METAL NANOPARTICLES AND METHOD FOR MANUFACTURING THEREOF

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ABSTRACT

The present invention provides a method of producing metal nanoparticles, having a high yield rate and uniform size achieved by employing a heterologous reducing agent that considerably reduces unreactant, and using ethylene glycol that allows effective separation of desired metal nanoparticles. In addition, the present invention provides metal nanoparticles having high dispersion stability achieved by capping with polyvinyl pyrrolidone(PVP) and conductive ink including these metal nanoparticles. One aspect of the invention may provide a method of producing nanoparticles comprising, (a) mixing ethylene glycol, capping molecules and a reducing agent, (b) mixing a metal precursor with alcohol-based compound and reacting it with the mixture of (a), and (c) finishing the reaction by adding acetone and ethylene glycol to the reaction solution (b).
Fig. 4

Absorbance

Wave length (nm)
METAL NANOPARTICLES AND METHOD FOR MANUFACTURING THEREOF

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of Korean Patent Application No. 10-2005-0085708 filed on Sep. 14, 2005, with the Korea Intellectual Property Office, 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, in particular, to a method of producing metal nanoparticles with the solution method.

[0004] 2. Description of the Related Art

[0005] Major ways to produce metal nanoparticles are the chemical synthesis method, the mechanical production method and the electrical production method. However, in case of the mechanical production method which uses mechanical power for comminuting, it is hard to produce highly pure particles because of intrusion of impurities during the process and impossible to form uniform-sized metal nanoparticles. Further, the electrical production method by electrolysis has shortcomings in that it requires a long period for production time and provides a low yield rate caused by low concentration. The chemical synthesis method includes the vapor-phase method and the solution (colloid) method, where the vapor-phase method which uses plasma or gas evaporation has shortcomings in that it requires highly expensive equipments, so the solution method which is possible to generate uniform particles with low cost is generally used.

[0006] A method of producing metal nanoparticles by the solution method up to now comprises dissociating metal compound and then producing metal nanoparticles in the form of hydroxyl using a reducing agent or a surfactant. However, the production of metal nanoparticles by this existing solution method 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 mM. 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 needed. This represents a limitation to efficient mass production. In addition, the un-reactant remaining after completion of the reaction reduces the yield rate, and a vast amount of loss which occurs during the separation step of formed metal nanoparticles results in further reduction of the yield rate. Furthermore, when the generated metal nanoparticles are re-dispersed in order to use them in various areas, the dispersion stability is important, but the existing method provides a very low dispersion rate of 0.1 weight %.

[0007] Approaches to solve such existing problems and to produce a high yield rate of metal nanoparticles with uniform size are in progress.

SUMMARY

[0008] The present invention provides a method of producing metal nanoparticles, having a high yield rate and uniform size achieved by employing a heterologous reducing agent that considerably reduces un-reactant, and using ethylene glycol that allows effective separation of desired metal nanoparticles. In addition, the present invention provides metal nanoparticles having high dispersion stability achieved by capping with polyvinyl pyrrolidone (PVP) and conductive ink including these metal nanoparticles.

[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 nanoparticles comprising, (a) mixing ethylene glycol, capping molecules and a reducing agent, (b) reacting a mixture of a metal precursor and an alcohol-based compound with the mixture of (a), and (c) adding acetone and ethylene glycol to the reaction solution of (b).

[0011] Here, it may be possible to raise a temperature of the mixed solution of (a) up to 100-140°C before the step of (b), the ethylene glycol in the step (a) may be mixed in 100 to 200 parts by weight with respect to 10 parts by weight of the metal precursor.

[0012] Also here, in the step (b), the mixed solution of the metal precursor and the alcohol-based compound may react with the mixture of (a) by adding together within a short period of time, and a step of recovering metal nanoparticles by centrifuging the reaction solution after the step (c) may further be included.

[0013] Here, the capping molecule may be preferably polyvinyl pyrrolidone and according to a preferred embodiment, the polyvinyl pyrrolidone may be mixed in 30-70 parts by weight with respect to 10 parts by weight of the metal precursor.

[0014] Here, the reducing agent may include one or more compounds selected from the group consisting of glucose, ascorbic acid, tannic acid, dimethylformamide, tetrahydroammonium borohydride, NaBH4, LiBH4 and N2H4. According to a preferred embodiment, the reducing agent is preferably glucose and mixed in a mole ratio of 0.2 to 0.5 with respect to the metal precursor.

[0015] Here, the metal precursor may include one or more metals selected from the group consisting of gold, silver, copper, nickel, zinc, platinum, palladium, rhodium, ruthenium, iridium, osmium, tungsten, tantalum, titanium, aluminum, cobalt, iron and a mixture thereof. In a preferred embodiment, the metal precursor is one or more compounds selected from the group consisting of AgNO3, AgBF4, AgPF6, Ag2O, CH3COOAg, AgCF3SO3, AgClO4, AgCl, and CH3COCH==COCH3Ag.

[0016] Here, the alcohol-based compound may be one or more compounds selected from the group consisting of methanol, ethanol, ethylene glycol and diethylene glycol. In a preferred embodiment, the alcohol-based compound may be mixed in 30-50 parts by weight with respect to 10 parts by weight of the metal precursor.

[0017] Here, the ethylene glycol in the step (c) may be added in 2-10 parts by weight with respect to 1 part by weight of the capping molecule, and preferably, a reaction time in the step (b) ranges from 30 minutes to 4 hours.
Another aspect of the invention may provide metal nanoparticles produced by the method for producing metal nanoparticles set forth above.

Here, the metal nanoparticles may be metal nanoparticles capped with the polyvinyl pyrrolidone, and according to a preferred embodiment, the particles of polyvinyl pyrrolidone are 5-10 weight %.

Another aspect of the invention may provide conductive ink including metal nanoparticles set forth above.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a data representing the result of TGA analysis for the metal nanoparticles produced according to an embodiment of the invention;

FIGS. 2 and 3 are FE-SEM images of the metal nanoparticles produced according to preferred embodiments of the invention;

FIG. 4 is a graph that represents the result of UV-Vis spectroscopy (UV spectrum) of the metal nanoparticles produced according to a preferred embodiment of the invention; and

FIG. 5 is a graph that represents the result of particle size analysis of the metal nanoparticles produced according to a preferred embodiment of the invention.

DETAILED DESCRIPTION

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

To produce metal nanoparticles of the present invention, the invention include a step of mixing ethylene glycol, capping molecules, and a reducing agent.

In the invention, ethylene glycol along with the reducing agent reduces the metal precursor to prevent formation of un-reactants and allow production of metal nanoparticles in a high yield rate. Ethylene glycol may be also used as a solvent that dissolves the metal precursor. Also, ethylene glycol is added with excess amount of acetone so that removes un-reacted PVP and terminates the reaction. So far, though ethylene glycol has been used to act as both a solvent and a reducing agent, it performs poor in the reducing capacity, to result in a low yield rate. But in the invention, ethylene glycol plays various roles mentioned above and is used as an important compound for producing metal nanoparticles at a high concentration and a high yield rate.

Here, the capping molecules refer to molecules that allow metal particles to grow stably in a solvent and form nano-sized particles by encapsulating the metal particles. Any known compounds may be used as such capping molecules, and compounds having oxygen, nitrogen, and sulfur atoms may be typically used. More specifically, compounds having thiol group (—SH), amine group (—NH2), carboxyl group (—COOH) may be used as capping molecules, and according to an embodiment of the invention, PVP (Polyvinyl pyrrolidone) is preferable. This is because the PVP strongly adheres to metal nanoparticles to enhance the dispersion stability of metal nanoparticles thus obtained, and allows the metal nanoparticles to have a high dispersion rate when they are re-dispersed.

If the metal precursor is reduced only with ethylene glycol, the yield rate of metal nanoparticles becomes declined since an excess amount of un-reactant is generated. Thus a reducing agent may be added to increase the yield rate of metal nanoparticles in the invention. Example of this reducing agent, but not limited to these, may include borate hydroxides such as NaBH4, LiBH4, and tetrabutylammonium borohydride(TBAB), hydrazines such as N2H4, glucose, acids such as ascorbic acid, tannic acid etc., and dimethylformamide(DMF) etc. In a preferred embodiment of the invention, glucose is used since it is low in price, environment-friendly, and easily dissolved in water or an alcohol-based compound. Glucose is used as a reducing agent because when a hydroxyl group of glucose is oxidized, it may release electrons during its conversion to the corresponding aldehyde.

In this step, ethylene glycol is added to dissolve PVP while functioning as a reducing agent, where ethylene glycol is preferably added in 100-200 parts by weight with respect to 10 parts by weight of the metal precursor since this is the most optimal amount for reducing the metal precursor with the reducing agent. Here, since the addition of more than 200 parts by weight of ethylene glycol does not result in an increased yield of nanoparticles, the addition of more ethylene glycol than the desired amount is not economical.

Also, it is preferable that the capping molecules be added in 30-70 parts by weight with respect to 10 parts by weight of the metal nanoparticles. If the capping molecule is added less than 30 parts by weight, metal nanoparticles thus formed become larger than nano size and lack of uniformity and further deteriorates the dispersion stability since it is impossible to obtain fully capped metal nanoparticles. On the other hand, if the capping molecules is added more than 70 parts by weight, the yield rate does not increase as much as of that extent, which just results in an increase of unit cost. Here, when PVP is used as a capping molecule, it is preferable that the PVP be mixed in 30-50 parts by weight with respect to 10 parts by weight of the metal precursor.

Preferably, the reducing agent is added in a mole ratio of 0.2-0.5 with respect to 1 mole of the metal precursor. Because the addition within this ratio allows the formation of uniform metal nanoparticles and reduces un-reactant to increase the yield rate. When the reducing agent is added more than 0.5 mole ratio, it results in precipitation of metal particles and unequal growth of particles. When glucose is used as a reducing agent, it is preferable that it be mixed in 1-4 parts by weight with respect to 10 parts by weight of the metal precursor.

After thoroughly dissolving PVP and the reducing agent in ethylene glycol, the mixed solution is heated up to 100-140°C. If a mixture of the metal precursor and ethylene glycol is added at this temperature, uniform metal nanoparticles may be obtained with desired size. If the heating-up is performed after adding the mixture of the metal precursor and ethylene glycol to the mixed solution of ethylene glycol, PVP and the reducing agent, it causes unequal formation of metal nanoparticles and undesirable large size of particles.

Any metal precursor, that is known and used for the production of metal nanoparticles, may be used without
limitation in the present invention, preferably that is suitable for the alcohol reduction method. But not limited to these, preferable example of the metal precursor may include one or more metals selected from the group consisting of gold, silver, copper, nickel, zinc, platinum, palladium, rhodium, ruthenium, iridium, osmium, tungsten, tantalum, titanium, aluminum, cobalt, iron and a mixture thereof.

Specific example may include inorganic acid salts such as nitrates, carbonates, chlorides, phosphates, borates, oxides, sulfonates, and sulfates, etc., and organic acid salts, such as stearates, myristates, and acetates, etc. The use of nitrates may be more preferable, as they are economical and widely used. More specific examples of the metal precursor may include silver precursors such as AgNO₃, AgBF₄, AgPF₆, Ag₂O, CH₃COOAg, AgCl₂, AgCl, and CuCl₂, which copper salts such as of Cu(NO₃)₂, CuCl₂, and CuSO₄, and nickel salts such as of NiCl₂, Ni(NO₃)₂, and NiSO₄, etc.

After such a metal precursor is thoroughly dissolved in an alcohol-based compound, it is mixed with the mixed solution of ethylene glycol, capping molecules and the reducing agent because addition of the metal precursor in solid phase may result in an unequal reaction. Here, the solution of the metal precursor is preferably added once within a short time to the mixed solution set forth above. That is because when the metal precursor is added several times, the size of metal nanoparticles varies with addition time, which results in formation of metal nanoparticles having an unidentified particle distribution.

Here, the alcohol-based compound refers to a compound having alcohol group (—OH), but not limited to these, of which example may include methanol, ethanol, ethylene glycol, and diethylene glycol. These alcohol-based solvents may readily be mixed with PVP or ethylene glycol that is used as a reducing agent. These alcohol-based compounds may be preferably mixed in 30-50 parts by weight with respect to 10 parts by weight of the metal precursor, which is enough amount to dissolve the metal precursor.

The reaction set forth above is preferably performed for 30 minutes to 4 hours. An excess reaction over 4 hours is not preferable because it causes precipitation of the metal particles on the wall of a reaction chamber.

The compounds react with each other, the cores of particles are formed and then the cores grow to form metal nanoparticles. When the reaction is completed to form metal nanoparticles with desired size, ethylene glycol is added again and subsequently excess amount of acetone is added. They separate out metal nanoparticles from by-products and unreactants of the reaction by using difference of solubility.

According to a preferred embodiment, the acetone is preferably used in 200-300 parts by weight with respect to 100 parts by weight of total weight of the solution in the previous step. Besides acetone, methanol, ethanol, or a mixed solution thereof may be used. In addition, the additionally added ethylene glycol is preferably added in more than 2 parts by weight with respect to 1 part by weight of the capping molecule, more preferably 2-10 parts by weight. When ethylene glycol and acetone are added within the range, the metal nanoparticles capped with PVP may be selectively separated from the unreactants and the by-products by using difference of solubility. In a highly effective production of the metal nanoparticles, the metal nanoparticles are not readily separated from the by-products when using acetone alone in the end stage of the reaction, the additional annexing of ethylene glycol is required. Thus, to obtain the metal nanoparticles having high concentration and high efficiency like the present invention, ethylene glycol should be added in the end stage of the reaction.

When the metal nanoparticles obtained by this production method are dispersed in ethanol in a concentration of more than 50 weight % and centrifuged at 5000 rpm for 10 minutes, the dispersion stability is more than 98%. When the metal nanoparticles are obtained by the existing method and then centrifuged, the dispersion stability becomes very low of 0.1 weight %.

FIG. 1 is a data representing the result of TGA analysis (Thermo Gravimetric Analysis) for the metal nanoparticles produced according to an embodiment of the invention. Referring to FIG. 1, when metal nanoparticles are fully dried and analyzed with TGA, the result confirms that 7 weight % of PVP attach to 93 weight % of silver particles. FIGS. 2 and 3 are FE-SEM images of the metal nanoparticles produced according to preferred embodiments of the invention. FIG. 4 is a graph that represents the result of UV-VIS spectroscopy (UV spectrum) of the metal nanoparticles produced according to preferred embodiments of the invention. FIG. 5 is a graph that represents the result of particle size analysis of the metal nanoparticles produced according to preferred embodiments of the invention. This particle size analysis shows that average 10-30 nm of the metal nanoparticles may be obtained and the particle distribution rate are even.

The method for producing metal nanoparticles were generally set forth above, hereinafter, explanations will be given in greater detail with reference to specific examples.

While the embodiments of the invention have been described 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.

EXAMPLE 1

PVP 30 g and glucose 6.5 g were thoroughly dissolved in ethylene glycol 200 g and the mixture was poured to a flask. The temperature was raised up to 120°C. Silver nitrate 20 g was thoroughly dissolved in 60 g of ethylene glycol and the mixture was then promptly added into the reaction flask and agitated for 35 minutes. 200 g of ethylene glycol was added to the reaction product, 1200 ml of acetone was added and silver nanoparticles were selectively separated through centrifugation. When the silver nanoparticles were completely dried, 10.3 g of powder was obtained. As shown in FIG. 1, the examination of particle distribution through FE-SEM confirmed that uniform nanoparticles of 16 nm were generated.

EXAMPLE 2

PVP 30 g and glucose 1 g were thoroughly dissolved in ethylene glycol 200 g and the mixture was poured to the reaction flask. The temperature was raised up to 120°C. Silver nitrate 10 g was thoroughly dissolved in 50 g of ethylene glycol and the mixture was then promptly put into a flask and agitated for 30 minutes. After cooling to room temperature, 200 g of ethylene glycol was added to the reaction product, 1500 ml of acetone was added and silver nanoparticles were selectively separated through centrifugation. When the silver nanoparticles were completely dried,
5 g of powder was obtained. As shown in FIG. 2, the examination of particle distribution through FE-SEM confirmed that uniform nanoparticles of 25 nm were generated.

**COMPARISON EXAMPLE 1**

[0047] After PVP 100 g was thoroughly dissolved in ethylene glycol 200 g and the mixture solution was placed into a flask, the temperature was raised up to 120°C while the mixture solution was agitated. Silver nitrate 20 g was thoroughly dissolved in 60 g of ethylene glycol and the mixture was then promptly put into the reaction flask and reacted for 35 minutes. After the reaction was completed, the reaction was completely stopped by adding 150 g of ethylene glycol to the flask, and silver nanoparticles were selectively separated and perfectly dried. Finally, 12 g of silver nanoparticles were obtained. The result of the examination of particle distribution was average 15 nm size of the particles.

[0048] The metal nanoparticles obtained from the examples had more than 50% of yield rate, while the yield rate of the metal nanoparticles from the comparison example was lower than this.

[0049] In addition, when the metal nanoparticles obtained from the examples were dispersed at a high concentration of more than 50% in ethanol and centrifuged at 5000 rpm for 10 minutes, they retained more than 98% of dispersion stability. On the other hand, when the metal nanoparticles obtained from the comparison example was centrifuged like above, only 0.1 weight % remained.

[Production of Conductive Ink]

[0050] 100 g of 10-30 nm silver nanoparticles produced by example 1 or 2 was added to an aqueous solution of ethanol and diethylene glycol butyl ether acetate, and dispersed with an ultrasonicator to produce 20 eps of conductive ink. The conductive ink thus produced may be printed on a circuit board via inkjet techniques to form conductive wiring.

[0051] 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.

[0052] As described above, the method of production of metal nanoparticles according to the present invention significantly can reduce the unreacted to produce uniform metal nanoparticles with a high yield rate. In addition, the method of production of metal nanoparticles according to the present invention can separate desired metal nanoparticles efficiently with ethylene glycol. Again, the metal nanoparticles of the invention have high dispersion stability as they are capped with polyvinyl pyrrolidone (PVP). The invention also provides conductive ink including these metal nanoparticles.

What is claimed is:

1. A method of producing metal nanoparticles, said method comprising:
   (a) mixing ethylene glycol, capping molecules and a reducing agent;
   (b) reacting a mixture of a metal precursor and an alcohol-based compound with the mixture in the step (a); and
   (c) adding acetone and ethylene glycol to the reacting solution in the step (b).
2. The method of claim 1, wherein the mixture in the step (a) is heated to a temperature of 100-140°C before the step (b).
3. The method of claim 1, wherein the ethylene glycol in the step (a) is mixed in 100 to 200 parts by weight with respect to 10 parts by weight of the metal precursor.
4. The method of claim 1, wherein in the step of (b), the mixture of the metal precursor and the alcohol-based compound and the mixture in the step (a) are added together within a short period of time to react.
5. The method of claim 1, wherein recovering metal nanoparticles by centrifuging the solution after the step of (c) is further included.
6. The method of claim 1, wherein the capping molecule is polyvinyl pyrrolidone.
7. The method of claim 6, wherein the polyvinyl pyrrolidone is mixed in 30-70 parts by weight with respect to 10 parts by weight of the metal precursor.
8. The method of claim 1, wherein the reducing agent includes one or more compounds selected from the group consisting of glucose, ascorbic acid, tannic acid, dimethylformamide, tetrabutyl ammonium borohydride, NaBH₄, LiBH₄ and N₃H₄.
9. The method of claim 8, wherein the reducing agent is glucose.
10. The method of claim 1, wherein the reducing agent is mixed in a molar ratio of 0.2 to 0.5 with respect to the metal precursor.
11. The method of claim 1, wherein the metal precursor includes one or more metals selected from the group consisting of gold, silver, copper, nickel, zinc, platinum, palladium, rhodium, ruthenium, iridium, osmium, tungsten, tantalum, titanium, aluminum, cobalt, iron and a mixture thereof.
12. The method of claim 1, wherein the metal precursor is one or more compound selected from the group consisting of AgNO₃, AgBF₄, AgPF₆, Ag₂O, CH₃COOAg, AgCF₃SO₃, AgClO₄, AgCl and CH₃COCH═COCH₃Ag.
13. The method of claim 1, wherein the alcohol-based compound is one or more compounds selected from the group consisting of methanol, ethanol, ethylene glycol and diethylene glycol.
14. The method of claim 1, wherein the alcohol-based compound is mixed in 30-50 parts by weight with respect to 10 parts by weight of the metal precursor.
15. The method of claim 1, wherein the ethylene glycol in the step (c) is added in 2-10 parts by weight with respect to 1 part by weight of the capping molecule.
16. The method of claim 1, wherein the reaction time of the step (b) ranges from 30 minutes to 4 hours.
18. The metal nanoparticles of claim 17, wherein the metal nanoparticles are capped with polyvinyl pyrrolidone.
19. The metal nanoparticles of claim 18, wherein the particles of the polyvinyl pyrrolidone are 5-10 weight %.
20. Conductive ink including metal nanoparticles according to claim 17.