

Colloidal Dispersion of Gold Nanoparticles

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Abstract Stable sols of gold nanoparticles with an average diameter of about 13 nm were prepared from hydrogen tetrachloroaurate (prepared starting from bulk metallic gold) and trisodium citrate dihydrate. The organic salt acts as reducing as well as stabilizing agent for the gold nanoparticles, having an average diameter of 13 ± 4 nm. The deep purple colloidal suspension is stable for several weeks. UV-Vis absorption spectra shows the typical surface plasmon resonance band of nanosized gold with an absorption maximum at 521.5 ± 0.5 nm.

Classification

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|--------------|-------------------------------------|
| form: | colloid |
| function: | pigment |
| preparation: | reduction of aqueous metal solution |
| composition: | citrate-stabilized Au nanoparticles |

Introduction

Gold colloids have been known since ancient times for their fascinating properties and colors, which nowadays can be related to the presence of metal nanoparticles.[1] Starting from the pioneering investigations of M. Faraday[2] and W. Ostwald,[3] gold nanoparticles have been the topic of much interest due to their easy preparation and high stability.[4] An extensive review on their synthesis, properties and applications has been recently published.[1] Nucleation and growth of colloidal gold was thoroughly investigated by Turkevich *et al.*[5,6,7]

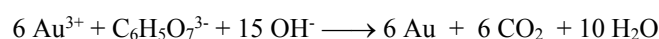
Gold nanoparticles are well-known for producing a strong optical response (plasmon) due to the excitation of free electrons at the metal surface which results in typical surface plasmon resonance (SPR) bands.[8] These outstanding optical properties of gold nanoparticles make them suitable for several uses. Furthermore, gold nanoparticles are appealing systems for their invaluable chemical, supramolecular, recognition and catalytic properties.[1] Au nanoparticles-oligonucleotide conjugates are currently attracting great interest because of their potential use in

DNA detection. Gold colloids have also found application as non-cytotoxic labels, biolabels and in optical biosensors.[9] Colloidal gold, labeled to various biological materials like lectins, antibodies, antigens, enzymes, or lipoproteins allows to observe these systems by transmission or scanning electron microscopic methods.[9]

Two main approaches can be used to generate metal colloids, the first based on dispersion of larger particles (*dispersion method*), the second relying on the condensation of smaller units (*reduction method*).[9] While the former affords only unstable sols, characterized by particles with a wide size distribution, the latter allows to prepare stable sols through reduction of metal salts in solution.[9] Several routes have been proposed to prepare stable suspensions of gold nanoparticles,[1,6,10,11,12,13] mainly based on reduction of Au(III) derivatives.

For example, gold colloids are easily prepared by reduction of HAuCl_4 in diluted aqueous solution with citric acid or trisodium citrate. A very narrow size distribution can be obtained when the latter reducing agent is used which is oxidized to carbon dioxide in the course of the reaction. Carbon dioxide is formed after different oxidative steps; intermediates and by-products such as acetone dicarboxylic acid have been reported.[5]

The method described here allows obtaining very stable gold nanoparticles with a diameter of about 13 nm and a quite narrow size distribution, starting from a solution of hydrogen tetrachloroaurate and trisodium citrate. Trisodium citrate acts both as reducing as well as stabilizing agent.



The proposed method presents, with respect to other routes, several advantages, mainly related to i) easy synthetic procedure, ii) reproducibility of the method iii) stability of the prepared sol. The aqueous medium used is another advantage, since water solvates both reagents very well.

Variation of the experimental conditions allows, in principle, tailoring the particles size up to 900 nm.[9] In particular, Turkevich *et al.* [5] have extensively described the effect of various parameters, such as the temperature, amount of citrate added or the dilution of the solution, on the formation of colloidal gold. Lowering the temperature at which the sodium citrate solution is added to the hydrogen tetrachloroaurate solution by 10°C, increases the time required for completion of the reaction by a factor of two. The amount of citrate added or the dilution of the solution can dramatically affect the average size and size distribution of the gold nanoparticles. The latter is additionally depending on the relative rates of nucleation and growth.[5]

However, although variation of the above mentioned parameters over a large range yields sols of nanoparticles of different size and size distribution, the general outcome of the procedure (colloidal gold) remains unaffected. It should furthermore be pointed out that, by using the described procedure, the variation of the citrate/hydrogen tetrachloroaurate(III)·3H₂O molar ratio within a limited range does not dramatically affect the size and size distribution. However, the prepared

gold colloids are only stable in solution, because they are protected by ligand molecules and electric charges preventing coagulation.

Materials

- Metallic gold foil purchased from Nuova Franco Suisse Italia
- Hydrogen chloride, HCl, 37% (Aldrich), used as received
- Nitric acid, HNO₃, 65% (Carlo Erba), used as received
- Sulfuric acid, H₂SO₄, 98% (Carlo Erba), used as received
- Sodium citrate dihydrate, HOC(COONa)(CH₂COONa)₂·2H₂O, 99.0% ACS reagent (Merck) used as received

Safety and Disposals

Safety and handling instructions for the chemicals, especially those involved in the preparation of H₂AuCl₄ (strong acids), are reported in the corresponding materials safety data sheets (MSDS). The employed chemicals should be handled with care and with protective gloves. Preparation of H₂AuCl₄ should be carried out in well ventilated areas and under an aspirated fume hood due to the development of toxic nitric vapors. Gloves and safety glasses should be worn when working with the precursor solutions as well as with the colloidal sol.

Procedures

All the procedures were performed in air, at room temperature and atmospheric pressure, using de-ionised water..

A. Preparation of H₂AuCl₄·3H₂O

Synonyms: Hydrogen tetrachloroaurate trihydrate, tetrachloroauric acid trihydrate; chloroauric acid trihydrate.

The reported procedure allows preparing about 1.3 g of H₂AuCl₄·3H₂O and requires about one week for the preparation and about two weeks for the crystallization of the product.

For all concentration/evaporation steps, a wide flask (Petri dish) should be used, because otherwise condensation of the acid will require considerably more time.

- (1) About 0.7 g of metallic gold is cut in very small pieces ($\sim 1 \times 2$ mm) and put into a 250 ml beaker. 70 ml of aqua regia (75% v/v HCl, 25% v/v HNO₃) are slowly added.
- (2) The mixture is stirred and gradually heated to 50°C. When dissolution of gold slows down, the temperature is gradually increased to 70-80°C.
- (3) Once metallic gold is completely dissolved (after about 2 h), the solution is continuously heated until it is concentrated to 30 ml.
- (4) HCl is slowly added to the hot solution, until brown nitric vapors are completely eliminated and the volume is about 60 ml.
- (5) The procedure described in 3. and 4. is repeated about 5 times, until, after addition of HCl, no brown nitric vapor is developed.
- (6) The solution is concentrated (by heating) to 30 ml.
- (7) Bidistilled de-ionised water is added to the solution under stirring which is kept at about 70-80°C, until a volume of about 50 ml is obtained and until acid vapors are completely absent. The presence of acid vapors is checked by a litmus paper (pH indicator) which is put into the vapors; this operation (addition of water, concentration of the solution under heating) is repeated until pH 7 is reached.
- (8) The magnetic stirrer is removed from the beaker and the solution is concentrated to 15 ml by heating at 70°C;
- (9) The solution is cooled to room temperature.
- (10) The beaker is put into a desiccator; on the bottom of the desiccator a crystallizing dish containing concentrated H₂SO₄ is placed;
- (11) The desiccator is put in vacuum by using a water pump and protected from sunlight by an aluminum foil;
- (12) The vacuum is periodically checked and the desiccator is left standing for about 15 d, until crystals of an intense yellow color are formed.

B. Preparation of Gold Nanoparticles Colloidal Suspension

The reported procedure allows the preparation of a stable suspension of monodisperse gold nanoparticles having a diameter of about 13 nm.

A 1 mM aqueous solution of H₂AuCl₄ is prepared by dissolving 0.39 g of H₂AuCl₄·3H₂O in 1 L of de-ionised water, and a 38 mM solution of sodium citrate dihydrate by dissolving 11.41 g in 1 L de-ionised water. An amount of 20 ml of the H₂AuCl₄ solution is put in a 50 ml beaker equipped with a magnetic bar. The solution is heated to the boiling point and then 2 ml of the citrate solution are added (Au : citrate molar ratio 1:3.8) under stirring. The yellow color of the solution originating from hydrogen tetrachloroaurate first turns colorless. The solution remains clear for about 10 sec and then turns grayish-blue. After about 1 min a deep wine-red sol is obtained. No further change of color upon prolonged boiling is observed. Deionised water is added drop wise to keep the volume at 22 ml. The solution is then cooled to room temperature. The pH of the final solution is about 6.7.

Characterization

A purple red, stable sol is obtained.

UV-Vis characterization: The UV-Vis absorption spectra of the colloidal sol were acquired in the 200-800 nm wavelength range, using a 2 nm spectral band width and a 0.5 nm data interval. The absorption maximum is at 521.5 ± 0.5 nm, in agreement with values reported in literature (Fig. 1).[1,9,12]

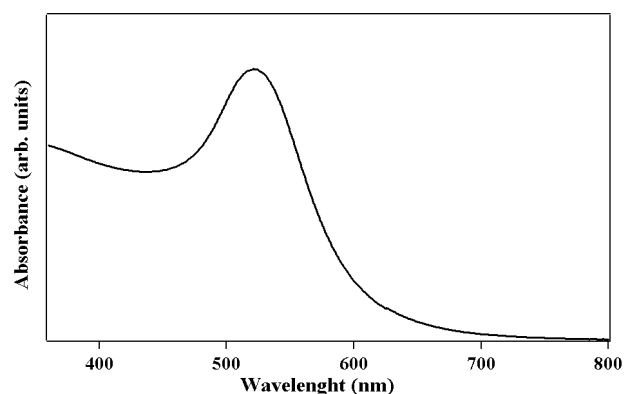


Fig. 1. UV-Vis spectrum of the gold colloid (molar Au: citrate ratio: 1: 3.8).

Dynamic light scattering measurements (Particle Sizing Systems Nicomp Model 370 correlator equipped with a thermostated cell holder and a Spectra Physics Series 2016 Ar laser operating at 488 nm): Hydrodynamic particle diameters were obtained from cumulated fits of the autocorrelation functions at 90° scattering angle. DLS measurements were performed on the gold sol diluted twice in Milli-Q water. The sol was filtered through a Sartorius Minisart single use filter ($0.2 \mu\text{m}$) before measurements. The average particle size (number-weighted) was 12 ± 4 nm (Fig. 2).

Comments

- (1) The prepared sol is stable for several weeks.
- (2) The replacement of sodium citrate by other reducing agents would result in other nanoparticles sizes and dispersions.

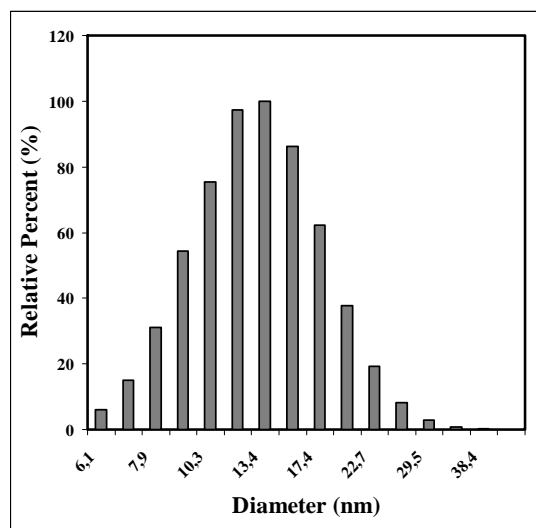


Fig. 2. Number-weighted Gaussian analysis of the gold sol (Au: citrate molar ratio: 3.8) as determined by light scattering measurements.

- (3) The addition of sodium citrate should be performed when the HAuCl_4 solution is boiling, otherwise longer reaction times are required to achieve the purple red sol.
- (4) The slightly basic pH of the solution ensures that the adsorbed citrate groups on the gold nanoparticles are completely deprotonated.
- (5) The features of the colloidal sols obtained by this procedure are affected by experimental parameters, such as the temperature: lowering the temperature at which trisodium citrate is added to the chloroauric acid solution by 10°C increases the time required to observe the deepening of the solution color, which indicates the completion of the reaction, by a factor of 2.[1]
- (6) The preparation of colloidal gold by this procedure starting from hydrogen tetrachloroaurate and trisodium citrate solutions is easy, safe, not dangerous, and can be performed in a reproducible way also by undergraduate chemistry students.
- (7) Addition of strong electrolytes to the gold colloids results in their fast coagulation and precipitation.

References

- [1] M. C. Daniel, D. Astruc, *Chem. Rev.* 2004, **104**, 293, and references therein.
- [2] M. Faraday, *Philos. Trans.* 1857, **147**, 145.
- [3] W. Ostwald, *Kolloid Z.* 1909, **4**, 5.

- [4] M. A. Hayat, *Colloidal Gold, Principles, Methods and Applications*, Vol. 1; Academic Press, New York, 1989. G. Schmid, *Clusters and Colloids. From Theory to Application*, VCH, Weinheim, 1994.
- [5] J. Turkevich, P. C. Stevenson, J. Hillier, *Discuss. Faraday Soc.* 1958, **11**, 55.
- [6] B. V. Enüstün, J. Turkevich, *J. Am. Chem. Soc.* 1963, **85**, 3317.
- [7] D. Beischer, F. Krause, *Angew. Chem.* 1938, **51**, 331.
- [8] U. Kreibig, M. Vollmer, *Optical Properties of Metal Clusters*, Springer, Berlin, 1995.
- [9] G. Schmid, *Chem. Rev.* 1992, **92**, 1709.
- [10] J. Turkevich, J. Hillier, *Anal. Chem.* 1949, **21**, 475.
- [11] G. Schmid, B. Corain, *Eur. J. Inorg. Chem.* 2003, 3081.
- [12] A. D. McFarland, C. L. Haynes, C. A. Mirkin, R. P. Van Duyne, H. A. Godwin, *J. Chem. Educ.* 2004, **81**, 544A.
- [13] S. L. Cumberland, G. F. Strouse, *Langmuir* 2002, **18**, 269.