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Short Communication

# The synthesis of gold nanoparticles by a citrate-radiolytical method

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## HIGHLIGHTS

- Gold nanoparticles were synthesised by classical and citrate-radiolytical methods.
- The size of gold nanoparticles was controlled by different saturated gases.
- Radiolytically intensified citrate oxidation is advantageous for Au(III) reduction.
- A comparison of particle sizes between classical and radiolytical methods was made.

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## ABSTRACT

The classical citrate method is based on the reduction of an Au(III) precursor with sodium citrate in an aqueous solution near the boiling point. In this work gold nanoparticles (GNPs) were synthesised *via* a citrate method using reduction by gamma-irradiation at room temperature. The Au(III)–citrate aqueous precursor solution was gamma-irradiated to doses of up to 30 kGy. The dose rate of gamma-irradiation was $\sim$8 kGy h$^{-1}$. The GNP size was controlled by the adsorbed dose as well as by different saturated gases (air or nitrogen) present in precursor solutions. The results showed that gamma-irradiation produced smaller GNPs in the presence of precursor solutions saturated with nitrogen compared with the ones saturated with air. By increasing both the gold(III) and citrate concentrations in precursor solutions, stable and highly concentrated colloidal gold/citrate suspensions were synthesised using classical and citrate-radiolytical reduction methods. Gamma-irradiation thus produced well-dispersed and highly concentrated GNPs in an aqueous citrate solution in the presence of dissolved oxygen and without adding any reducing or stabilising agents. Radiolytically intensified citrate oxidation and decarboxylation to acetone and other products by dissolved oxygen was advantageous for Au(III) reduction and subsequent formation of gold nanoparticles. Since the completely same precursor solutions were used both in the classical and citrate-radiolytical reduction methods, a real comparison of GNP sizes between these two methods was given.



## 1. Introduction

A chemical reduction of the Au(III) aqueous solution by citrate ions, the so called Turkevich–Frens method or "the classical citrate reduction method", is one of the most widely used synthesis procedures for obtaining rather uniform gold nanoparticles (GNPs). The classical citrate method (Turkevich et al., 1951; Frens, 1973) is based on the reduction of an Au(III) precursor with sodium citrate in an aqueous solution near the boiling point (100 °C). This synthesis produces GNPs in the form of a stable aqueous solution (colloidal gold or gold sol), since the citrate ions act both as reducing and protective agents. Citrate synthesised GNPs have been frequently used in various applications, especially biomedical. For instance, the surface of citrate coated GNPs can be modified by a biocompatible polymer or by anti-epidermal growth factor receptors in order to prolong the circulation time of GNPs in the bloodstream and/or for active cancer cell targeting (Reuveni et al., 2011). Apart from applications, the citrate reduction synthesis is one of the best model systems to study the GNPs nucleation-growth mechanism. Moreover, the new synthesis routes significantly contribute to a better understanding of the Au(III) reduction and GNPs formation mechanisms. For instance, Ji et al. (2007) emphasised the importance of adjusting the pH of the Au(III)/citrate solution above 6.2 in order to obtain nearly monodisperse GNPs. In addition to acting as reducing and protective agents, the citrate ions have thus played the third important role as pH mediators that determine the final size and size distribution of the GNPs. Kimling et al. (2006) and Plech et al. (2008) observed

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that GNPs could be obtained by the citrate method *via* UV or X-ray reduction at room temperature. It was found that smaller and larger GNPs coexisted in the solution during growth and that electrostatic stabilisation defined their final size and shape. Ojea-Jiménez et al. (2010) synthesised GNPs by citrate reduction in the presence of heavy water ($D_2O$). The presence of deuterium increased the reducing strength of citrate molecules and as a consequence faster reduction produced smaller sized GNPs. Mikhlin et al. (2011) proposed a new mechanism of GNP formation by citrate reduction on the analogy of the originally proposed mechanism for the crystallisation of proteins. They proposed the formation of domains ("dense droplets") enriched by gold and the formation of GNP-containing globules that prevent the uncontrolled growth of gold nanoparticles. In a recent paper Doyen et al. (2013) suggest that citrate forms aggregates with Au(I) and/or Au(0) atoms and behaves as a "molecular linker", helping thus in the formation of GNPs. In this work we show that γ-irradiation could produce well-dispersed GNPs in an aqueous citrate solution in the presence of dissolved oxygen at room temperature and without adding any reducing agent or stabiliser. The enhanced radiolytical degradation (oxidation/decarboxylation) of citrate by dissolved oxygen and catalysed by gold had an advantage effect in the formation of gold nanoparticles.

## 2. Materials and methods

In this work the GNPs were synthesised by γ-irradiation of a gold/citrate aqueous precursor solution commonly used in case of a classical citrate reduction method. The auric acid ($HAuCl_4 \cdot 3H_2O$, Aldrich), trisodium citrate ($Na_3C_6H_5O_7$, Kemika) and Millipore deionised water (18.2 MΩ cm) were used. Glassware used in the experiments was cleaned by freshly prepared aqua regia (conc. HCl/conc. $HNO_3$=3:1 by volume). The precursor solution was prepared as follows: 20.5 μL of 4 wt% $HAuCl_4 \cdot 3H_2O$ was added to 10 mL of water in a glass vial while stirring with magnetic stirrer, then 200 μL of 1% citrate solution was added and stirred for additional 15 min. The molar ratio of gold to citrate was 1:3.2, which corresponds to the GNP sizes of approximately 12 nm. The concentrated samples were prepared by increasing the gold and citrate concentrations by three and ten times, respectively, whereas the $H_2O$ volume and cit/Au ratio were kept fixed. Such

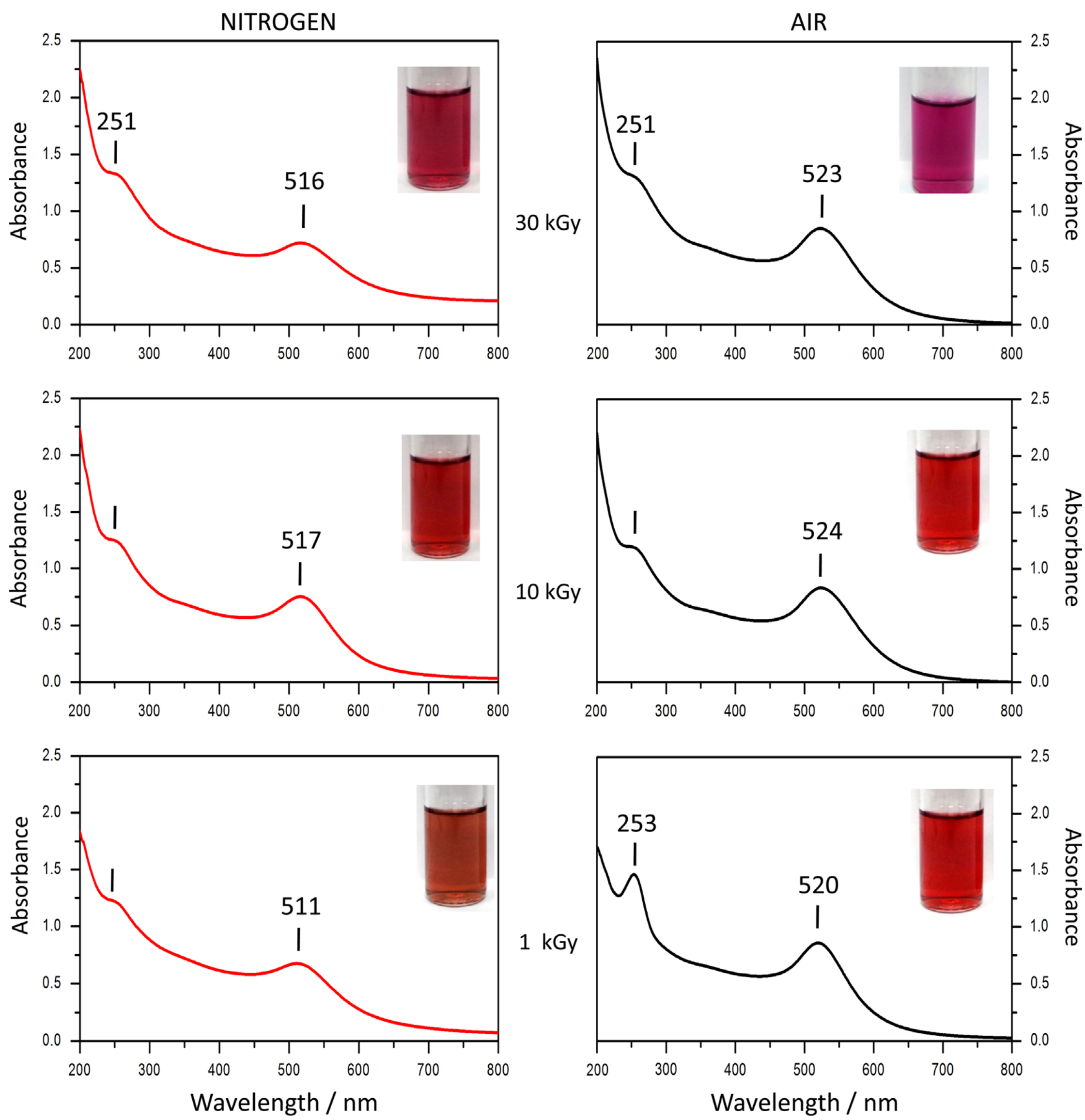


**Fig. 1.** UV–vis spectra of gold nanoparticle (GNP) samples synthesised by γ-irradiation of Au(III)/citrate solutions (absorbed doses of 1, 10 and 30 kGy). The left panel shows GNP samples synthesised in the presence of nitrogen gas ($N_2$), whereas the right one shows corresponding GNP samples synthesised by γ-irradiation in the presence of dissolved oxygen (air). Inset images show the colours of GNP samples.