Nitrilotriacetic acid: A novel reducing agent for synthesizing colloidal gold

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ABSTRACT

We report for the first time that nitrilotriacetic acid (NTA) is an effective reductant for the preparation of stable dispersions of uniform gold nanoparticles. The method described is capable of generating stable sols with a metal concentration as high as 1.5×10^{-3} mol dm^{-3}. The size of gold nanoparticles can be tuned from 10 to 160 nm by adjusting the stoichiometric excess of NTA. For a constant [Au]/[NTA] ratio the temperature affects the reduction kinetics but has little impact on the size of gold nanoparticles. The mechanisms of the reduction of Au(III) species and the formation and stabilization of gold nanoparticles are discussed.

1. Introduction

The unique optical properties of colloidal gold have been known and exploited for centuries, as the famous Lycurgus cup testifies [1]. Even its therapeutic action, a prelude to today's applications in the bio-medical field, has been suggested as early as 16th century by Parcellus [2]. Today, dispersed gold nanoparticles are widely used in catalysis [3,4], nonlinear optics [4–6], electronics [7,8], surface enhanced Raman spectroscopy (SERS) [9,10], pigments [11], biology [12–15], sensors [16], biosensors [17–19], drug delivery [12,13,20], dentistry, heat reflecting coatings, detection of sequence specific DNA molecules [21] and other domains of high technology and medicine. The rapid progress of these applications has been facilitated by the availability of a variety of methods to synthesize colloidal gold. Stable dispersions of uniform gold nanoparticles with controlled size and shape can be obtained by many routes [22], the majority involving the reduction of gold salts in liquid media. The reducing electrons may come either from the molecules containing the gold ions or from other species present in the system. In the first case, the electrons transfer is triggered by the exposure of a precursor gold solution (most often HAuCl$_4$) to ultraviolet [23,24] or visible [25] light, γ-rays [26], pulse radiolysis, or laser beams [27]. In the second case, the electrons are supplied by molecules with reducing properties. Ascorbic, citric, and salicylic acids [7,28,29], polyols [30–32], hydrazine [33,34], borohydrides [35], hydrogen, acetylene, phosphorous [36], amines

[37,38], and ethylenediaminetetraacetic acid (EDTA) [39,40] are some of the most popular compounds used for this purpose.

The stability of prepared gold dispersions, essential in most applications, is easily provided in dilute systems due to an effective electrostatic stabilization mechanism. As the range of repulsive electrostatic forces diminishes at high ionic strength, the preparation of concentrated stable gold sols inevitably involves the use of stabilizers. While effective, these additives tend to attach to the surface of gold nanoparticles affecting their performance. For this reason, the preparation of stable dispersions of gold nanoparticles with a clean surface or one which can be easily functionalized is of significant value for many applications. A widely used such method is the one developed by Turkevich et al. [29,36,41,42] and further refined by Frens [43]. The approach consists adding sodium citrate into a stirred tertrachloroauric acid (HAuCl$_4$) solution at elevated temperature (~80 °C). While popular, the citrate method has two limitations. The first is its inability to generate stable gold sols at concentrations above 0.3×10^{-3} mol dm^{-3} [43] in absence of dedicated stabilizing agents. The second relates to the limited options for subsequent surface functionalization due to the relatively chemically inert backbone of adsorbed citrate molecules. Thus, a method that addresses these shortcomings is likely to be a valuable addition to the tool box of scientists interested in the synthesis and applications of colloidal gold.

In this paper, we describe for the first time the preparation of stable gold dispersions using tri-sodium salt of nitrilotriacetic acid (Na$_3$-NTA) as both reducing agent and colloid stabilizer. Nitrilotriacetic acid, a biodegradable tetradentate trianionic ligand has for longtime been used in water softening and as a replacement of

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Table 1
Experimental conditions used to evaluate the effect of $[Au^{3+}]/[NTA]$ molar ratio.

Sample	HAuCl$_4$ solution		NTA solution		$[Au^{3+}]/[NTA]$ ratio	Au concentration (mol dm^{-3})[a]
	Volume of working solution (cm^3)	Final concentration (mol dm^{-3})[a]	Volume of working solution (cm^3)	Final concentration (mol dm^{-3})[a]		
1	0.8	2×10^{-4}	0.6	6×10^{-4}	1:3	2×10^{-4}
2	0.8	2×10^{-4}	0.8	8×10^{-4}	1:4	2×10^{-4}
3	0.8	2×10^{-4}	1.2	1.2×10^{-3}	1:6	2×10^{-4}
4	0.8	2×10^{-4}	2	2×10^{-3}	1:10	2×10^{-4}
5	0.8	2×10^{-4}	4	4×10^{-3}	1:20	2×10^{-4}
6	0.8	2×10^{-4}	8	8×10^{-3}	1:40	2×10^{-4}

[a] Values refer to the final reaction volume.

sodium and potassium triphosphate in 'biologically friendly' detergents [44]. It has also been used in biomedical applications to link Ni ions to citrate prepared gold nanoparticles for site specific labeling in protein complexes [45,46]. The described method has several advantages over the citrate process. First, the presence of the nitrogen atom in the backbone of the NTA molecules adsorbed on gold offers enhanced possibilities for subsequent surface functionalization [45,46]. Secondly, the method can generate uniform dispersed gold particles in a broader size range (10–160 nm). Finally, the process yields stable gold sols with higher metal concentrations than the Turkevich/Frens approach. These features make the method described an attractive route to generate dispersed gold particles for biomedical applications.

2. Experimental

2.1. Reagents and solutions

The concentrated solution of tetrachloroauric acid (HAuCl$_4$, 23.11 wt.% Au) was supplied by Umicore (S. Plainfield/NJ). Nitrilotriacetic acid trisodium salt monohydrate (N(CH$_2$CO$_2$Na)$_3$·H$_2$O) [NTA] was purchased from Alfa Aesar (Ward Hill/MA). Stock solutions containing 5×10^{-2} mol dm^{-3} Au and 2×10^{-1} mol dm^{-3} NTA were prepared by adding 2.13 g of concentrated HAuCl$_4$ solution and respectively 2.75 g NTA in 50 cm^3 deionized (DI) water. Lower concentration gold dispersions were prepared by diluting the stock solutions as needed. The gold stock solution was stable for several weeks. The NTA stock solution was used within 24 h of its preparation.

2.2. Preparation of gold sols

A volume of 200 cm^3 DI water was introduced into a 3-neck 500 cm^3 spherical flask and heated to the reaction temperature (between 20 and 90 °C). The HAuCl$_4$ and NTA solutions maintained at the same temperature were added rapidly into the flask and the reaction mixture was stirred until the color and UV–Vis spectra of gold sols stabilized. The [Au]:[NTA] molar ratio was adjusted by varying the volumes of HAuCl$_4$ and NTA stock solutions. The role of reactants ratio was investigated first at 80 °C and a gold concentration of 2×10^{-4} mol dm^{-3} in the conditions given in Table 1. The effects of gold concentration and reaction temperature were assessed in separate sets of experiments.

2.3. Characterization methods

The size and morphology of gold nanoparticles were assessed by both transmission electron microscopy (TEM, JEOL – JEM 2010) and field emission electron microscopy (FESEM, JEOL 7400). The optical properties of gold sols were recorded using a Perkin Elmer Lambda 35 UV–Vis double beam spectrophotometer (Perkin Elmer, Waltham, MA). The zeta potential and size distribution of metal nanoparticles were measured with a Brookhaven ZetaPals dynamic light scattering (DLS) analyzer.

3. Results and discussion

In all experiments summarized in Table 1, the color of the reaction mixture evolved from pale yellow, to colorless, and finally to dark blue or ruby red. The sequence of color changes varied widely in length with the reactants molar ratio. At 80 °C, it took 6 h for the $[Au^{3+}]/[NTA]$ ratio of 1:1 (sample #1) to complete the reduction of gold but only ~3 min at the ratio of 1:40 (sample #6). To illustrate the evolution of optical properties, the UV–Vis spectra of reactants and reaction mixture at different times are given in Fig. 1 for the $[Au^{3+}]/[NTA]$ ratio of 1:6 (sample #3). The electron transfer from the reductant to the Au(III) species causes the disappearance of the 218 and 289 nm absorption bands (red curve) corresponding to the $p\pi \rightarrow 5dx^2 - y^2$ and $p\sigma \rightarrow 5dx^2 - y^2$ transitions in the square planar $[AuCl_2^-]$ complex ion [28] and the emergence of a new absorption band at 212 nm (blue curve). These changes suggest that the Au^{3+} ions are first reduced to Au$^+$ to form a colorless Au(I)-NTA complex. The Au(I) species are subsequently reduced by NTA to Au^0, as indicated by the disappearance of the Au(I)-NTA absorption band at 212 nm. The nuclei generated once the concentration of gold atoms exceeds the critical supersaturation grow by diffusional capture of Au atoms to form the final nanoparticles [47]. The presence of the latter is clearly indicated by the red color of the dispersion and the distinct absorption peak at 544 nm (green line).

3.1. The effect of reactants molar ratio

The color of gold dispersions, their UV–Vis spectra, and the TEM images of the isolated nanoparticles prepared in the conditions given in Table 1 are presented in Figs. 2–4.

The sols prepared at $[Au^{3+}]/[NTA]$ ratios of 1:3 and 1:4 (examples #1 and #2) were less intense in color and slightly turbid (Fig. 2). Their UV–Vis spectra revealed the presence of a single broad plasmon band, which shifted from 589 nm to 569 nm as the excess of reductant increased (Fig. 3). The pronounced background absorption at higher wavelengths in both cases indicated the presence of large particles/aggregates. Not surprising, the solids completely settled in less than 2 h. In the case of $[Au^{3+}]/[NTA]$ ratio of 1:6 (sample #3), the background absorption at higher wavelengths was greatly diminished while the plasmon band was narrower and blue-shifted to 544 nm. The color of the sol was clear red and it was stable for several days. The sols prepared at higher stoichiometric excess of NTA ($[Au^{3+}]/[NTA]$ ratios 1:10, 1:20, and 1:40) were all clear and red-wine in color. The position of their plasmon band blue-shifted gradually from 536 nm, to 530 nm, and 520 nm as the excess of reductant increased. In all