Gold nanoparticles and method of synthesizing the same

The present invention relates to gold nanoparticles which can be produced at low costs with high yields in large amounts by a liquid phase synthesis method and have a controlled size, as well as a synthesis method thereof. The inventive gold nanoparticles consist of gold nanoparticles having a polygonal or circular plate structure.

FIG. 1

Stirring and heating an aqueous solution of HAuCl₄·3H₂O

Adding a dispersion stabilizer to the HAuCl₄·3H₂O solution

Adding a reducing agent to HAuCl₄·3H₂O solution to which the dispersion stabilizer had been added

Heating and cooling the resulting mixture so as to form gold nanoparticles

Inducing precipitation at room temperature and then treating the upper layer solution with a filter
Description

BACKGROUND OF THE INVENTION

1. Field of the invention

[0001] The present invention relates to gold nanoparticles and a synthesis method thereof, and more particularly to gold nanoparticles which can be produced at low costs, high yields and large amounts by a liquid phase synthesis and has a planar shape with a controlled size, as well as a synthesis method thereof.

2. Description of the Prior Art

[0002] As generally known in the art, gold nanoparticles are widely used in various fields, such as catalysts, chemical sensors, biosensors, optoelectronic devices, optical devices, nano-devices, and surface enhanced Raman scattering (SERS).

[0003] Such gold nanoparticles show various optical properties depending on their shape. For example, spherical gold nanoparticles have a strong absorbance peak at 500 - 600 nm, whereas nanorods and nanoboxes show absorbance peaks at 500 - 1,500 nm. Such optical properties are very important variables in various application fields of the gold nanoparticles, particularly in applications to biosensors or optical devices.

[0004] The shape of the gold nanoparticles determines their physical and chemical properties. Gold nanoparticles with a certain shape have the properties according to their shape. Therefore the shape control of the gold nanoparticles means the control of their properties.

[0005] Since the 1990s, the gold nanoparticles have been produced and studied in many fields, mostly in the form of spherical particles. However, attempts to produce planar gold nanoparticles as two-dimensional nanoplates and apply such nanoplates in the development of new materials are still insufficient in spite of their technological importance in the applications to optical devices, electronic devices, nanomechanical devices, etc.

[0006] Meanwhile, triangular plate-shaped gold nanoparticles were observed at an extremely small amount as a by-product in the synthesis of spherical nanoparticles (Chem. Lett. 2003, 32, 1114-1115), which cannot be considered as the synthesis of plate-shaped gold nanoparticles. There are no reports indicating that gold nanoparticles consisting of high-yield gold nanoplates without spherical nanoparticles were synthesized. Particularly, there is no example of reproducible preparation of gold nanoplates which have a thickness of a few to several tens of nanometers and a edge length ranging from several tens of nanometers to several thousands of nanometers and show characteristic optical spectra as in the present invention.

SUMMARY OF THE INVENTION

[0007] Accordingly, the present invention has been made to solve the above-mentioned problems occurring in the prior art. An advantage of the present invention is to provide gold nanoparticles consisting of gold nanoplates, which can be produced at low cost with high yields in large amounts by a liquid-phase synthesis and whose size can be controlled, as well as a synthesis method thereof.

[0008] Another advantage of the present invention is to provide gold nanoparticles consisting of gold nanoplates, which are highly crystalline and have the size controlled in the nanometer range.

[0009] In order to accomplish the above object, in one aspect, the present invention provides gold nanoplates, which have a polygonal or circular plate structure.

[0010] The edge length or diameter of the gold nanoplates is preferably 10 nm - 2,000 nm, and the thickness of the gold nanoplates is preferably 1 nm - 100 nm.

[0011] In another aspect, the present invention provides a method for preparing such gold nanoplates, which comprises the steps of stirring and heating an aqueous solution of HAuCl₄·3H₂O; adding a dispersion stabilizer to the HAuCl₄·3H₂O solution; adding a reducing agent to the HAuCl₄·3H₂O solution to which the dispersion stabilizer had been added; and heating and cooling the resulting mixture so as to form gold nanoplates.

[0012] The inventive method may further comprise the step of inducing the precipitation of the aqueous solution having the gold nanoplates formed therein, and then treating the upper layer with a filter.

[0013] The concentration of the HAuCl₄·3H₂O solution is preferably 0.1 mM to 10 mM. The dispersion stabilizer is preferably any one selected from the group consisting of citric acid, polyacrylic acid (PVA), polyethylene glycol (PEG) and polyvinylpyrrolidone (PVP). If polyvinylpyrrolidone is used as the dispersion stabilizer, the molar ratio between the gold ions of the HAuCl₄·3H₂O solution and the polyvinylpyrrolidone is preferably 1:0.05 to 1:15, and more preferably 1:0.1 to 1:10.

[0014] The reducing agent is preferably sodium citrate. In this case, the molar ratio between the gold ions of the
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HAuCl₄·3H₂O solution and sodium citrate is preferably 1:0.1 to 1:10, and more preferably 1:0.1 to 1:1.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] The above and other objects, features, and advantages of the present invention will be more apparent from the following detailed description taken in conjunction with the accompanying drawings, in which:

FIG. 1 is a flow chart for illustrating a method for synthesizing gold nanoplates according to one embodiment of the present invention;
FIG. 2 shows the shape of gold nanoplates according to an embodiment of the present invention, which was measured by a scanning electron microscope;
FIG. 3a shows the shape and crystallinity of gold nanoplates according to an embodiment of the present invention, which were measured by a scanning electron microscope, a transmission electron microscope, and X-ray diffraction (XRD) analysis;
FIG. 3b illustrates that the size of gold nanoplates can be controlled by controlling synthetic conditions;
FIG. 4a shows the results of energy dispersive spectrometry for the nanoplates according to an embodiment of the present invention; and
FIG. 4b shows the UV-Vis NIR spectra of gold nanoplates according to the size of the nanoplates.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0016] Hereinafter, a preferred embodiment of the present invention will be described with reference to the accompanying drawings.

[0017] In a preferred embodiment, the present invention provides gold nanoparticles in the form of gold nanoplates, which are highly crystalline and have the size controlled in the nanometer range. In another embodiment, the present invention provides gold nanoparticles in the form of gold nanoplates which can be produced at low cost with high yields in large amounts by a liquid phase synthesis method.

[0018] FIG. 1 is a flow chart for illustrating a method for synthesizing gold nanoparticles in the form of gold nanoplates according to one embodiment of the present invention.

[0019] As shown in FIG. 1, the inventive method for synthesizing gold nanoplates comprises the steps of: (S1) stirring and heating an aqueous solution of HAuCl₄·3H₂O; (S2) adding a dispersion stabilizer to the HAuCl₄·3H₂O solution; (S3) adding a reducing agent to the HAuCl₄·3H₂O solution to which the dispersion stabilizer had been added; and (S4) heating and cooling the resulting mixture so as to form gold nanoplates.

[0020] The inventive preparation method may further comprise the step (S5) of inducing the precipitation of the aqueous solution having the gold nanoplates formed therein, at room temperature, and then treating the upper layer with a filter, thus obtaining high-purity gold nanoplates.

[0021] In the step (S1) of heating the HAuCl₄·3H₂O solution with stirring, an aqueous solution of HAuCl₄·3H₂O is prepared from HAuCl₄·3H₂O with a purity of more than 99.9%, and heated in a reflux system with vigorous stirring. At this time, the concentration of the HAuCl₄·3H₂O solution is preferably 0.1 mM to 10 mM, and most preferably 1 mM.

[0022] In the step (S2) of adding the dispersion stabilizer to the HAuCl₄·3H₂O solution, the dispersion stabilizer, such as citric acid, polyacrylic acid (PPA), polyethylene glycol (PEG) or polyvinylpyrrolidone (PVP), is added to the HAuCl₄·3H₂O solution being stirred and heated. In a preferred embodiment of the present invention, polyvinylpyrrolidone is used as the dispersion stabilizer. The polyvinylpyrrolidone is a kind of polymer with a molecular weight of about 50,000 and has a characteristic in that it is easily dissolved in water.

[0023] In this case, the molar ratio between the gold ions of the HAuCl₄·3H₂O solution and the polyvinylpyrrolidone is preferably 1:0.05 to 1:15, more preferably 1:0.1 to 1:10, and most preferably 1:10 to 1:7.

[0024] The step (S3) is the step where the reducing agent is added to the HAuCl₄·3H₂O solution to which the dispersion stabilizer had been added.

[0025] As the reducing agent, sodium citrate (C₆H₅Na₃O₇) is preferably used. The molar ratio between the gold ions of the HAuCl₄·3H₂O solution and the sodium citrate is preferably 1:0.1 to 1:10, more preferably 1:0.1 to 1:1, and most preferably 1:0.5.

[0026] The sodium citrate has the following formula 1:
In the step (S4) of heating and cooling the HAuCl₄·3H₂O solution to which the reducing agent had been added, the solution is heated with vigorous stirring, and then cooled with stirring at room temperature, so as to form gold nanoplates.

In this case, the gold nanoplates are formed via the following reaction scheme:

\[
\text{HAuCl}_4 + \text{HO-} - \text{CO}_2\cdot - \text{CO}_2\cdot - \text{CO}_2\cdot \xrightarrow{\text{heating}} \text{Au nanoparticles} + \text{CO}_2 + \text{HCO}_2\cdot
\]

Namely, Au³⁺ is reduced into Au⁰ by the sodium citrate so as to induce the nucleation of gold nanoplates, and the anisotropic growth of the nuclei leads to form gold nanoplates.

In the step (S5) of inducing the precipitation of the solution at room temperature and then treating the upper layer of the solution with a filter, the HAuCl₄·3H₂O solution in which gold nanoplates had been formed is kept at room temperature to induce the precipitation, and then the upper layer portion in which the gold nanoplates are suspended are collected and filtered. In this case, in order to obtain high-quality, gold nanoplates, the upper layer solution in which the gold nanoplates are suspended is filtered several times using deionized water as a cleaning solvent. This is because the gold nanoplates with high purity are suspended in the upper layer portion of the solution.

Meanwhile, FIG. 2 shows the shape of gold nanoplates according to an embodiment of the present invention, which was measured with a field emission scanning electron microscope (FS-SEM).

As shown in FIG. 2, the gold nanoplates according to an embodiment of the present invention have a thickness of 10 - 50 nm and a side length of 50 - 1,000 nm. Furthermore, gold nanoplates with various sizes, which vary depending on filters used in the filtering step, can be obtained.

FIG. 3a shows the shape and crystallinity of gold nanoplates according to an embodiment of the present invention, which were measured by a scanning electron microscope, a transmission electron microscope, and X-ray diffraction (XRD) analysis. FIG. 3b illustrates that the size of gold nanoplates can be controlled by controlling synthesis conditions.

In FIG. 3a, (a) and (b) are a low-magnification and a high-magnification SEM photograph, respectively. As can be seen in (a) and (b) of FIG. 3a, the gold nanoplates according to the embodiment of the present invention have an edge length of 50 - 1,000 nm.

In FIG. 3a, (c) is a TEM photograph. The inset in (c) is a diffraction pattern taken along a direction perpendicular to the surface of the gold nanoplate, and shows (220) and (422) Bragg diffraction peaks corresponding to lattice constants 1.44 Å and 0.83 Å, respectively, relative to [111] axis. Also, in FIG. 3a, (d) shows the diffraction pattern of the gold nanoplates according to the embodiment of the present invention. The comparison of (d) with the JCPDS card shows that the inventive nanoplates have the crystalline structure of pure gold.

In FIG. 3b, (a), (b), (c), and (d) are electron microscope photographs of gold nanoplates formed when the molar ratios between HAuCl₄·3H₂O and polyvinylpyrrolidone are 1:9, 1:5, 1:2, and 1:0.1, respectively.

As can be seen in (a) to (d) of FIG. 3b, although the size of gold nanoplates can be slightly controlled depending on the kind of a filter used in the filtering step, the size of the gold nanoplates is strongly dependent upon the ratio of polyvinylpyrrolidone, a dispersion stabilizer, to HAuCl₄·3H₂O. More specifically, it is found that an increase in the ratio of polyvinylpyrrolidone to HAuCl₄·3H₂O leads to an increase in the size of the gold nanoplates formed.

FIG. 4a shows the results of analysis using an energy dispersive spectrometer for the nanoplates according to the inventive embodiment, and FIG. 4b shows the UV-Vis NIR spectra of the gold nanoplates according to the size
of the nanoplates.

[0039] As can be seen in FIG. 4a and 4b, the nanoplates according to the embodiment of the present invention show peaks at the characteristic wavelength of gold. Namely, the nanoplates according to the embodiment of the present invention are made of gold.

[0040] Moreover, the spectra 1 to 4 in FIG. 4b represent the spectra of the gold nanoplates shown in (a) to (d) of FIG. 3b, respectively. As can be seen in FIG. 4b, the gold nanoplates according to the embodiment of the present invention have two characteristic and strong absorbance peaks at visible and near infrared region (wavelength region of 500-2,000 nm), indicating that they have thin and planar shapes.

[0041] According to the above-described method for synthesizing the gold nanoplates, high purity gold nanoplates with a very small thickness and various sizes can be produced at high yields by a simple liquid phase synthesis and separation process.

[0042] Furthermore, the above-described method for synthesizing the gold nanoplates allows the provision of gold nanoplates of various sizes and shapes, as well as the provision of gold nanoplates having various physical and chemical properties.

[0043] Moreover, it is considered that the above-described nanoplates can be widely applied for the development of new materials, catalysts, photosensors, optical and electronic devices, nanomechanical parts, etc. Particularly, it is expected that the present invention will provide a synthesis method which allows the gold nanoplates to be produced at low costs, with high yields and in large amounts.

[0044] As described above, the present invention can provide the gold nanoplates which can be produced at low costs, high yields and large amounts by the liquid phase synthesis method, as well as the synthesis method thereof.

[0045] In addition, the present invention can provide the gold nanoplates with a single-crystalline structure and a size controlled in the nanometer range.

[0046] Although a preferred embodiment of the present invention has been described for illustrative purposes, those skilled in the art will appreciate that various modifications, additions and substitutions are possible, without departing from the scope and spirit of the invention as disclosed in the accompanying claims.

Claims

1. Gold nanoplates having a polygonal or circular plate structure.

2. The gold nanoplates according to Claim 1, wherein the length of any one edge or diameter thereof is 10 - 2,000 nm.

3. The gold nanoplates according to any of claims 1 and 2, wherein the thickness thereof is 1 - 200 nm.

4. A method for synthesizing gold nanoplates, which comprises the steps of:

   - stirring and heating an aqueous solution of HAuCl₄·3H₂O;
   - adding a dispersion stabilizer to the HAuCl₄·3H₂O solution;
   - adding a reducing agent to the HAuCl₄·3H₂O solution to which the dispersion stabilizer had been added; and
   - heating and cooling the resulting mixture so as to form gold nanoplates.

5. The method according to Claim 4, which further comprises the step of inducing the precipitation of the aqueous solution having the gold nanoplates formed therein, and then treating the upper layer solution with a filter.

6. The method according to any of claims 4 and 5, wherein the concentration of the HAuCl₄·3H₂O solution is 0.1 mM to 10 mM.

7. The method according to any of claims 4 to 6, wherein the dispersion stabilizer is any one selected from the group consisting of citric acid, polyacrylic acid (PVA), polyethylene glycol (PEG) and polyvinylpyrrolidone (PVP).

8. The method according to Claim 7, wherein the molar ratio between the gold ions of the HAuCl₄·3H₂O solution and the polyvinylpyrrolidone is 1:0.05 to 1:15.

9. The method according to Claim 8, wherein the molar ratio between the gold ions of the HAuCl₄·3H₂O solution and the polyvinylpyrrolidone is 1:0.1 to 1:10.

10. The method according to any of claims 4 to 9, wherein the reducing agent is sodium citrate.
11. The method according to Claim 10, wherein the molar ratio between the gold ions of the HauCl₄·3H₂O solution and sodium citrate is 1:0.1 to 1:10.

12. The method according to Claim 10, wherein the molar ratio between the gold ions of the HauCl₄·3H₂O solution and sodium citrate is 1:0.1 to 1:1.
FIG. 1

1. Stirring and heating an aqueous solution of HAuCl₄·3H₂O
2. Adding a dispersion stabilizer to the HAuCl₄·3H₂O solution
3. Adding a reducing agent to HAuCl₄·3H₂O solution to which the dispersion stabilizer had been added
4. Heating and cooling the resulting mixture so as to form gold nanoparticles
5. Inducing precipitation at room temperature and then treating the upper layer solution with a filter