Journal of Molecular Structure xxx (2016) 1–8

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Light wavelength influence on surface plasmon resonance in citrate–gold nanosystems

Raoul-Vasile Lupusoru [a], Daniela A. Pricop [b, *], Maria Andries [b], Dorina Creanga [b]

[a] Department of Pathophysiology, Faculty of Medicine, “Gr.T. Popa” University of Medicine and Pharmacy, 16, Str. Universitatii, Iasi, Romania
[b] Faculty of Physics, “Alexandru Ioan Cuza” University, 11, Carol I Bd., 700506, Iasi, Romania

ARTICLE INFO

Article history:
Received 29 November 2015
Received in revised form
18 February 2016
Accepted 22 February 2016
Available online xxx

Keywords:
Gold colloidal suspension
Citrate gold interaction
Microstructural analysis
Visible radiation effect

ABSTRACT

Citrate–gold particles were yielded according to classical method of auric salt reduction in two different synthesis media aiming to use them further applications in biomedical and environmental domains. The analysis of citrate–gold interaction was done through UV–vis and IR spectroscopy as well as by Transmission Electron Microscopy (TEM) and Dark Field (DF) Microscopy. Average particle size was higher for citrate–gold NPs synthesized with NaOH (32.5 nm) than for NPs synthesized with NaCl (15 nm). Dimensional histograms of one year aged colloidal suspensions presented mean size of 29 nm and respectively 18 nm. The influence of 90 min light exposure, analyzed by UV–vis, evidenced that for both NaOH synthesis protocol and NaCl protocol, plasmon band maxima at 528 nm and respectively 538 nm didn't changed, neither for white nor for green light. For one year aged samples this band shifted to 540 nm for green light irradiation in the case of citrate–gold NPs synthesized with NaOH. Also, for these NPs, both green and white light exposures resulted in plasmon band intensity changes for native as well as for aged samples. FTIR investigation showed also different changes at the level of the intensity of main vibration bands of citrate–gold after exposure to light, suggesting stronger adsorption of citrate in the case of NaCl addition in the initial reaction medium than in the case of NaOH. Finally, the utilization of NaCl in the synthesis protocol seems to favor the synthesis of more stable and lower toxicity colloidal suspensions, both during time and under the light irradiation.

1. Introduction

The investigation of citrate–gold interaction in the context of Au nanoparticle synthesis attired the attention of several research groups due to wide utilization of such nanosized systems in technical and life science applications. Prior to gold colloid nucleation, the induction period is associated with the formation of citrate oxidation products such as dicarboxy acetone that acts as a multidentate chelating agent generating Au(I) clusters [1]. The authors of [1] corroborated theoretical findings with experimental UV–vis absorption spectroscopy and TEM analysis to describe AuNPs formation and final particle morphology; thus some steps of the molecular mechanism of the reduction of Au(III) and decarboxylation of citrate were studied, aiming better understanding of basic molecular interactions essential for the improvements of experimental efficiency.

In some scientific reports [2–5], the electromagnetic radiation in the visible range was found as having stimulation influence in the photochemical synthesis of molecular shell/metal core particles. The exposure to visible radiation was shown to induce redox processes by activating the molecular components with role of reducing agents during colloidal metal formation [6].

The electromagnetic radiation in the visible range was found as having stimulating influence in the photochemical synthesis of metal particles [7]. UV irradiation was applied during synthesis of gold nanoparticles with polyetylene glycol as protector agent; it was found that nanoparticle size, shape and dispersion efficiency depend on the polymerization degree [8]. UV exposure was used in the generation of metal seeds as nucleation centers of final nanoparticles [9]. Monodispersed colloidal Au seeds were prepared by applying 300 nm UV radiation being further used in the growth of higher particles under solar light by progressive adding of Au (III) ions [9].

Optical radiation can influence the silver particles yielding efficiency due to the possibility of energetically adjusting of local surface plasmon resonance (LSPR) occurring in metal electrons

---

* Corresponding author.
E-mail address: daniela.a.pricop@gmail.com (D.A. Pricop).

http://dx.doi.org/10.1016/j.molstruc.2016.02.081
0022-2860/© 2016 Elsevier B.V. All rights reserved.

Please cite this article in press as: R.-V. Lupusoru, et al., Light wavelength influence on surface plasmon resonance in citrate–gold nanosystems, Journal of Molecular Structure (2016), http://dx.doi.org/10.1016/j.molstruc.2016.02.081

[10]. This phenomenon is related to some metal nanoparticles absorption in the optical range resulting in new distribution of energized electrons over the Fermi level [11]. According to [12] significant concentration of energized electrons remain in the "hot" state for 0.5–1 ps, their energetic gain activating the molecules adsorbed at nanoparticle surface -thus inducing chemical transformations [13].

In the study presented below light absorption was shown to induce some changes of citrate interaction with gold ions at the surface of colloidal nanoparticles which resulted mainly in particle association and partial flocculation and precipitation from the irradiated suspension.

AuNPs were exposed to green light due to LSPR effect induced at NP surface [6] aiming to study the way how energy gain of gold electrons could generate changes in absorbed citrate, depending on the used reagent: NaOH or NaCl respectively. White light—including green one, was chosen for comparison since the stability of citrate/gold binding has practical importance for the storage and manipulation of gold suspensions in ambient light.

2. Materials and methods

2.1. Citrate–gold nanoparticle synthesis

Hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4 \times 3H_2O$), sodium hydroxide (NaOH), sodium chloride (NaCl) and sodium citrate dihydrate ($C_6H_9Na_3O_9$) were purchased from Sigma Aldrich being used without further purification. The solutions were prepared using Milli-Q deionized water (18.2MOhm, Barnstead Easy-PureII purification system).

The pH measurements were performed using Sartorius professional meter pp-50 device.

- Citrate–gold in NaOH–G(NaOH): 5 ml $HAuCl_4 \times 3H_2O$ (1 mM solution) were mixed with 0.5 ml NaOH solution (20 mM) and filled with deionized water up to 50 ml in a suitable glass bowl. The bowl was immersed in a water bath preheated to 110 °C using a thermostated heat source. After the temperature reached 85 °C, 3 ml sodium citrate dihydrate (50 mg/ml) was added. The mixture remained on the thermostated source, under magnetic stirring, for about 30 min at 85 °C to get completed nucleation in the G(NaOH) sample; final pH about 6.8.
- Citrate–gold in NaCl–G(NaCl): 5 ml $HAuCl_4 \times 3H_2O$ (1 mM solution) were mixed with 1 ml NaCl solution (20 mM) and deionized water, up to 50 ml, was added in the reaction round-bottom glass. As above, the bowl was let on thermostated heat source preheated at 110 °C until the temperature lowered at 85 °C, then 1.5 ml sodium citrate dihydrate (50 mg/ml) being added. Completely nucleated G(NaCl) colloidal nanoparticles were yielded after 30 min; final pH about 4.5.

2.2. Citrate–gold nanoparticle characterization

Malvern Zetasizer Nano ZS Zen-3500 was used to determine the hydrodynamic diameter and polydispersity index of the nanoparticles within the colloidal solution; measurements were performed at room temperature. Transmission electron microscopy (Hitachi High-Tech HT7700-TEM device) was used to characterize the morphology and determine the size and size distribution of the synthesized citrate–gold nanoparticles. Nikon Ti-Eclipse Optical Microscope working in dark field (DF) techniques was also used for imaging nanoparticles. NIS Elements BR (NIS–BR) specialized software was utilized to measure and compare DF data provided by TEM micrographs and optical microscope recordings.

2.3. Citrate–gold nanoparticle irradiation

50 W halogen lamp was used to irradiate the citrate–gold suspension samples at 24.5 cm height over each Petri dish containing 10 ml colloidal suspension (Table 1). Illumination at the suspension level and light energy dose was measured with Solar Light PMA 2100 device and PMA 2130 sensor in the visible light. G(NaOH) and G(NaCl) prepared suspensions were divided in equal volumes (10 ml) and poured in geometrically identical Petri dishes as follows:

- G(NaOH)C and G(NaCl)C-control samples, non-irradiated;
- G(NaOH)WL and G(NaCl)WL-samples exposed to white light;
- G(NaOH)GF and G(NaCl)GF-samples exposed to green light (photographic filter).

Table 1 displays lighting, and energy dose absorbed by the nanoparticles. Light exposed samples were let under the halogen lamp for 5 min time durations alternated with 5 min breaks in order to avoid sample heating. Total exposure time was of 90 min in each case-except control non-irradiated samples.

2.4. Spectral investigation

The electronic spectra were recorded with Shimadzu UV–vis Spectrophotometer type Pharma Speck, provided with 1 cm quartz cells. FTIR spectra were recorded with FTIR spectrometer, Bruker Vertex 70 model and water spectrum was automatically extracted from those of analyzed samples.

2.5. Structural modeling

Molecular optimized geometry by quantum chemical simulations was done using Gaussian 0.9 with DFT B3LYP level of theory with 6-31++G (d,p) basis set; partial electric charges on molecule atoms were estimated as well as vibration spectra; representation of calculated data were done in VMD (Visual Molecular Dynamics) 1.9.2 program.

3. Results and discussions

DFT modeling provided optimized citrate geometry (Fig. 1a) with hydrogen bond developed intramolecularly (Table 2) [14].

The relatively high negative fractional charges of oxygen from carboxylate groups are ranging from −0.59 to −0.66 (Fig. 1b) suggesting the ability of citrate to interaction with Au ions through these oxygens. In Table 2 energetic and structural parameters resulted from citrate modeling are presented-for isolated citrate (in vapor state).

According to [1] that developed a synthesis reaction model based on pH role in NP formation, in the range of neutral pH citrate ions have three negative charges while in the range of acidic pH only two negative charges can be found on citrate ions. Thus we propose the two synthesis schemes corresponding to possibly different citrate binding to gold NPs (Schemes 1 and 2).

In Scheme 1, the synthesis protocol resulted in neutral pH characterizing NP colloidal suspension ((G)NaOH) while in Scheme 2, the resulted suspension (G(NaCl)) is characterized by acidic pH. According to Table 3, G(NaOH) NPs show, at 6.8 pH, lower polydispersity index (0.57) compared to G(NaCl) NPs (at 4.5 pH the polydispersity index is 0.74); hydrodynamic diameter is larger (70.5 nm) for G(NaOH) sample compared to G(NaCl) (61.2 nm).

In Fig. 2 a the citrate IR modeled spectrum is given as provided by mathematical approach while in Fig. 2 b the vibration spectrum recorded in citrate aqueous solution is presented for comparison. In

Please cite this article in press as: R.-V. Lupusoru, et al., Light wavelength influence on surface plasmon resonance in citrate–gold nanosystems, Journal of Molecular Structure (2016), http://dx.doi.org/10.1016/j.molstruc.2016.02.081