



## Effect of thermal treatments on the morphology, chemical state and lattice structure of gold nanoparticles deposited onto carbon structured monoliths



Diego Ballestero<sup>a,\*</sup>, Roberto Juan<sup>b</sup>, Alfonso Ibarra<sup>c</sup>, Carmen Gómez-Giménez<sup>b</sup>, Carmen Ruiz<sup>b</sup>, Begoña Rubio<sup>b</sup>, María Teresa Izquierdo<sup>b</sup>

<sup>a</sup> Instituto de Medioambiente, Universidad San Jorge, Autovía A-23 PK 299, 50830 Villanueva de Gállego (Zaragoza), Spain

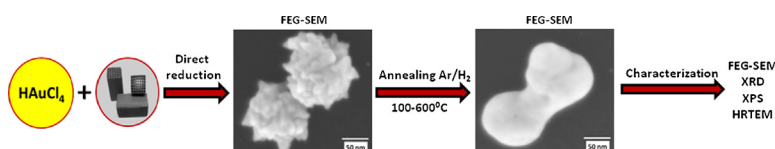
<sup>b</sup> Instituto de Carboquímica, ICB-CSIC, c/ Miguel Luesma, 4, 50018 Zaragoza, Spain

<sup>c</sup> Instituto de Nanociencia de Aragón INA-LMA, Edificio I+D – Campus Río Ebro, c/ Mariano Esquillor s/n, 50018 Zaragoza, Spain

### HIGHLIGHTS

- Gold nanoparticles are deposited onto carbon monoliths.
- Gold is reduced by the carbon support itself.
- Materials are characterized by different techniques FEG–SEM, XRD, XPS and HRTEM.
- Heat treatment led to changes in gold particle morphology.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Gold nanoparticles (GNPs) were deposited onto carbon monoliths through direct chemical reduction of cationic gold sources. Colloidal gold particles were also deposited onto the same type of support to prepare a reference material. The Au/C structured materials were subjected to thermal treatment (annealing) up to 600 °C. Transformations in size, shape, chemical state and possible modifications in the lattice structure of GNPs due to thermal effects were evaluated by field emission gun (FEG), scanning electron microscopy (SEM), X-ray diffraction, X-ray photoelectron spectroscopy (XPS) and high resolution transmission electron microscopy (HRTEM). Evolution in size and shape of GNPs is compared with some of the models described in the bibliography for the melting of nanoparticles. No modification to either the lattice parameter or atomic structure in gold crystals was detected following annealing. The sintering process among gold nanoparticles could be observed in situ through HRTEM showing the aggregation mechanism for these particles.

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## 1. Introduction

Nanomaterials have recently become of increasing interest owing to their unique physical and chemical attributes which are significantly different from their bulk state. Among these

nanomaterials, gold nanoparticles (GNPs) have drawn a great deal of attention from researchers because of their various promising properties. In recent years, gold has attracted growing interest since it has been shown that GNPs exhibit enhanced activity as catalysts, i.e. in CO oxidation at room temperature [1].

At the nanoscale level, GNPs exhibit a distinctly different color and appearance and they are reported to provide many potential applications in electronic and optical detection systems [2,3], therapeutics [4], catalysis [5,6], and the environment [7–9].

\* Corresponding author. Tel.: +34 976060100; fax: +34 976077584.  
E-mail address: [dballestero@usj.es](mailto:dballestero@usj.es) (D. Ballestero).

The optical, electronic, and catalytic properties of GNPs correlate to the physical characteristics of the particles, such as size [10,11] and shape [12–14]. Therefore, GNP properties are strongly related to the core size of the particles and, as the size of the particles decreases, the fraction of the atoms present on the vertex and edge sites increases in comparison to the terrace sites [15]. Precise control of the structural properties of GNPs, such as size, surface chemistry, and even crystalline character, is a key goal for improved understanding of their optical, electronic, chemical, and electrochemical properties [16].

Surface atoms of GNPs have a great effect/influence on physical and chemical properties; these atoms present less cohesive energy [17] than bulk material because they have fewer neighboring atoms compared to atoms in the bulk. Each chemical bond provides chemical energy, so atoms with fewer bonds and neighboring atoms have lower cohesive energy.

In recent years, there has been growing interest in GNPs deposited onto different supports, especially in catalyst applications where the presence of a support plays an important role in controlling the morphology of the particle. Preparation of the catalysts usually includes treatment at high temperatures (800–1000 °C) [18], with the catalysts being stable under thermal treatment.

Other applications of GNPs deposited onto supports are focused on environmental applications, such as materials for mercury capture which are subjected to thermal treatment at 300–350 °C during preparation [19,20]; however no mention is made about possible changes in the GNPs of the materials due to the thermal treatment involved in their preparation (annealing).

Thus, it is known that the melting point is a physical property that is affected by the size of the material. In effect, the melting temperature of a bulk metal is not dependent on its macroscopic size but it can decrease for metals at nanometric scale [21]. In other words, the physical properties of nanoparticles differ greatly from those of their bulk counterparts due to the enhanced surface-to-volume ratio in small sizes. Takagi was the first to observe the melting point depression of several types of metal nanoparticles [22] where the diffraction patterns changed from characteristic crystalline patterns to liquid patterns. Nanoparticle shape also impacts on the melting point of a nanoparticle. Facets, edges and deviations from a sphere all change the magnitude of melting point depression [23]. Different shapes affect the surface to volume ratio, which affects the cohesive energy and thermal properties of a nanostructure.

The specific melting process for nanoparticles is currently unknown. There are several models for possible mechanisms of nanoparticle melting [24]. The liquid drop model (LDM) assumes all atoms have the same cohesive energy so that an entire nanoparticle will melt at a single temperature [23]. Moreover, this model assumes that the surface atoms of a nanoparticle dominate the properties of all atoms in the particle. The liquid shell nucleation model (LSN) predicts that a surface layer of atoms melts prior to the bulk of the particle [25], the melting process depends on its radius of curvature, and therefore, large nanoparticles melt at higher temperatures than smaller ones. The liquid nucleation and growth model (LNG) treats the melting of nanoparticles as a surface-initiated process [26] with the liquid–solid interface advancing quickly through the entire nanoparticle. The bond order length strength (BOLS) model employs an atomistic approach focused on the cohesive energy of individual atoms [27]. This model predicts that surface layers of a nanoparticle will melt at lower temperatures than the bulk of the nanoparticle.

The LSN model applied to the melting temperature of gold particles is in strong agreement with one of the phenomenological models proposed some time ago to explain experimental results obtained by scanning electron-diffraction [28]. In effect, those

results are found to be in satisfactory agreement with that model, which assumes the pre-existence of a liquid layer surrounding the solid particle.

On the other hand, it is known that when two or more gold particles are very close, and subjected to heat, coalescence begins and another irregular particle is formed from regular particles. This phenomenon can be considered as a manifestation of the model based on the neck growth rate [29] used to describe the evolution of sintering of particles of equal size during the early stages, although these simulations [30] and models use much smaller particles (under 5 nm) than the average size of those in the materials studied here. The mechanism for sintering nanosized particles is different from simulations for micronized particles using molecular dynamics (MD), due to the fact that nanocrystals are faceted, while the sintering theories are formulated for macroscopically smooth crystallites. Similar simulations for particles which present quite different sizes suggest that they can also be sintered in the early stages by surface diffusion [31] and by grain boundary diffusion, this last being commonly used for particles larger than 4 nm [32].

If heating the particle after early sintering is continued, a gradual tendency to reach a spherical shape (hemisphere) would occur after the neck growth with energy release due to the surface area reduction; this fact has been shown in a graphical view by simulation of the coalescence of GNPs at high temperature [32]. These simulated processes have recently been investigated for supported GNPs sized approximately 100 nm [33], using FEG–SEM and optical techniques for monitoring the coalescence, concluding that melting is the major mechanism involved in coalescence. Melting has been found [30] to primarily affect the surface (“premelting”), then proceed inwards.

This work studies the influence of annealing on the size, shape, crystalline structure and chemical state of the GNPs deposited on carbon monoliths using a novel methodology described elsewhere [34] which involves the carbon acting as a reductor to avoid the use of other chemicals that can be harmful for environment. Furthermore, morphological changes on GNPs are contrasted with the behavior of deposited colloidal GNPs (particle size <30 nm and almost circular in shape) under similar thermal treatment. GNPs will be characterized by FEG–SEM, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and HRTEM. The novelty of this research deals with the final characteristics of the GNPs depending on the deposition method and the structured carbon support used in this work, because no studies have been reported previously in the literature on this topic.

## 2. Methodology

### 2.1. Preparation of samples

Two kinds of materials based on carbon monoliths (CM) with gold nanoparticles deposited into channels were prepared by different procedures: (1) direct reduction of Au<sup>3+</sup> solution and (2) deposition of colloidal gold.

The first preparation was carried out according to the methodology described in a previous paper [34] using HAuCl<sub>4</sub>·3H<sub>2</sub>O as a gold source dissolved into a water/ethanol (1:1, vol) mixture and depositing the gold onto CM under the specific conditions described for MC–Au–2 material, also appearing in that paper.

Colloidal gold was prepared by citrate reduction based on the Turkevich recipe [35] and taking into account the results found by other researchers on the influence of pH [36] and molar ratio gold/citrate [37,38] on the final particle size. Some changes were introduced in the recipe in order to combine a higher gold concentration with an average particle size of about 20 nm under stable conditions: A 100 ml gold solution (0.8 g HAuCl<sub>4</sub>·3H<sub>2</sub>O/l) with an

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