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# Kinetic study of gold nanoparticles synthesized in the presence of chitosan and citric acid

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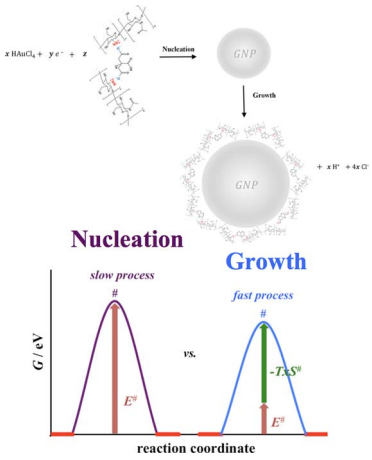
## GRAPHICAL ABSTRACT

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## ABSTRACT

In this work colloidal gold nanoparticles (GNPs) are prepared using a citrate-reduction route, in which citric acid serves as reductive agent for the gold precursor $HAuCl_4$. We demonstrate that a temperature variation on the one hand enables to tune the reaction rate of GNP formation and on the other hand allows modifying the morphology of the resulting metal nanoparticles. The use of chitosan, a biocompatible and biodegradable polymer with a multitude of functional amino and hydroxyl groups, facilitates the simultaneous synthesis and surface modification of GNPs in one pot. The resulting GNPs, which are stabilized by a network of chitosan and ß-ketoglutaric acid units, are characterized by UV–vis spectroscopy, atomic force microscopy (AFM), transmission electron microscopy (TEM) as well as fluorescence correlation spectroscopy (FCS) and reveal an average diameter of about 10 nm at the end of the synthesis. The kinetics of GNP formation is studied by calculating

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activation parameters based on UV–vis and AFM data such as the apparent activation energy, entropy and free energy applying the concept of the Finke-Watzky model and harmonic transition state theory.

## 1. Introduction

Due to their unique physical and chemical properties gold nanoparticles (GNPs) have attracted considerable scientific interest in several fields of chemistry, physics, material science, medicine or photonics since the second half of the 20th century [1–6]. In the literature various synthesis methods for producing GNPs are reported, such as micro emulsions, reversed micelles, seeding growth, sono-chemistry, photochemistry, radiolysis or direct chemical reduction [7–9]. From all these methods, the most efficient approach according to its simplicity constitutes the method of direct chemical reduction, in which gold-containing precursors are reduced by a reducing agent [10]. The majority of synthesis protocols for the production of GNPs rely on a reduction of Au(III), e.g. $HAuCl_4$ or $AuCl_4$–, to gold with oxidation state zero when a suitable reductant, commonly citrate [11] or borohydride [12] is added or generated in situ, e.g. by radiolysis of appropriate oligomers [13,14] into the reaction mixture. The so-called citrate synthesis, in which citrate serves as reductant, was introduced by Turkevich et al. [11] and later reinvestigated by Frens [15].

One of the key issues in colloid synthesis displays avoiding the aggregation of GNPs in order to obtain a monodisperse solution. In fact, sodium citrate in Turkevich's synthesis [11] is playing an important role as stabilizing agent, which prevents aggregation and precipitation of the GNPs that reveal a compelling tendency to flocculate as a result of van der Waals interactions. Consequently, GNPs are successfully stabilized if an appropriate support or anions or polymers are available, which are shielding the surface of each nanoparticle [16]. The use of polymers in nanoparticle encapsulation for their further release by means of a semi-crystalline polymer matrix, which allows a better dispersion of the synthesized material, is one of the most promising techniques for the stabilization of nanoparticles' dispersions [17,18].

Biosynthesis and green synthesis are other significant areas in GNPs preparation via in situ synthesis, in which the biomolecule may act as stabilizer and reductant both. Suitable sources for bio- and green preparations of GNPs are natural source extracts, for instance chitosan and microbes. Polysaccharides may also serve as stabilizing agents [19] according to their ability to coordinate metal ions. The resulting polymer-metal ion complex can then be reduced under mild conditions, yielding particles with smaller size and narrower size distribution in comparison to those synthesized in the absence of polymers, since the polysaccharide chains prevent the aggregation of the nanoparticles formed. Chitosan [20], starch [21], gum arabic [22] and alginate [23] are some examples of polysaccharides that were reported as stabilizing agents for the synthesis of metal nanoparticles. Chitosan constitutes a biocompatible, biodegradable, mucoadhesive, pH-dependent cationic polymer, which is insoluble in water at alkaline and neutral pH, and displays the second most abundant biopolymer in nature after cellulose. It consists of β–1,4 linked glucosamine and N-glucosamine units and can be synthesized by deacetylation of chitin. In acidic media chitosan's amine groups become protonated ($R–NH_3^+$) so that the polymer is positively charged, which enables to solvate it in water. Furthermore, the ionic repulsion between the charged amine groups causes an extended linear polymer configuration. As polyelectrolyte chitosan is able to form electrostatic complexes under acidic conditions [24]. In presence of primary amino, hydroxyl or ester groups, chitosan is reconciled as excellent support material for metal nanoparticles by building networks with the above-mentioned functionalities that may protect the nanoparticle surface from aggregation. Chitosan stabilization of GNPs by adding $NaBH_4$ as reductant was first published in 2003 [25], while Huang et al. proposed a complete green synthesis of GNPs in 2004 claiming that chitosan acts both as reductive and stabilizing agent [26]. From this time onwards, chitosan-stabilized GNPs have found various applications in catalysis [27], biomedicine [28] and sensing [29].

In this article we report for a new synthesis of GNPs in presence of chitosan dissolved in citric acid, which enables the simultaneous synthesis and surface modification of GNPs in one pot. While so far in the literature either synthesis protocols for the formation of GNPs in presence of chitosan and acetic acid or in the presence of citric acid but in the absence of chitosan can be found, we demonstrate in this communication that the combination of citric acid and chitosan reveals major consequences in the size and shape of the produced GNPs as well as in the ongoing reaction mechanism as discussed in Section 3. We study the reaction kinetics of GNP formation by applying the Finke-Watzky model [30] and harmonic transition state theory in order to gains insights into activation parameters such as the apparent activation energy, entropy and free energy. The synthesized GNPs are characterized by different methods (cf. Section 2), such as ultraviolet-visible spectroscopy ((UV–vis)), atomic force microscopy (AFM), transmission electron microscopy (TEM) and fluorescence correlation spectroscopy (FCS).

## 2. Materials and methods

### 2.1. Chemicals and reagents

Analytical grade tetrachloroauric acid ($HAuCl_4 \cdot 3H_2O$) and trisodium citrate ($Na_3C_3H_5O(COO)_3 \cdot 2H_2O$) were obtained from Panreac Química S.A.U. (Spain) and Merck (Germany), respectively, while medium-molecular-weight chitosan, composed of β-(1–4)-linked D-glucosamine and *N*-acetyl-D-glucosamine with a deacetylation degree of about 75–85%, as well as citric acid (CA; $C_6H_8O_7$) were purchased from Sigma–Aldrich®. All solutions were prepared with deionized water.

### 2.2. Synthesis procedure

In our synthesis protocol, 1.0 wt. % of chitosan was dissolved in an aqueous solution of CA (1.0 wt. %) by stirring and heating the system at 50 °C for 24 h. Besides, a second solution was prepared, in which 10 mL of a 2.5 mM solution of tetrachloroauric acid ($HAuCl_4$) was added to 85 mL deionized water. The second mixture was stirred at 350 rpm and heated up to various temperatures, namely 50 °C, 60 °C, 70 °C, 80 °C and 90 °C. After that 5 mL of the first solution containing chitosan and CA was added to the solution of tetrachloroauric acid. During the synthesis of the GNPs the color of the solution changed from pink to red-violet.

### 2.3. Experimental methods

The obtained GNPs according to the above-presented synthesis procedure were characterized by ultraviolet–visible spectroscopy ((UV–vis)), atomic force microscopy (AFM), transmission electron microscopy (TEM) and fluorescence correlation spectroscopy (FCS).

#### 2.3.1. Ultraviolet-visible spectroscopy ((UV–vis))

(UV–vis) absorption spectra of GNP dispersions were recorded by a spectrophotometer (*Thermo Scientific Evolution 300, USA)* at different reaction time intervals. Deionized water was used as reference sample.

#### 2.3.2. Atomic force microscopy (AFM)

AFM imaging was performed on the NanoScope V system (*Bruker Ltd, Germany*) operating in tapping mode in air at room temperature.