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FOR MANUFACTURING THEM AND
CONDUCTIVE INK**

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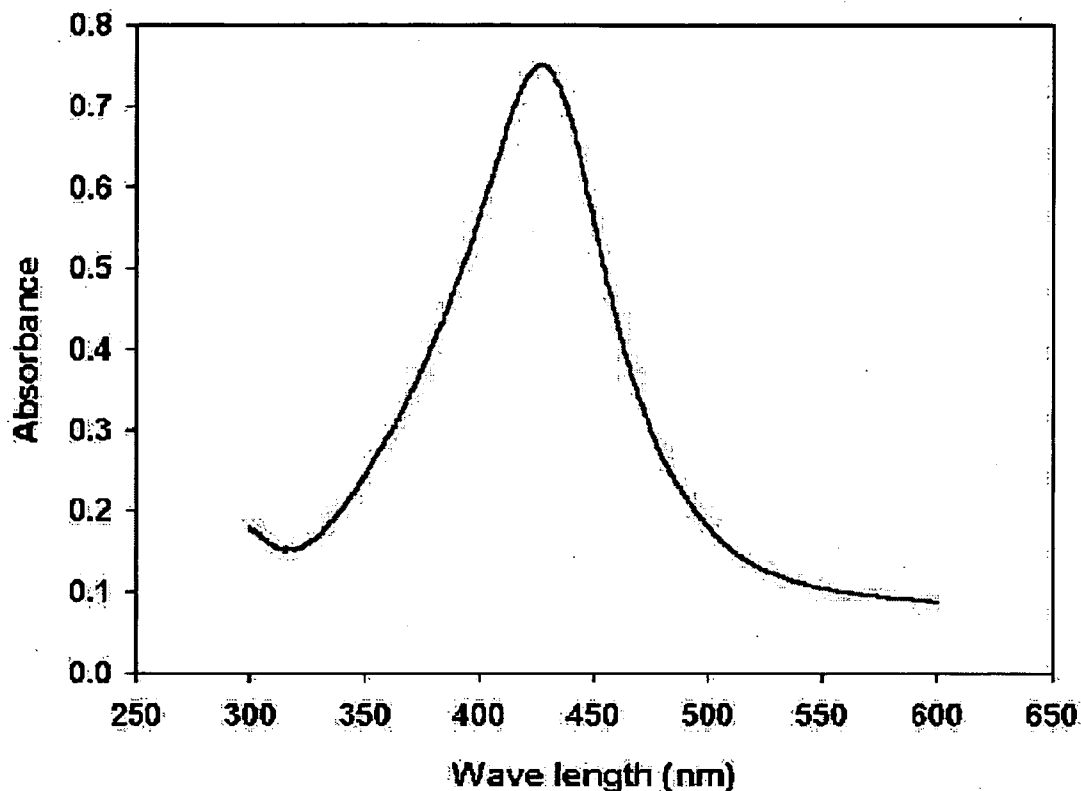
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(57) **ABSTRACT**

A method of producing hydrophobic metal nanoparticles using a hydrophobic solvent, having uniform particle size distribution and high yield rate to allow mass production; the metal nanoparticles thus produced; and conductive ink including the metal nanoparticles are disclosed. According to one aspect of the invention, a method of producing metal nanoparticles is provided, comprising dissociating a metal compound with an amine-based compound, and adding a hydrocarbon-based compound and either one of an alkanolic acid or a thiol-based compound to the dissociated metal ion solution.



Figures

Figure 1

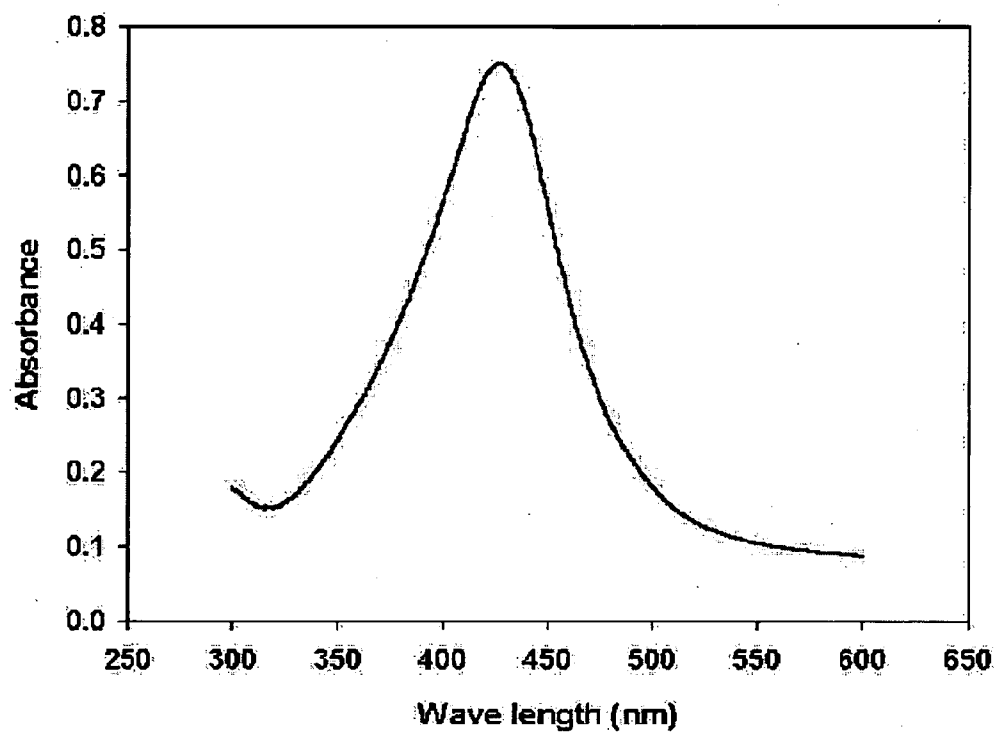


Figure 2

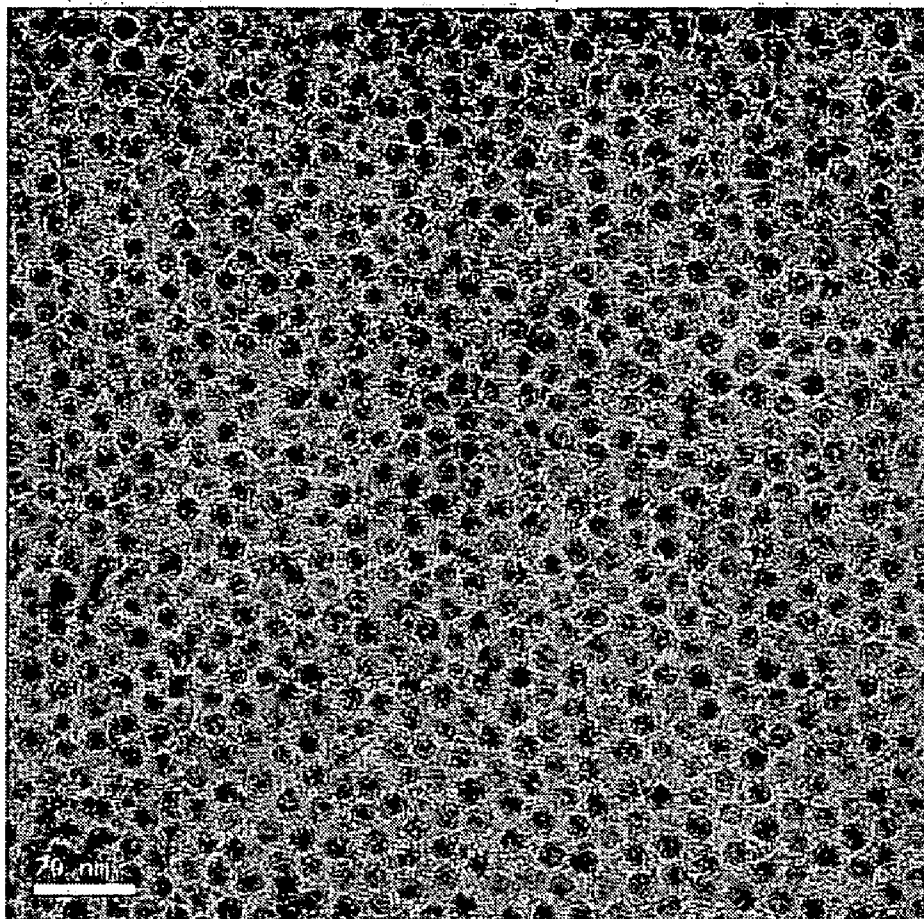


Figure 3

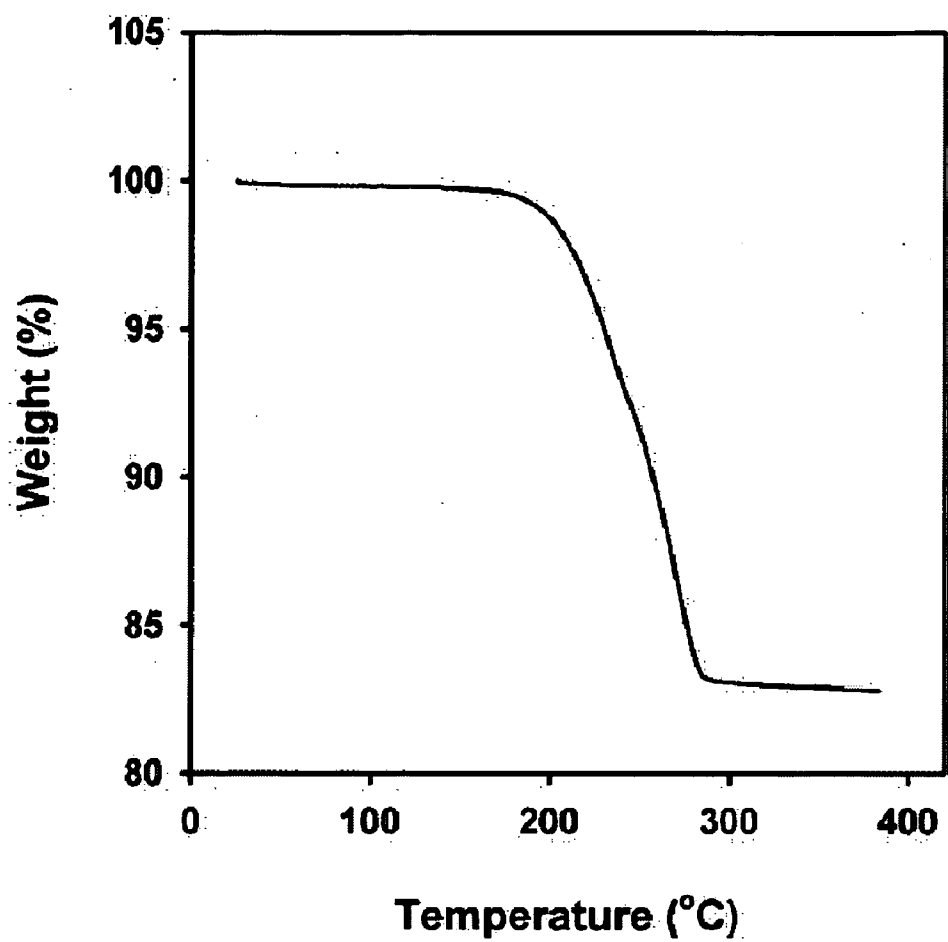


Figure 4

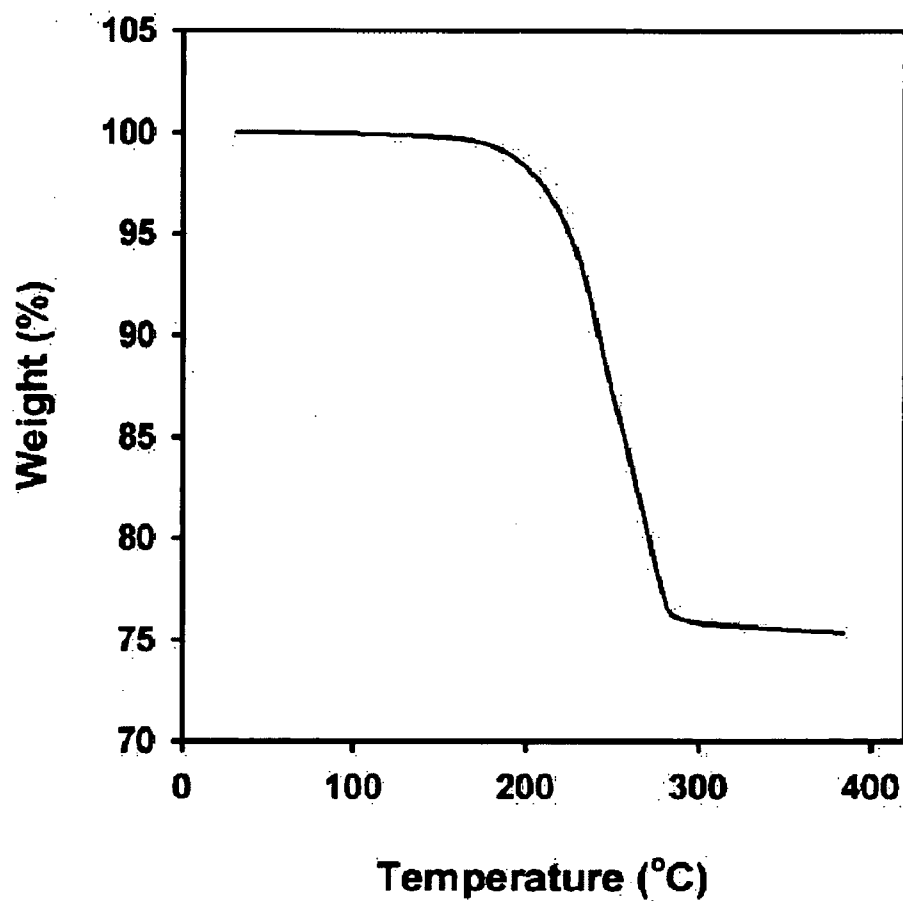


Figure 5

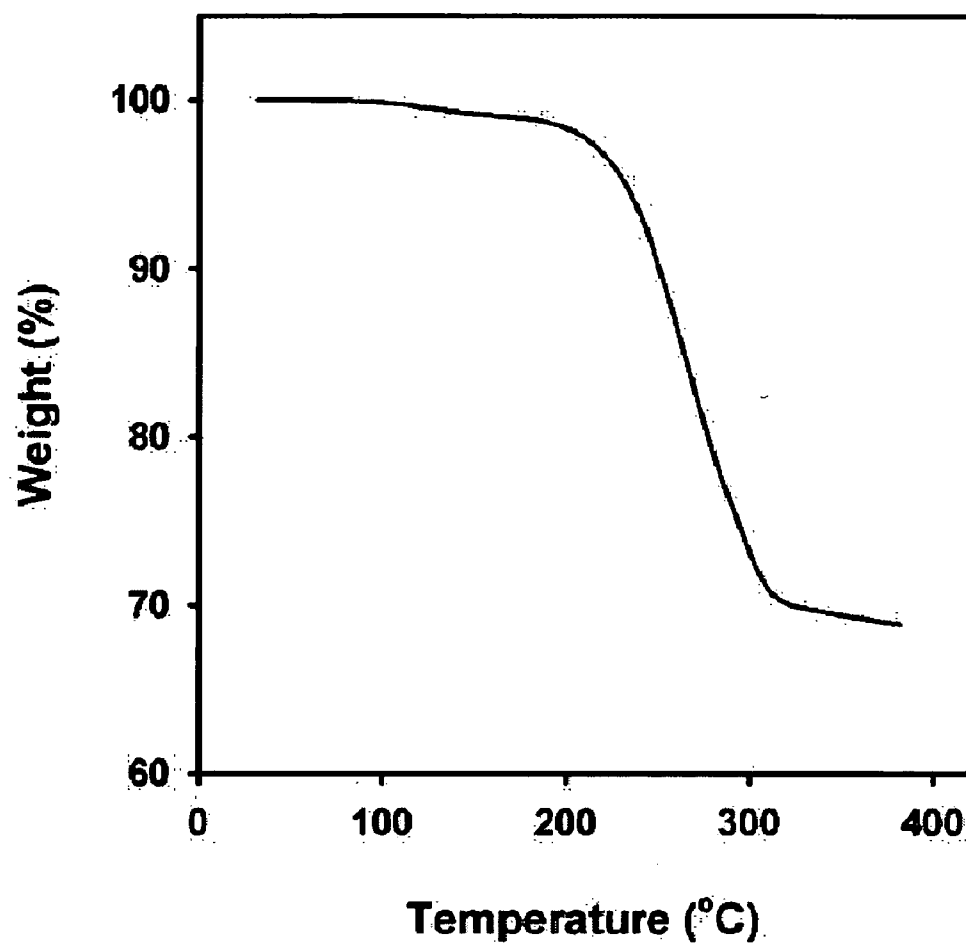


Figure 6

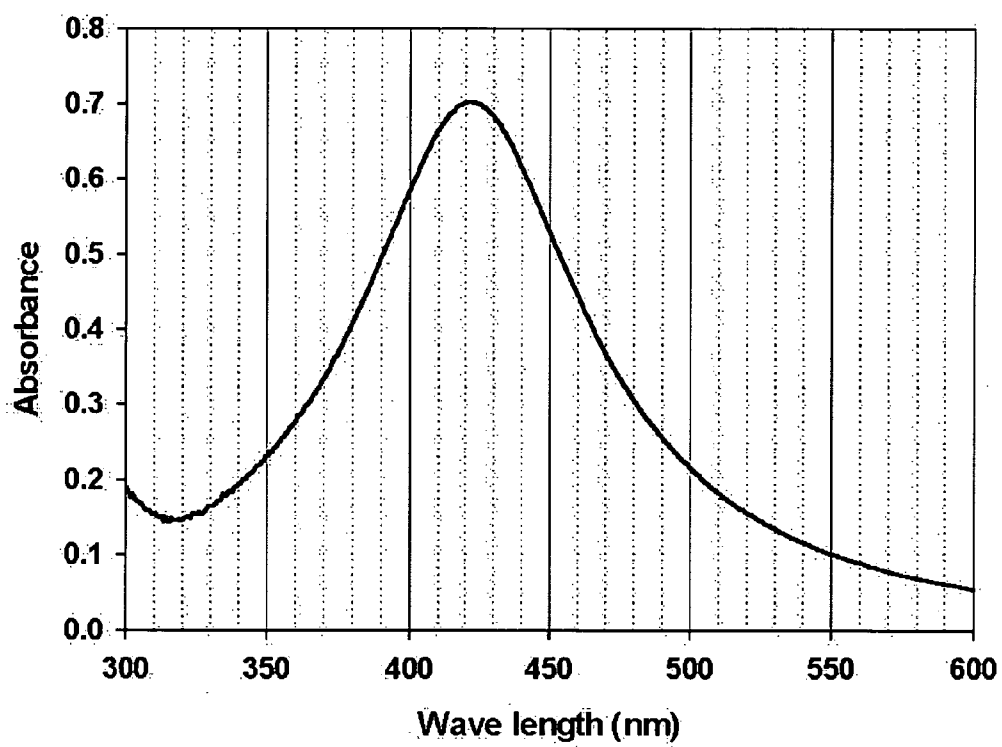


Figure 7

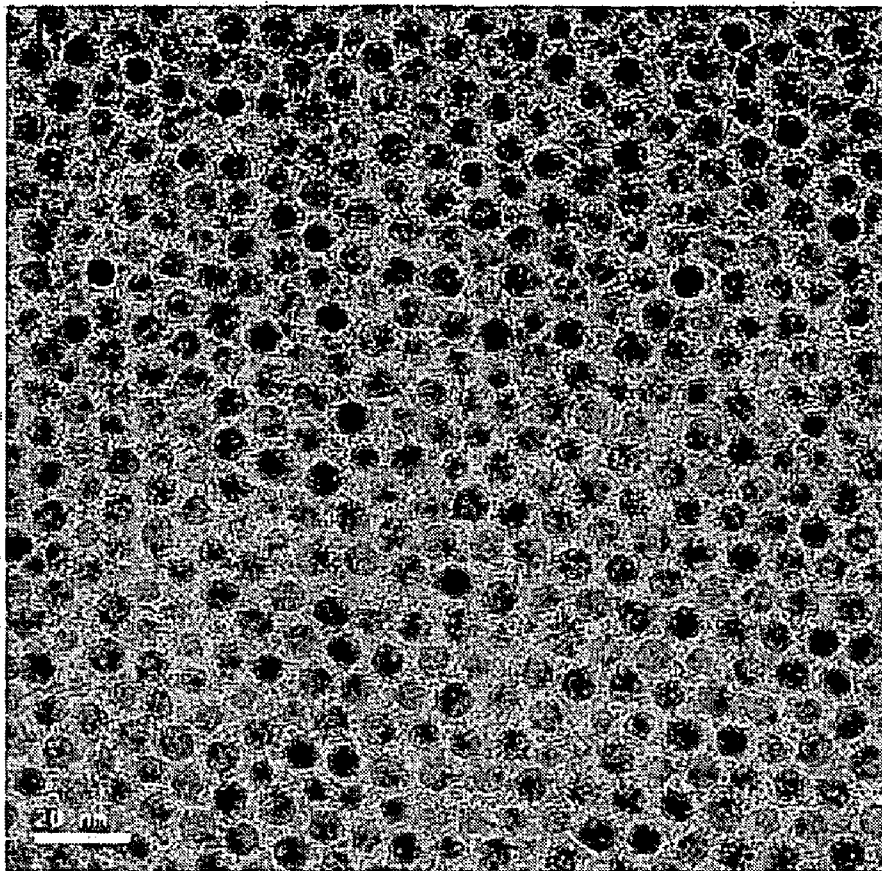


Figure 8

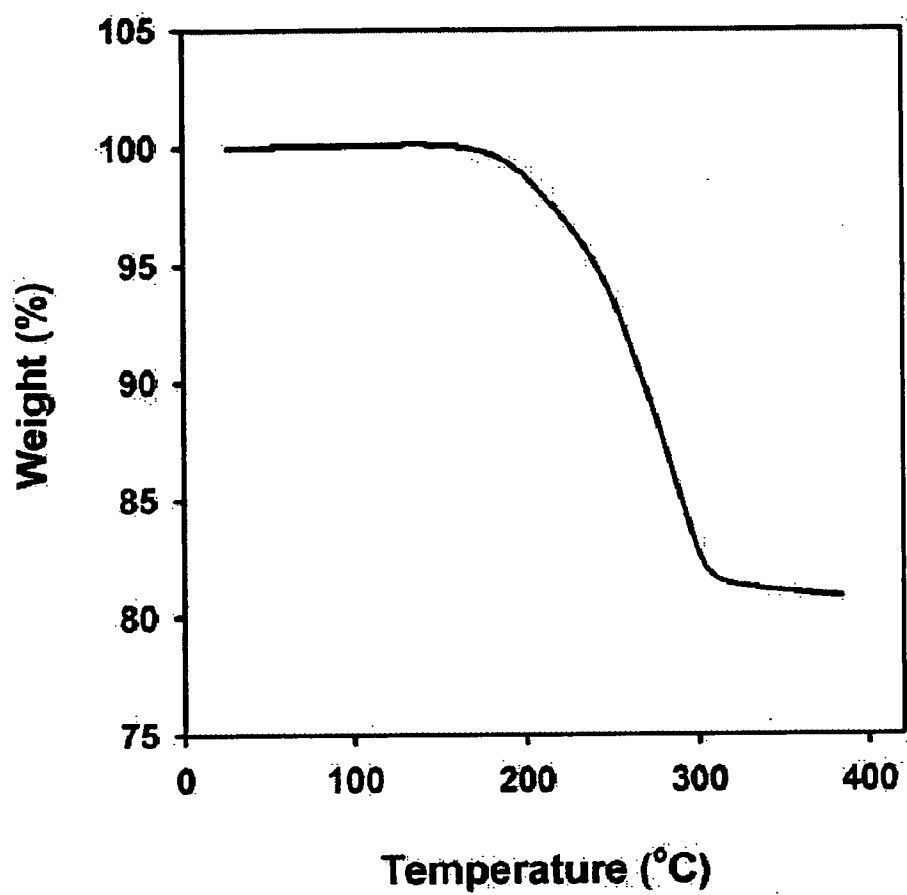
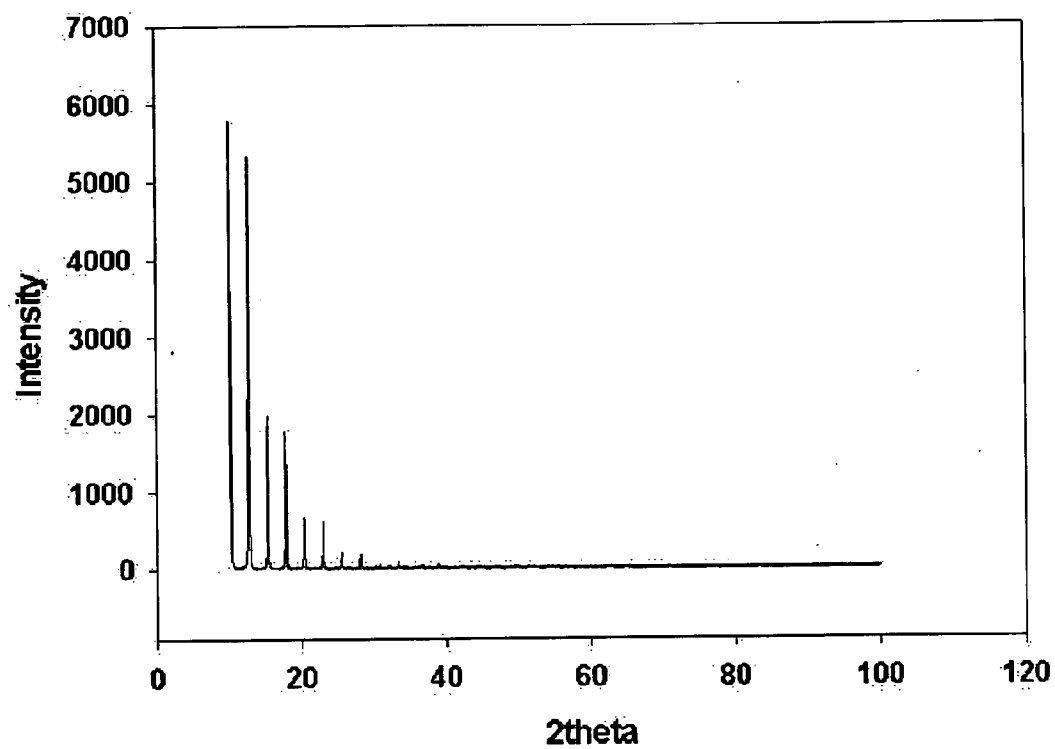


Figure 9



METAL NANO PARTICLE AND METHOD FOR MANUFACTURING THEM AND CONDUCTIVE INK

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of Korean Patent Application No. 2005-39013 filed on May 10, 2005 and Korean Patent Application No. 2005-55186 filed on Jun. 24, 2005, the contents of which are incorporated here by reference in their entirety.

BACKGROUND

[0002] 1. Technical Field

[0003] The present invention relates to a method of producing metal nanoparticles and the metal nanoparticles thus produced, and in particular, to a method of producing metal nanoparticles by the solution method.

[0004] 2. Description of the Related Art

[0005] There are two major methods of producing metal nanoparticles, namely the vapor method and the solution method (colloid method). However, since the vapor method which uses plasma or gas evaporation requires highly expensive equipment, the solution method is generally used, which is more easily utilized in mass production.

[0006] One existing method of producing metal nanoparticles by the solution method is to dissociate a metal compound in a hydrophilic solvent and apply reducing agents or surfactants to produce the metal nanoparticles in the form of a hydrosol. Another method is the phase transfer method, which involves moving the compound from a hydrophilic solvent to a hydrophobic solvent to form metal nanoparticles that may be dispersed in a hydrophobic solvent. However, the production of metal nanoparticles by such existing methods provides a very low yield rate, as it is limited by the concentration of the metal compound solution. That is, it is possible to form metal nanoparticles of uniform size only when the concentration of the metal compound is less than or equal to 0.01M. Thus, there is a limit also on the yield of metal nanoparticles, and to obtain metal nanoparticles of uniform size in quantities of several grams, 1000 liters or more of functional group are need. This presents a limitation to efficient mass production. Moreover, the phase transfer method necessarily requires a phase transfer, which is a cause of increased production costs.

[0007] Further, the production of metal nanoparticles having alkanoates as capping molecules using existing methods entails a complicated process, as it includes at least two or more steps. For example, the existing production method of silver nanoparticles must proceed through a step of adding NaOH in an alkanolic acid solution to synthesize Na-alkanoate, a step of reacting the Na-alkanoate with silver salt dissociated in water to form Ag-alkanoate powder, and a step of dissolving the Ag-alkanoate powder in an organic solvent for heating, to obtain silver nanoparticles. The several steps thus needed for the production of metal nanoparticles can be a waste of time and effort.

SUMMARY

[0008] The present invention provides a method of producing metal nanoparticles using a hydrophobic solvent,

having uniform particle size distribution and high yield rate to allow mass production. Also, the present invention provides metal nanoparticles having alkanoate molecules or sulfur molecules, produced at a low cost by an integrated procedure, and provides conductive ink including the metal nanoparticles thus obtained.

[0009] Additional aspects and advantages of the present invention will be set forth in part in the description which follows and, in part, will be obvious from the description, or may be learned by practice of the invention.

[0010] One aspect of the invention may provide a method of producing metal nanoparticles, comprising dissociating a metal compound with an amine-based compound, and adding a hydrocarbon-based compound and either one of an alkanolic acid or a thiol-based compound to the dissociated metal ion solution.

[0011] Here, the metal compound may include one or more metals selected from a group consisting of silver (Ag), copper (Cu), nickel (Ni), gold (Au), platinum (Pt), palladium (Pd), and iron (Fe). In a preferred embodiment, the metal compound may include one or more compounds selected from a group consisting of AgNO₃, AgBF₄, AgPF₆, Ag₂O, CH₃COOAg, AgCF₃SO₃, and AgClO₄.

[0012] Also, the amine-based compound may have a composition of C_xH_{2x+1}NH₂, where x may be an integer from 2 to 20. In a preferred embodiment, the amine-based compound may be one or more compounds selected from a group consisting of butylamine, propylamine, octylamine, decylamine, dodecylamine, hexadecylamine, and oleylamine. Further, the mole ratio of the amine-based compound to the metal compound may range from 1 to 100.

[0013] In addition, the hydrocarbon-based compound may be one or more compounds selected from a group consisting of hexane, octane, decane, tetradecane, hexadecane, 1-hexadecene, 1-octadecene, toluene, xylene, and chlorobenzoic acid. Here, the hydrocarbon-based compound may be added so that the concentration of the metal compound becomes a mole ratio of 0.001 to 10.

[0014] The alkanolic acid may have a composition of RCOOH, where R may be a saturated or unsaturated aliphatic hydrocarbon from C1 to C20. In a preferred embodiment, the alkanolic acid may be one or more acids selected from a group consisting of lauric acid, oleic acid, decanoic acid, and palmitic acid. Also, the mole ratio of the alkanolic acid to the metal compound may range from 0.1 to 1.

[0015] The thiol-based compound may have a composition of C_yH_{2y+1}SH, where y may be an integer from 2 to 20. In a preferred embodiment, the thiol-based compound may be one or compounds selected from a group consisting of linear-structure octanethiol, decanethiol, dodecanethiol, tetradecanethiol, hexadecanethiol, octadecanethiol and branched-structure 2-methyl-2-propanethiol. Also, the mole ratio of the thiol-based compound to the metal compound may range from 0.1 to 1.

[0016] In addition, a reducing agent may further be added during the adding of a hydrocarbon-based compound and either one of an alkanolic acid or a thiol-based compound to the dissociated metal ion solution. Here, the reducing agent may be one or more compounds selected from a group consisting of boron hydroxide, hydrazine, alcohol, amide,

acid, and glucose. In a preferred embodiment, the reducing agent may be one or more compounds selected from a group consisting of NaBH₄, LiBH₄, tetrabutylammonium borohydride, N₂H₄, glycol, glycerol, dimethylformamide, tannic acid, citrate, and glucose. Also, the mole ratio of the reducing agent to the metal compound may range from 0.1 to 1.

[0017] Another aspect of the invention may provide metal nanoparticles produced by a method comprising dissociating a metal compound with an amine-based compound, and adding a hydrocarbon-based compound and an alkanolic acid to the dissociated metal ion solution.

[0018] Here, the size of the metal nanoparticles may be 1 to 40 nm, and the metal nanoparticles may include 10 to 40 weight % organic components among the metal nanoparticles. Further, the metal nanoparticles may be used as an antibiotic, a deodorant, a disinfectant, a conductive adhesive, a conductive ink, or an electromagnetic shield coating for a display device.

[0019] Still another aspect of the invention may provide metal nanoparticles produced by a method comprising dissociating a metal compound with an amine-based compound, and adding a hydrocarbon-based compound and a thiol-based compound to the dissociated metal ion solution.

[0020] Here, the size of the metal nanoparticles may be 1 to 20 nm, and the metal nanoparticles may have 1 to 6 weight % of sulfur. The metal nanoparticles may be used as an antibiotic, a deodorant, a disinfectant, a conductive adhesive, a conductive ink, or an electromagnetic shield for a display device.

[0021] Yet another aspect of the invention may provide conductive ink including metal nanoparticles produced by a method comprising dissociating a metal compound with an amine-based compound, and adding a hydrocarbon-based compound and either one of an alkanolic acid or a thiol-based compound to the dissociated metal ion solution.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022] These and/or other aspects and advantages of the present invention will become apparent and more readily appreciated from the following description of the embodiments, taken in conjunction with the accompanying drawings of which:

[0023] **FIG. 1** is a graph representing the results of UV-VIS spectroscopy for metal nanoparticles produced according to an embodiment of the invention;

[0024] **FIG. 2** is a TEM (transmission electron microscope) image of metal nanoparticles produced according to an embodiment of the invention;

[0025] **FIGS. 3 to 5** are graphs representing the results of TGA (thermo-gravimetric analysis) for metal nanoparticles produced according to embodiments of the invention;

[0026] **FIG. 6** is a graph representing the results of UV-VIS spectroscopy for metal nanoparticles produced according to an embodiment of the invention;

[0027] **FIG. 7** is a TEM image of metal nanoparticles produced according to an embodiment of the invention;

[0028] **FIG. 8** is a graph representing the results of TGA (thermo-gravimetric analysis) for metal nanoparticles produced according to an embodiment of the invention; and

[0029] **FIG. 9** is a graph representing the results of WAXS (wide-angle X-ray scattering) analysis of silver thiolate for producing metal nanoparticles according to an embodiment of the invention.

DETAILED DESCRIPTION

[0030] Hereinafter, preferred embodiments will be described in detail of the method of producing metal nanoparticles and the metal nanoparticles thus produced according to the present invention.

[0031] Any precursor including metals, as generally used in the production of metal nanoparticles, may be used as the metal compound in the present invention, preferably that which is dissociated well in a hydrophobic solvent. Here, examples of such a metal compound include at least one metal selected from a group consisting of silver, copper, nickel, gold, platinum, palladium, iron, or an alloy thereof. Specific examples may include inorganic acid salts, such as nitrates, carbonates, chlorides, phosphates, borates, oxides, sulfonates, and sulfates, etc., and organic acid salts, such as stearate, myristate, and acetate, etc. The use of nitrates may be more preferable, as they are economical and widely used. More specific examples for the metal compound may include silver compound solutions, such as of AgNO₃, AgBF₄, AgPF₆, Ag₂O, CH₃COOAg, AgCF₃SO₃, and AgClO₄, copper compound solutions, such as of Cu(NO₃), CuCl₂, and CuSO₄, and nickel compound solutions, such as of NiCl₂, Ni(NO₃)₂, and NiSO₄, etc.

[0032] Although these metal compounds are generally known to dissociate well in a hydrophilic solvent, the present invention presents a method by which the metal compound is dissociated in a hydrophobic solvent. An amine-based compound was selected as this hydrophobic solvent. Thus, when a hydrocarbon-based compound was added later as a reflux solvent, the solubility is increased between the metal ion solution dissociated by the amine-based compound and the hydrocarbon-based compound. Therefore, the metal nanoparticles may consequently be retrieved with a high yield rate.

[0033] The amine-based compound may have a composition of C_xH_{2x+1}NH₂, where x is an integer between 2 to 20. To dissociate the metal compound, it may be preferable for the amine-based compound to be in a liquid state. Examples of such an amine-based compound include propylamine (C₃H₇NH₂), butylamine (C₄H₉NH₂), octylamine (C₈H₁₇NH₂), decylamine (C₁₀H₂₁NH₂), dodecylamine (C₁₂H₂₅NH₂), hexadecylamine (C₁₆H₃₃NH₂), and oleylamine (C₁₈H₃₅NH₂), preferably butylamine and propylamine, and more preferably propylamine, because butylamine and propylamine have superior characteristics of dissociating metal compounds, where propylamine has a greater ability of dissociating silver salts than does butylamine. Although octylamine and oleylamine are also liquids, their abilities to dissociate silver salts are inferior compared to that of butylamine or propylamine. Among the above amine-based compounds, decylamine (C₁₀H₂₁NH₂), dodecylamine (C₁₂H₂₅NH₂), and hexadecylamine (C₁₆H₃₃NH₂) are solid, and may be used by applying heat or dissolving in an organic solvent.

[0034] In a preferred embodiment, the amine-based compound may be mixed with the metal compound in a mole ratio of 1 or greater. For the amine-based compounds of

propylamine and butylamine, a mole ratio of 1 to 100 is preferable, considering the reaction conditions and yield rate, etc. Thus, the amine-based compound may be mixed in a mole ratio of 1 to 100 with respect to the metal compound, where it may be preferable in terms of economy to mix as little as possible, within a range where the metal compound can be dissociated.

[0035] The reflux solvent and capping molecules are added to the metal ion solution dissociated via the process set forth above.

[0036] A variety of organic solvents may be selected for the reflux solvent added to adjust the reflux temperature. Since an amine-based compound, which is a hydrophobic solvent, is used as the dissociation solvent in the present invention, it is preferable that a hydrophobic organic solvent be used also for the reflux solvent. A representative hydrophobic solvent is the hydrocarbon-based compound. Thus, the type of hydrocarbon-based compound is selected based on the desired reflux conditions. Preferred examples of a hydrocarbon-based compound include hexane, octane, decane, tetradecane, hexadecane, 1-hexadecene, 1-octadecene, toluene, xylene, and chlorobenzoic acid, etc. For the reflux solvent, toluene, xylene, 1-hexadecene, chlorobenzoic acid, or 1-octadecene is more preferable. This is because it is preferable for the mixed solution to be refluxed at a temperature of 100° C. or above to produce the desired forms of metal nanoparticles of the present invention, and the boiling point is 110.6° C. for toluene, 140° C. for xylene, 274° C. for 1-hexadecene, 320° C. for 1-octadecene, and 190° C. for chlorobenzoic acid, to be in correspondence with such temperature condition. The reflux solvents listed as examples set forth above are preferable also in terms of economy. The reflux temperatures are selected to range from 100 to 400° C.

[0037] It may be preferable that the hydrocarbon-based compound, such as described above, be added to the dissociated metal ion solution so that the concentration of the metal compound ranges from 0.001 to 10 mole ratio, since the reflux conditions may be formed within this range of mole ratio that are suitable for obtaining metal nanoparticles. The higher concentration of the metal compound, the smaller size of the functional group, to be preferable in terms of economy as mass production is made possible. The concentration of the metal compound is ultimately related to the yield rate of the metal nanoparticles, and in the existing solution method, the metal nanoparticles are formed only at a low concentration of 0.01 mole ratio or less, to result in a low yield rate. Using the present invention, however, the metal nanoparticles may be formed at a high concentration to ensure a high yield rate.

[0038] In the solution method, capping molecules are required to produce metal nanoparticles, where compounds having oxygen, nitrogen, and sulfur atoms may be used as such capping molecules. More specifically, compounds of the thiol group ($-\text{SH}$), amine group ($-\text{NH}_2$), or carboxyl group ($-\text{COOH}$) may be used, and in the present invention, compounds having alkanoate molecules ($-\text{COOR}$) or thiol-based compounds are used as the capping molecules.

[0039] According to an embodiment of the invention, the alkanoate molecules when used as capping molecules mix readily with hydrophobic solvents, and bond with metal nanoparticles by a certain strength to form metal nanopar-

ticles that are stable. Also, when metal nanoparticles having alkanoate molecules are used as conductive ink, the capping molecules may be removed easily by firing, to form wiring that is superior in electrical conductivity.

[0040] In the present invention, alkanoic acid is used as the compound having alkanoate molecules. Alkanoic acid has a composition of RCOOH , where R is a saturated or unsaturated aliphatic hydrocarbon from C_1 to C_{20} . That is, R may be an alkyl group from C_1 to C_{20} , an alkenyl group from C_1 to C_{20} , or an alkylene group from C_1 to C_{20} .

[0041] Examples of such an alkanoic acid include lauric acid ($\text{C}_{11}\text{H}_{23}\text{COOH}$), oleic acid ($\text{C}_{17}\text{H}_{33}\text{COOH}$), decanoic acid ($\text{C}_9\text{H}_{19}\text{COOH}$), and palmitic acid ($\text{C}_{15}\text{H}_{31}\text{COOH}$), etc. In a preferred embodiment of the invention, lauric acid and oleic acid are used for their advantages in terms of yield rate and conductivity.

[0042] Preferably, the alkanoic acid is added in a mole ratio of 1 or lower with respect to the metal compound, since the addition in a higher ratio will result in left-over alkanoic acid after a 1:1 reaction with the metal compound to produce side reactions, or incur a waste of the alkanoic acid. Thus, adding the alkanoic acid in a mole ratio of 1 with respect to the metal compound is preferable in terms of economy. In addition, for capping the metal nanoparticles, the alkanoic acid must be added in a mole ratio of 0.1 or higher with respect to the metal compound.

[0043] Compared to the existing method of producing metal nanoparticles having alkanoate molecules, it is not necessary to proceed through the step of forming alkanoate compounds of alkali metals in the present invention, and the metal nanoparticles may be produced in an integrated procedure, so that the production process may be simplified and the production costs reduced.

[0044] According to another embodiment of the invention, a thiol-based compound is used as the capping molecules. The thiol-based compound has a composition of $\text{C}_y\text{H}_{2y+1}\text{SH}$, where y may be selected from 2 to 20. Preferred examples of a thiol-based compound include linear-structure octanethiol ($\text{C}_8\text{H}_{17}\text{SH}$), decanethiol ($\text{C}_{10}\text{H}_{21}\text{SH}$), dodecanethiol ($\text{C}_{12}\text{H}_{25}\text{SH}$), tetradecanethiol ($\text{C}_{14}\text{H}_{29}\text{SH}$), hexadecanethiol ($\text{C}_{16}\text{H}_{33}\text{SH}$), octadecanethiol ($\text{C}_{18}\text{H}_{37}\text{SH}$) and branched-structure 2-methyl-2-propanethiol ($\text{C}_4\text{H}_9\text{SH}$). In a preferred embodiment of the invention, dodecanethiol ($\text{C}_{12}\text{H}_{25}\text{SH}$) or 2-methyl-2-propanethiol ($\text{C}_4\text{H}_9\text{SH}$) is used as the thiol-based compound. Preferably, the thiol-based compound is added in a mole ratio of 1 or lower with respect to the metal compound, since the addition of the thiol-based compound in a higher ratio makes it difficult for the metal nanoparticles to be created. More preferably, a mole ratio of 0.5 is used. Also, for capping the metal nanoparticles, the thiol-based compound must be added in a mole ratio of at least 0.1.

[0045] To use a hydrocarbon-based compound having a boiling point of 50° C. or more as the reflux solvent in the present invention, or in order to increase the yield rate of the metal nanoparticles produced, the reducing agent may be added further. Examples of such reducing agent include borate hydroxide, hydrazine, alcohol, amide, acid, and glucose, etc. More specific examples may include borate hydroxides such as NaBH_4 , LiBH_4 , and tetrabutylammonium borohydride (TBAB), hydrazines such as N_2H_4 , alco-

hol such as glycol and glycerol, amides such as dimethylformamide (DMF), acids such as tannic acid and citrate, and glucose. In general, TBAB is preferable for a reducing agent used in a hydrophobic solvent.

[0046] When a reducing agent is added, rapid exothermic reactions may occur, as well as rapid fusion and growth of the particles. It may thus be difficult to control the metal particles, and side reactions may occur, so that care is needed in using a reducing agent.

[0047] Preferably, the reducing agent should be added in a mole ratio of 1 or lower with respect to the metal compound, since the addition of a reducing agent in a higher mole ratio causes fusion between the metal particles to decrease the yield rate of nano-sized metal particles, and may also cause an explosion due to rapid exothermic reactions. Also, in order for the reducing agent to function as a reducing agent, it must be added in a mole ratio of 0.1 or higher. Therefore, it is preferable that the reducing agent be added in a mole ratio of 0.1 to 1 with respect to the metal compound.

[0048] In a preferred embodiment of the invention, a hydrocarbon-based compound and an alkanolic acid are added to the metal ion solution dissociated with an amine-based compound as described above, and the mixed solution is refluxed, where a reducing agent may optionally be added further. The reflux temperature is determined according to the boiling point of the selected hydrocarbon-based compound. The reflux starts at 18° C. with a temperature range of 100° C. to 400° C., and proceeds for 1 to 24 hours. Preferably, the metal nanoparticles will be obtained after 2 to 4 hours at 100° C.

[0049] At the initial stage of the reflux reaction, the mixed solution is a white slurry, turning more and more yellow, and as the reaction progresses, transforms from a transparent yellow to a red, and then a brown color. Whether or not the metal nanoparticles have formed may be determined by this change in color. The metal nanoparticles thus formed may be retrieved without a sorting process, by precipitating in a polar solvent and performing centrifugal separation. This is because the formed metal nanoparticles are uniform in size, to render the sorting process unnecessary. The polar solvent may include acetone, ethanol, methanol, or a mixed solution thereof.

[0050] The metal nanoparticles thus retrieved have a size of 1 to 40 nm, and preferably, metal nanoparticles were obtained that had a uniform size of 5 to 10 nm. FIG. 1 is a graph representing the results of UV-VIS spectroscopy for metal nanoparticles produced according to a preferred embodiment of the invention. Referring to FIG. 1, a graph is shown for the analysis results of silver nanoparticles obtained by a production method according to the present invention, having a maximum light absorbance in the wavelength region of 420 nm. Considering the fact that the maximum light absorbance is shown in the wavelength region of 380 to 240 nm for silver particulates of several or several tens of nm, it is seen that the graph of FIG. 1 shows a typical silver plasmon peak. FIG. 2 is a TEM (transmission electron microscope) image of the metal nanoparticles produced according to a preferred embodiment of the invention. Referring to FIG. 2, the analysis results of the silver nanoparticles obtained by a production method according to the present invention show that silver nanoparticles are

formed that have a uniform size of 7 nm. The image further shows that the silver nanoparticles obtained are superior also in terms of dispersion stability.

[0051] Also, among the metal nanoparticles obtained using alkanolates as capping molecules, organic components occupy 10 to 40 weight %. FIGS. 3 to 5 are graphs representing the results of TGA (thermo-gravimetric analysis) for metal nanoparticles produced according to preferred embodiments of the invention. Referring to FIG. 3, the results of thermo-gravimetric analysis on silver nanoparticles obtained by a production method according to the present invention and capped with decanoic acid show a weight reduction of about 17 weight % at a high temperature of 300° C. or more. Also, referring to FIG. 4, the results of thermo-gravimetric analysis on silver nanoparticles obtained by a production method according to the present invention and capped with lauric acid show a weight reduction of about 25 weight %, and referring to FIG. 5, the results of thermo-gravimetric analysis on silver nanoparticles obtained by a production method according to the present invention and capped with oleic acid show a weight reduction of about 33 weight %. Thus, it is seen that among the silver nanoparticles obtained by a production method according to the present invention, the weight occupied by organic components is 10 to 40 weight %, preferably 15 to 35 weight %. Among the organic components in FIGS. 3 to 5 respectively, the oxygen content was 3 to 4 weight %. In an embodiment of the present invention, the oxygen content among the organic components is 1 to 6 weight %, preferably 2 to 5 weight %.

[0052] In another preferred embodiment of the invention, a hydrocarbon-based compound and a thiol-based compound are added to the metal ion solution dissociated with an amine-based compound as described above, and the mixed solution, in which a reducing agent may optionally be added, is refluxed according to the boiling point of the added hydrocarbon-based compound. This reflux is performed at 18 to 200° C. for 1 to 24 hours, preferably at 130° C. or more for 2 to 4 hours.

[0053] At the initial stage of the reflux reaction, the mixed solution is a white slurry, turning more and more yellow, and as the reaction progresses, transforms from a transparent yellow to a red, and then a brown color. Whether or not the metal nanoparticles have formed may be determined by this change in color. The metal nanoparticles thus formed may be retrieved without a sorting process, by precipitating in a polar solvent and performing centrifugal separation. This is because the formed metal nanoparticles are uniform in size, to render the sorting process unnecessary. Examples of the polar solvent may include acetone, ethanol, methanol, or a mixed solution thereof, etc.

[0054] The metal nanoparticles thus retrieved have a size of 1 to 50 nm, and preferably, metal nanoparticles were obtained that had a uniform size of 3 to 20 nm. Moreover, the metal nanoparticles are produced in a high-viscosity hydrophobic hydrocarbon-based compound, for a superior yield rate of 10 to 20 %. Also, since thiol is used for the capping molecules, the metal nanoparticles obtained have a 1 to 5 weight % of sulfur (S).

[0055] FIG. 6 is a graph representing the results of UV-VIS spectroscopy for metal nanoparticles produced according to an embodiment of the invention. Referring to FIG. 6,

the graph shows a maximum light absorbance in the wavelength region of 420 nm. Considering the fact that the peak occurs in the wavelength region of 380 to 240 nm for silver particulates of several or several tens of nm, it is seen that the graph of **FIG. 4** shows a typical silver plasmon peak.

[0056] **FIG. 7** is a TEM image of metal nanoparticles produced according to an embodiment of the invention. Referring to **FIG. 7**, it is seen that silver nanoparticles are formed that have a uniform size of 5 nm. It is also seen that the dispersion stability is highly superior.

[0057] **FIG. 8** is a graph representing the results of TGA for metal nanoparticles produced according to an embodiment of the invention. Referring to **FIG. 8**, the results of thermo-gravimetric analysis on silver nanoparticles obtained by a production method according to the present invention and capped with dodecanethiol show a weight reduction of about 19 weight % at a high temperature of 300° C. or more. Thus, it is seen that among the silver nanoparticles obtained by a production method according to the present invention, the weight occupied by organic components is 10 to 40 weight %. Among the organic components, the content of sulfur was about 3 weight %. In an embodiment of the present invention, the oxygen content among the organic components is 1 to 6 weight %, preferably 2 to 5 weight %.

[0058] The yield rate may also be increased to 40% or higher, for metal nanoparticles produced in a high-viscosity hydrophobic hydrocarbon-based compound as in the present invention. This would be a benefit of four times the efficiency, when compared with existing production methods which provide yield rates of about 10% only. Until now, the maximum amount of metal nanoparticles obtainable in a single process, when producing metal nanoparticles in a laboratory scale was known to be about 40 g. Using a production method of the present invention, however, more than 100 g of metal nanoparticles may be obtained.

[0059] The metal nanoparticles thus obtained may be used as desired as an antibiotic, a deodorant, a disinfectant, conductive adhesive, conductive ink, or an electromagnetic shield for a display device. When the metal nanoparticles are used as conductive ink, the metal nanoparticles may be dispersed in a hydrophobic hydrocarbon-based solvent. This is because the solubility of the metal nanoparticles is high in hydrocarbon-based solvents, since they are produced in a hydrophobic solvent.

[0060] Embodiments relating methods of producing metal nanoparticles were set forth above, and hereinafter, explanations will be given in greater detail with reference to specific examples.

EXAMPLE 1

[0061] 5 g of AgNO₃ was dissociated in 20 g of butylamine. The color of the solution was transparent. Here, 50 ml of toluene and 5.6 g of lauric acid were added. This mixed solution was heated to 110° C., which is the boiling point of toluene. After refluxing for 4 hours, the solution turned into a red color, and ultimately into a thick brown color. A mixture of acetone, ethanol, and methanol was added to the thick brown solution, to precipitate silver nanoparticles. These precipitates were collected after centrifugal separation. Analyzing these precipitates with a UV-VIS spectroscope provided a graph having a peak such as

that in **FIG. 1**, by which it was found that 0.3 g of silver nanoparticles having sizes of 1 to 40 nm were obtained. From the results of TEM analysis on the particles after centrifugal separation, it was found that particles having a uniform size of 7 nm were obtained, as in **FIG. 2**.

EXAMPLE 2

[0062] 5 g of AgNO₃ was dissociated in 20 g of butylamine. The color of the solution was transparent. Here, 50 ml of toluene and 5.6 g of lauric acid were added. Here, 1.6 g of TBAB was added further, which is a reducing agent. With the addition of TBAB, the color of the solution turned red. As the solution was heated up to 110° C., the boiling point of toluene, and refluxed for 2 hours, the solution gradually turned into a thick brown color. A mixture of acetone, ethanol, and methanol was added to the thick brown solution, to precipitate silver nanoparticles. After centrifugal separation of the precipitates, 1.2 g of silver nanoparticles were obtained. From the results of TEM analysis on the particles, it was found that particles having a uniform size of 7 nm were formed.

EXAMPLE 3

[0063] 16 g of AgNO₃ was dissociated in 30 g of butylamine. The color of the solution was a faint yellow. Here, 100 g of xylene was added and the mixture stirred. Here, 20 g of lauric acid was further added, and the solution was refluxed for 20 minutes while being heated up to 140° C., the boiling point of xylene. As the reaction progressed, the solution turned into a red color, and ultimately into a thick brown color. A mixture of acetone, ethanol, and methanol was added to the thick brown solution, to precipitate silver nanoparticles. After centrifugal separation of the precipitates, 1.6 g of silver nanoparticles were obtained. From the results of TEM analysis on the particles, it was found that particles having a uniform size of 6 nm were formed.

EXAMPLE 4

[0064] 16 g of AgNO₃ was dissociated in 30 g of butylamine. The color of the solution was a faint yellow. The mixture was stirred after adding 100 g of xylene. Here, 20 g of oleic acid was further added, and the solution was refluxed for 20 minutes while being heated up to 140° C., the boiling point of xylene. As the reaction progressed, the solution turned into a red color, and ultimately into a thick brown color. A mixture of acetone, ethanol, and methanol was added to the thick brown solution, to precipitate silver nanoparticles. After centrifugal separation of the precipitates, 3 g of silver nanoparticles were obtained. From the results of TEM analysis on the particles, it was found that particles having a uniform size of 7 nm were formed.

EXAMPLE 5

[0065] 16 g of AgNO₃ was dissociated in 30 g of butylamine. The color of the solution was a faint yellow. The mixture was stirred after adding 100 g of xylene. Here, 20 g of lauric acid was added, and 3.2 g of TBAB, which is a reducing agent, was added further. With the addition of TBAB, the color of the solution turned dark red. The solution was refluxed for 90 minutes while being heated up to 140° C., the boiling point of xylene. The solution turned into a thick brown color. A mixture of acetone, ethanol, and methanol was added to the thick brown solution, to precipi-

tate silver nanoparticles. After centrifugal separation of the precipitates, 5 g of silver nanoparticles were obtained. From the results of TEM analysis on the particles, it was found that particles having a uniform size of 7 nm were formed.

EXAMPLE 6

[0066] 16 g of AgNO_3 was dissociated in 30 g of butylamine. The color of the solution was a faint yellow. The mixture was stirred after adding 100 g of xylene. Here, 20 g of oleic acid was added, and 3.2 g of TBAB, which is a reducing agent, was added further. With the addition of TBAB, the color of the solution turned dark red. The solution was refluxed for 90 minutes while being heated up to 140°C ., the boiling point of xylene. The solution turned into a thick brown color. A mixture of acetone, ethanol, and methanol was added to the thick brown solution, to precipitate silver nanoparticles. After centrifugal separation of the precipitates, 6 g of silver nanoparticles were obtained. From the results of TEM analysis on the particles, it was found that particles having a uniform size of 7 nm were formed.

EXAMPLE 7

[0067] 16 g of AgNO_3 was dissociated in 30 g of butylamine. The color of the solution was a faint yellow. The mixture was stirred after adding 100 g of hexane. Here, 20 g of lauric acid was added, and 3.2 g of TBAB, which is a reducing agent, was added further. With the addition of TBAB, the color of the solution turned dark red. As the solution was refluxed for 2 hours while being heated up to 69°C ., the boiling point of hexane, the solution turned into a thick brown color. A mixture of acetone, ethanol, and methanol was added to the thick brown solution, to precipitate silver nanoparticles. After centrifugal separation of the precipitates, 0.8 g of silver nanoparticles were obtained. From the results of TEM analysis on the particles, it was found that particles having a uniform size of 7 nm were formed.

EXAMPLE 8

[0068] 16 g of AgNO_3 was dissociated in 30 g of butylamine. The color of the solution was a faint yellow. The mixture was stirred after adding 100 g of hexane. Here, 20 g of oleic acid was added, and 3.2 g of TBAB, which is a reducing agent, was added further. With the addition of TBAB, the color of the solution turned dark red. As the solution was refluxed for 2 hours while being heated up to 69°C ., the boiling point of hexane, the solution turned into a thick brown color. A mixture of acetone, ethanol, and methanol was added to the thick brown solution, to precipitate silver nanoparticles. After centrifugal separation of the precipitates, 1.2 g of silver nanoparticles were obtained. From the results of TEM analysis on the particles, it was found that particles having a uniform size of 7 nm were formed.

COMPARISON 1

[0069] 10 g of NaOH was added to 50 g of an aqueous lauric acid solution to synthesize Na-dodecanoate of $\text{C}_{11}\text{H}_{23}\text{COO}^-\text{Na}^+$. 22 g of this Na-dodecanoate was mixed with 16 g of an aqueous AgNO_3 solution for a cation exchange reaction to obtain Ag-dodecanoate in the form of a white powder. When 6 g of Ag-dodecanoate is mixed with 100 g of a 1-octadecene solvent at normal temperature, the

mixed solution was untransparent. As the temperature was increased to 120°C ., and higher, the Ag-dodecanoate is dissolved to form a transparent solution, and as the temperature was increased to 150°C ., and higher, the solution turned into a faint red color and ultimately into a dark red color. Here, an organic solvent was added and silver nanoparticles precipitated, after which 0.2 g of metal nanoparticles were retrieved by centrifugal separation.

COMPARISON 2

[0070] 13 g of KOH was added to 70 g of an aqueous oleic acid solution to synthesize K-oleate of $\text{C}_{17}\text{H}_{33}\text{COO}^-\text{K}^+$. 39 g of this K-oleate was mixed with 16 g of an aqueous AgNO_3 solution for a cation exchange reaction to obtain Ag-oleate in the form of a white powder. When 8 g of Ag-oleate is mixed with 100 g of a 1-octadecene solvent at normal temperature, the mixed solution was untransparent. As the temperature was increased to 150°C ., and higher, the Ag-dodecanoate is dissolved to form a transparent solution, and as the temperature was increased to 200°C ., and higher, the solution turned into a faint red color and ultimately into a dark red color. Here, a polar solvent was added and silver nanoparticles precipitated, after which 0.8 g of metal nanoparticles were retrieved by centrifugal separation.

Production of Conductive Ink

[0071] 100 g of silver nanoparticles 6 to 7 nm in size, produced by Examples 1 through 8, were placed in an aqueous diethylene glycol butyl ether acetate and ethanol solution, and dispersed with an ultra-sonicator to produce 20 cps of conductive ink. The conductive ink thus produced may be printed on a circuit board via inkjet techniques to form conductive wiring.

[0072] According to the Comparison examples set forth above, the production of metal nanoparticles with alkanoate molecules as capping molecules takes a long time and requires several procedures, so that the process is complicated and the amount of metal nanoparticles retrieved is little.

REFERENCE EXAMPLE

[0073] 5 g of AgNO_3 was dissociated in 30 g of propylamine. The color of the solution was transparent or a faint yellow. With the addition of 4.2 g of dodecanethiol, white sediments were formed. The sediments were insoluble not only in a hydrophilic solvent such as water and alcohol, but also in hydrophobic solvents such as toluene. The dried white sediments were analyzed via WAXS (wide-angle X-ray scattering), DSC (differential scanning calorimetry) and TGA (thermo-gravimetric analysis). The analysis results of DSC revealed that the melting point was 133°C ., and the results of WAXS revealed that they had a lamellar structure. Also, the results of TGA revealed that silver ions and dodecanethiol underwent a 1:1 reaction. Therefore, it is found that the white sediments formed is silver thiolate ($\text{C}_{12}\text{H}_{25}\text{S}-\text{Ag}$).

[0074] FIG. 9 is a graph representing the results of WAXS (wide-angle X-ray scattering) analysis of silver thiolate for producing metal nanoparticles according to an embodiment of the invention. FIG. 9 is a graph representing the analysis results of WAXS for the white sediments obtained in the Reference Example set forth above.

EXAMPLE 9

[0075] 5 g of AgNO_3 was dissociated in 20 g of propylamine. The color of the solution was transparent or a faint yellow. The mixture was stirred after adding 50 g of xylene, and then 4.2 g of dodecanethiol was added, at which white sediments were formed. The temperature was raised to the boiling point of xylene, and at 130° C. and higher, the white sediments started to disappear. The solution was yellow, and turned red after about 1 hour of the reaction, to consequently turn into a thick brown color. The total reaction time was about 4 hours, and after adding ethanol to the thick brown solution and precipitating, the particles were collected by centrifugal separation. The results of analyzing the particles with a UV-VIS spectroscope are the same as those in FIG. 1, and the TEM image is the same as that in FIG. 2. These analyses reveal that ultimately, silver nanoparticles having a uniform size of 5 nm were formed.

EXAMPLE 10

[0076] 1-hexadecene was used instead of xylene as the reflux medium of Example 9. Ultimately, it was found that silver nanoparticles having a uniform size of 5 nm were formed.

EXAMPLE 11

[0077] 5 g of AgNO_3 was dissociated in 20 g of propylamine. The color of the solution was transparent or a faint yellow. The mixture was stirred after adding 50 g of xylene, and then 8.4 g of dodecanethiol was added, at which white sediments were formed. The temperature was raised to the boiling point of xylene, and at 130° C. and higher, the white sediments started to disappear. The solution was yellow, and turned red after about 1 hour of the reaction, to consequently turn into a thick brown color. The total reaction time was about 4 hours, and after adding ethanol to the thick brown solution and precipitating, the particles were collected by centrifugal separation. Ultimately, it was found that silver nanoparticles having a uniform size of 5 nm were formed.

EXAMPLE 12

[0078] 1-hexadecene was used instead of xylene as the reflux medium of Example 11, and it was found that, ultimately, silver nanoparticles having a uniform size of 5 nm were formed.

EXAMPLE 13

[0079] 5 g of AgNO_3 was dissociated in 20 g of propylamine. The color of the solution was transparent or a faint yellow. The mixture was stirred after adding 50 g of n-hexane, and then 4.2 g of dodecanethiol was added, at which white sediments were formed. The temperature was raised to the boiling point of n-hexane, and as soon as 1 g of TBAB was added, the solution turned into a red color, and ultimately into a thick brown color. After the completion of the reaction, it was found that silver nanoparticles having a uniform size of 5 nm were formed.

EXAMPLE 14

[0080] Toluene was used instead of n-hexane as the reflux medium of Example 13, and it was found that, at the completion of the reaction, silver nanoparticles having a uniform size of 5 nm were formed.

EXAMPLE 15

[0081] Xylene was used instead of n-hexane as the reflux medium of Example 13, and it was found that, at the completion of the reaction, silver nanoparticles having a uniform size of 5 nm were formed.

EXAMPLE 16

[0082] 1-hexadecene was used instead of n-hexane as the reflux medium of Example 13, and it was found that, at the completion of the reaction, silver nanoparticles having a uniform size of 5 nm were formed.

EXAMPLE 17

[0083] 5 g of AgNO_3 was dissociated in 20 g of propylamine. The color of the solution was transparent or a faint yellow. The mixture was stirred after adding 50 g of xylene, and then 8.4 g of dodecanethiol was added, at which white sediments were formed. The temperature was raised to the boiling point of xylene, and at 130° C. and higher, the white sediments started to disappear. As soon as 1 g of TBAB was added, the solution turned into a red color, and ultimately into a thick brown color. After the completion of the reaction, it was found that silver nanoparticles having a uniform size of 5 nm were formed.

EXAMPLE 18

[0084] 1-hexadecene was used instead of xylene as the reflux medium of Example 17, and it was found that, at the completion of the reaction, silver nanoparticles having a uniform size of 5 nm were formed.

COMPARISONS 3, 4, 5

[0085] In Comparison 3, 5 g of AgNO_3 was dissociated in 20 g of propylamine. The color of the solution was transparent or a faint yellow. The mixture was stirred after adding 50 g of n-hexane, and then 16.8 g of dodecanethiol was added, at which white sediments were formed. The temperature was raised to the boiling point of n-hexane, for a reaction time of 8 hours. As a result, the white sediments were not dissolved, and hence silver nanoparticles were not formed.

[0086] In Comparison 4, toluene was used instead of n-hexane as the reflux medium of Comparison 3, and in Comparison 5, xylene was used instead of n-hexane. Similarly, the white sediments were not dissolved, and hence silver nanoparticles were not formed.

[0087] Here, it is found that silver nanoparticles are not formed when dodecanethiol is added in a mole ratio of 2 with respect to AgNO_3 .

COMPARISONS 6, 7, 8

[0088] In Comparison 6, 5 g of AgNO_3 was dissociated in 20 g of propylamine. The color of the solution was transparent or a faint yellow. The mixture was stirred after adding 50 g of n-hexane, and then 16.8 g of dodecanethiol was added, at which white sediments were formed. The temperature was raised to the boiling point of n-hexane, and 1 g of TBAB was added. As a result, the white sediments were not dissolved, and hence silver nanoparticles were not formed.

[0089] In Comparison 7, toluene was used instead of n-hexane as the reflux medium, and in Comparison 8, xylene was used instead of n-hexane. As a result, the white sediments were not dissolved, and hence silver nanoparticles were not formed. Here, it is found that silver nanoparticles are not formed when dodecanethiol is added in a mole ratio of 2 with respect to AgNO_3 , even when a reducing agent of TBAB is added.

Production of Conductive Ink

[0090] 100 g of silver nanoparticles 5 nm in size, produced by Examples 9 through 18, were placed in an aqueous diethylene glycol butyl ether acetate and ethanol solution, and dispersed with an ultra-sonicator to produce 20 cps of conductive ink. The conductive ink thus produced may be printed on a circuit board via inkjet techniques to form conductive wiring.

[0091] While the embodiments of the present invention have been described with reference to methods of producing silver nanoparticles, it is apparent that the methods may be applied equally to metal compounds including metals mentioned above besides silver salt, to produce metal nanoparticles in a manner described in one of the embodiments.

[0092] The present invention provides a method of producing metal nanoparticles using a hydrophobic solvent, having uniform particle size distribution and high yield rate to allow mass production. Also, the present invention provides metal nanoparticles having alkanoate molecules or sulfur molecules, produced at a low cost by an integrated procedure, and provides conductive ink including the metal nanoparticles thus obtained.

[0093] Although a few embodiments of the present invention have been shown and described, it will be appreciated by those skilled in the art that changes may be made in these embodiments without departing from the principles and spirit of the present invention, the scope of which is defined in the appended claims and their equivalents.

What is claimed is:

1. A method of producing metal nanoparticles, said method comprising:

dissociating a metal compound with an amine-based compound; and

adding a hydrocarbon-based compound and either one of an alkanolic acid or a thiol-based compound to the dissociated metal ion solution.

2. The method of claim 1, wherein the metal compound includes one or more metals selected from a group consisting of silver (Ag), copper (Cu), nickel (Ni), gold (Au), platinum (Pt), palladium (Pd), and iron (Fe).

3. The method of claim 2, wherein the metal compound includes one or more compounds selected from a group consisting of AgNO_3 , AgBF_4 , AgPF_6 , Ag_2O , CH_3COOAg , AgCF_3SO_3 , and AgClO_4 .

4. The method of claim 1, wherein the amine-based compound has a composition of $\text{C}_x\text{H}_{2x+1}\text{NH}_2$, where x is an integer from 2 to 20.

5. The method of claim 4, wherein the amine-based compound is one or more compounds selected from a group consisting of butylamine, propylamine, octylamine, decylamine, dodecylamine, hexadecylamine, and oleylamine.

6. The method of claim 1, wherein the mole ratio of the amine-based compound to the metal compound ranges from 1 to 100.

7. The method of claim 1, wherein the hydrocarbon-based compound is one or more compounds selected from a group consisting of hexane, octane, decane, tetradecane, hexadecane, 1-hexadecene, 1-octadecene, toluene, xylene, and chlorobenzoic acid.

8. The method of claim 1, wherein the hydrocarbon-based compound is added so that the concentration of the metal compound becomes a mole ratio of 0.001 to 10.

9. The method of claim 1, wherein the alkanolic acid has a composition of RCOOH , where R is a saturated or unsaturated aliphatic hydrocarbon from C_1 to C_{20} .

10. The method of claim 9, wherein the alkanolic acid is one or more acids selected from a group consisting of lauric acid, oleic acid, decanoic acid, and palmitic acid.

11. The method of claim 1, wherein the mole ratio of the alkanolic acid to the metal compound ranges from 0.1 to 1.

12. The method of claim 1, wherein the thiol-based compound has a composition of $\text{C}_y\text{H}_{2y+1}\text{SH}$, where y is an integer from 2 to 20.

13. The method of claim 12, wherein the thiol-based compound is one or more compounds selected from a group consisting of linear-structure octanethiol, decanethiol, dodecanethiol, tetradecanethiol, hexadecanethiol, octadecanethiol and branched-structure 2-methyl-2-propanethiol.

14. The method of claim 1, wherein the mole ratio of the thiol-based compound to the metal compound ranges from 0.1 to 1.

15. The method of claim 1, wherein a reducing agent is further added during the adding of a hydrocarbon-based compound and either one of an alkanolic acid or a thiol-based compound to the dissociated metal ion solution.

16. The method of claim 15, wherein the reducing agent is one or more compounds selected from a group consisting of boron hydroxide, hydrazine, alcohol, amide, acid, and glucose.

17. The method of claim 15, wherein the reducing agent is one or more compounds selected from a group consisting of NaBH_4 , LiBH_4 , tetrabutylammonium borohydride, N_2H_4 , glycol, glycerol, dimethylformamide, tannic acid, citrate, and glucose.

18. The method of claim 15, wherein the mole ratio of the reducing agent to the metal compound ranges from 0.1 to 1.

19. Metal nanoparticles, produced by a method comprising:

dissociating a metal compound with an amine-based compound; and

adding a hydrocarbon-based compound and an alkanolic acid to the dissociated metal ion solution.

20. The metal nanoparticles of claim 19, wherein the size of the metal nanoparticles is 1 to 40 nm.

21. The metal nanoparticles of claim 19, including 10 to 40 weight % organic components among the metal nanoparticles.

22. The metal nanoparticles of claim 19, used an antibiotic, a deodorant, a disinfectant, a conductive adhesive, a conductive ink, or an electromagnetic shield for a display device.

23. Metal nanoparticles, produced by a method comprising:

dissociating a metal compound with an amine-based compound; and

adding a hydrocarbon-based compound and a thiol-based compound to the dissociated metal ion solution.

24. The metal nanoparticles of claim 23, wherein the size of the metal nanoparticles is 1 to 20 nm.

25. The metal nanoparticles of claim 23, having 1 to 6 weight % of sulfur.

26. The metal nanoparticles of claim 23, used an antibiotic, a deodorant, a disinfectant, conductive adhesive, con-

ductive ink, or an electromagnetic shield for a display device.

27. Conductive ink including metal nanoparticles produced by a method comprising:

dissociating a metal compound with an amine-based compound; and

adding a hydrocarbon-based compound and either one of an alkanolic acid or a thiol-based compound to the dissociated metal ion solution.

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