E-04	11.0
Example 29	AC	8.00E-05	10.9
Example 30	AD	6.55E-05	11.2
Comparative Example 1	AE	8.60E+04	14.6
Comparative Example 2	AF	1.10E+04	15.1
Comparative Example 3	AG	5.50E+02	11.5

[0136] Next, metallic copper-containing films were prepared in the same manner as "Production 1 of Metallic Copper-Containing Film" described above, except that the metallic copper particles each of which was prepared by mixing the sample W and the sample X in a ratio as shown in Table 6 were used, and the volume resistance values were measured for the metallic copper-containing films. The results are shown in Table 6. The volume resistance values can be further reduced by mixing the sample W and the sample X in a manner as described in the Table and preparing pastes thereof. The similar effect can be also expected by mixing the metallic copper particle according to the present invention and a commercially available copper powder.

[Table 6]

	Sample W[g]	Sample X[g]	Volume resistance value [$\Omega\cdot$cm]
Example 31	5	0	5.10E-05
Example 32	4	1	2.15E-05
Example 33	3	2	2.20E-05
Example 34	2	3	5.30E-05
Example 35	1	4	6.40E-05
Example 36	0	5	1.20E-04

Production 2 of Metallic Copper-Containing Film (Sintering with Plasma)

[0137] Copper pastes were prepared using sample A obtained in the Examples and sample AF obtained in the Comparative Examples according to the above method. Each copper paste was applied on a PET film with an applicator to prepare each metallic copper-containing film. Thereafter, plasma treatment was performed using Micro Labo-PS manufactured by Nissin Inc. under the following condition, and thereby each metallic copper-sintered film was obtained.

[0138] First of all, the metallic copper-containing film was placed on a stage heated at 100°C in the plasma apparatus to perform heating at a predetermined time of 180 seconds or 30 seconds. Thereafter, the pressure inside the apparatus was reduced for 60 seconds, 3% H_2-He gas was introduced to the apparatus for 30 seconds, and plasma irradiation was performed for 180 seconds. After performing the plasma treatment, cooling was performed by purging N_2 gas for

90 seconds to obtain a metallic copper-sintered film (film thickness of 10 μm). The results are shown in Table 7. It has been found that a metallic copper-containing film having a low resistance can be produced, even through plasma treatment is performed, by the use of the metallic copper particle according to the present invention.

[Table 7]

	Sample	Treated base material	Heater temperature	Volume resistance value [Ω·cm]
Example 1	A	PET	100°C	2.26E-04
Comparative Example 2	AF	PET	100°C	O.L.
* In the table, O.L. represents a value equal to or more than the upper limit of measurement of the measurement apparatus. The value is roughly 1 × 10^{+4} Ω·cm or more, while it depends on the film thickness.				

Production 3 of Metallic Copper-Containing Film (Heating at 120°C in the Air)

[0139] Copper pastes were prepared by mixing 5 g of each of the samples (A to AH) obtained in the Examples and the Comparative Examples, a phenol resin (0.62 g of Resitop: PL-5208 (containing 59% by weight of phenol resin as an active ingredient)), and 0.26 g of ethylene glycol monobutyl ether acetate using a deaerating stirrer, and then kneading the resultant mixture with a three-roll mill. Each of the prepared copper pastes was applied on an alumina substrate with an applicator, and fired at 120°C for 10 minutes in a natural convection type drier to prepare metallic copper-containing films each of which has a film thickness of about 25 μm. The specific resistance values of the obtained metallic copper-containing films were measured using MCP-T610 Loresta GP manufactured by Mitsubishi Chemical Analytech Co., Ltd. by a direct current four-terminal method. Thereafter, the cross sections were observed with a scanning electron microscope to measure the film thicknesses, and the volume resistance values were calculated based on the specific resistance values. The results are shown in Table 8. From the fact that low volume resistance values are obtained by firing at a low temperature of 120°C, it can be said that the material according to the present invention is excellent in sinterability at a low temperature. Moreover, Figs. 36 and 37 show an SEM image of the cross section in the metallic copper-containing film of the sample Q produced in Example 17. It was confirmed from these SEM images that the metallic copper particles according to the present invention are sintered by firing at a low temperature of 120°C in the air.

[Table 8]

	Sample	Volume resistance value
		[Ω·cm]
Example 1	A	1.90E-02
Example 2	B	5.00E-02
Example 3	C	8.20E-02
Example 4	D	7.50E-02
Example 5	E	9.80E-02
Example 7	G	1.30E-01
Example 8	H	2.50E-01
Example 9	I	2.50E-01
Example 10	J	3.10E-01
Example 11	K	9.50E-02
Example 12	L	9.20E-02
Example 13	M	8.30E-02
Example 14	N	4.40E+01
Example 15	O	5.90E-02
Example 16	P	4.80E-02
Example 17	Q	2.10E-03

(continued)

	Sample	Volume resistance value
		[Ω·cm]
Example 18	R	3.70E-01
Example 19	S	1.60E-01
Example 20	T	2.80E+00
Example 21	U	6.70E-02
Example 22	V	7.40E-03
Example 23	W	5.10E-03
Example 24	X	2.00E-03
Example 25	Y	2.00E-03
Example 26	Z	3.10E-03
Example 27	AA	5.00E-03
Example 29	AC	8.05E-03
Example 30	AD	1.20E-02
Comparative Example 1	AE	O.L.
Comparative Example 2	AF	O.L.
Comparative Example 3	AG	O.L.
Comparative Example 4	AH	O.L.
* In the table, O.L. represents a value equal to or more than the upper limit of measurement of the measurement apparatus. The value is roughly $1\times10^{+4}$ Ω·cm or more, while it depends on the film thickness.		

Production of Metallic Paste

[0140] Metallic pastes (Cu solid content of 75% by mass) were prepared by mixing 9 g of each of the samples (A, C, E, J, N, Q, AB, AF, AG) obtained in the Examples and the Comparative Examples, 1 g of a vehicle (resin: 20% by mass of ethyl cellulose N200 and solvent: terpineol), and 2 g of terpineol and kneading the resultant mixture with a three-roll mill. The viscosity of the metallic paste was measured for each paste produced with a B type viscometer (model HB DV-I+) manufactured by Brookfield AMETEK setting the measurement temperature at 20°C and using CPE-52 as a corn spindle. The viscosity (ηa) at a low shear rate (10 [1/sec]) and the viscosity (ηb) at a high shear rate (100 [1/sec]) were measured, and the value of the viscosity (ηa) was divided by the value of the viscosity (ηb) to calculate a thixotropy index (TI) value. These results are shown in Table 9.

[0141] In the pastes (i.e. metallic pastes) using the metallic copper particles of the Examples according to the present invention, the TI values are dominantly higher (specifically, TI values are 3.0 or more) than those in the Comparative Examples. For this reason, for example, in the screen printing, the fluidity of the metallic paste during continuous printing becomes favorable, and a thick film can be obtained after completion of patterning on a substrate. Moreover, cracks, disconnection, short-circuits, bleeding, and the like are suppressed, and thick films are reproducibly obtained during continuous printing. Furthermore, in printing, such as inkjet printing, during which a high shear force is applied to the metallic paste, ejection of the metallic paste from holes can be made smooth, and fixing of the metallic paste to a printing medium becomes favorable.

[Table 9]

	Sample	Viscosity [mPa·s]		TI (η a / η b)
		η a	η b	
Example 1	A	31500	6415	4.91
Example 3	C	26500	6000	4.42

(continued)

	Sample	Viscosity [mPa·s]		TI (η a / η b)
		η a	η b	
Example 5	E	28500	5500	5.18
Example 10	J	35146	5015	7.01
Example 14	N	25152	7055	3.57
Example 17	Q	22700	5159	4.40
Example 28	AB	58260	10820	5.38
Comparative Example 2	AF	23300	8200	2.84
Comparative Example 3	AG	35688	12000	2.97

Industrial Applicability

[0142] According to the present invention, a metallic copper particle which can be fired under a nonreducing atmosphere such as nitrogen and which is excellent in sinterability at a lower temperature can be simply produced. The metallic copper particle can be used in materials for securing electrical conduction, materials for antistatic, materials for shielding electromagnetic waves, materials for giving metallic luster or antibacterial properties, and other materials, and can be used particularly in uses for forming a fine electrode and a fine circuit-wiring pattern such as a printed wiring board, making use of the electrical conductivity of the metallic copper-containing film, in uses for joining chips and substrates, and in design and decoration uses making use of metallic color tone of the metallic copper-containing film.

Claims

1. A metallic copper particle comprising a large diameter metallic copper particle and at least one fine metallic copper particle wherein the at least one fine metallic copper particle is adhered on a surface of the large diameter metallic copper particle.

2. The metallic copper particle according to claim 1, wherein an aggregate of the fine metallic copper particles is adhered on the surface of the large diameter metallic copper particle.

3. The metallic copper particle according to claim 1 or 2, further comprising a small metallic copper particle in a mixed state.

4. The metallic copper particle according to claim 1 or 2, wherein a gelatin and/or a collagen peptide exist on at least one selected from the group consisting of the metallic copper particle, the large diameter metallic copper particle, and the at least one fine metallic copper particle.

5. The metallic copper particle according to claim 3, wherein a gelatin and/or a collagen peptide exist on at least one selected from the group consisting of the metallic copper particle, the large diameter metallic copper particle, the at least one fine metallic copper particle e, and the small metallic copper particle.

6. The metallic copper particle according to claim 1, 2, or 4, wherein at least one selected from the group consisting of the metallic copper particle, the large diameter metallic copper particle, and the at least one fine metallic copper particle comprises an organic acid and/or a salt thereof.

7. The metallic copper particle according to claim 3 or 5, wherein at least one selected from the group consisting of the metallic copper particle, the large diameter metallic copper particle, the at least one fine metallic copper particle, and the small metallic copper particle comprises an organic acid and/or a salt thereof.

8. The metallic copper particle according to any one of claims 1 to 7, having a specific surface area of 0.1 to 10 m^2/g.

9. A process for producing a metallic copper particle having a volume resistance value of 1×10^{-2} Ω·cm or less after

heating the metallic copper particle at a temperature of 300°C under a nitrogen atmosphere, the process comprising mixing a copper oxide and a hypophosphorous acid and/or a salt thereof in a solvent in the presence of a gelatin and/or a collagen peptide, thereby reducing the copper oxide.

10. The process for producing a metallic copper particle according to claim 9, wherein the gelatin and/or the collagen peptide exist in 1 to 500 parts by mass with regard to 100 parts by mass of the metallic copper particle.

11. The process for producing a metallic copper particle according to claim 9 or 10, wherein the reduction reaction is performed in a temperature range of 40 to 95°C.

12. The process for producing a metallic copper particle according to any one of claims 9 to 11, comprising mixing the copper oxide and the hypophosphorous acid and/or the salt thereof in the solvent in the presence of the gelatin and/or the collagen peptide, and an amine complexing agent, thereby reducing the copper oxide.

13. The process for producing a metallic copper particle according to any one of claims 9 to 12, comprising mixing the copper oxide and the hypophosphorous acid and/or the salt thereof in the solvent in the presence of the gelatin and/or the collagen peptide, and an organic acid, thereby reducing the copper oxide.

14. The process for producing a metallic copper particle according to any one of claims 9 to 13, comprising mixing the copper oxide and hypophosphorous acid and/or the salt thereof in the solvent in the presence of the gelatin and/or the collagen peptide, an amine complexing agent, and an organic acid, thereby reducing the copper oxide.

15. The process for producing a metallic copper particle according to any one of claims 9 to 14, wherein the reduction reaction is performed at a pH of 3 or lower.

16. A metallic copper dispersion comprising the metallic copper particle according to any one of claims 1 to 8.

FIG.1

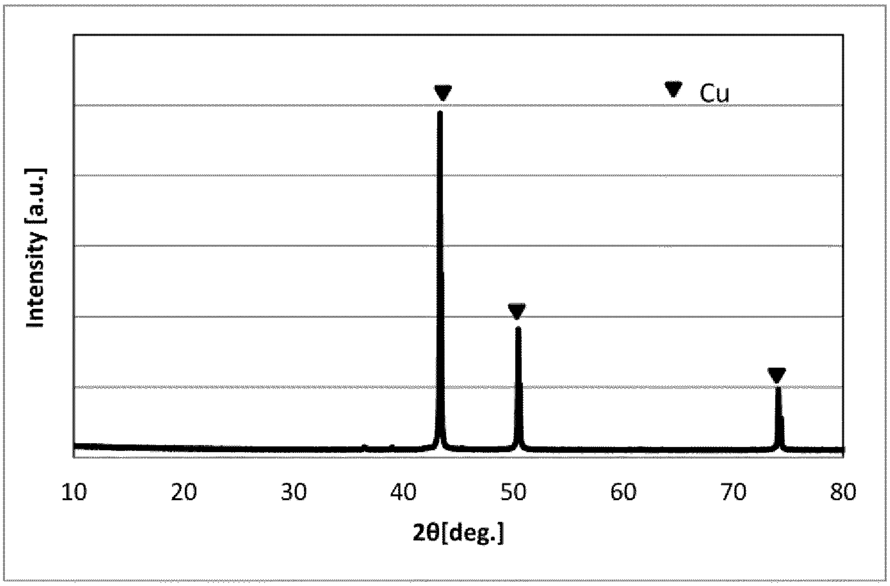

▼ Cu
Intensity [a.u.]
10
20
30
40
50
60
70
80
2θ[deg.]

FIG.2

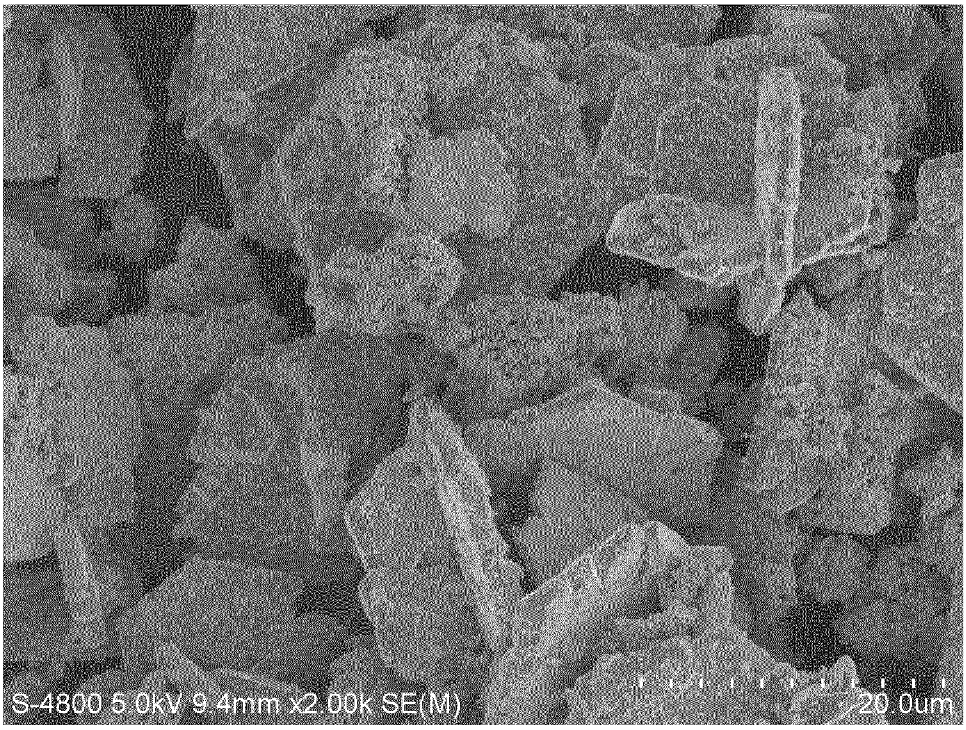

S-4800 5.0kV 9.4mm x2.00k SE(M)
20.0um

FIG.3

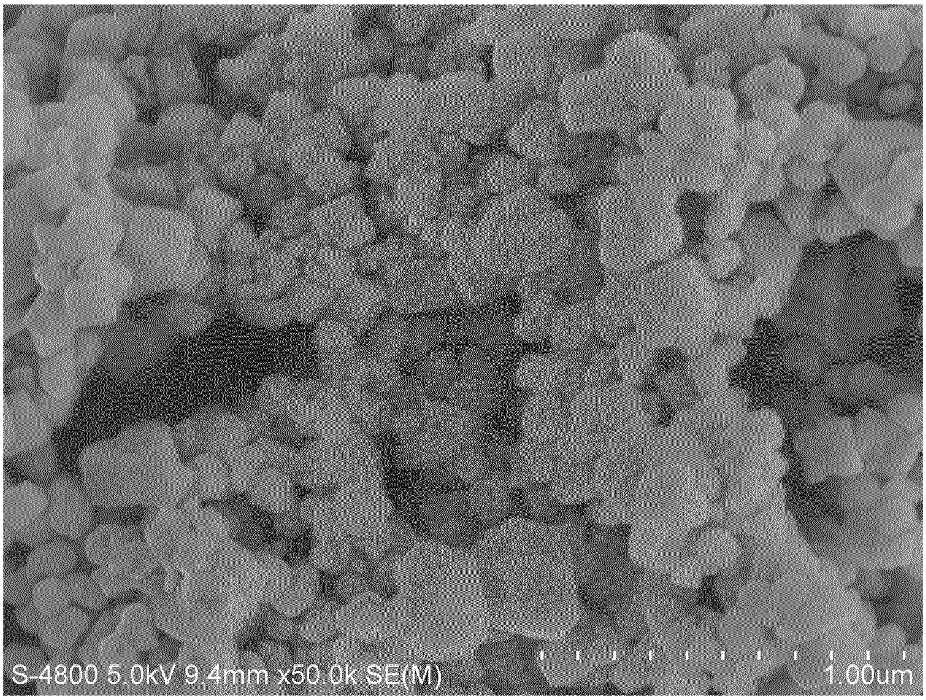

S-4800 5.0kV 9.4mm x50.0k SE(M)
1.00um

FIG.4

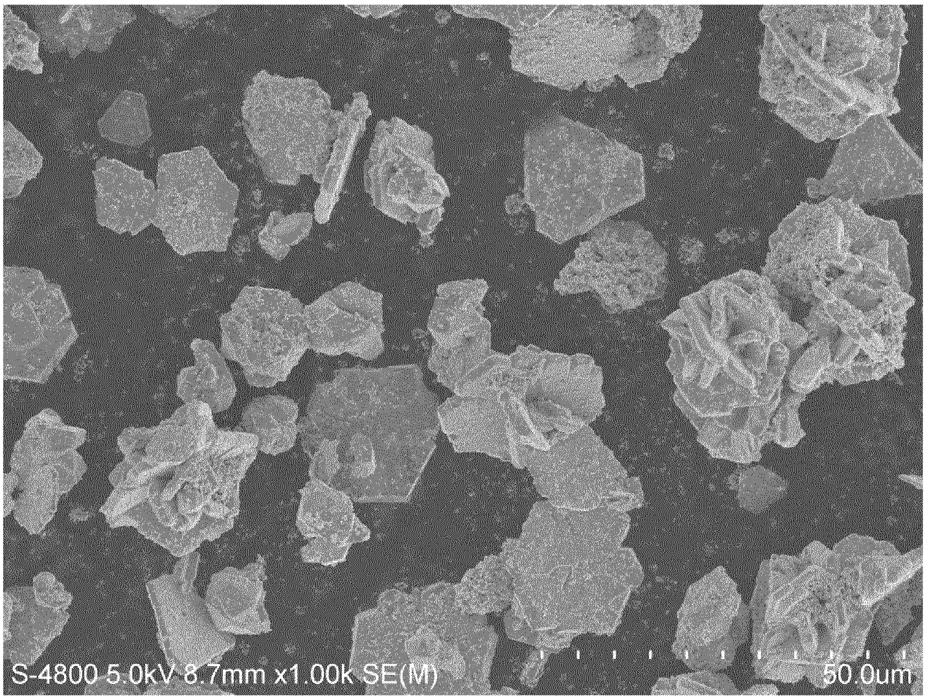

S-4800 5.0kV 8.7mm x1.00k SE(M)
50.0um

FIG.5

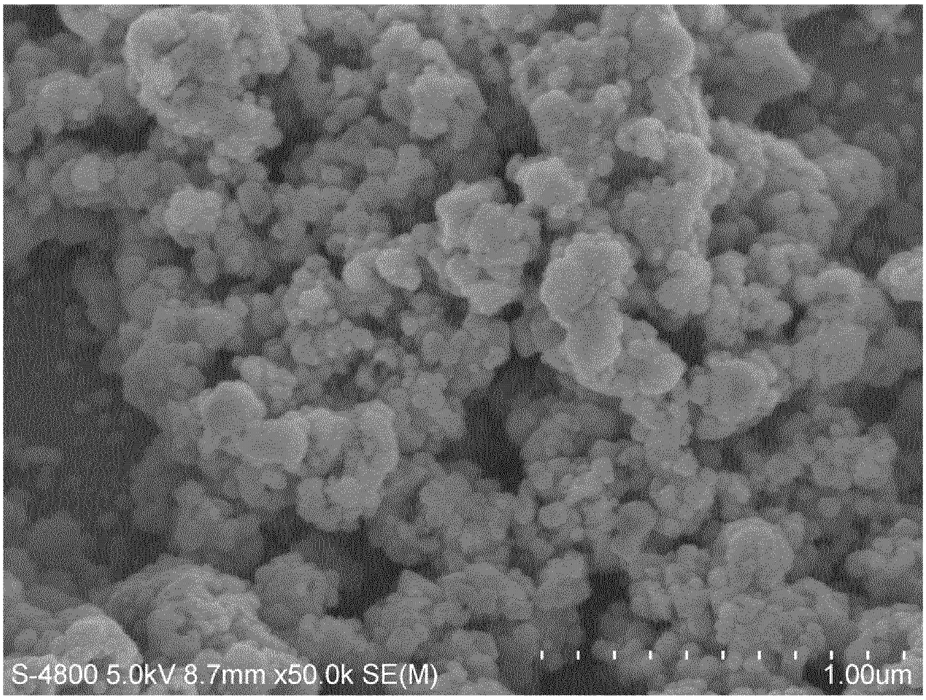

S-4800 5.0kV 8.7mm x50.0k SE(M)
1.00um

FIG.6

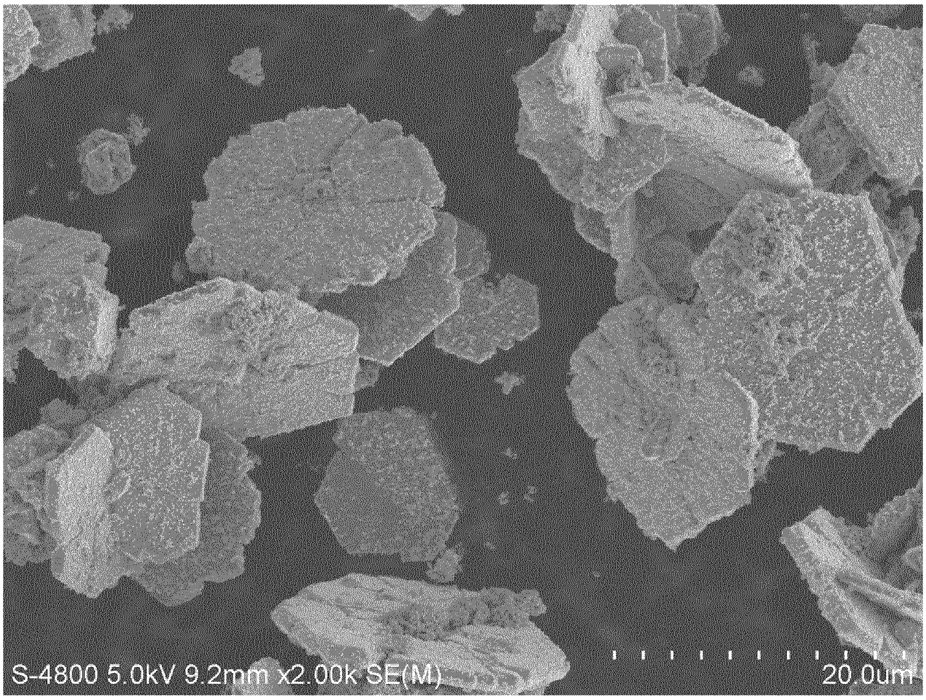

S-4800 5.0kV 9.2mm x2.00k SE(M)
20.0um

FIG.7

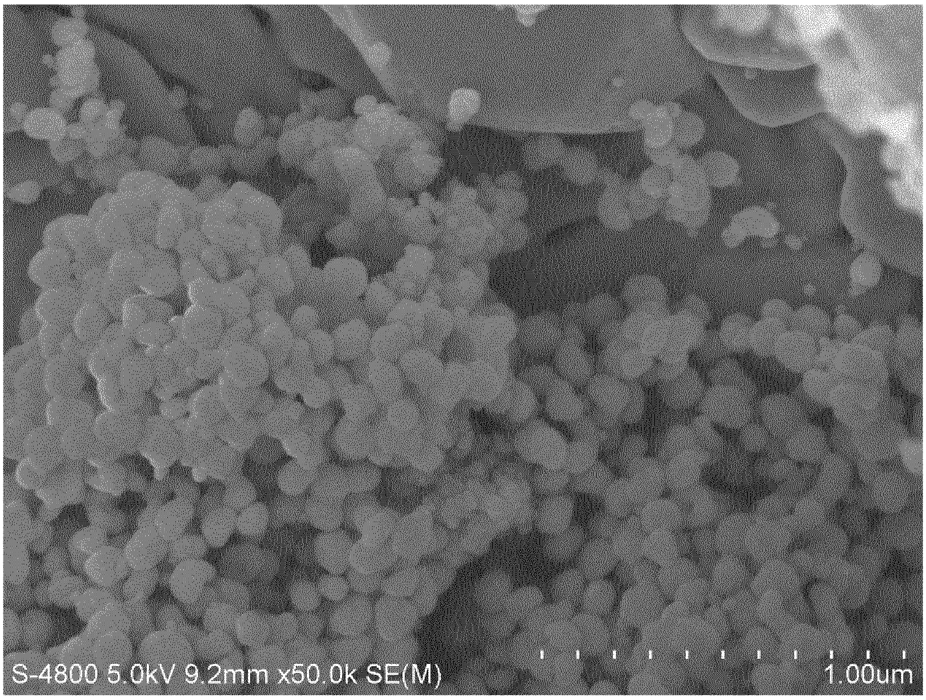

S-4800 5.0kV 9.2mm x50.0k SE(M)
1.00um

FIG.8

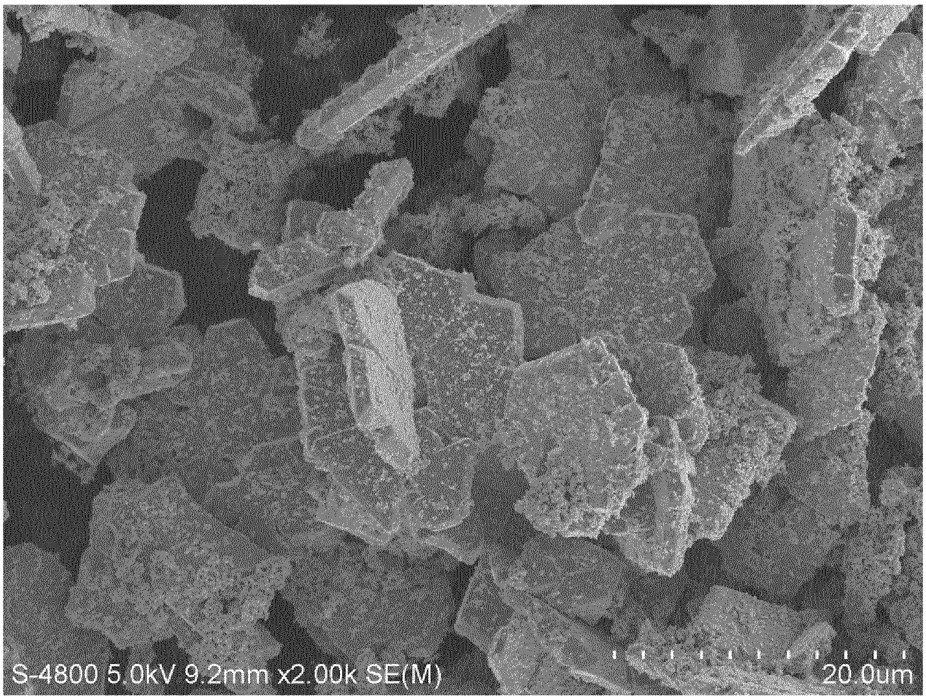

S-4800 5.0kV 9.2mm x2.00k SE(M)
20.0um

FIG.9

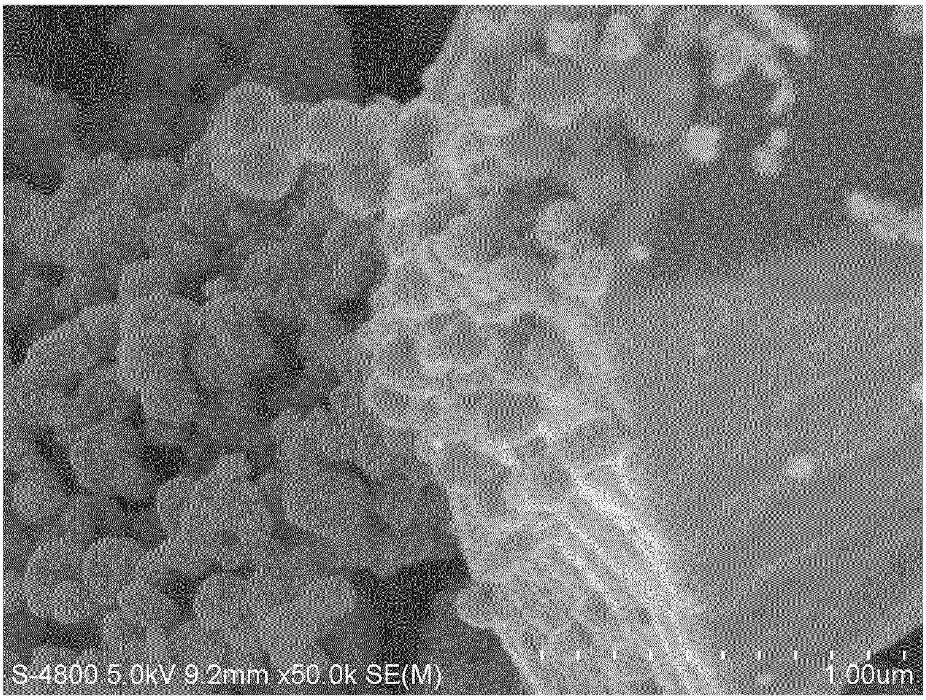

S-4800 5.0kV 9.2mm x50.0k SE(M)
1.00um

FIG.10

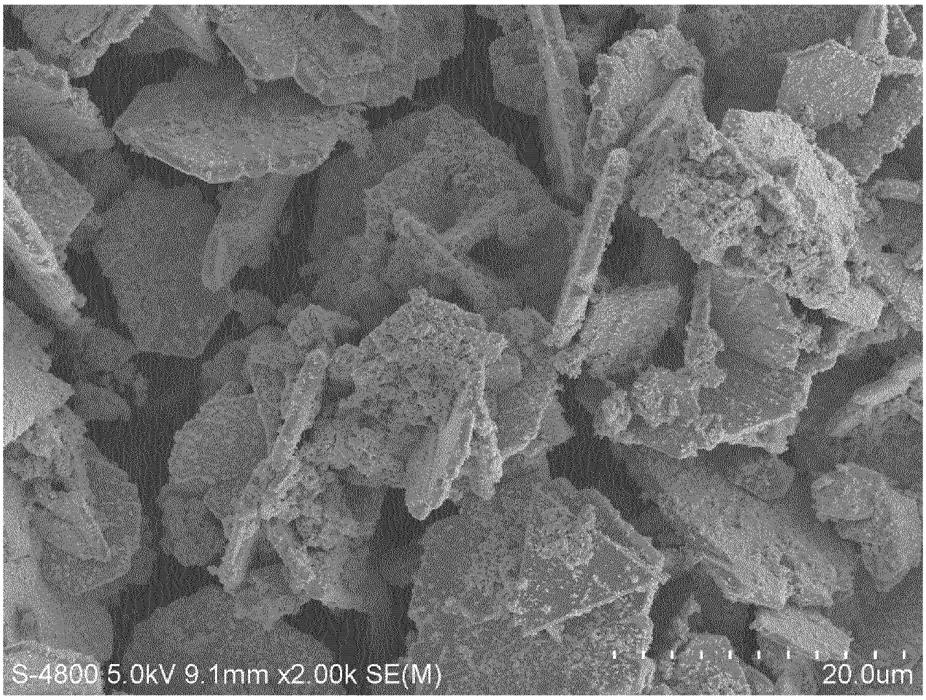

S-4800 5.0kV 9.1mm x2.00k SE(M)
20.0um

FIG.11

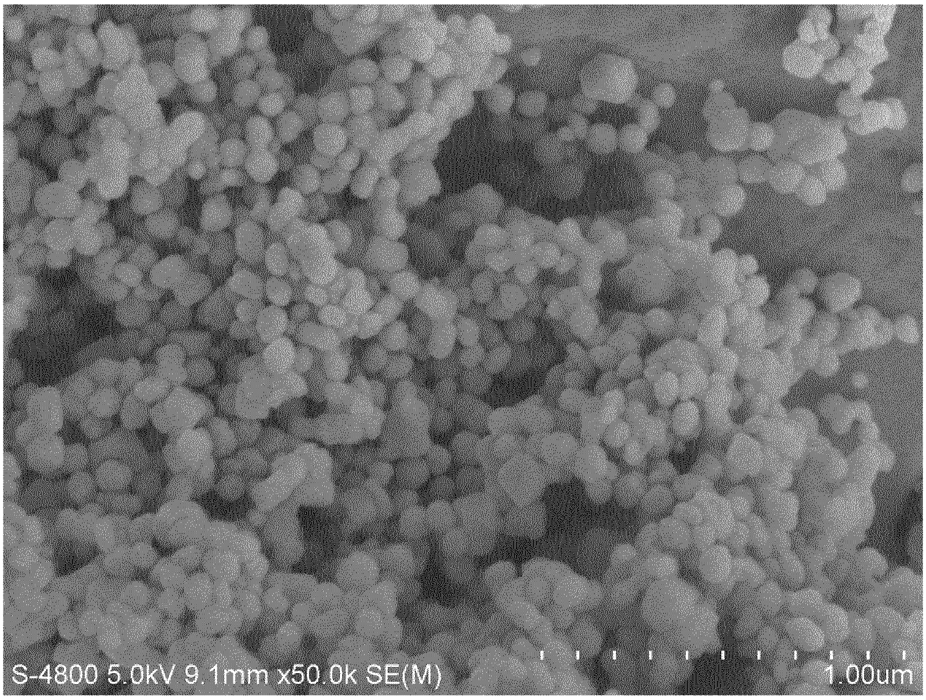

S-4800 5.0kV 9.1mm x50.0k SE(M)
1.00um

FIG.12

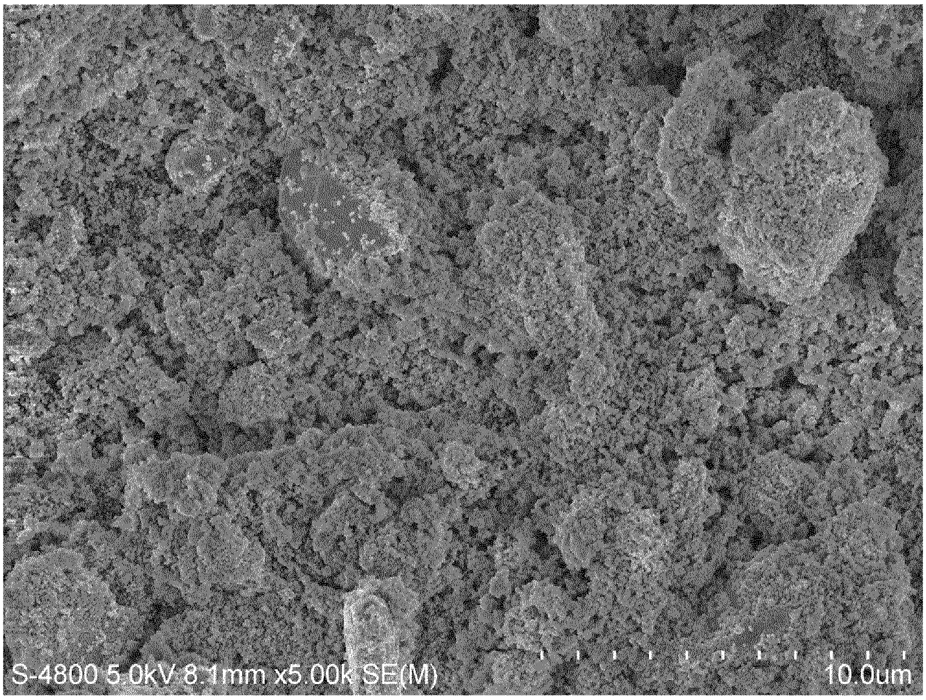

S-4800 5.0kV 8.1mm x5.00k SE(M)
10.0um

FIG.13

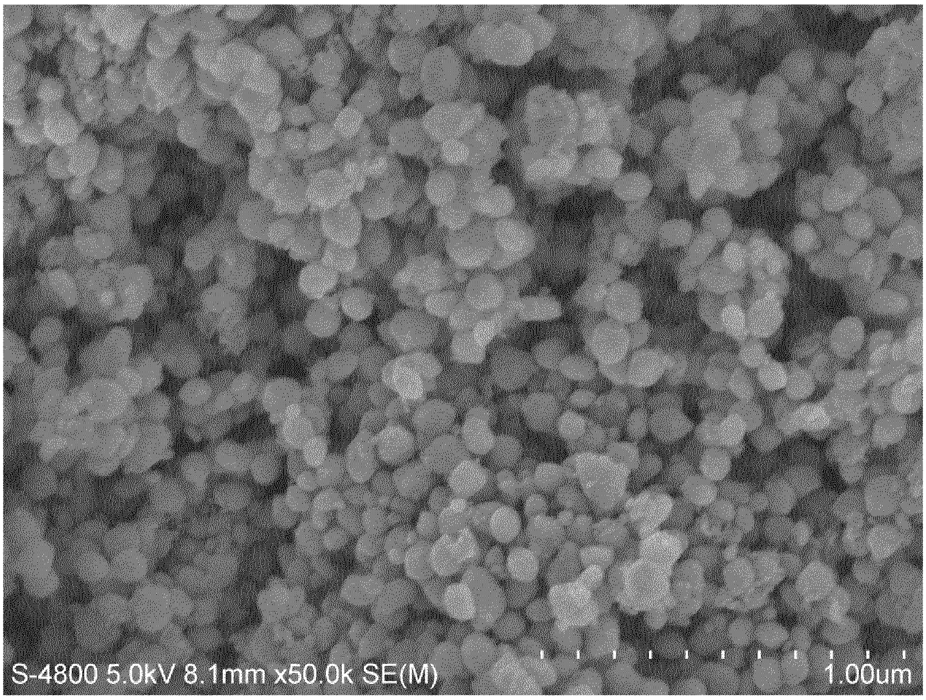

S-4800 5.0kV 8.1mm x50.0k SE(M)
1.00um

FIG.14

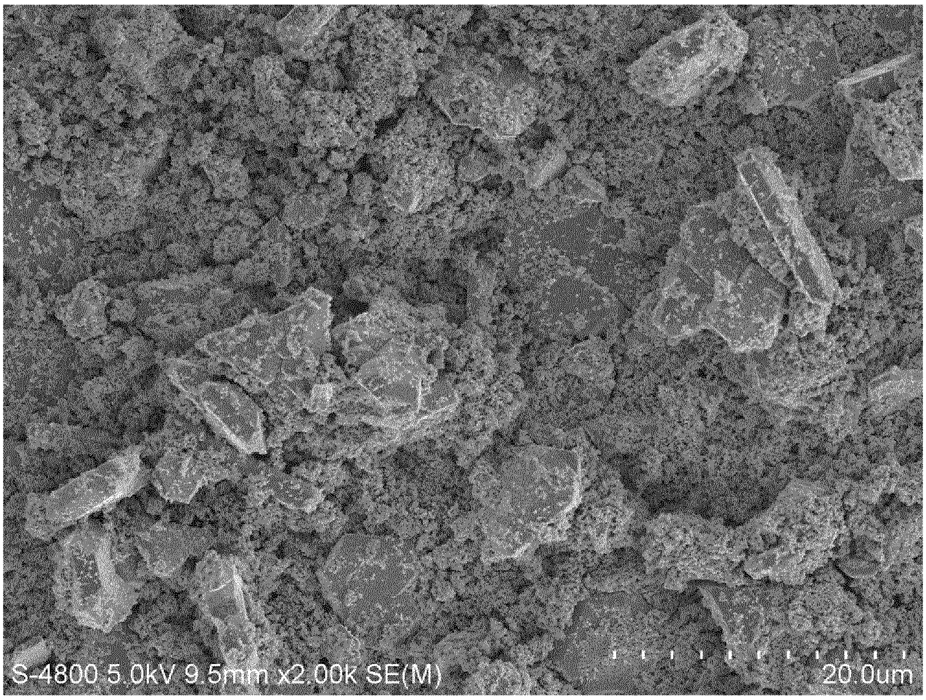

S-4800 5.0kV 9.5mm x2.00k SE(M)
20.0um

FIG.15

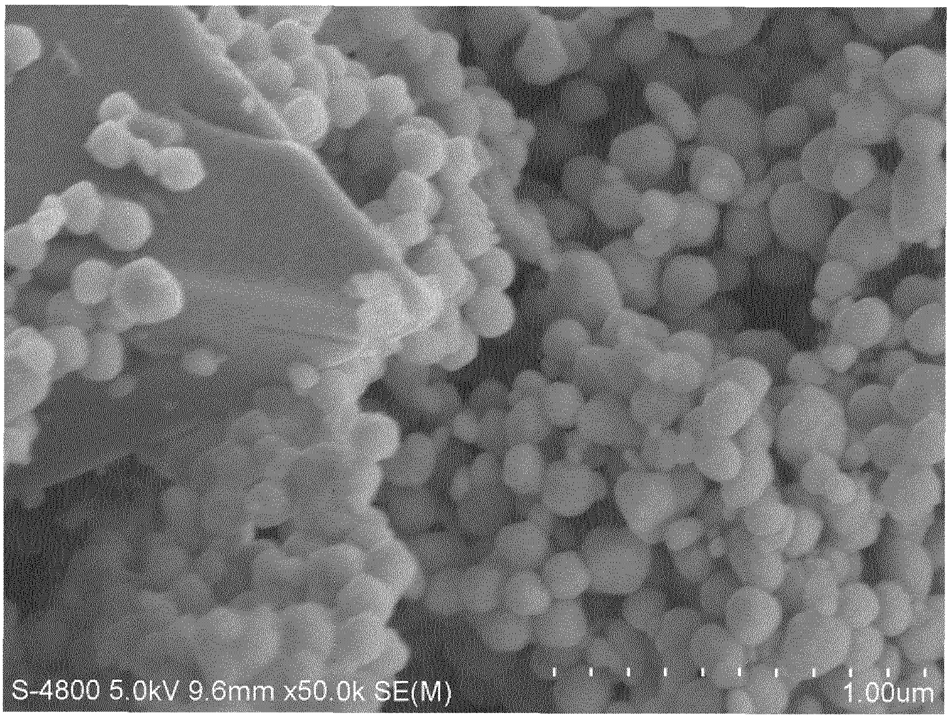

S-4800 5.0kV 9.6mm x50.0k SE(M)
1.00um

FIG.16

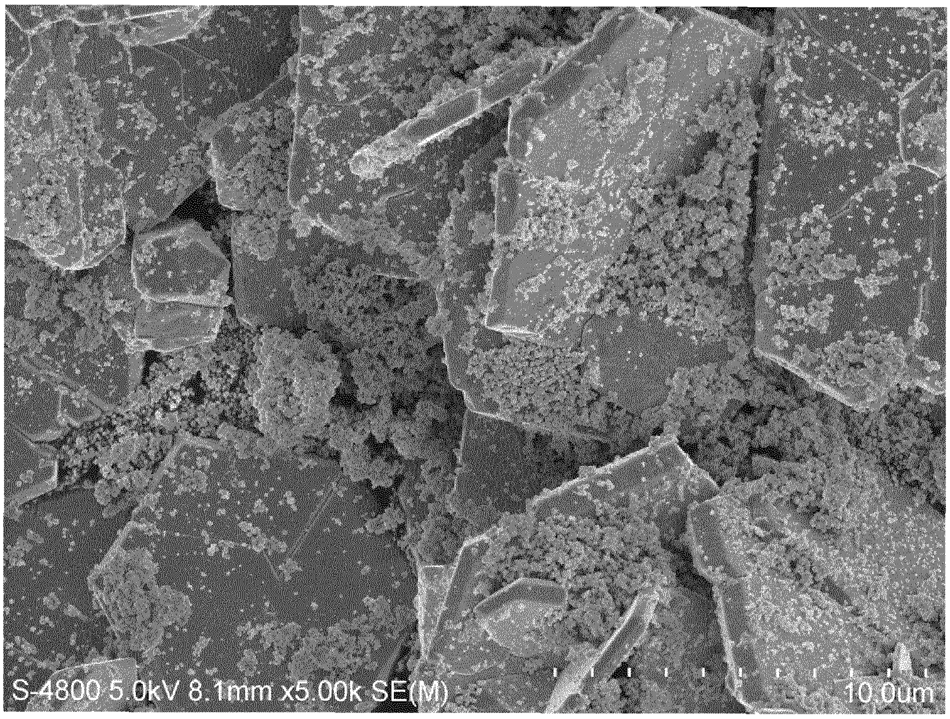

S-4800 5.0kV 8.1mm x5.00k SE(M)
10.0um

FIG.17

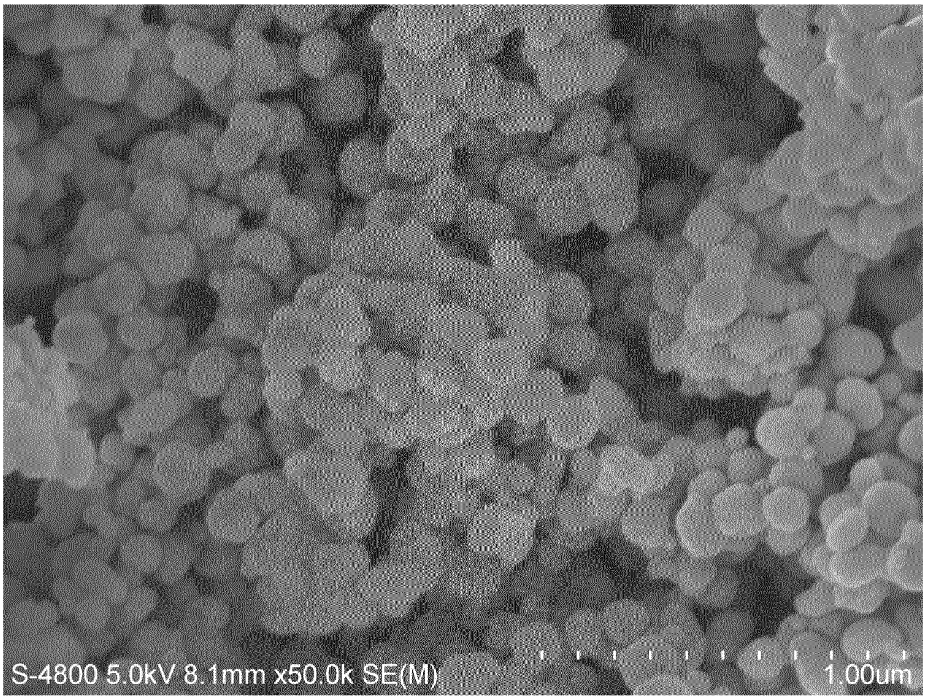

S-4800 5.0kV 8.1mm x50.0k SE(M)
1.00um

FIG.18

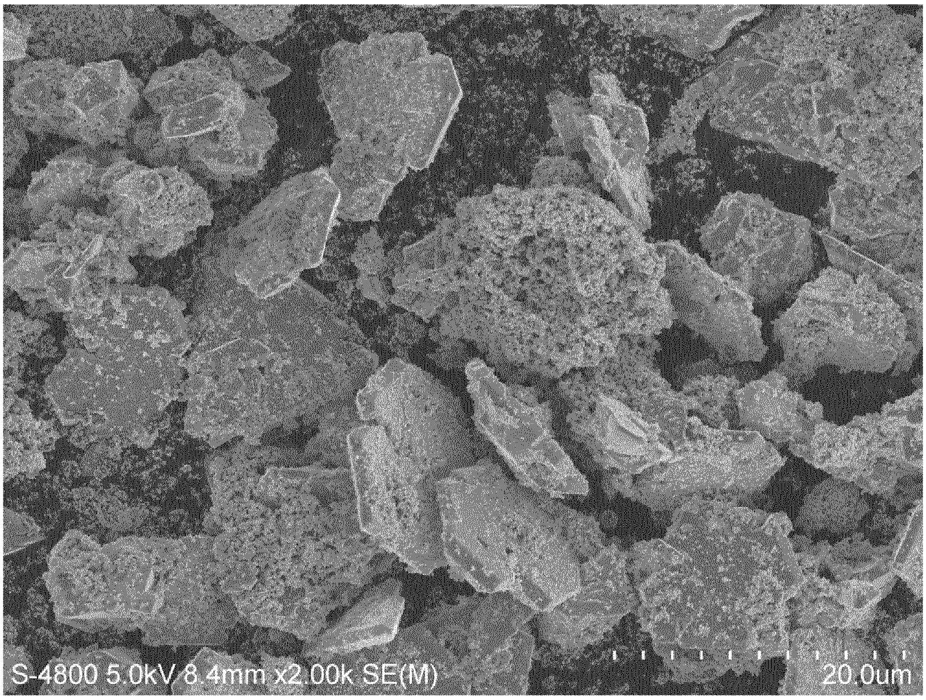

S-4800 5.0kV 8.4mm x2.00k SE(M)
20.0um

FIG.19

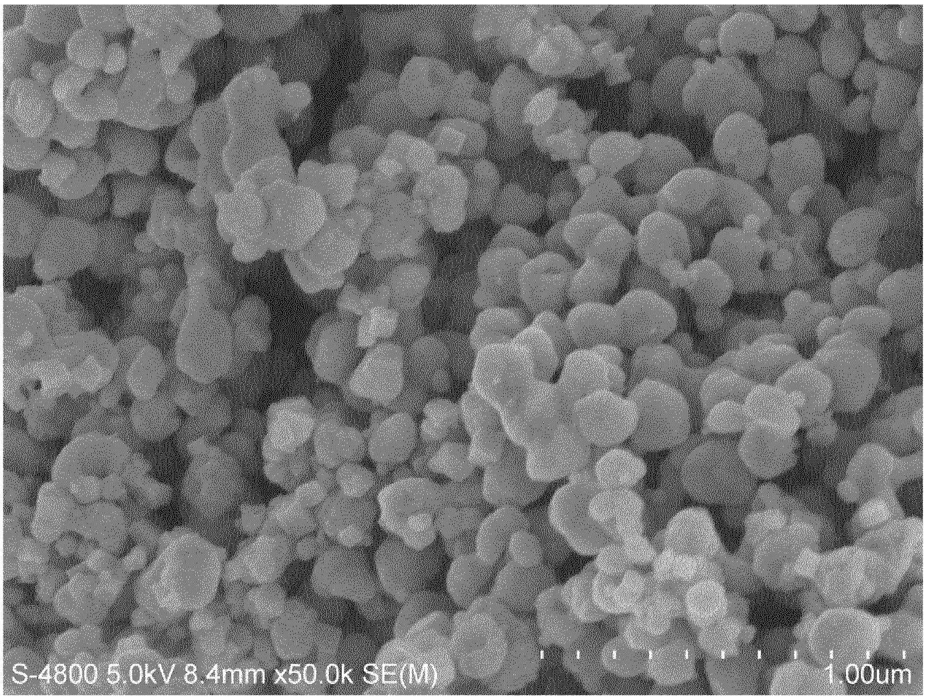

S-4800 5.0kV 8.4mm x50.0k SE(M)
1.00um

FIG.20

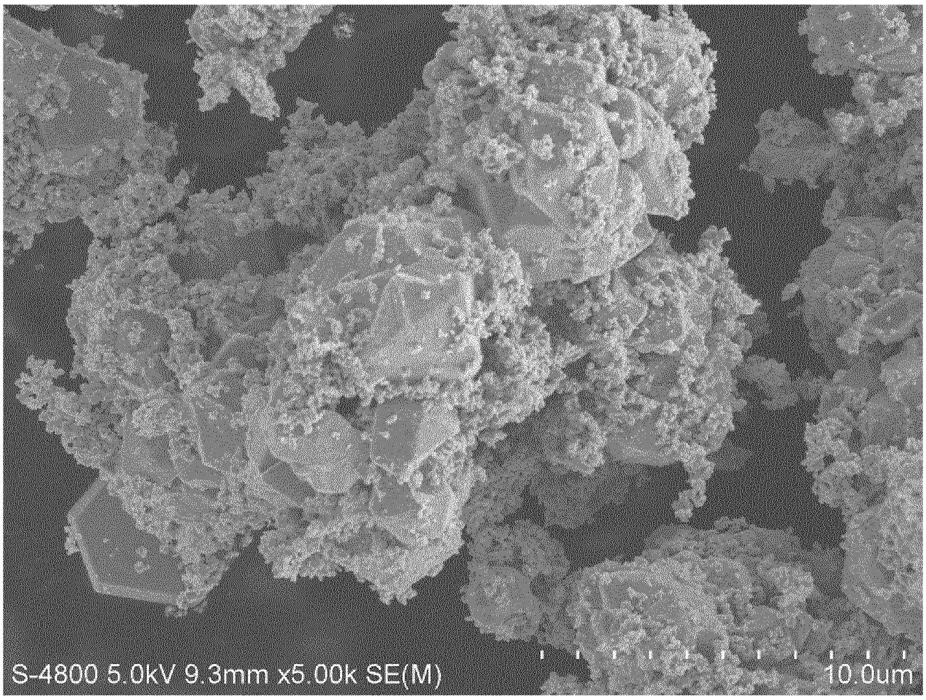

S-4800 5.0kV 9.3mm x5.00k SE(M)
10.0um

FIG.21

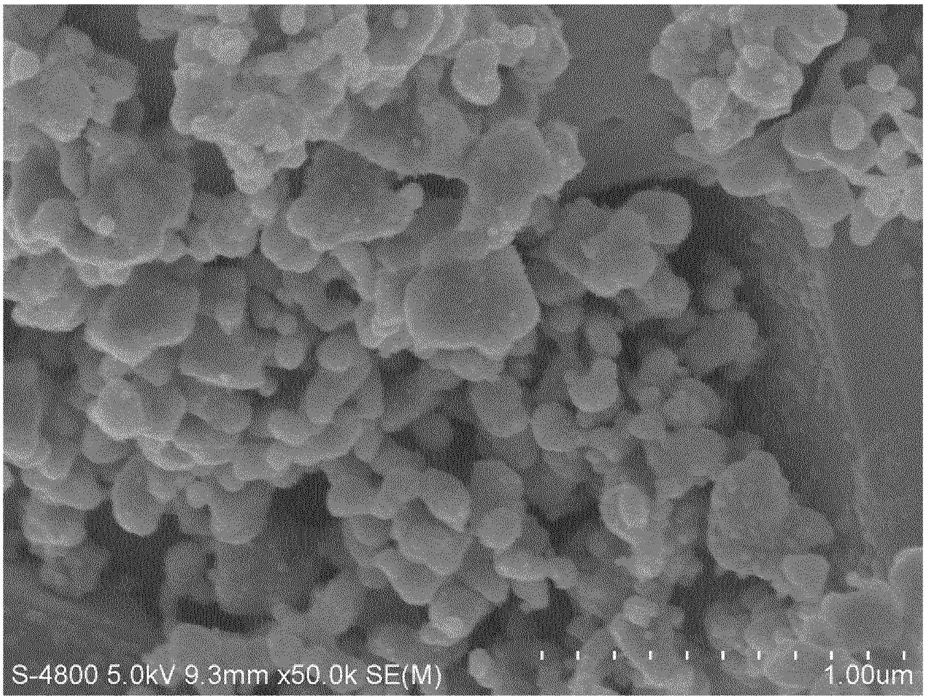

S-4800 5.0kV 9.3mm x50.0k SE(M)
1.00um

FIG.22

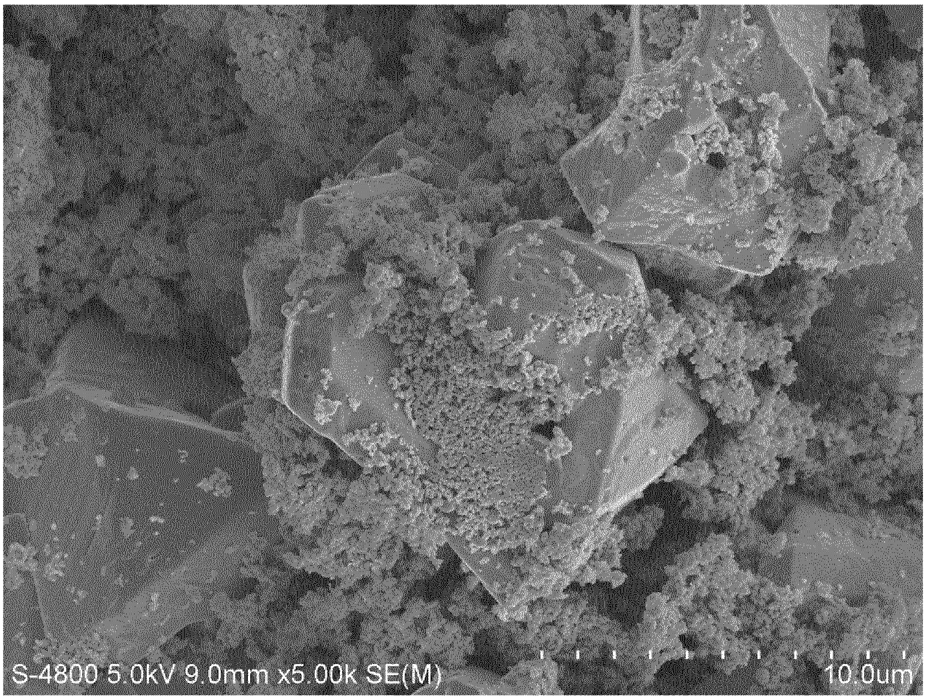

S-4800 5.0kV 9.0mm x5.00k SE(M)
10.0um

FIG.23

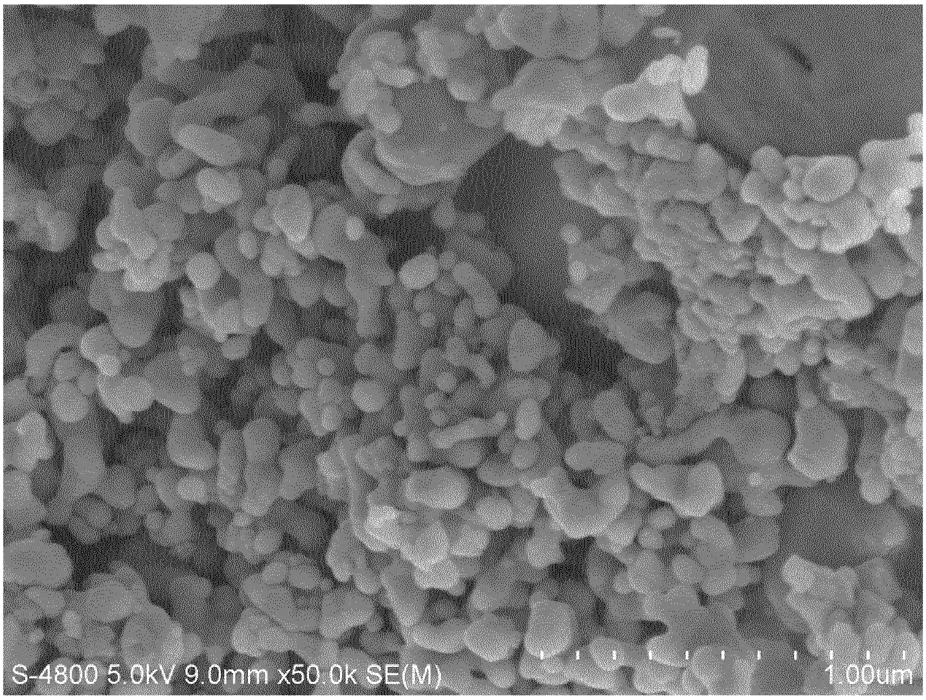

S-4800 5.0kV 9.0mm x50.0k SE(M)
1.00um

FIG.24

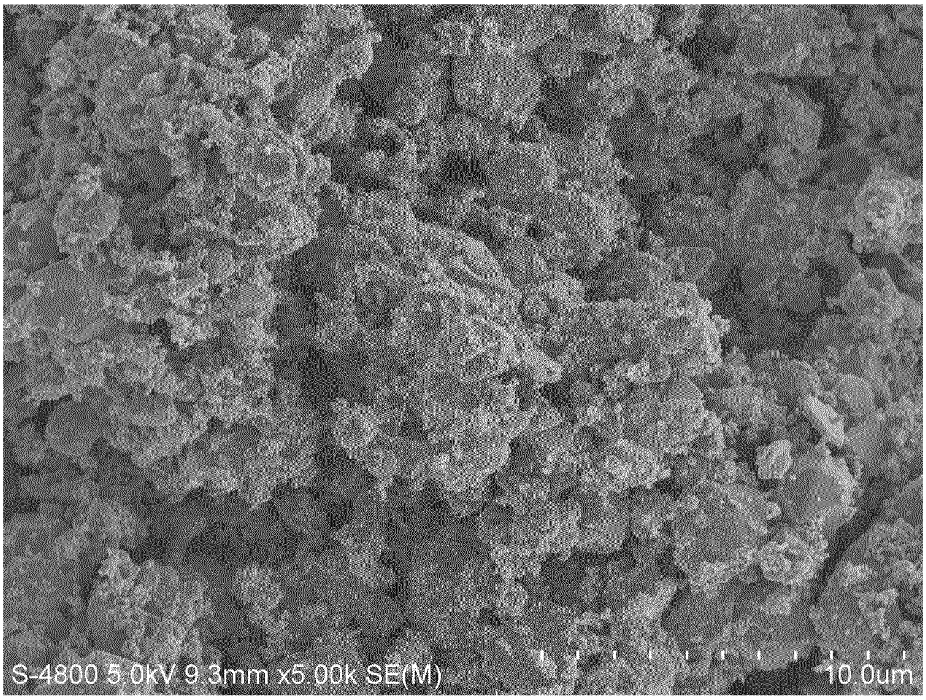

S-4800 5.0kV 9.3mm x5.00k SE(M)
10.0um

FIG.25

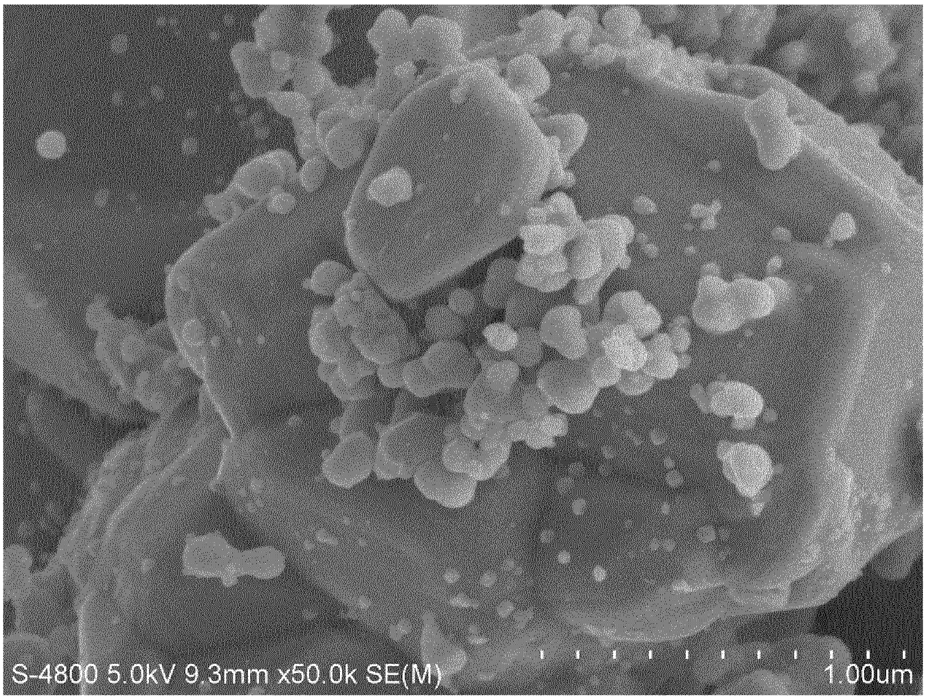

S-4800 5.0kV 9.3mm x50.0k SE(M)
1.00um

FIG.26

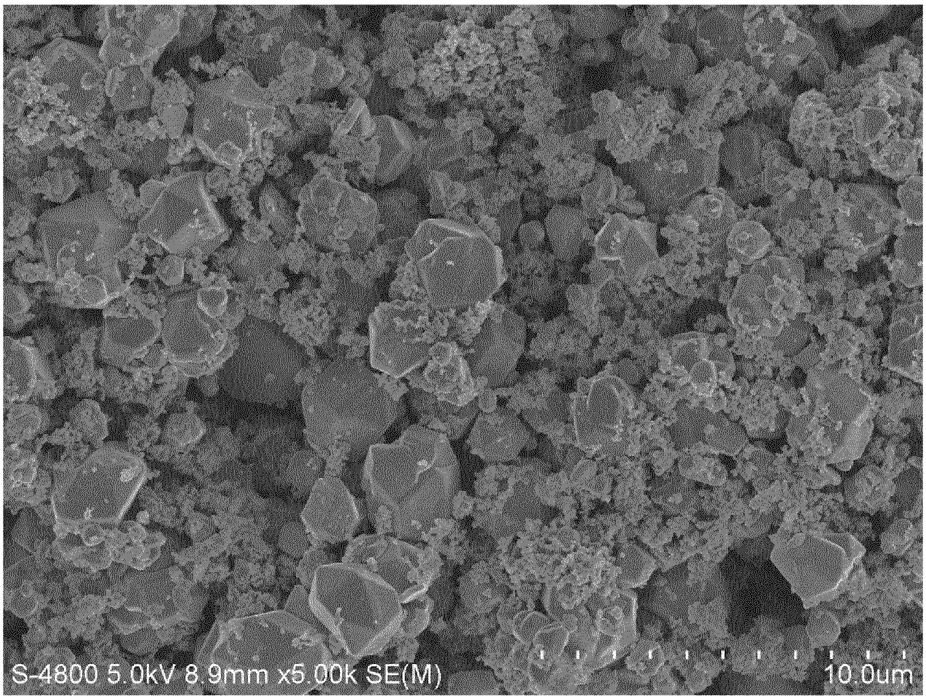

S-4800 5.0kV 8.9mm x5.00k SE(M)
10.0um

FIG.27

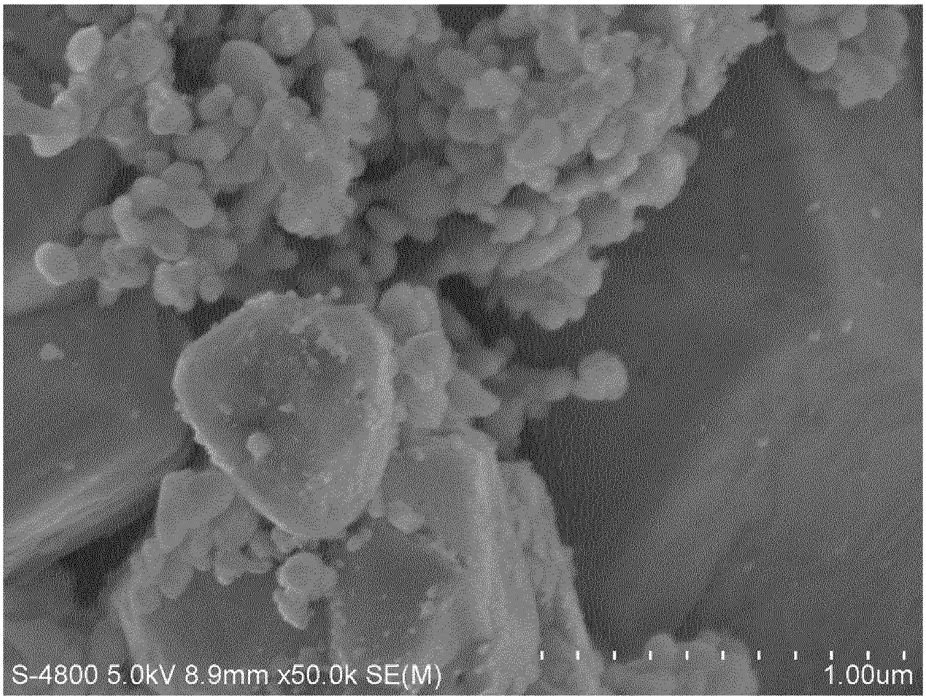

S-4800 5.0kV 8.9mm x50.0k SE(M)
1.00um

FIG.28

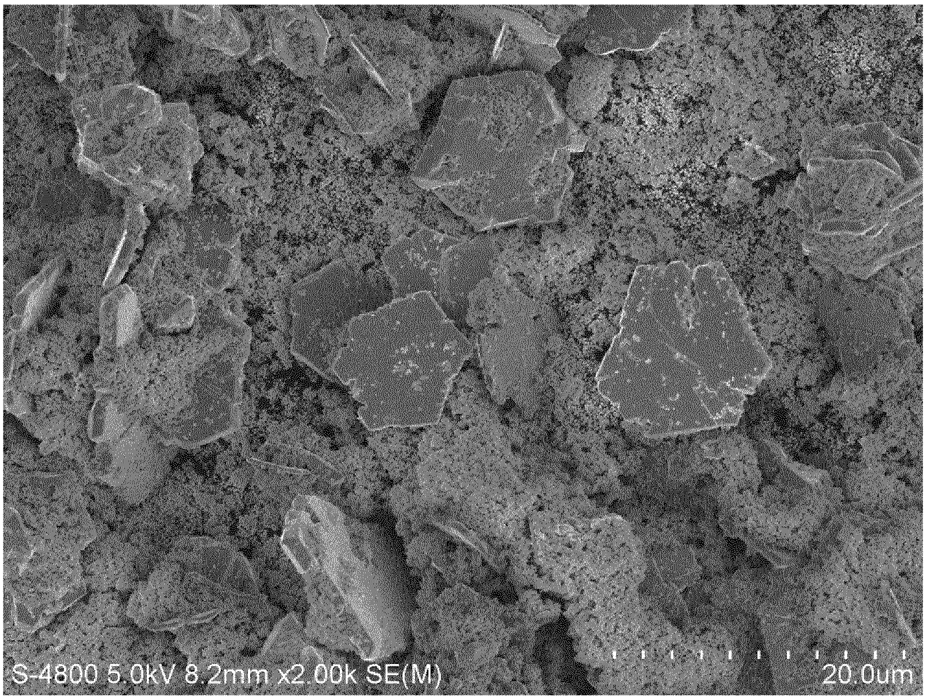

S-4800 5.0kV 8.2mm x2.00k SE(M)
20.0um

FIG.29

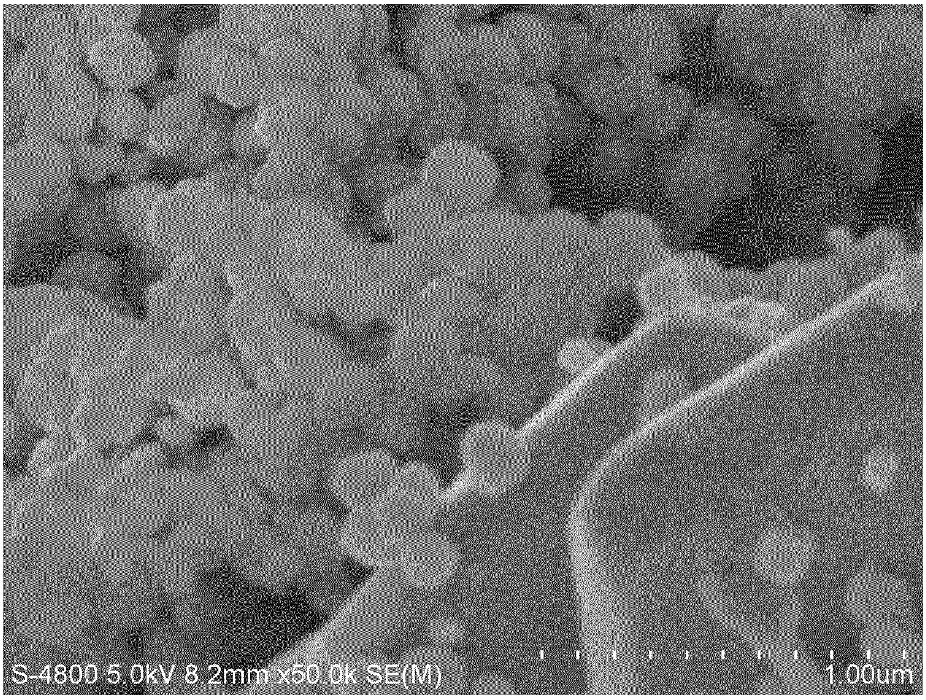

S-4800 5.0kV 8.2mm x50.0k SE(M)
1.00um

FIG.30

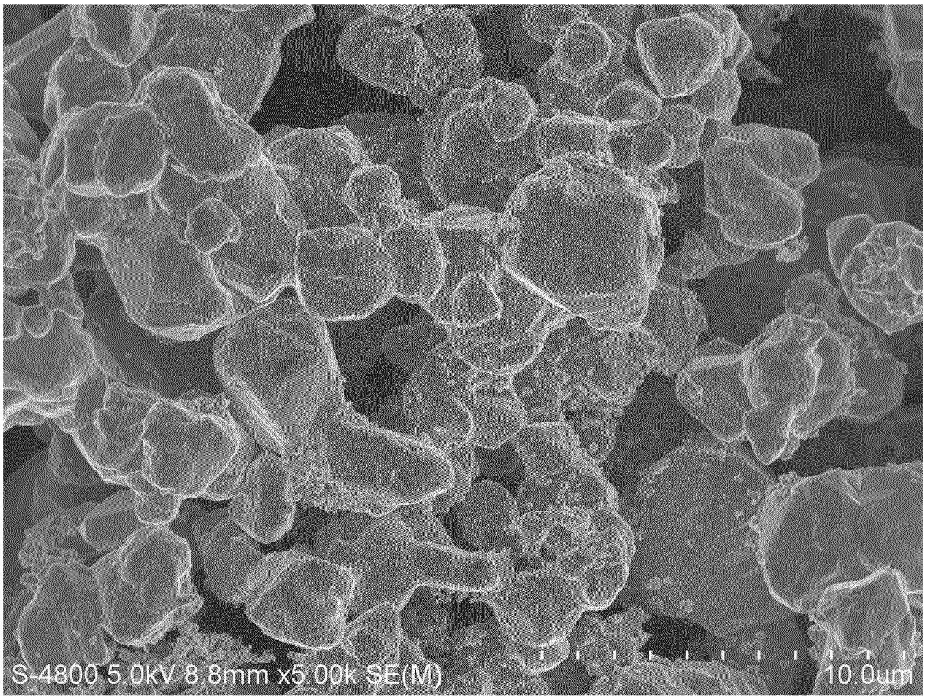

S-4800 5.0kV 8.8mm x5.00k SE(M)
10.0um

FIG.31

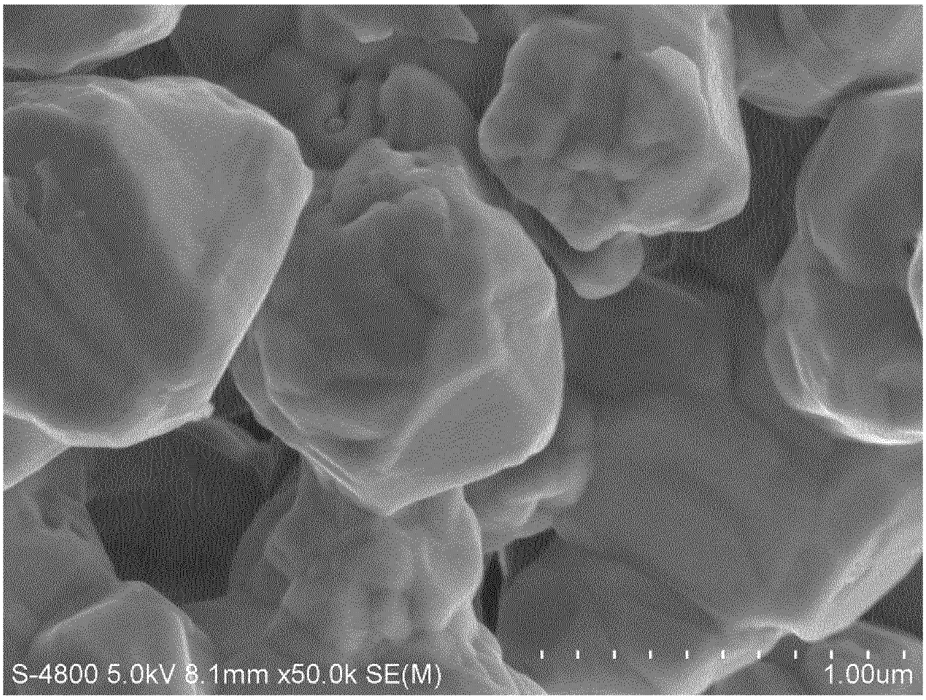

S-4800 5.0kV 8.1mm x50.0k SE(M)
1.00um

FIG.32

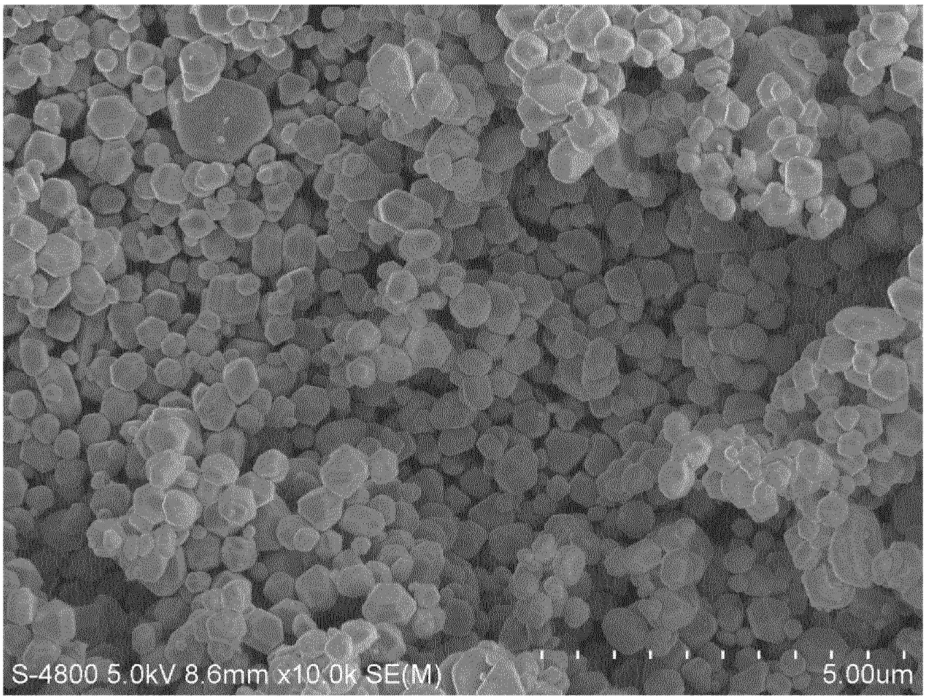

S-4800 5.0kV 8.6mm x10.0k SE(M)
5.00um

FIG.33

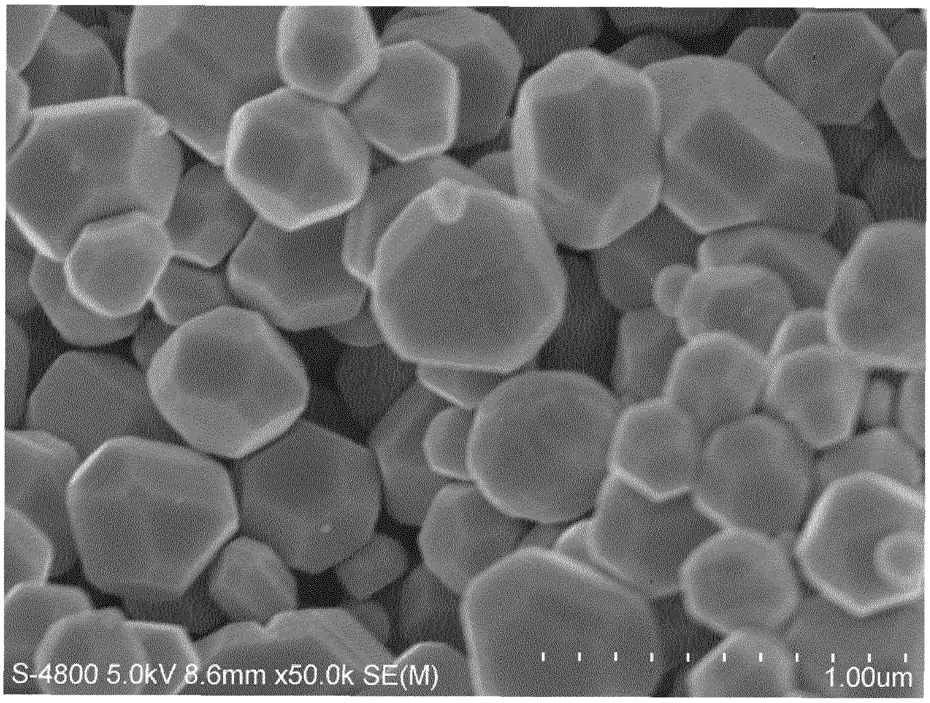

S-4800 5.0kV 8.6mm x50.0k SE(M)
1.00um

FIG.34

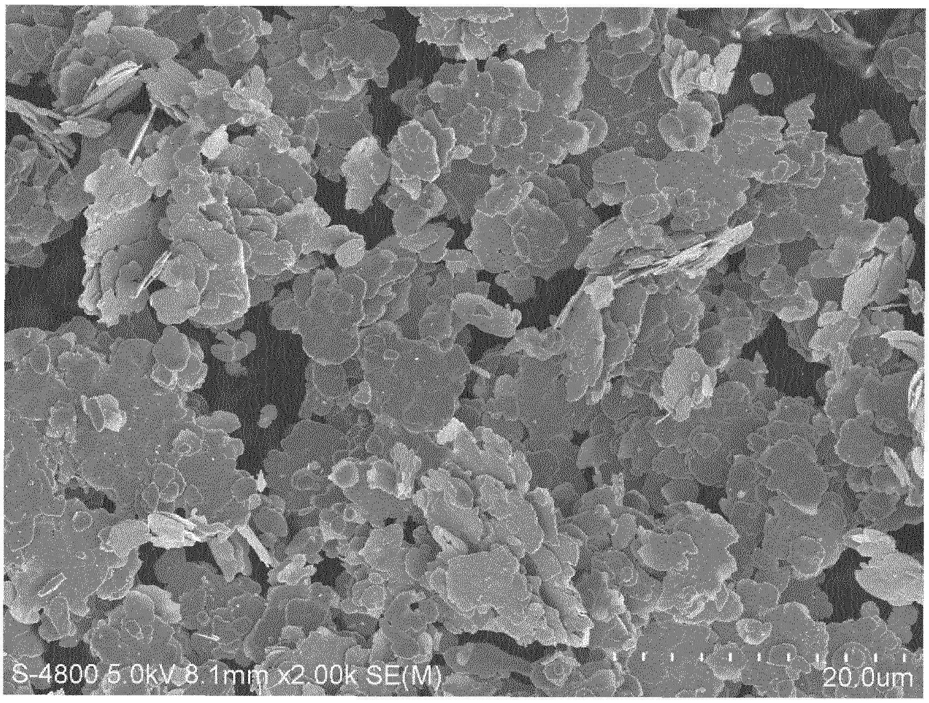

S-4800 5.0kV 8.1mm x2.00k SE(M)
20.0um

FIG.35

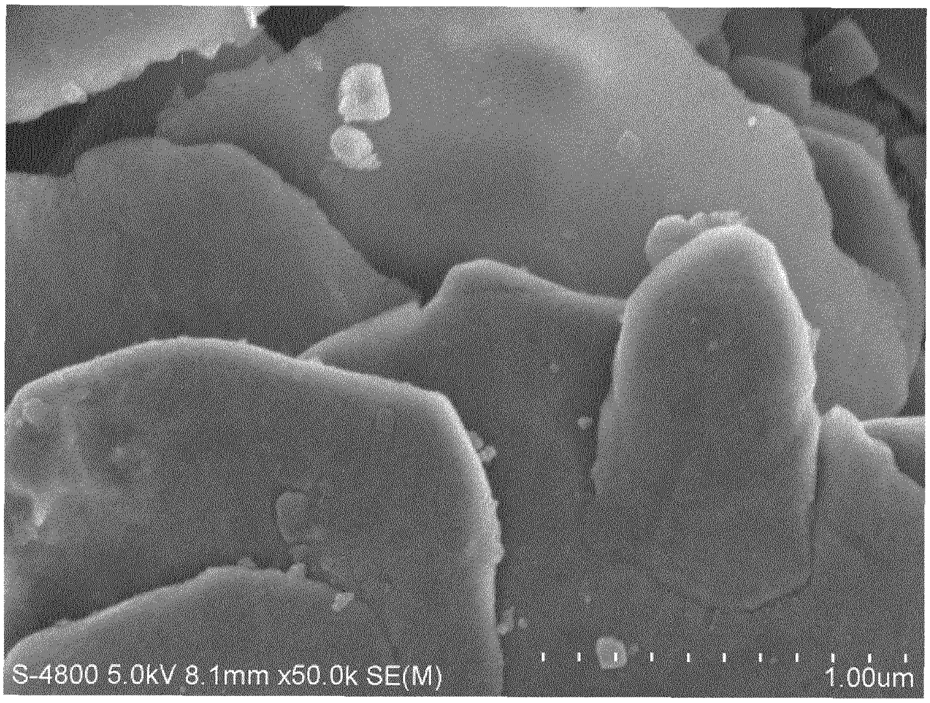

S-4800 5.0kV 8.1mm x50.0k SE(M)
1.00um

FIG.36

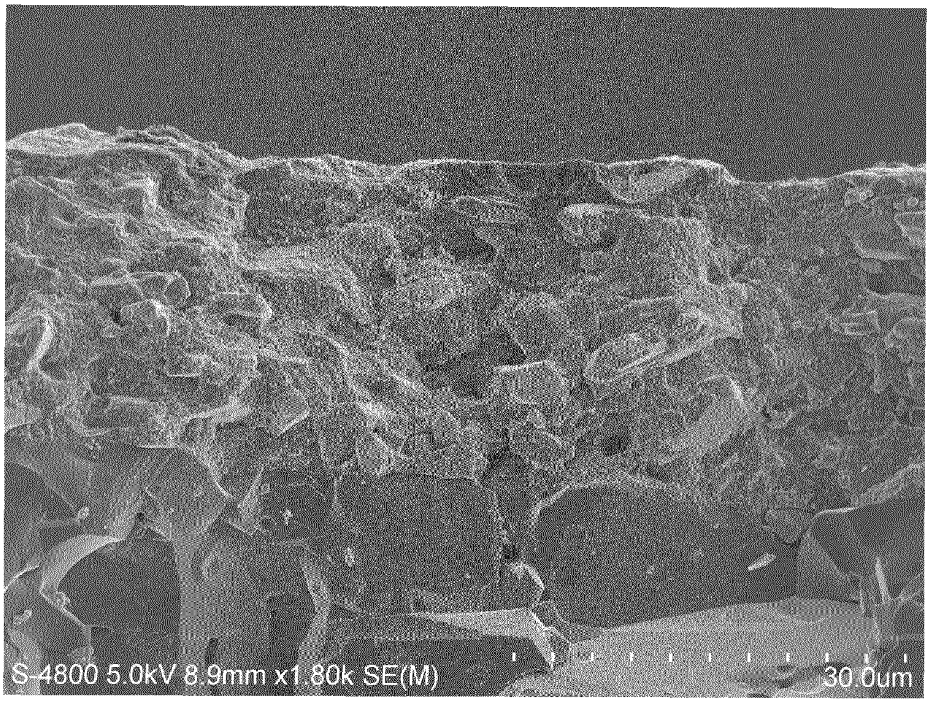
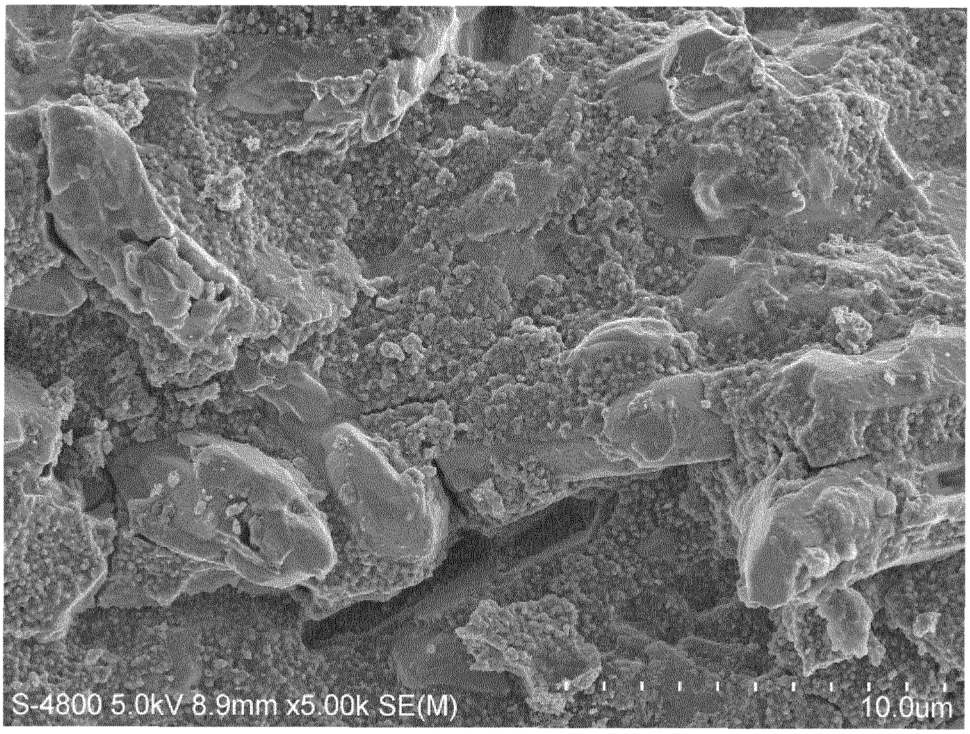

S-4800 5.0kV 8.9mm x1.80k SE(M)
30.0um

FIG.37



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/074025

A. CLASSIFICATION OF SUBJECT MATTER
B22F9/20(2006.01)i, *B22F1/00*(2006.01)i, *H01B1/00*(2006.01)i, *H01B1/22*(2006.01)i, *H01B5/00*(2006.01)i, *H01B13/00*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B22F9/20, B22F1/00, H01B1/00, H01B1/22, H01B5/00, H01B13/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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Kokai Jitsuyo Shinan Koho	1971-2015	Toroku Jitsuyo Shinan Koho	1994-2015

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	WO 2009/116349 A1 (Asahi Glass Co., Ltd.), 24 September 2009 (24.09.2009), claims 1, 6 to 9; paragraphs [0002] to [0005], [0011], [0018] to [0035] & TW 200946446 A	1-3,6-8,16 4-5
X Y	WO 2010/032841 A1 (Asahi Glass Co., Ltd.), 25 March 2010 (25.03.2010), claims 1 to 5; paragraphs [0006], [0012] to [0031] & TW 201022152 A	1-3,6-8,16 4-5
X Y	WO 2012/161201 A1 (Asahi Glass Co., Ltd.), 29 November 2012 (29.11.2012), claims 1 to 4; paragraphs [0040] to [0058] & CN 103582918 A & KR 10-2014-0038413 A & TW 201301303 A	1-3,6-8,16 4-5

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search 16 November 2015 (16.11.15)	Date of mailing of the international search report 24 November 2015 (24.11.15)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/074025

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	WO 2010/024385 A1 (Ishihara Sangyo Kaisha, Ltd.), 04 March 2010 (04.03.2010), claim 7; paragraphs [0020] to [0027], [0051], [0062] to [0063] & JP 5355577 B2 & US 2011/0155432 A1 claim 7; paragraphs [0091] to [0094]; table 8 & EP 2319643 A1 & CA 2735151 A & CN 102137728 A & KR 10-2011-0052657 A	9-15 4-5
X Y	JP 2013-64191 A (Fujifilm Corp.), 11 April 2013 (11.04.2013), claims 1 to 14; paragraphs [0030], [0062], [0073] & EP 2564954 A1 claim 8; example 10 & KR 10-2013-0024771 A	9-15 4-5

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- WO 2006019144 A1 **[0007]**
- WO 2010024385 A1 **[0007]**
- JP 4848674 B **[0007]**