



One-pot eco-friendly synthesis of gold nanoparticles by glycerol in alkaline medium: Role of synthesis parameters on the nanoparticles characteristics



Eduardo B. Ferreira, Janaina F. Gomes, Germano Tremiliosi-Filho, Luiz H.S. Gasparotto*

Instituto de Química de São Carlos, Universidade de São Paulo, Caixa Postal 780, 13560-970 São Carlos, Brazil

ARTICLE INFO

Article history:

Received 9 September 2013
Received in revised form 12 March 2014
Accepted 3 April 2014
Available online 5 April 2014

Keywords:

A. Metals
A. Nanostructures
B. Chemical synthesis
C. Electron microscopy

ABSTRACT

In this work we studied the role of experimental variables in an ecologically-correct synthesis of gold nanoparticles carried out by glycerol in alkaline medium at ordinary temperatures (25 °C and 0 °C). Variation of pH allowed the production of spherical and anisotropic nanoparticles. Different concentrations of polyvinylpyrrolidone (PVP) directly impacted the size and stability of the nanoparticles. In contrast, glycerol concentration had little influence on the synthetic process. The empirical rate law was determined for the process with respect to glycerol and gold ions. From the kinetic study it was possible to establish that the rate of nanoparticle formation is only slightly more dependent on gold ions than on glycerol. Thus, to increase the rate of nanoparticles formation, it is economically and environmentally more advantageous to increase the glycerol concentration than the Au³⁺ concentration.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Huge attention has been devoted to gold nanoparticles (AuNPs) due to their broad potential application in photonics [1,2], electrocatalysis [3,4], chemical sensing [5], biosensing [6] and cancer therapy [7]. Haruta [8] quoted gold as the “novel catalyst of 21st century”, due to its application in CO oxidation. Popular nanogold synthesis involves reducing agents such as sodium borohydride [9,10], sodium citrate [11] and hydrazine [12]. In particular, the citrate procedure is inconvenient because gold nanoparticles are formed only upon heating the solution (80–100 °C). Hydrazine is quite efficient as a reducing agent, however intrinsic drawbacks such as carcinogenicity, environmental hazard, and instability (specially in its anhydrous form) [13] pose a major problem to scalability. Quite recently we reported an environmentally correct route to produce gold [14] and silver [15] nanoparticles for borohydride electro-oxidation and oxygen electro-reduction, respectively, using glycerol in alkaline medium as reducing agent. Seeking for environmentally green routes of nanoparticle preparation has been a trend in the past

years [16–20]. Glycerol's non-toxicity and biodegradability make it an excellent alternative to commonly used reducing agents. Although the generation of AuNPs by glycerol is possible, the influence of experimental variables (e.g. pH, stabilizer concentration) on the process is still unknown.

In this paper we studied the influence of different experimental parameters such as glycerol concentration, pH, stabilizer concentration and temperature on the synthetic process. It is known that shape, size and spatial arrangement of nanomaterials strongly impact their properties. Therefore, it is important to determine how the synthesis variables generate nanoparticles with distinct characteristics. Glycerol concentration was found to influence the least the synthetic process. A minimal of 5.0 g/L polyvinylpyrrolidone (PVP) is necessary to achieve complete nanoparticle stabilization. It was found that pH plays a major role in regulating size and shape of gold nanoparticles, being possible to obtain spherical and anisotropic nanoparticles depending on the pH employed. Finally, we discuss the empirical rate order determined as a function of glycerol and gold ions.

2. Experimental

2.1. Reagents and instrumentation

All chemicals (Aldrich) used in this work were of analytical grade and used without further purification. A Varian/Cary 5G spectrophotometer was used to acquire UV–vis spectra of the

* Corresponding author. Current address: Instituto de Química, Universidade Federal do Rio Grande do Norte, Lagoa Nova, 59078-970, Natal, RN, Brazil. Tel.: +55 84 33422323.

E-mail addresses: eduardoferreira@iqsc.usp.br (E.B. Ferreira), janainafg@iqsc.usp.br (J.F. Gomes), germano@iqsc.usp.br (G. Tremiliosi-Filho), lhgasparotto@ufrnet.br (L.H. Gasparotto).

AuNPs colloidal suspensions. For the transmission electron microscopy (TEM) experiments, copper grids coated with carbon film were immersed into the nanoparticle colloidal suspensions and allowed to dry overnight in a desiccator. The grids were then analyzed with a TEM FEI Tecnai (200 kV accelerating voltage).

2.2. Preparation of AuNPs

In a typical experiment for AuNPs synthesis, known amounts of polyvinylpyrrolidone (PVP, molecular weight = 10,000) with AuCl_3 (30 wt% in HCl) were dissolved in 5 mL of ultrapure water. In a separate flask, determined quantities of a glycerol and NaOH were dissolved in 5 mL of ultrapure water. The glycerol–NaOH solution was then added to the AuCl_3 –PVP solution to yield 10 mL of solution with final concentrations shown in Table 1. The effect of pH was investigated at two temperatures (25 °C and 0 °C). 0 °C was achieved with an ice bath. To follow the reaction kinetics (Table 1, Set 4#), the wavelength of 520 nm was fixed and the absorbance followed as a function of time with the reaction conducted directly in the UV–vis cuvette.

3. Results and discussion

3.1. Influence of glycerol concentration

Fig. 1A shows a collection of the UV–vis spectra of the colloidal AuNPs prepared at room temperature ($\sim 25^\circ\text{C}$) at different glycerol concentrations with all other parameter held constant. It was attempted to produce gold nanoparticles in absence of PVP, however, they tended to agglomerate and precipitate in the bottom of the reaction vessel. Unlike citrate and borohydride anions, glycerol itself lacks capability of stabilizing the nanoparticles. Increasing the glycerol concentration caused an increase in AuNPs concentration, as shown by the consistent increments in absorbance in Fig. 1A. Red-colored solutions were immediately obtained upon mixing glycerol/NaOH with Au^{3+} /PVP. The red color is due to the surface plasmon band (SPB) as a result of the resonant coherent dipolar oscillations of the electron gas (electrons of the conduction band) at the surface of nanoparticles. The SPB is a valuable tool for inference about the size regime of some metal particles (e.g. Ag and Au). The colloidal AuNPs spectra had a maximum absorbance (λ_{max}) at around 520 nm regardless of the concentration, a value typical for spherical gold nanoparticles [21,22]. The symmetry of the bands implies a fair similarity in the shape of the nanoparticles and low degree of aggregation in the solution [23]. From these results one can conclude that glycerol concentration has practically no influence on size and distribution of AuNPs. Non-spherical gold nanoparticles display multiple SPR bands correlated with their multiple axes, with one of the absorption bands appearing towards the near infrared region [24]. The fact that the absorbance tends to fade out for wavelengths higher than 600 nm is an indicative that there are no other particle geometries in the solution (e.g. nanorods, pentagons, truncated triangle plates). Fig. 1B shows a representative TEM image of AuNPs produced at an intermediate glycerol concentration of $6.6 \times 10^{-2} \text{ mol L}^{-1}$. The nanoparticles

were spherical in shape with mean particle size of $7.6 \text{ nm} \pm 1.4 \text{ nm}$, thus corroborating the UV–vis results. Fig. 1C, which was obtained by acquiring many images as that of Fig. 1B (100 particles counted), shows that size of the AuNPs lie indeed between 6 nm and 9 nm. It can be seen in the high-resolution TEM (inset of Fig. 1B) that the particles are polycrystalline.

3.2. Influence of pH

Fig. 2 presents UV–vis spectra of AuNPs produced at different pH and 25°C with the other parameters kept constant. Two groups of spectra can be observed: one centered at about 540 nm (pH 9 and 11) and another at around 520 nm (pH 12–14). The inset of Fig. 2 displays photographs of the AuNPs colloidal solutions at different pH and 25°C . The higher the alkalinity, the deeper the red-wine color. For pH 9 and 11 the redshift (compared to 520 nm) is a diagnostic of an increase in the nanoparticle size [21,25]. Another contribution for this redshift might be an incomplete reduction of metal ions adsorbed on the surface of the nanoparticle and/or in the solution, as argued by Moskovits et al. [22]. At relative low alkalinity the reducing power of glycerol must be also low, tending to increase with the pH. This is supported by the fact that at pH higher than 12 the λ_{max} centered back at 520 nm, which is the typical value for fully reduced gold nanoparticles. Another interesting feature is that at pH 9 and 11 the absorbance does not tend to vanish at wavelengths higher than 600 nm, in contrast to pH 12–14. This behavior can be attributed to the existence of other-than-spherical shaped nanoparticles. For anisotropic AuNPs such as pentagon, truncated triangle plate and cuboctahedron the absorption starts at around 600 nm and develop peaks in the NIR region [24]. A TEM image of AuNPs synthesized at pH 9 (bottom left) reveals significantly larger nanoparticles with truncated triangle, hexagonal particles and nanorods, thus corroborating the UV–vis results. Production of anisotropic gold nanoparticles can thus be achieved by simple reduction of pH. A TEM image of AuNPs synthesized at pH 14 (bottom right) shows that at high pH values their size can be substantially decreased, hence confirming the qualitative UV–vis results.

The temperature was found to dramatically impact the synthetic process. At 0°C (Fig. 3) the absorptions at pH 9 and 11 are practically non-existent compared to pH 12–14. This can also be readily realized in the photographs of the AuNPs colloidal solutions (Fig. 3, bottom). At pH 9 and 11 the solutions still display a pale-yellow color characteristic of gold salt, denoting that the concentration of AuNPs, if any formed at all, must be very low. When zooming in on the region between 500 nm and 700 nm for pH 9 and 11 (inset of Fig. 3) one can actually see broad reshifted bands centered at about 558 nm and 567 nm, respectively. This is an indicative that at 0°C and pH 9 and 11 the AuCl_3 has been hardly reduced and the nanoparticles are larger than those shown in Fig. 1. Upon increasing the pH, the center of the band tends to go back to 520 nm.

3.3. Impact of the PVP concentration

Fig. 4A shows UV–vis spectra acquired at distinct PVP concentrations with all other parameters held constant. The

Table 1

Experimental conditions employed in this work. Temperature was kept constant at 25°C unless otherwise indicated.

Parameters				
Experiments	Glycerol concentration (mol L^{-1})	PVP (g L^{-1})	pH	AuCl_3 (mmol L^{-1})
Set 1#	6.6×10^{-4} ; 6.6×10^{-3} ; 6.6×10^{-2} ; 1.0	10	13	0.50
Set 2#	0.10	10	9;11–14 (at 25°C and 0°C)	0.50
Set 3#	0.10	0.040; 0.20; 1.0; 5.0	13	0.50
Set 4#	0.10 and 0.50	10	13	0.10; 0.25; 0.50; 0.75

Download English Version:

<https://daneshyari.com/en/article/1487970>

Download Persian Version:

<https://daneshyari.com/article/1487970>

[Daneshyari.com](https://daneshyari.com)