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Synthesis and characterization of gallium colloidal nanoparticles

M.F. Meléndrez [a], G. Cárdenas [b,*], J. Arbiol [c]

[a] International Center for Nanotechnology and Advanced Materials (ICNAM), Department of Physics & Astronomy, University of Texas at San Antonio, One UTSA circle, TX 78249, USA
[b] CIPA, Polymer Department, Metallic Atoms Laboratory, Universidad de Concepción, Casilla 160-C, Chile
[c] GAEN – CeMARC, Group of Advanced Electron Nanoscopy – Centre de Microscòpia d'Alta Resolució de Catalunya, Universitat de Barcelona, C/Lluís Solé i Sabarís, 1-3, 08028 Barcelona CAT, Spain

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ABSTRACT

In this work, gallium colloidal nanoparticles (Ga-Nps) were synthesized by chemical liquid deposition (CLD). This method involved the deposition of metallic atoms with organic solvents (THF, acetone and 2-propanol) in a freezing matrix of the solvent at 77 K, in order to obtain core–shell Ga-Nps which were characterized by: FT-IR, UV–Vis, TEM, SAED and electrophoretic mobility measurements. TEM images revealed a wide distribution of the apparent size of the particles and apparent average size of 5.65, 8.11 and 13.87 nm for Ga-Nps obtained with 2-propanol, THF and acetone, respectively. UV spectra showed absorption bands of metal plasmons, interesting quantum size effects and plasmon absorption bands of particles aggregated to λ_{280} and λ_{325}. Electrophoretic mobility allowed to evidence that nanoparticles had a negative charge as well as to observe that the zeta potential of the colloidal dispersions decreased over time, showing a significant tendency to the aggregation of Ga-Nps. The importance of the functionalization of metal nanoparticles with high dielectric constant solvents in the stabilization of colloidal systems was also observed. FT-IR spectroscopy revealed that the interaction of Ga surface with the solvent possibly produces a (Ga—C) bond. Experimental details, structural and thermal stability studies were also analyzed in this work.

1. Introduction

Nanoparticles often exhibit novel properties which are different from the bulk material properties [1]. Many of these properties show a strong dependence on size, shape and surface preparation [2]. These systems of reduced dimensions have been extensively investigated and are attractive for technological applications. For example, their size-dependent reactivity and interaction with other atoms and molecules [3,4], make them suitable for the development of new biophysical sensors [5,6], as well as also for thermoelectronic, nanoelectronic and nanophotonic devices [7–9]. Furthermore, the chemical properties of metal Nps make them potential candidates for use as novel catalysts with optimized selectivity [10,11]. Other future applications of Nps include enhanced absorption of light in thin photodetectors and organic solar cells [12,13] of particular interest have long been the optical properties of nanoparticles. The main feature of the optical extinction spectra of metal Nps is the excitation of plasmon polaritons, i.e., collective oscillations of the free electrons driven by the electromagnetic field. The surface plasmon resonances (SPR) can be used for a variety of optical applications such as waveguides [14]. Metal Nps with pronounced SPR can also serve as optical filters, which selectively block radiation in specific wavelength intervals and in integrated optical devices for ultrafast switching of light [15,16]. Moreover, the optical properties of Ga-Nps have been attracting increasing interest for various photonic applications such as nanoscale antennas for sensing, directional emitters or plasmonic waveguiding [17]. Unlike Ag or Au nanoparticles, the surface plasmon resonance of Ga metal droplets can be tuned from the UV to the near-infrared wavelength regime by changing the size of the droplets on various substrates with the appropriate dielectric constant [18].

On the other side, among the most common methods used for preparing nanoparticles electrochemical synthesis [19], thermal decomposition [20], chemical reduction [21] and metal vapor deposition [22] are present. Most of the nanoparticle synthesis methods present disadvantages for the nanoparticle purification process [23]. This is the reason why chemical liquid deposition (CLD) represents one of the more versatile techniques in order to obtain metal Nps. One of the most important advantages of this CLD technique is that no by-products of metal salt reduction are present and pure metal colloids are formed. Another advantage is control of surface composition by use of different organic molecules for the coating. Furthermore, the material obtained is easy to handle for analysis. An additional improvement of the CLD technique is the synthesis of useful amounts of nanoparticles and the possibility of scaling up the process [24]. This technique consists of the co-deposition of metallic vapors and organic solvents in a

* Corresponding author. Fax: +56 412203337.
E-mail address: galocardenas@udec.cl (G. Cárdenas).

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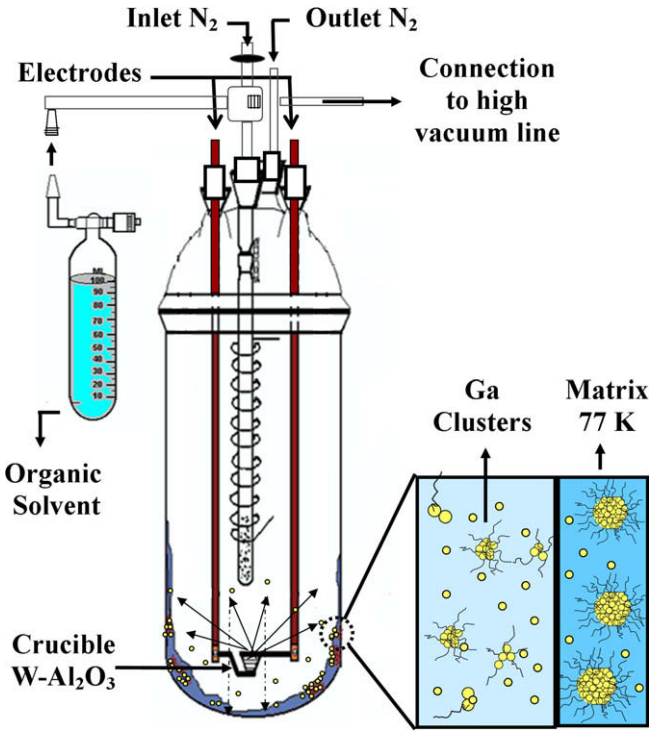
freezing matrix at 77 K. Direct contact between metal atoms and solvent molecules (from gas state) allows a better functionalization of the nanoparticles, obtaining lower size particles, stable colloid dispersions and *a narrow particle size distribution* [25–29]. The aim of this study was to obtain colloidal Ga nanoparticles by CLD with different solvents (acetone, THF and 2-propanol) as well as to study the synthesis parameters such as: latency time, the amount of metal evaporated moles, the colloid concentration and their effects on particle size and the stability of colloidal dispersions, also was analyzed the Ga-Nps agglomeration tendency, its optical properties and its thermal stability. Control over these processes and the interesting optical properties of Ga, would eventually allow its applications in optoelectronic devices.

2. Experimental

2.1. Ga-Nps synthesis by CLD

Ga-Nps were prepared by chemical liquid deposition (CLD) method [30], which involves the physical vapors deposition of metallic Ga in organic vapor media. Reaction was carried out in a glass reactor of metallic atoms. A W—Al_2O_3 crucible loaded with Ga was assembled in the metallic atom reactor and the whole system was evacuated (see Scheme 1). A glass device with organic solvent (2-propanol, acetone and THF p.a. grade, purchased from Fisher), dried with molecular sieves and further degasified three times by standard freeze–thaw procedure [31] was attached to the neck of the reactor. The whole system was immersed in liquid nitrogen (77 K) and evacuated on reaching a vacuum of 10^{-5} bars. The crucible was heated at 40 A to Ga boiling point. In the reaction, metallic Ga and the solvent were co-deposited for over half an hour. The freezing matrix, obtained on the reactor walls, was allowed to warm slowly for 1/2 h. Once this time was completed, the reactor was filled with extra pure nitrogen gas. After 30 min under a nitrogen flow, Ga colloidal dispersions in organic media were obtained. In a CLD reaction, 1.43×10^{-3} mol of Ga (purchased from Aldrich) was evaporated with 100 mL of 2-propanol (dried and degassed) to obtain the Ga colloidal nanoparticles.



Scheme 1. Metallic atom reactor. Simultaneous metal and solvent evaporation.

2.2. Electron microscopy studies

Particle size for the Ga-Nps was obtained by means an image histogram analysis by a TEM (JEOL-JEM 1200EXII) with 4 Å resolution. A drop of each colloid was placed on a dry copper grid (150 mesh), previously coated with carbon, in an inert atmosphere. TEM software Digital Micrograph (DM)™ 3.7.0 by Gatan Inc. was used for the TEM image processing. The measurement of the particle size population diameter was randomly chosen and the obtained data was plotted as frequency histograms using the Microcal™ Origin 6.0 software (Microcal Software, Inc.). The average particle size was fitted with normal curves and the standard deviation was also calculated.

2.3. UV spectroscopy

UV absorption spectra of Ga-Nps (0.01% v/v) were analyzed by UV spectrophotometer (Shimadzu Corp., Kyoto, Japan). Absorption spectra were recorded from 190 to 400 nm using quartz cells. Colloids were diluted with anhydrous and degasified solvents. Samples were prepared in an inert atmosphere and the quarts cells were sealed in order to avoid the contact of the Ga-Nps with the surrounding oxidant environment.

2.4. FT-IR spectroscopy

FT-IR was performed in a Nicolet Nexus spectrometer at room temperature (Nicolet Instrument Co., USA). The colloids were dried under vacuum and the samples were prepared in a KBr pellet (~2%, w/w). The spectra were carried out between 400 and 4000 cm^{-1}, with an accumulation of 64 scans, collected and processed with the Omnic 5.2a software package.

2.5. Electrophoresis

Electrophoresis experiments at 1, 24, 72, 120 and 168 h were carried out in a zeta meter system 3.0+ (Zeta Meter Inc., Staunton, USA) at 25 °C. Quartz cells were used, previously rinsed with deionised water and later with the corresponding solvent.

3. Results and discussion

3.1. Gallium colloid stability obtained by CLD

Yellow colloidal dispersions of Ga were obtained with the different solvents used in the synthesis (2-propanol, acetone and THF). A reaction scheme for the solids, nanostructured colloids and thin layers are shown in Fig. 1a. In the CLD reaction, the solvent forms a freezing matrix on the reactor walls at liquid nitrogen temperature, in which Ga metallic atoms are deposited by resistive evaporation. Besides, in Fig. 1b metallic atoms reactor at the time of co-deposition after the nucleation process and the gallium colloid formed are also observed.

Table 1 shows the stability data of the obtained colloids. Stability studies with solvents follow the tendency: 2-propanol > THF > acetone. Gallium colloids obtained with 2-propanol (Ga-Colls–2-propanol) showed a stabilization time of over 150 days. Ga-Colls–acetone was the least stable, with stabilization times under 20 days. Most of the colloids are kinetically unstable due to the high reactivity of nanoparticles caused by the high fraction of the atoms located on the surface. The high reactivity of the metallic surface of the particles allows their functionalization with solvent molecules from the