Preparation of gold nanoparticles and determination of their particles size via different methods

Muhammad Iqbal[a], Gisele Usanase[a], Kafia Oulmi[b], Fairouz Aberkane[b], Tahar Bendaikha[b], Hatem Fessi[a], Nadia Zine[c], Géraldine Agusti[a], El-Salhi Errachid[c], Abdelhamid Elaissari[a,*]

[a] University of Lyon, University Lyon-1, CNRS, UMR-5007, LAGEP, F-69622 Villeurbanne, France
[b] Laboratory of Chemistry and Environmental Chemistry(LCCE), Faculty of Science, Material Science Department, University of Batna, 05000, Algeria
[c] Institut des Sciences Analytiques (ISA), Université Lyon, Université Claude Bernard Lyon-1, UMR-5180, 5 rue de la Doua, F-69100 Villeurbanne, France

ABSTRACT

Gold nanoparticles have been used in various applications covering both electronics, biosensors, in vivo biomedical imaging and in vitro biomedical diagnosis. As a general requirement, gold nanoparticles should be prepared in large scale, easy to be functionalized by chemical compound of by specific ligands or biomolecules. In this study, gold nanoparticles were prepared by using different concentrations of reducing agent ($NaBH_4$) in various formulations and their effect on the particle size, size distribution and morphology was investigated. Moreover, special attention has been dedicated to comparison of particles size measured by various techniques, such as, light scattering, transmission electron microscopy, UV spectrum using standard curve and particles size calculated by using Mie theory and UV spectrum of gold nanoparticles dispersion. Particle size determined by various techniques can be correlated for monodispersed particles and excess of reducing agent leads to increase in the particle size.

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1. Introduction

Over the last three decades, nanoparticles research has received an increasing interest. This is due to the unique size dependent properties of nanoparticles, which are often thought as a separate and intermediate state of matter between individual atoms and bulk material [1]. Metal nanostructures present a wide variety of remarkable physical and chemical properties, which can be modified by changing their size, morphology, composition, and various preparation parameters [2,3]. Gold nanostructure have attracted considerable attention for many years because of their extensive use in various applications such as catalysis, photonics, electronics, optoelectronics, diagnostic, delivery, chemical, biological and biomedical sensing, photothermal therapy, surface plasmon resonance and surface-enhanced raman scattering (SERS) detection [4–11]. Gold nanoparticles (AuNPs) are considered as good candidate for labeling applications due to its ability of strong interaction with visible light. Upon interaction with light, the excitation of free electrons in gold atoms lead to a state of collective oscillation called surface plasmon resonance (SPR), which provide gold the ability to absorb and scatter visible light depending upon its size, shape and agglomeration state [12,13]. AuNPs can be targeted and accumulated at specific tissue of interest thus enable visualization of that area under study. They can be detected by several techniques including phase contrast optical microscopy, dark field microscopy, photothermal imaging [14,15] and confocal scanning optical microscopy [16,17]. AuNPs have been reported to lack the capability to induce adverse and acute toxicity, thus, they are considered biocompatible device for biomedical applications [18–21]. These properties of nanoparticles result from the extremely high proportion of surface atoms, this factor is directly dependent on the size of the nanoparticle. Indeed, the possibility to control these properties by adjusting the size of the nanoparticle, has been the cause of extensive investigation. Contrary to bulk materials that have constant physical properties regardless of mass, nanoparticles offer unique opportunities to control the electrical, magnetic and optical properties by modifying their diameter.

Nanoparticles can be prepared from various materials by relatively simple methods. In recent years, several types of methods have been published and reviewed. Currently, there are two kinds of approaches commonly used to prepare nanoparticles, the "top down approach", which involves the constant division of bulk metals into nanoparticles and the "bottom-up

* Corresponding author.
  E-mail address: elaissari@lagep.univ-lyon1.fr (A. Elaissari).

approach", which involves the building up of nanoparticles from the atomic level (metal ions) [3,8,22]. Various techniques such as, chemical, electrochemical, irradiation, sonochemical, solvothermal, photochemical and laser ablation have been used to prepare nanoparticles from metal ions precursors in the presence or absence of a capping agent [9,23–27]. Michael Faraday was the first to study the formation of colloidal gold particles from a scientific point of view and used phosphorus agent for the reduction of [AuCl$_4$]$^-$ ions [28]. During the last century, numerous easy to handle reducers were found, such as sodium borohydride, thiosulfate, or organic ones like, sodium citrate, ascorbic acid, alcohols (polyalcohol) and amines [9,29–33]. The Turkevich method is still one of the most applied procedures, in which, sodium citrate reduces [AuCl$_4$]$^-$ in hot aqueous solution to give colloids of 15–20 nm [34]. Citrate itself and its oxidation products can act as protecting agents, even if no other stabilizer is used. However one of the most popular methods for preparation of gold nanoparticles of various sizes comes from Brust et al. It uses NaBH$_4$ to reduce gold salts in the presence of alkanethiols to yield gold particles of 1–3 nm. And, by varying the thiol concentration, the particles sizes can be controlled between 2 and 5 nm [35].

Characterization methods for analysis and measurement of nanomaterials are essential in the development of nanotechnology; as the sizes, shapes, and structures of nanomaterials influence their physicochemical properties. The most common technique used for characterization of metallic nanoparticles is high-resolution transmission electron microscopy (HRTEM), which generates a photomicrograph of the core of the nanoparticles, providing information regarding the particle size, size distribution and polydispersity of the samples. UV–vis (optical) spectroscopy is used for analysis of the intensely colored colloidal dispersions having characteristic surface plasmon absorption [2,36,37]. In a given preparation of nanoparticles, there is usually a mixture of different size particles, which, have characteristic surface plasmon resonance peaks and thus their UV–vis spectra are usually significantly different, which may help in determining the nanoparticle size [38].

The aim of this work is to characterize the prepared nanoparticles in terms of morphology, size and size distribution. Special attention was dedicated to comparison of particles size measured by light scattering, transmission electron microscopy, by UV using standard curve and the particles size was calculated using Mie theory and UV spectrum of gold dispersion.

2. Materials and methods

2.1. Materials

Gold(III) chloride hydrate ($\geq$99.999%) was purchased from Sigma–Aldrich, and sodium borohydride (NaBH$_4$), 98 +%, was purchased from Acros Organics. Water was deionized using (Aquadem$^\circledR$ from Veolia Water, France). Nitric acid (68%) and hydrochloric Acid (35%) were obtained from BDH Prolabo-VWR International.

2.2. Preparation of gold nanoparticles

The preparation of gold nanoparticles was performed by NaBH$_4$ reduction method as described in literature [39]. Briefly, 10 mg of HAuCl$_4$ was dissolved in 100 ml of deionized water ($\approx$0.25 mM), and shaken properly to mix the solution. And, 0.1 M solution of reducing agent (NaBH$_4$) was prepared by dissolving 1.891 g of NaBH$_4$ in 500 ml of deionized water. Then, 100 ml of HAuCl$_4$ (0.25 mM) were taken in 250 ml flask with magnetic stirring at 750 rpm (230 V, IKA$^\circledR$ RET, Germany) and the reducing agent solution was added drop by drop with continuous stirring. The color of HAuCl$_4$ solution changed from pale yellow to dark red over several minutes. Stirring process was continued for another 10 min for complete homogenization. Since the HAuCl$_4$ is corrosive, a glass spatula was used to avoid the contact with metal. In the preparation of gold nanoparticles, cleaning of glassware is very crucial. Thus, all the glassware and stir magnetic bars were thoroughly cleaned in freshly prepared aqua regia (HCl/HNO$_3$ 3:1, v/v) and then rinse with distilled water and dried, to avoid aggregation of residual gold particle and to avoid unwanted nucleation during synthesis. After preparation of the particles, the dispersions were centrifuge at 14000 rpm for 15 min and the collected particles were redispersed in deionized water before any characterization. All the gold nanoparticles batches were store in the dark to minimize the photo induced oxidation.

2.3. Physicochemical characterization of nanoparticles

2.3.1. Hydrodynamic particle size measurement

The hydrodynamic particles size (Dh) of the colloidal dispersions was determined by dynamic light scattering (DLS) using zetasizer from Malvern (England) at room temperature (25 °C). The mean hydrodynamic diameter is calculated by using the Stokes–Einstein's equation:

$$Dh = \frac{kT}{3\pi\eta D} \tag{1}$$

Table 1
Data from Ghosh et al.[40] in which particle size and maximum wavelengths absorption of gold nanoparticles are reported as a function of trisodium citrate concentration.

Run	HAuCl$_4$ solution (10 mM, mL)	Trisodium citrate solution (1%, mL)	Color	λ_{max}	Average diameter (nm)	
					Reported	Observed
A	1.25	2.000	Dark red	518	–	8.00
B	1.25	1.600	Red	519	–	10.0
C	1.25	1.300	Red	520	–	13.0
D	1.25	1.000	Red	522	16.0	16.0
E	1.25	0.875	Red	526	–	20.0
F	1.25	0.750	Red	528	24.5	25.0
G	1.25	0.625	Pinkish red	529	–	32.0
H	1.25	0.500	Pink	532	41.0	41.0
I	1.25	0.400	Pink	534	–	55.0
J	1.25	0.300	Orange	545	71.5	73.0