

Stabilizer-free nanosized gold sols

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Abstract

The paper describes a convenient, rapid, and reproducible method for the synthesis of stable dispersions of uniform gold nanoparticles at ambient temperatures by mixing aqueous solutions of tetrachloroauric acid and iso-ascorbic acid. The influence of the experimental conditions on the size of the gold particles and the stability of the final sols was monitored by dynamic light scattering and UV–vis spectrophotometry. It was found that the size of the resulting nanoparticles is affected by the concentration and the pH of gold solution, while the stability of the electrostatically stabilized final sols is strongly dependent on the excess of reductant in the system, the ionic strength, and the temperature of the precipitation. Since the preparation process does not require the addition of a dispersing agent, the surface of the resulting gold nanoparticles can be easily functionalized to make them suitable for applications in medicine, biology, and catalysis.

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1. Introduction

Due to its presence in a readily accessible pure form in nature, esthetically pleasing properties, and exceptional resistance to tarnishing and corrosion, gold has captured the attention of both primitive and modern societies. While the bulk metal itself can be used successfully in various applications, the dispersions of fine gold particles are, by far, more important for both scientific and practical applications. The interest in such dispersions can be traced back to ancient times when their preparation and use for decorative and therapeutic purposes was quite common. Faraday's gold sols, produced in mid-nineteenth century [1], represent the first documented scientific investigation of dispersions of fine particles of this metal. Since then, the preoccupation with these systems has progressively escalated, fueled primarily by their fascinating properties (especially optical) and their potential for new applications in catalysis [2–6], nonlinear optics [5,7–10], electronics [11–13], pigments [14,15], biology [16–20], sensors [21], biosensors [22] dentistry, heat reflecting coatings, and other domains of high technology and medicine [23,24].

Since Faraday's pioneering work, many different routes to produce colloidal gold have been reported, including the condensation of metal vapors in solvents [25–28], in polymers [29] or other matrices, as well as the thermal decomposition of precursor metallic compounds suspended in either liquids [30] or gas streams (aerosol thermolysis). The vast majority of the processes, however, involve the reduction of gold compounds in solutions. The electrons needed in the latter process can be either generated 'in situ,' as for example in cases where HAuCl_4 solutions are subjected to γ rays [31–33], pulse radiolysis [34], ultraviolet [35], and visible [36] radiation, or can be supplied by various reducing chemical species present in solution. Since the redox potential of gold is high, the list of compounds capable to reduce the oxidized metallic species to the elemental state is quite extensive. Thus, borohydrides [37,38], hydroxylamine [39,40], hydrazine [41], formaldehyde [42–44], saturated and unsaturated alcohols [45–47], polyols [48], organic acids and their salts [49–54], hydrogen [49], acetylene [49], and phosphorous [1,49] have been used as reducing agents in the preparation of colloidal dispersions of gold particles. Despite the fact that sugars are very common reducing agents for many metal ions, they are rather ineffective in yielding gold particles from HAuCl_4 solutions. Ascorbic and iso-ascorbic acids (or erythorbic acid), however, which have a very similar chemical structure but contains a carbon–carbon double bond, are very strong re-

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ducing agents in a striking similarity with the difference in the behavior between saturated and unsaturated alcohols. Despite its desirable reducing properties, these compounds have been used in the case of gold mostly for analytical determinations [55–57], metal recovery [58,59], electroless plating [60–62], and only a few attempts were made to produce stable dispersions of gold particles [63,64].

In the vast majority of the precipitation processes, especially in concentrated solutions and non-aqueous media, the addition of protective species is necessary in order to obtain stable gold colloids. Being readily available, natural polymers (gelatin, dextrin) and polyelectrolytes (gums) have been historically the first and probably the most frequently used additives for this purpose. Large molecules of water-soluble synthetic polyelectrolytes (polycarbonates, polysulfonates, and polyphosphates) and polymers (polyvinyl alcohol, polyvinylpyrrolidone, polyacrylates, and polyacrylamides) can also be equally effective in stabilizing aqueous metal dispersions [65,66] and can be often tailored to specific experimental conditions. While the use of such additives greatly improves the ability to generate stable dispersions of gold particles, in many cases the presence of these compounds on the surface of the metal affects the physical and chemical properties of the solid surface in undesirable ways. For this reason, there is a significant interest in the preparation of electrostatically stabilized gold colloids in which the surface of the metal is amenable to various subsequent physical and chemical processes. Probably the most well-known and thoroughly investigated example of such system is the colloidal gold dispersion obtained by the reduction of tetrachloroauric acid with sodium citrate. In this case, the excess citrate ions adsorbed on the surface of the metallic particles provide a high enough surface charge to prevent the aggregation during the precipitation process. However, because of the fact that citric acid is a rather mild reducing agent, the reduction reaction must be conducted at elevated temperature (70–80 °C) and may take up to an hour. This paper describes a very simple and rapid precipitation process that uses iso-ascorbic acid (i-Asc) as reductant and yields in several seconds at ambient temperature electrostatically stabilized gold sols in the absence of dispersing agents.

2. Materials and procedures

2.1. Materials and solutions

The $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ stock solution of tetrachloroauric(III) acid used throughout the work was prepared by diluting into a 100.0 mL volumetric flask 0.855 g of concentrated gold chloride solution (23.03 wt% Au, 6.5 wt% free HCl) obtained from Degussa Corporation (South Plainfield, New Jersey). The stock solution of iso-ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$, Fluka) with the same concentration of $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ was prepared by dissolving 0.444 g of this compound in 250.0 cm^3 deionized water. While the stock solution of gold was stable for several months, the stock solution of iso-ascorbic acid was prepared fresh every time to eliminate the risk of degradation by oxidation. The *reacting solutions* of gold and iso-ascorbic acid,

which were actually used for the preparation of gold sols, were prepared in all cases by diluting appropriate volumes of the corresponding *stock solutions* into two separate 25.0 mL volumetric flasks. When required, the pH of the *reacting solutions* of gold was adjusted with $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ hydrochloric acid and sodium hydroxide solutions. All glass equipment (pipettes, beakers) was thoroughly washed with DI water, rinsed with acetone, and dried before use.

2.2. Preparation of gold sols

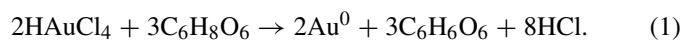
Immediately after their preparation, the *working solutions* of tetrachloroauric(III) acid and iso-ascorbic acid were transferred into two 50-mL glass beakers. Without delay, the content of the two beakers was added simultaneously and very rapidly into a 100- cm^3 glass beaker where the stable sols of gold nanoparticles developed in a few seconds.

2.3. Characterization of gold particles and sols

The UV–vis spectra of the reactant solutions, intermediate species, and gold sols were generated using either a Perkin–Elmer Lambda 35 UV–vis spectrophotometer or, when rapid scans were needed, a HP 5624 diode array spectrophotometer. The size and size distribution of the metallic particles were measured by dynamic light scattering using a simultaneous static and dynamic light scattering (SSDLS) goniometer built by ALV laser (Langen, Germany) and by transmission electron microscopy using a Jeol 1200EX. The electrokinetic properties of the gold particles were measured using a Brookhaven Zeta Plus analyzer.

3. Results and discussions

The simultaneous mixing of the tetrachloroauric acid and iso-ascorbic acid solutions results in the rapid formation of stable gold sols as indicated by the appearance of the typical red color of the final dispersion. The overall reduction reaction responsible for the formation of the dispersed gold is given by



Under all experimental conditions investigated, the emergence of the red color and the surface plasmon band is preceded by a short phase (induction period) during which the initially pale yellow AuCl_4^- aqueous solution becomes colorless. This typical evolution of the optical properties of the system is illustrated in Fig. 1, which presents the UV–vis spectra of the two reactant solutions immediately prior to mixing, two seconds after mixing, and after the red color of the sol has fully developed and stabilized. Shortly after the reactants are brought in contact (2 s), the 226 and 313 nm absorption bands characteristic of Au(III) species (corresponding to the $p_\pi \rightarrow 5d_{x^2-y^2}$ and $p_\sigma \rightarrow 5d_{x^2-y^2}$ transitions in the square planar AuCl_4^- complex ion) disappear and the absorbance of the peak for the remaining unreacted iso-ascorbic acid is reduced. These findings suggest that the Au^{3+} ions are reduced first to Au^+ according to Eq. (2),

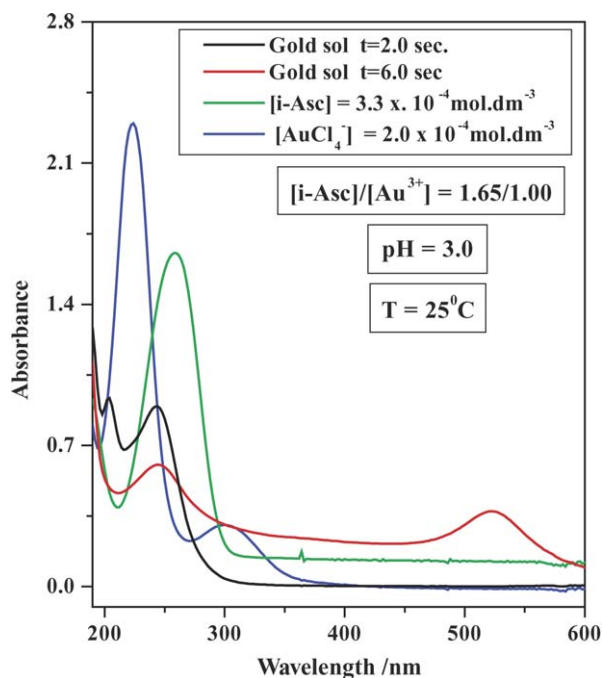


Fig. 1. The evolution of the UV–vis spectra with time during the reduction of gold species with iso-ascorbic acid at $T = 25^\circ\text{C}$ and $\text{pH} = 3.0$.

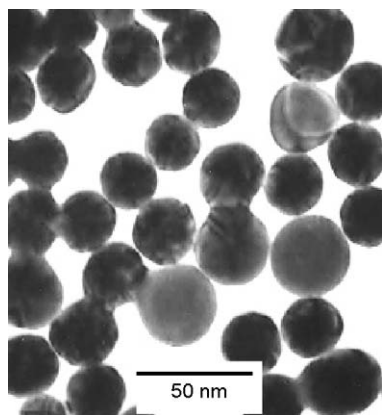
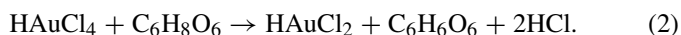


Fig. 2. TEM image of Au nanoparticles obtained by reducing HAuCl_4 with iso-ascorbic acid in the experimental conditions given in Fig. 1.

resulting in the formation of linear AuCl_2^- complex ions that do not absorb in UV–vis.



In a subsequent step, these Au(I) species are reduced to gold atoms, which undergo nucleation immediately after the critical supersaturation concentration is reached and form the final gold nanoparticles by rapid diffusional growth. The resulting gold nanoparticles, which are responsible for the absorption peak at 523, are quite uniform and range in size between 30 and 40 nm as demonstrated by the TEM image in Fig. 2.

3.1. The effect of gold concentration

The fact that the resulting gold sols prepared by this methods are stable for very long periods of time (at least a year), in spite

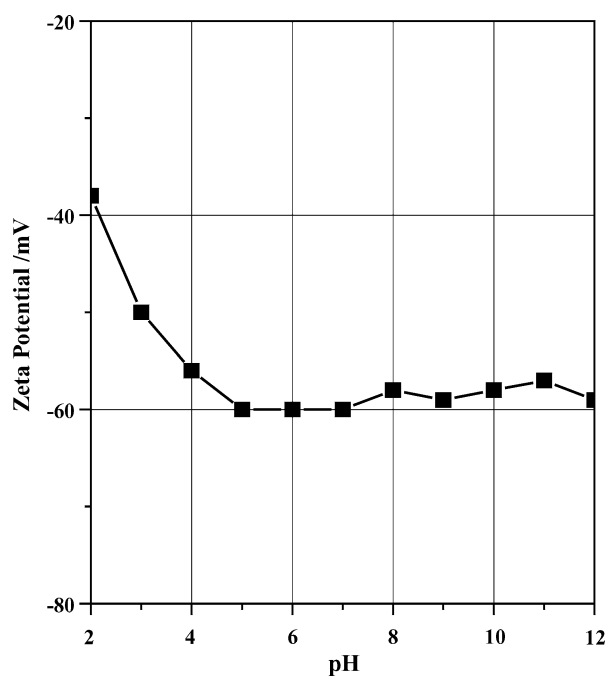


Fig. 3. The pH dependence of the zeta potential (ζ) of the gold particles shown in Fig. 2.

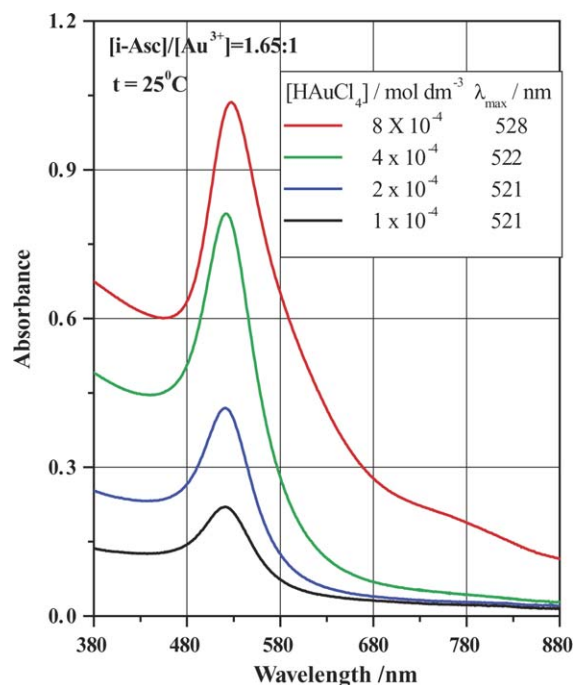


Fig. 4. UV–vis spectra of gold sols prepared by reducing solutions containing $1, 2, 4,$ and $8 \times 10^{-4} \text{ mol dm}^{-3}$ HAuCl_4 with iso-ascorbic acid at an $[\text{i-Asc}]/[\text{Au}^{3+}]$ molar ratio of 1.65:1 and 25°C .

of the absence of any additives, indicates that the particles are electrostatically stabilized. The electrostatic stabilization mechanism is indeed supported by the quite high negative charge of the gold particles (Fig. 3).

Since the ionic strength plays an important role in the electrostatic stabilization, the stability of the sols was investigated as a function of the concentration of the gold solution. Thus, 1,

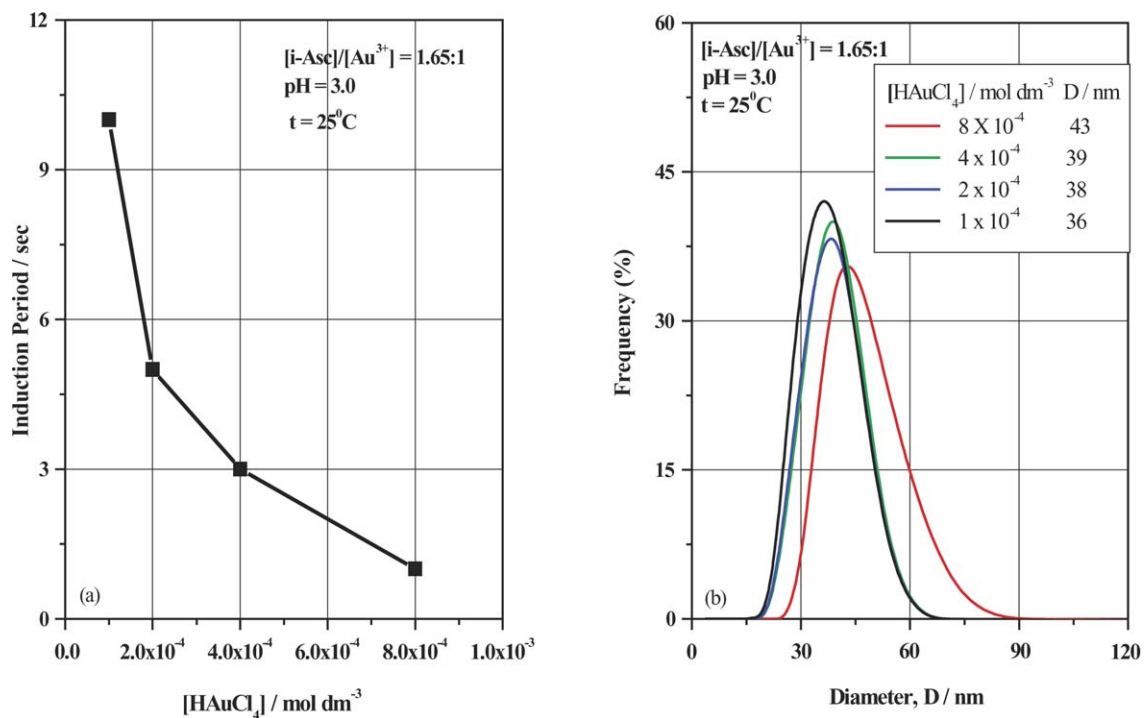


Fig. 5. The changes in the length of the induction period of the reduction reaction (a) and the particle size distributions of the resulting gold nanoparticles (b) for the gold sols shown in Fig. 4 as a function of the concentration of tetrachloroauric acid solutions.

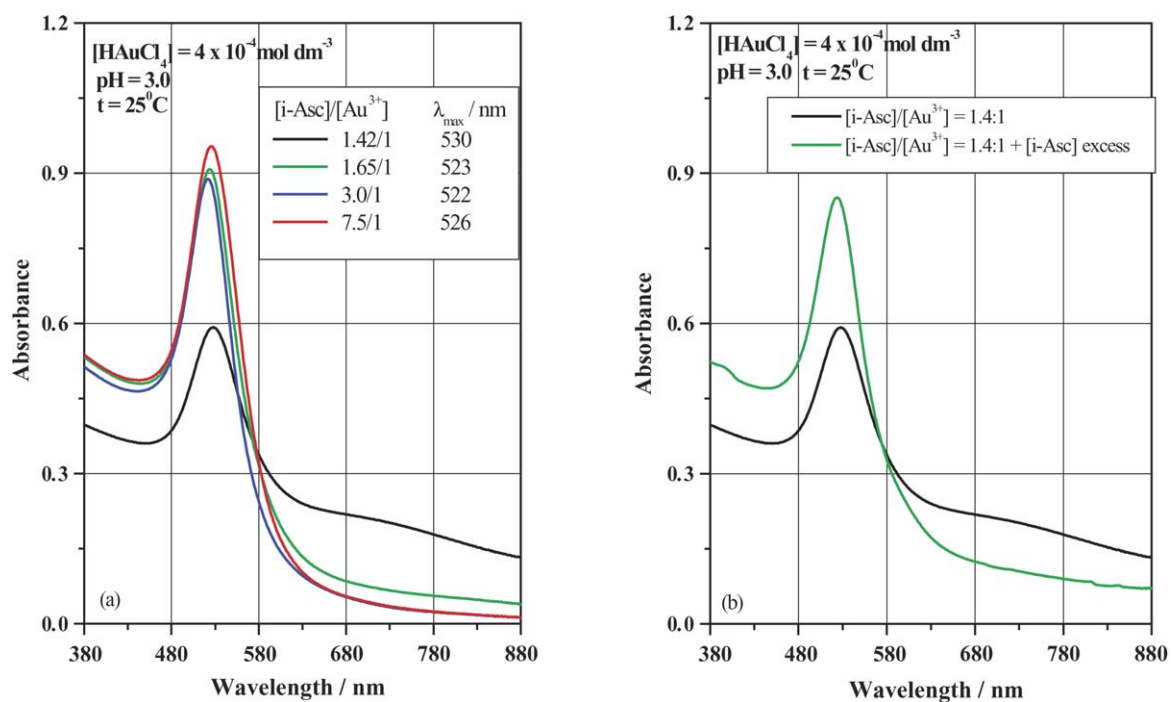


Fig. 6. The absorption spectra of gold sols prepared at different $[i-Asc]/[Au^{3+}]$ ratios (Table 1) measured 20 min after the reactant solutions were mixed (a) and absorption spectra of the gold sol prepared in stoichiometric excess of $HAuCl_4$ (sample 1, Table 1) immediately after precipitation and after the subsequent addition of an excess of iso-ascorbic acid (b).

$2, 4,$ and 8×10^{-4} mol dm⁻³ $HAuCl_4$ solutions were reduced with iso-ascorbic acid, at $25^\circ C$, at a constant ratio $[i-Asc]/[Au^{3+}]$ of 1.65:1, which corresponds to a 10% stoichiometric excess of reducing agent. The UV–vis spectra of the resulting

sols, containing 0.5, 1, 2, and 4×10^{-4} mol dm⁻³ Au, are shown in Fig. 4.

As expected, with the increase in the concentration of the gold solution, the resulting sols become progressively less

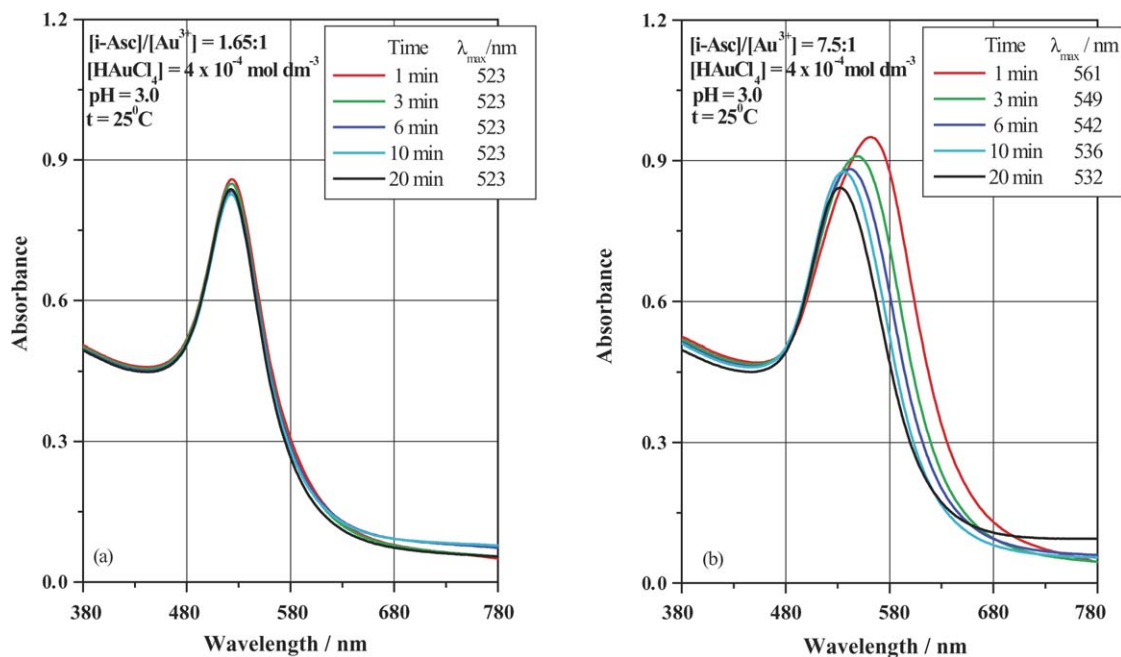


Fig. 7. The evolution with time of UV-vis spectra of gold sols prepared at 25 °C and an [i-Asc]/[Au³⁺] ratio of (a) 1.65:1 (sample 2, Table 1) and (b) 7.5:1 (sample 4, Table 1).

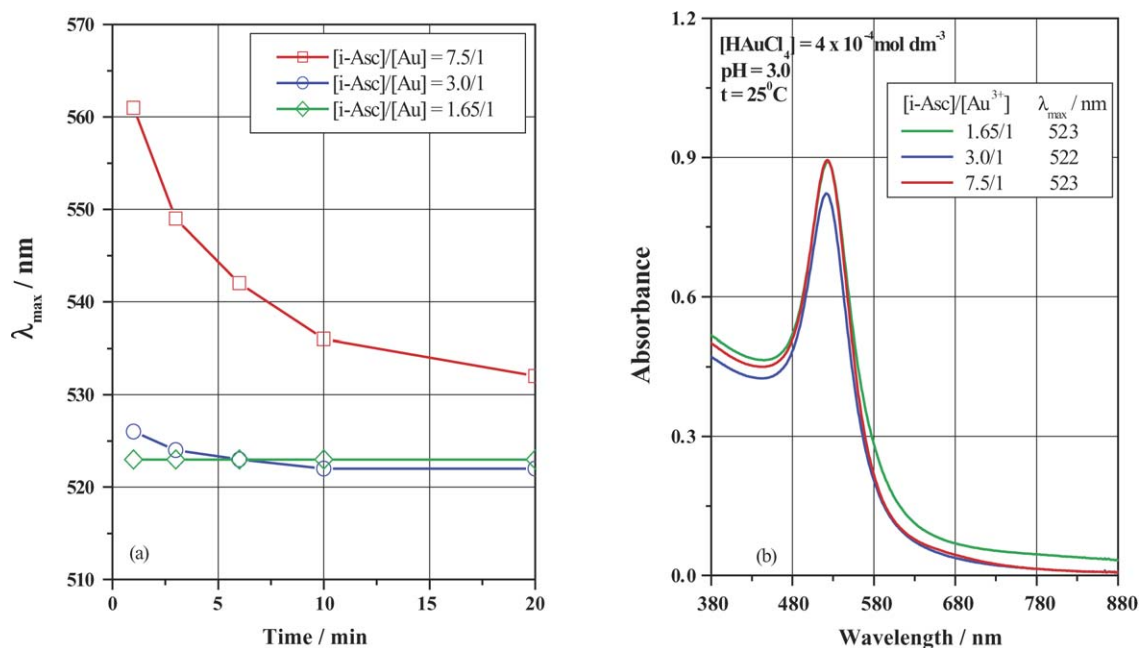


Fig. 8. (a) The shift as a function of time in the position of the gold plasmon band of the gold sols prepared at three different [i-Asc]/[Au³⁺] ratios (samples 2–4, Table 1) and (b) the UV-vis spectra of the same sols after 48 h.

Table 1
The experimental conditions used for the preparation of gold sols at different molar ratios iso-ascorbic acid/Au³⁺ ([i-Asc]/[Au³⁺])

Sample	HAuCl ₄ solution		Iso-ascorbic acid solution		[i-Asc]/[Au ³⁺] molar ratio	[i-Asc]/[Au ³⁺] stoichiometric ratio	Gold sol conc. (mol dm ⁻³)
	Vol. working solution (cm ³)	Final conc. (mol dm ⁻³)	Vol. working solution (cm ³)	Final conc. (mol dm ⁻³)			
1	1.0	4 × 10 ⁻⁴	1.42	5.7 × 10 ⁻⁴	1.42:1	0.95:1	2 × 10 ⁻⁴
2	1.0	4 × 10 ⁻⁴	1.65	6.6 × 10 ⁻⁴	1.65:1	1.1:1	2 × 10 ⁻⁴
3	1.0	4 × 10 ⁻⁴	3.00	1.2 × 10 ⁻³	3.00:1	2.0:1	2 × 10 ⁻⁴
4	1.0	4 × 10 ⁻⁴	7.50	3.0 × 10 ⁻³	7.50:1	5.0:1	2 × 10 ⁻⁴

stable as indicated by the broadening of the plasmon band and the increase in absorption at higher wavelengths due to scattering. At the same time, the increase in the concentration of the gold solution causes an acceleration of the reduction reactions in the homogeneous phase as confirmed by the shortening of the induction period that precedes the nucleation of gold (Fig. 5a). The size of the resulting metal particles increases only slightly with the concentration of the reacting gold solutions as confirmed by the size distribution data presented in Fig. 5b.

3.2. The effect of the molar ratio of reactants

The chemical reaction given by Eq. (1) is likely to be affected by the ratio of the reactant concentrations. For this reason, this parameter was investigated in more detail under the conditions given in Table 1.

While the gold sol prepared in conditions of a small stoichiometric excess of reducing agent (sample 2) displayed a nice red-wine color and was characterized by a narrow plasmon band, the sol obtained with an excess of HAuCl₄ (sample 1) was slightly aggregated as indicated by its turbidity, bluish-red color, and the significant absorption at higher wavelengths (Fig. 6a). The slight aggregation in the latter case is very likely due to the excess AuCl₄⁻ complex ions, which adsorb on the surface of the gold particles and cause a decrease in their charge. The fact that further addition of iso-ascorbic acid restores the red color and eliminates the absorption at higher wavelengths (Fig. 6b) supports this mechanism. It is noteworthy that a similar situation has been described in the literature in the case of the well-known citrate process in which the gold sol acquires the characteristic red color only after the Au(III) species are completely reacted [50].

Rather intriguing changes in the optical properties of the sols were detected both visually and by UV–vis spectrometry for the two gold sols prepared at larger stoichiometric excesses of reductant (samples 3 and 4, Table 1). While at an [i-Asc]/[Au³⁺] ratio of 1.65/1.0 (sample 2), the color of the sol immediately after its preparation was red and did not change with time, at a reactant ratio of 7.5:1 the initial color of the sol was blue–violet and changed gradually to red during the next several minutes. The differences in the evolution of the optical properties of the two sols are reflected in the changes of their UV–vis spectra (Figs. 7a and 7b). Similar but less pronounced changes in the color and the position of the plasmon band were also observed in the case of the [i-Asc]/[Au³⁺] ratio of 3.0/1.0. This gradual evolution of the optical properties, which is captured for the first 20 min in Fig. 8a, leads eventually to a situation in which after 48 h not only the color but the position of plasmon band for all three sols prepared in excess of reductant are practically identical (Fig. 8b).

The blue shift and the narrowing of the plasmon band of the gold sols with time indicate that in the presence of a high excess of iso-ascorbic acid the metallic particles first lose aggregates, which break apart with time. The fact that the magnitude of the shift increases with the excess of reductant, suggests that the iso-ascorbic acid molecules adsorb on the surface of the

gold and decrease their charge enough to cause the reversible coagulation of the particles. Indeed, this mechanism appears to be supported by the fact that the shift of the plasmon band mirrors the decay of the peak at 246 nm corresponding to the excess iso-ascorbic acid and stops when all excess reductant has been decomposed due to its auto-oxidation catalyzed by the gold (Fig. 9a). In contrast, when a surfactant (Solsperse 20000) was added to the reducing solution, it prevented the interaction of the ascorbic acid with the gold surface (as proven by the much slower decay of the iso-ascorbic peak) and thus the reversible coagulation of the metallic particles. As a result, the color of the gold sol is red from the beginning and the plasmon band does not change its position (Fig. 9b).

3.3. The effect of the pH of the gold solution

Due to the dissociation of the tetrachloroauric acid and the excess of free hydrochloric acid in the concentrated gold chloride solution, the pH of the gold *working solution* is typically quite low (2.9 ± 0.1). Below this value the pH was adjusted with a 1×10^{-2} mol dm⁻³ hydrochloric acid solution, while the higher values were obtained by adding a sodium hydroxide solution of the same concentration. While the addition of hydrochloric acid increases the stability of the AuCl₄⁻ complex ions, the addition of a base causes the stepwise substitution of Cl⁻ ions in the inner sphere of coordination of Au(III) by the OH⁻ ions (Eq. (3)), which translates in progressively more stable gold hydroxocomplexes [63]:



Since in the latter case the substitution is a slow process, the pH measurements were made after the complete equilibration of the solutions and the final values as well as the UV–vis spectra were recorded 24 h after the final adjustment.

As expected, the variation of the pH translates in significant changes in the UV–vis spectra of the gold solutions as illustrated in Fig. 10a. In the sample acidified with HCl, the absorption bands at 226 and 313 nm, corresponding to the allowed $p_\pi \rightarrow 5d_{x^2-y^2}$ and $p_\sigma \rightarrow 5d_{x^2-y^2}$ metal–ligand transitions, are well defined and in excellent agreement with the calculated ones [67], indicating the presence of AuCl₄⁻ square planar complex ions. With progressive insertion of OH⁻ ions in the inner coordination sphere of Au³⁺, both bands shift towards lower wavelengths due to the formation of a stronger metal–ligand bond. Concomitantly, the band at 313 nm decreases in intensity and finally disappears, possibly due to the progressive increase and equalization of the energy of the p_π and p_σ orbitals.

The reactivity of the solutions was also greatly affected by the pH as indicated by the length of the induction period, which represents a quite accurate measure of the rate of the reactions in the homogeneous phase that precede the nucleation of gold. The time needed for the emergence of the gold particles was the shortest at pH 3.5, at which all free hydrochloric acid is neutralized and the substitution of Cl⁻ with OH⁻ ions is still negligible [63], and increased sharply for solutions with both lower and

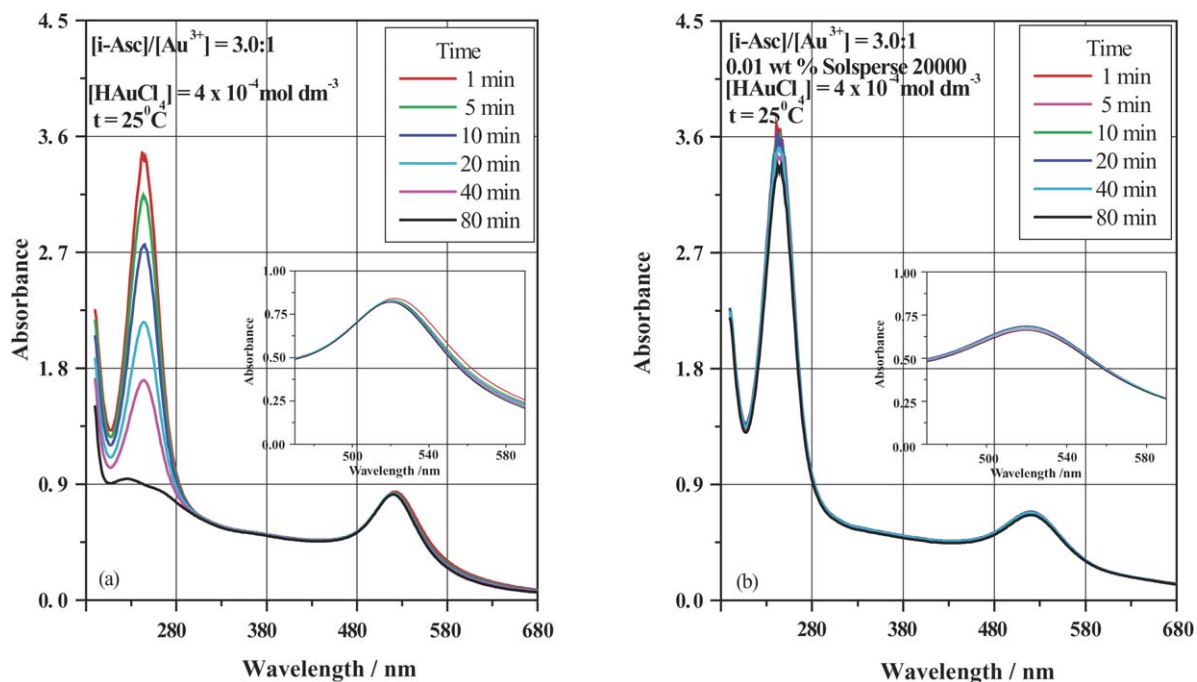


Fig. 9. The changes with time in the UV-vis spectrum of the gold sol prepared at an $[i\text{-Asc}]/[\text{Au}^{3+}]$ ratio of 3.0:1 (sample 2, Table 1) in absence of dispersant (a) and in the presence of 0.01% w/v Solsperse 20000 (b).

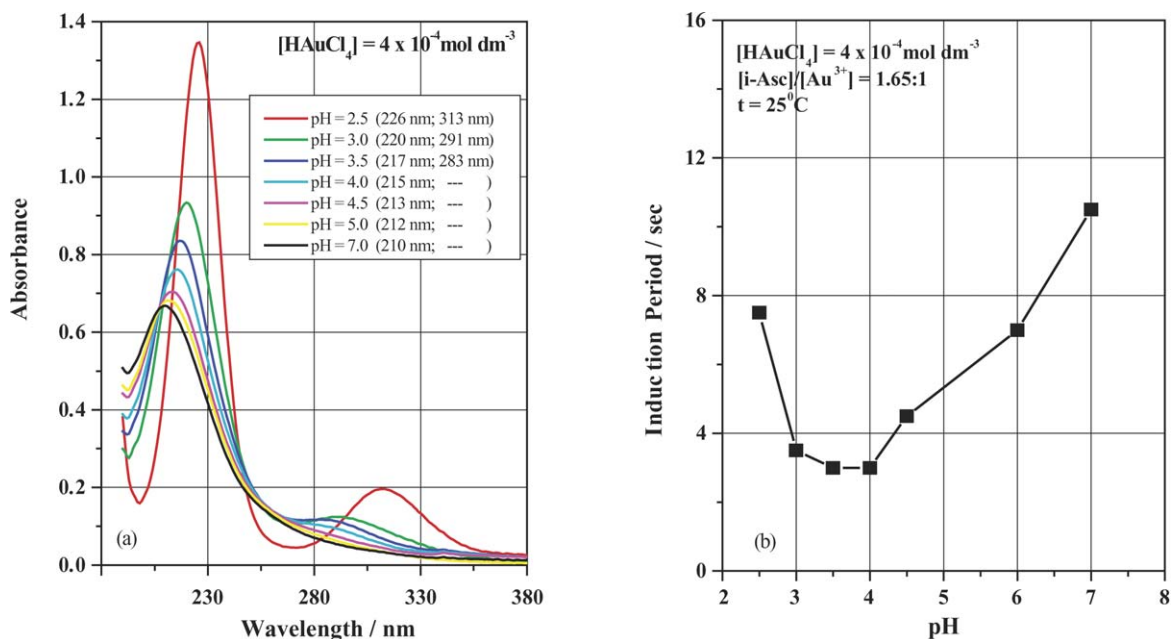


Fig. 10. (a) The UV-vis absorption spectra, measured in 2 mm path length quartz cells, of $4 \times 10^{-4} \text{ mol dm}^{-3}$ HAuCl_4 solutions adjusted at different pH values between 2.5 and 7.0, and (b) the variation in the length of the induction period recorded as a function of the pH.

higher pH (Fig. 10b). These trends can be explained in the former case by the increasing stability of the AuCl_4^- complex ions at higher concentrations of Cl^- ligands as well as the diminishing of the reducing abilities of iso-ascorbic acid in more acidic conditions and in the latter case by the formation of progressively more stable Au(III) hydroxocomplexes.

As expected, the rate of the ensuing nucleation process follows a similar pattern, the result being that the size of the

resulting gold particles decreases with the increase in the pH of the solutions, reaches a minimum at a value of ~ 4 , and then increases again (Fig. 11a). Similarly, the plot of the λ_{max} corresponding to the plasmon bands of the gold particles as a function of the pH displays the same pattern (Fig. 11b). As a result of the similarity in the variation of the diameter of the gold particles and the position of the corresponding plasmon bands with pH, a linear relationship between these two properties can

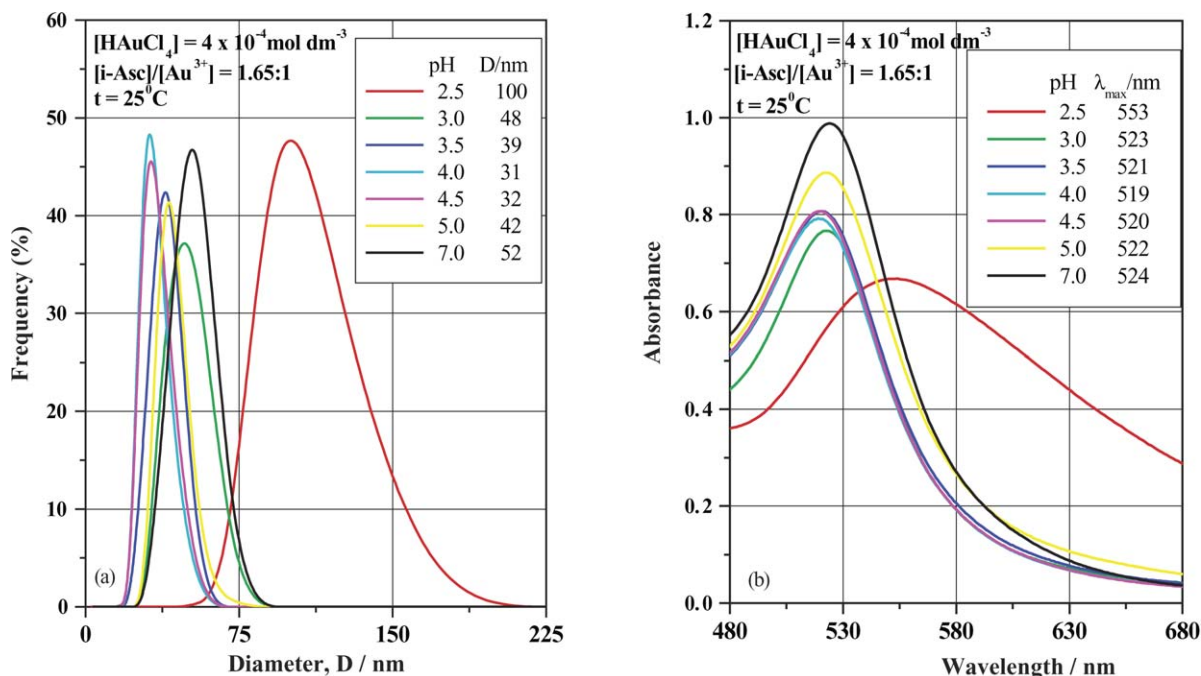


Fig. 11. The variation of (a) the particle size of gold measured by dynamic light scattering and (b) the position of the plasmon band for the gold sols prepared by mixing $4 \times 10^{-4} \text{ mol dm}^{-3}$ tetrachloroauric(III) acid solutions (adjusted at values ranging from 2.5 to 7.0) with $6.6 \times 10^{-4} \text{ mol dm}^{-3}$ iso-ascorbic acid at 25°C and an $[i\text{-Asc}]/[Au^{3+}]$ ratio of 1.65:1.

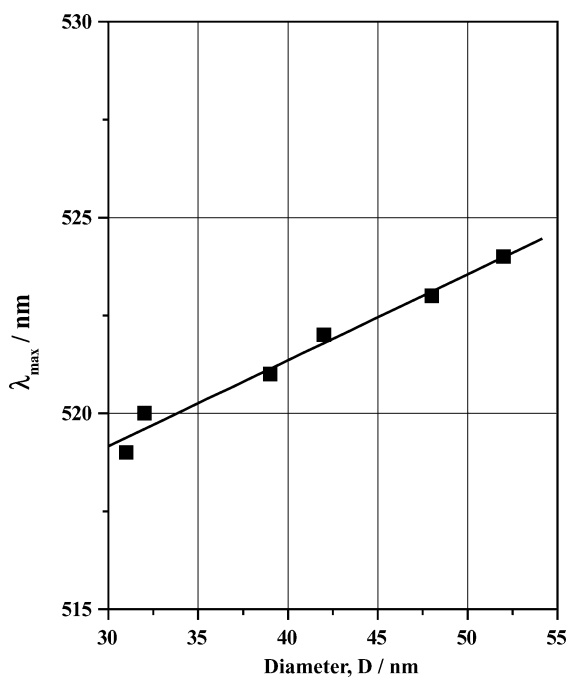


Fig. 12. The relationship between λ_{max} , the wavelength of the maximum absorption of the plasmon band of gold sols and the corresponding modal diameter of the gold particles.

be established. Indeed, the plot of the λ_{max} as a function of the modal diameter of the gold particles is a straight line (Fig. 12). This linear relationship, valid only if the gold sols are fully dispersed, can be used eventually in estimating the size of the gold particles based on a simple and very rapid spectrophotometric measurement.

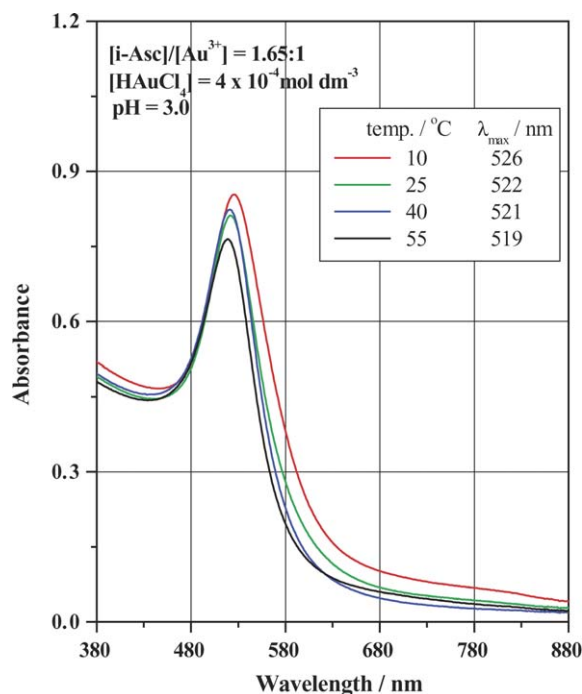


Fig. 13. UV-vis spectra of gold sols prepared by mixing a $4 \times 10^{-4} \text{ mol dm}^{-3}$ $HAuCl_4$ solution (pH 3.0) with a $6.6 \times 10^{-4} \text{ mol dm}^{-3}$ iso-ascorbic acid solution (sample 2 in Table 1) at 10, 25, 40, and 55°C .

3.4. The effect of temperature

To observe the effect of reaction temperature, the experiments were carried out at 10, 25, 40, and 55°C using the reacting solutions of tetrachloroauric(III) acid and iso-ascorbic acid prepared under the conditions given as sample 2 in Ta-

ble 1. The UV–vis spectra of the four sols (Fig. 13) indicate a progressively shorter wavelength of maximum absorption of gold particles with increasing temperature, very likely as a result of the decrease in the particle size caused by faster reactions in the homogeneous phase and nucleation at higher temperatures. Further increase in the temperature failed to yield stable sols, presumably because the increased kinetic energy of the particles was large enough to overcome the barrier of energy responsible for the electrostatic stabilization.

4. Summary

This paper describes a rapid, convenient, and reproducible method for the synthesis of stable gold sols by reducing tetrachloroauric acid with iso-ascorbic at room temperature. The resulting gold nanoparticles are quite uniform and their size can be adjusted by controlling the concentration and composition of Au(III) complexes, as well as by the reaction temperature. Since the preparation process does not require the addition of a dispersing agent, the surface of the nanoparticles is amenable to a wide range of modifications required for applications in medicine, biology, and catalysis.

Acknowledgment

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