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Preparation of gold nanoparticles (GNP) aqueous suspensions by a new method involving Tiron

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Abstract A new method is proposed to produce gold nanoparticles (GNP) by in situ reduction of a gold salt dissolved in water. The reducing agent used is Tiron instead of the citrate anion most often mentioned in literature. The influence of various parameters has been investigated, such as the content of Tiron with respect to that of the precursor of gold $HAuCl_4$, or the initial pH of the solution after mixing of reactants. It is shown that Tiron also exerts a positive influence as a dispersant, which impedes agglomeration of gold nanoparticles. The typical average size of GNP synthesized in the present work is close to 7 nm.

Introduction

In the context of nanosciences and nanotechnologies, gold nanoparticles (GNP) or gold colloids generates a great interest for several reasons. Some review articles describe the synthesis and assembly of functionalized GNP [1] and their potential applications, for instance in biology, catalysis and nanotechnology [2]. It has been widely demonstrated that the distribution of size, the shape and the surface behavior of the particles influence their properties. With their coloring properties, the GNP permits to confer some beautiful colors in the pink, red, purple, blue and green to glass, ceramic and porcelain products. The effects observed depend on the size, the shape [3] and then the refractive index of particles and also on the content of GNP in the sol.

The purpose of this present work was to propose new aqueous formulations for GNP sols in order to obtain useful suspensions to color glass substrates by heat treatment at high temperature. It can prove of interest to color the substrates by spraying a GNP sol before the final cooling of bottles. Presently, a further thermal treatment is necessary after the deposition of a color layer to permit adhesion on the substrate.

Generally, gold nanoparticles are prepared according to an oxidation/reduction process. In the latter case, attention must be paid not only to the reduction process of the gold ion involved but also to factors which keep the solid phase dispersed and prevent colloids from aggregation. Several conventional methods of synthesis have been developed but one of the most familiar processes is the citrate reduction technique, which has been introduced by Turkevitch in 1951 [4]. It consists of reducing $HAuCl_4$ in a boiling citrate solution according to the reaction (1) [5]:

Frens reported in 1973 that nanosized gold nanoparticles (from 15 nm to 150 nm) could be obtained through an adequate control of the ratio of trisodium citrate to $HAuCl_4$ [6] species, and also through the control of the ratio between gold ions and a surfactant which is added simultaneously to the citrate.

In the field of ceramics, consolidation of colloidal suspensions into dense and homogeneous green bodies is a central feature of colloidal processing research to

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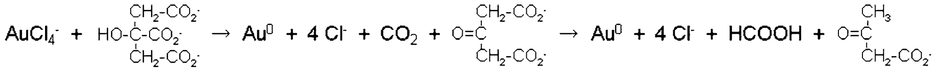


$$AuCl_4^- + HO\text{-}\overset{CH_2\text{-}CO_2^-}{\underset{CH_2\text{-}CO_2^-}{C}}\text{-}CO_2^- \rightarrow Au^0 + 4\,Cl^- + CO_2 + O{=}\overset{CH_2\text{-}CO_2^-}{\underset{CH_2\text{-}CO_2^-}{C}} \rightarrow Au^0 + 4\,Cl^- + HCOOH + O{=}\overset{CH_3}{\underset{CH_2\text{-}CO_2^-}{C}} \qquad (1)$$

manufacture components with a complex shape. In the most cases, to obtain stable suspensions with high solid loadings, surface modification, with a dispersant, of the raw material is necessary. Among these organic additives, citrate ion is a well known and efficient dispersant of alumina powder [7]. Use of Tiron and citric acid salts has allowed to develop, for example, the direct coagulation casting process [8].

The Tiron molecule $(OH)_2C_6H_2(SO_3Na)_2$ is an efficient dispersant of many oxide powders. Its ability to strongly complex several ions in water enhances its adsorption on the oxide surface by forming an inner sphere complex. Previous works describe the advantages of this molecule to stabilize oxide suspensions (Al_2O_3, ZrO_2, TiO_2) with respect to hydrosoluble polymers such as polyelectrolytes [9, 10]. Moreover its oxido-reduction properties have permitted the preparation of aqueous suspensions in view of the development of a process of electrophoretic deposition, which has been thoroughly investigated in the case of TiO_2 layer [11]. As citrate and Tiron present similar properties in the field of aqueous oxide suspensions, we have tested Tiron for the synthesis of GNP. We have studied the influence of the ratio $HAuCl_4$/Tiron concentrations and of the pH on the stability of the sol and on the size distribution of the particles. The UV–vis spectra, the measurement of size distribution by Photon Correlation Spectroscopy (PCS) and Transmission Electron Microscopy (TEM) proved to be powerful techniques to characterize such systems.

Materials and methods

Hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4 \cdot 3H_2O$), 5–dihydroxy-1,3-benzene-disulfonic acid (commercially called as Tiron), citric acid were purchased from Sigma–Aldrich. Sodium hydroxide was obtained from Prolabo.

UV–vis spectra were obtained with a spectrophotometer (Lambda 40; Perkin Elmer) in the 200–800 nm wavelength range using quartz cells with 1 cm path length.

Size distributions of solid particles were obtained by photon correlation spectroscopy (PCS), which was performed with the aid of a Malvern S4700 apparatus operated at room temperature. This technique is based upon the analysis of the Brownian motion of nanoparticles, with a He–Ne laser emitting at a 633 nm wavelength. Mie theory allows it to obtain size fractions from measured intensity distributions. Samples were analyzed without dilution.

High magnification observations were made by TEM using JEOL JEM-2010 equipment operated at 200 kV.

For the synthesis of gold nanoparticles, 25 ml of gold sol were prepared from $HAuCl_4$ (5×10^{-4} M), a mixture of Tiron (7.5×10^{-4}–4.8×10^{-3} M) and NaOH (8.0×10^{-4}–5.0×10^{-3} M) or tri sodium citrate (1.6×10^{-3} M). All formulations investigated are listed in Table 1. Reference numbers with A and B refer to citrate and Tiron reagents, respectively. The first digit corresponds to the concentration of the reducing agent

Table 1 Compositions used for synthesis of GNPs

Reference number	$HAuCl_4$ concentration (M)	Reductant agent	Reductant agent concentration (M)	NaOH concentration (M)	Final pH	Average diameter (nm)
A1	5×10^{-4}	Trisodium citrate	1.6×10^{-3}	None added	6.0	19
B1.1	5×10^{-4}	Tiron	7.5×10^{-4}	1.5×10^{-3}	2.2	Agglomeration
B1.2	5×10^{-4}	Tiron	7.5×10^{-4}	3.0×10^{-3}	7.4	36
B1.3	5×10^{-4}	Tiron	7.5×10^{-4}	4.0×10^{-3}	9.8	24
B1.4	5×10^{-4}	Tiron	7.5×10^{-4}	5.0×10^{-3}	10.6	25
B2.1	5×10^{-4}	Tiron	1.6×10^{-3}	8.0×10^{-4}	2.0	34
B2.2	5×10^{-4}	Tiron	1.6×10^{-3}	1.5×10^{-3}	3.2	33
B2.3	5×10^{-4}	Tiron	1.6×10^{-3}	2.4×10^{-3}	4.4	23
B2.4	5×10^{-4}	Tiron	1.6×10^{-3}	3.0×10^{-3}	7.8	16
B2.5	5×10^{-4}	Tiron	1.6×10^{-3}	4.0×10^{-3}	8.0	21
B3.1	5×10^{-4}	Tiron	1.0×10^{-3}	3.0×10^{-3}	7.5	18
B4.1	5×10^{-4}	Tiron	3.2×10^{-3}	3.0×10^{-3}	7.4	35
B5.1	5×10^{-4}	Tiron	4.8×10^{-3}	3.0×10^{-3}	7.1	39

and the second to the NaOH concentration tested. In this table, the final pH of the GNP sol and the average size of particles calculated from the software of the Malvern S4700 equipment are also given.

In the first method involving Tiron, Tiron and NaOH were mixed, and just kept for an hour. The presence of the basic form of Tiron resulted in a color change of the solution, which turned yellow. $HAuCl_4$ aqueous solution was boiled under continuous stirring. Then, heating was stopped and the gold solution added to the mixture of Tiron and NaOH. The solution turned black immediately and then changed to transparent red rapidly. Then it was gently cooled down to room temperature.

The former method involving sodium citrate, which was introduced by Turkevitch in 1951 [4] is now considered as conventional. Tri sodium citrate was made from citric acid and NaOH. The gold sol was prepared by boiling $HAuCl_4$ with Na citrate.

Results and discussion

Tiron stability versus pH

As the structure of the Tiron molecule includes a benzene ring, the compound can be detected by UV spectroscopy, and the evolution of its content estimated qualitatively. The values of pK_a for the two hydroxyl groups of Tiron are 7.6 and 12.5. The pH influences the absorption wavelength depending upon the protonation of the first alcohol group (i.e., pH < 7.6, $\lambda = 230$, 290 nm and pH > 7.6, $\lambda = 260$, 307 nm). The absorption wavelength of the oxidized form of Tiron is $\lambda = 435$ nm [12]. Figure 1 summarizes such data.

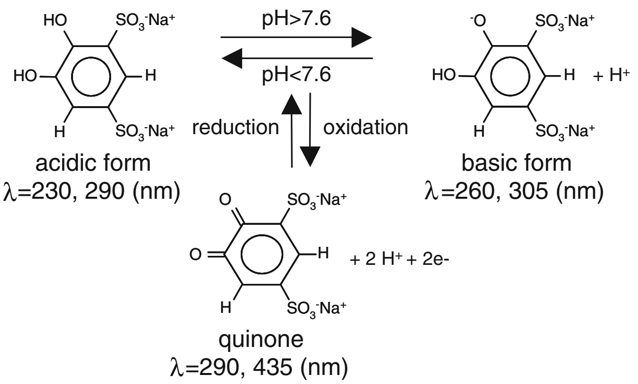
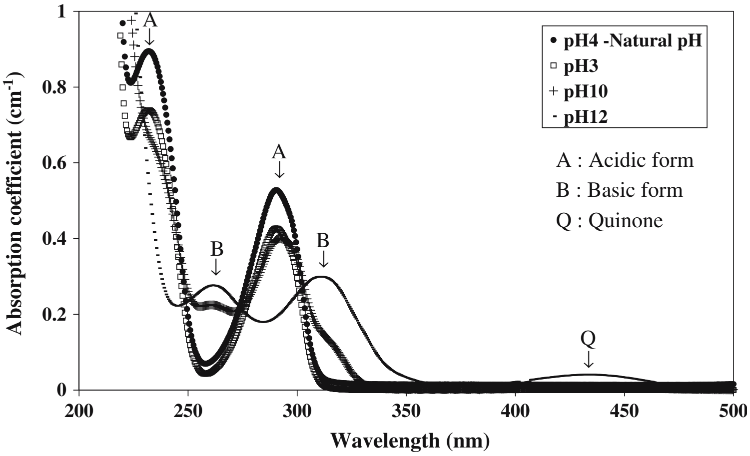


Fig. 1 The transformations of Tiron according to the pH of the aqueous solution

First, Tiron stability was studied versus pH. Four solutions with a Tiron concentration of 1×10^{-8} M were prepared. The natural pH of such solutions is 4. The pH of three samples was then adjusted at 3, 10 and 12, respectively with either HCl or NaOH. These solutions were left for 24 h to reach equilibrium, and their pH was again measured. Values obtained were 3, 4, 7 and 11. Figure 2 depicts the UV–vis spectra of such solutions.

For pH 3 and 4, only the acidic form is present (two peaks, $\lambda = 230$, 290 nm). One can conclude that no oxidation of Tiron occurs in acidic media. At pH 7, peaks of the basic form appear together with the peak corresponding to the oxidized form. At pH 11, both basic and oxidized forms are present. This increase of the peak intensity corresponding to the oxidized form indicates that a part of Tiron oxidizes under basic conditions. The oxidation potential of Tiron depends on the pH and decreases as pH increases. Then the anion can be oxidized by water in basic media. As Tiron oxidation produces hydronium ions, the final pH of the third solution, initially fixed at 10, becomes neutral (pH = 7). These results will help to interpret

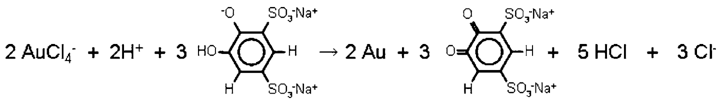
Fig. 2 UV–vis spectra of Tiron solutions versus pH



the UV spectra of GNP sols because depending on the formulation the final pH values are included in a pH domain ranging from 2.2 to 10.6 (cf Table 1).

Preparation of GNP

For the preparation of gold sols, two parameters were studied, namely the ratio of $HAuCl_4$ to Tiron concentrations and the NaOH concentration. We assumed that $AuCl^{-}_4$ ions can be reduced by Tiron according to the reaction (2).



(2)

For the formulations with reference numbers from B1.1 to B1.4, stoichiometric ratio ($[HAuCl_4]/[Tiron] = 1/1.5$) with several concentrations of NaOH was tested. Figure 3 depicts UV–vis spectra of gold sol prepared according to formulations B1.1–B1.4. Peaks around 517–550 nm, which indicate the existences of gold nanoparticles are observed. In the UV wavelength range, peaks due to oxidized form of Tiron can be observed. For the lowest NaOH concentration studied, B1.1 formulation, the final pH measured is 2.2. Under such conditions, the colloidal dispersion is not stable and agglomeration occurs. The small intensity peak due to GNP, centered at 550 nm, is quite broad. Only the acidic form of Tiron is observed. When the final pH is larger than 7.4, sols are stable. The peak of GNP is narrow and centered between 517 nm and 525 nm. The average size of particles is included in the range 24–36 nm. Formulations B1.3 and B1.4 lead to smaller sizes of colloids. This suggests that a basic pH is beneficial for the sol stability. Stability of gold sol depends on the final pH, and particles are well dispersed in neutral or basic media. We attribute this pH dependent behavior to the presence of an oxide monolayer on the particle surface. The reactivity of the metal surface with water leads to superficial oxidation. Then hydroxyl groups thus formed at the surface can exchange protons with the solution and their ionization induces a density of electrical charges. Measurements of the zeta potential of gold surfaces versus pH carried out by Giesbers et al. [13] have permitted to conclude that the zeta potential is pH dependent, and that the isoelectric point (IEP) of such surfaces is equal to 4.5.

The present work permits to check such an assumption about the surface oxidation of GNP and to ascertain the important role of H^+ and OH^- in controlling the electrical charge of the particles. If the IEP of our GNPs is close to 4.5, a pH shift towards neutral and basic values will stabilize the GNP dispersion by creating a repulsive potential due to the deprotonation of hydroxyl surface groups. For all the formulations, Tiron is nearly oxidized (according to the intensity of the peak centered at $\lambda = 435$ nm) except in acidic media where the reduction of quinone by water occurs after the Tiron oxidation by gold ions.

In a second set of experiments, gold sols were prepared with Tiron in excess. Several NaOH concentrations were tested likewise (B2.1–B2.5). The

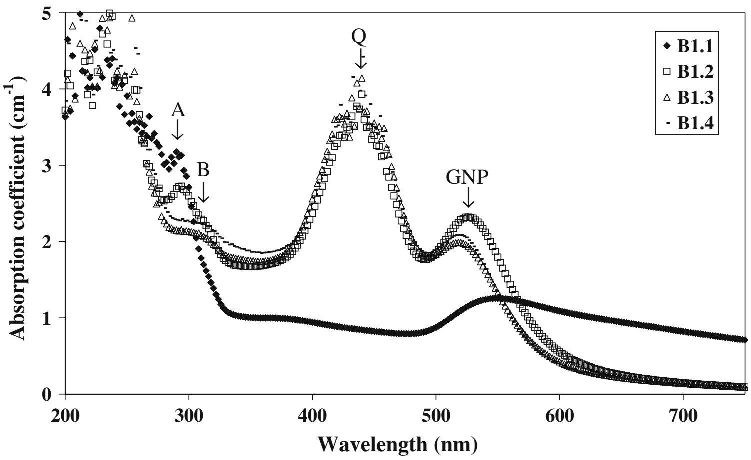


Fig. 3 UV–vis spectra of GNP prepared according to the Tiron route (with a stoichiometric ratio of $[HAuCl_4]$ and [Tiron])

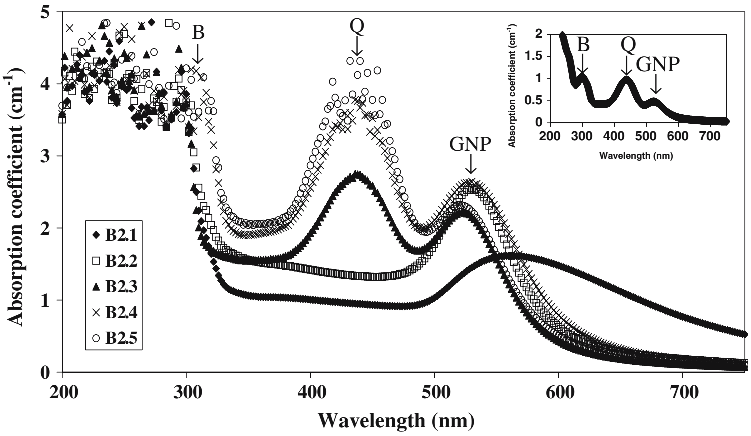


Fig. 4 UV–vis spectra of GNP prepared according to the Tiron route ([HAuCl$_4$]/[Tiron] = 1/3.2). Inset shows UV–vis spectrum of a diluted sol issued from composition B2.5

registered optical spectra are reported in Fig. 4. In these formulations, the ratio [HAuCl$_4$]/[Tiron] amounts to 1/3.2. Peaks at shorter wavelengths were too strong to be analyzed efficiently. So the sol (B2.5) was diluted and the spectrum obtained thereafter is showed in the inset. One then observes three peaks, which successively reveal the presence of GNP (λ = 522 nm), quinone (λ = 437 nm), and basic forms of Tiron (λ = 298 nm). This indicates that Tiron was not fully oxidized. The final pH of the sols derived from formulations B2.1 and B2.2 is acid, the absorption peak due to GNP is large, but no agglomeration occurs. The average particle size is beyond 30 nm. As the final pH increases, the particle size decreases and reaches a minimum value for formulation B2.4. The average size of GNP obtained with an excess of Tiron is smaller than previously, when a stoichiometric ratio was used between gold ion and Tiron. One concludes that Tiron acts not only as a reducing agent but also as a dispersant for colloids.

The mechanism of Tiron dispersion of oxide powders (Al$_2$O$_3$, TiO$_2$, ZrO$_2$) can be described as follows [14]. Tiron is a very efficient complexant for several cations (as Al^{3+}, Ti^{4+}, Fe^{3+}, Zr^{4+}, Sb^{3+}, etc) in aqueous media. Presumably this character enhances the adsorption onto the cationic surface sites of such oxides. In the vicinity of the IEP, adsorption occurs by ligand exchange between hydroxyl surface groups and the Tiron molecule and an inner sphere complex is formed. The ionized sulfonate groups confer a negative charge to the surface, which induces a repulsive potential between the particles. In turn this contributes to stabilize the powder dispersion. As the oxidation potential of Au^{3+}/Au is very low, Tiron reduces Au^{3+} in water, but according to the previous results we can assume that the organic molecule adsorbs on the gold nanoparticles in the same way as on oxide surfaces. This adsorption finally impedes agglomeration of solid particles, and thus limits any increase of the particle size. Basically Tiron works as a dispersant, and it keeps particles stable in aqueous suspension. The surface of the solid phase is negatively charged.

Then, in an additional set of experiments, the NaOH concentration was fixed at 3×10^{-3} M and several concentrations of Tiron were introduced (B1.2, B2.4, B3.1, B4.1, B5.1 formulations). Stable sols were obtained whatever the Tiron concentration and the UV–vis spectra are similar. Data presenting the evolution of average particle size versus Tiron concentration are reported in Fig. 5. The first number near the spot corresponds to the pH of the mixture of Tiron and NaOH before addition to the HAuCl$_4$ solution while the second is the final pH of GNP sols. The pH of the Tiron/NaOH mixture is basic, and it decreases as the concentration of Tiron (a weak acid) increases. Actually the Tiron concentration does not influence the final pH of the sols. A maximum value of 7.8 is reached in the case of the sol containing the smaller particles.

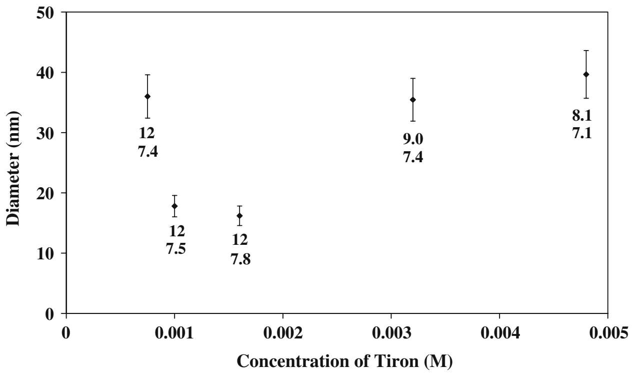


Fig. 5 Relation between the initial concentration of Tiron and the average size of GNPs. Concentration of HAuCl$_4$ and NaOH were fixed. The first value corresponds to the pH of the aqueous solution after mixing Tiron and NaOH while the second is the pH of the GNP sol

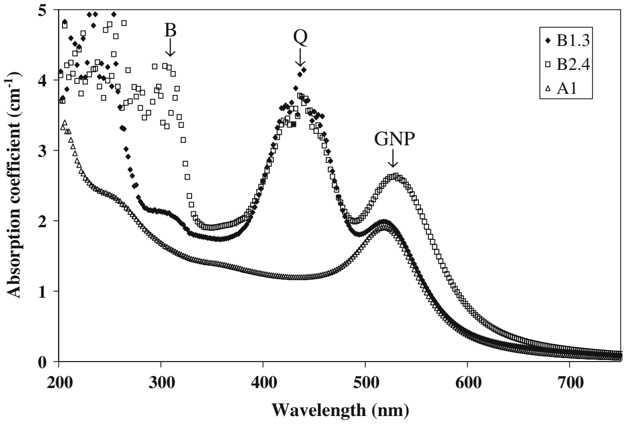


Fig. 6 Comparison between UV–vis spectra of GNP prepared according to Tiron and citrate routes. Optimum conditions for both a stoichiometric ratio (B1.3) and composition containing Tiron in excess (B2.4) were chosen

Likewise, when the Tiron concentration increases, the average size decreases for the ratio [$HAuCl_4$]/[Tiron] = 1/3.2 but further additions of Tiron result into larger sizes due to an increasing ionic strength in the solution.

Optimum conditions corresponding to stoichiometric and Tiron in excess were chosen (B1.3 and B2.4). Then the GNP sols obtained were compared to the material made according to the citrate route. Initial citrate concentration was similar to that corresponding to Tiron in excess (1.6×10^{-3} M). In Fig. 6, the peak positions of three kinds of GNPs are almost the same as those observed previously around 520 nm. The small difference in position is due to variations in particle size and to the refractive index of additives. There is also a difference at shorter wavelengths. It indicates a difference in concentrations of the basic form of Tiron. The sodium salt of citric acid is also used to disperse alumina suspensions. As for Tiron, the citrate molecule forms an inner sphere complex onto the oxide surface with the COO^- and OH groups bounded to the same carbon atom, while other ionized carboxylate groups produce a negative surface charge [15]. A difference with Tiron is that the molecule of citrate is often decomposed after the reduction of gold ions according to the reaction 1. The products issued from the citrate decomposition reaction cannot adsorb on the solid surfaces because their chemical structure does not lead to the formation of a stable complex by appropriate chemical bonds.

We then conclude that efficiencies of Tiron and citrate are similar to prepare stable sol of GNP. This is

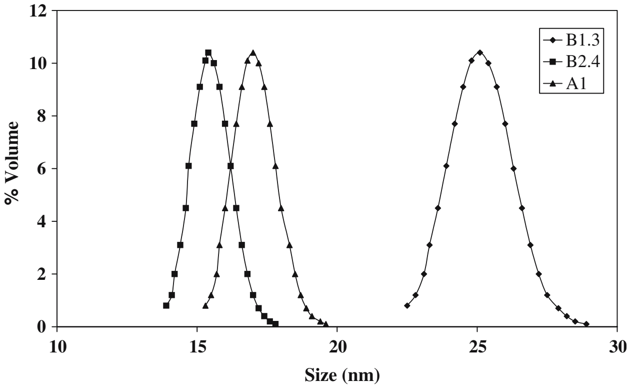


Fig. 7 Size distributions obtained with compositions A1, B1.3 and B2.4

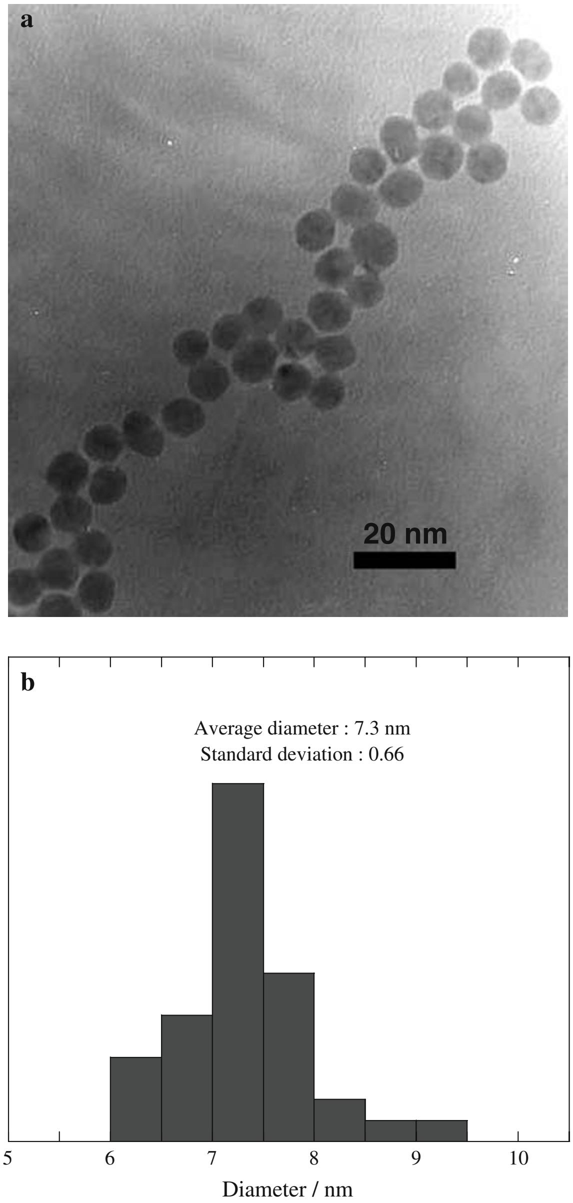


Fig. 8 (**a**) A TEM picture of GNP (B2.4). (**b**) The size distribution of GNP (B2.4) obtained from the image shown in Fig. 8a

confirmed by the measurements of size distributions performed through PCS, the results of which are reported on Fig. 7. Stoichiometric ratios of Au precursor/Tiron concentrations lead to a large size distribution, whereas those obtained with an excess of reactant (either Tiron or citrate) are similar and very narrow.

Then TEM pictures of particles prepared from composition B2.4 were taken (Fig. 8a) and the size distribution of colloids (Fig. 8b) estimated from the micrographs. Direct observation of Fig. 8 confirms the size of gold nanoparticles, which were successfully prepared by these techniques. The shape of particles is nearly spherical, whereas the size distribution is narrow and is similar to that derived from PCS.

Conclusion

In this work, spherical gold nanoparticles (GNP) were successfully prepared by using Tiron as a reducing agent of a gold inorganic precursor. By adjusting the pH conditions and the initial Tiron concentration, an average particle size as low as of 7 nm could be obtained together with a narrow size distribution. Tiron operates both as a reducing agent and a dispersant, and exhibits the same efficiency as citrate. This offers a new route to get metal nanoparticles in aqueous media. It is obviously expected that Tiron could replace citrate for the synthesis of other metal nanoparticles such as silver or platinum. As Tiron can also be adsorbed onto oxide particles such as Al_2O_3, TiO_2 or ZrO_2, it could prove possible to cover these materials by GNP prepared according to this new route.

This work also suggests that other organic additives, among which organic dispersants, currently used in ceramic processing could be tested for the preparation of nanoparticles.

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