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Preparation and microscopic characterization of magnetite–gold mesoparticles with tunable morphology

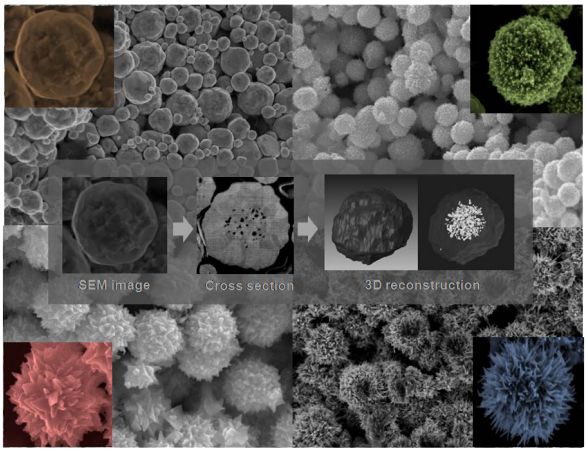
Paulina Lloret [a], Gabriel Ybarra [a], Pablo Granell [b], Leandro Socolovsky [c], Carlos Moina [a,*]

[a] Unidad Técnica Nanomateriales, INTI-Procesos Superficiales, Instituto Nacional de Tecnología Industrial, San Martín, Argentina
[b] Centro de Micro y Nanoelectrónica del Bicentenario, Instituto Nacional de Tecnología Industrial, San Martín, Argentina
[c] Laboratorio de Sólidos Amorfos, Facultad de Ingeniería, Universidad de Buenos Aires, Argentina

HIGHLIGHTS

- Magnetite-gold mesoparticles were prepared with controlled morphology by adjusting the concentration of reactants and surfactants used in the synthesis.
- A structural study was carried out by using FIB/SEM technology which revealed that the inner structured of the particles is composed by iron oxide nanoparticles and gold crystals.
- A tridimensional reconstruction was created from SEM images of sliced mesoparticles by focused ion beam.

GRAPHICAL ABSTRACT



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ABSTRACT

Composite magnetite–gold mesoscopic particles were prepared by deposition of Au onto magnetite nanoparticles. The surface morphology of the mesoparticles could be tuned by controlling the factors that affect the kinetics of the reactions and by adding surfactants that direct the growth of gold crystals. The internal structure of composite mesoparticles was analyzed by focused ion beam and scanning electron microscopy. A particle-mediated growth mechanism of formation was proposed.

1. Introduction

Despite their impressive wealth of applications [1–4], nanoparticles present drawbacks inherent to their nanoscale condition [5]. Their high area to volume ratio and extremely small size make them prone to suffer from problems in terms of thermal stability, shape preservation, and manipulation. One of the strategies currently being developed to mitigate these problems consists in the preparation of larger particles that only some of the properties characteristic of nanoscale materials are preserved. Therefore in recent years, there has been an increasing interest in the synthesis, characterization and applications of particles with a size in the mesoscale (roughly between 100 nm and 1 μm). Considerable effort has been made in order to obtain mesoscopic particles (mesoparticles) of controlled size and morphology formed by the

* Corresponding author.
E-mail address: moina@inti.gov.ar (C. Moina).

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controlled aggregation of nanoparticles [6]. Mesoparticles prepared in such a way are expected to show a higher stability and to be easier to handle, while other nanoscale properties are expected to be retained.

Important progress has been recently made in the preparation and the understanding of the mechanism of growth of mesoscopic particles formed by the aggregation of nanoparticles, especially regarding the formation of metallic mesocrystals [7]. A mesocrystal is a mesoscopic particle composed by a number of individual nanocrystals aligned along a common crystallographic direction, forming an ordered mesoscale superstructure [8]. A mechanism of formation has been proposed for gold [9] as well as for silver metallic mesocristals [10]. The proposed mechanism involves four stages: initially, Au atoms are formed by chemical reduction; subsequently, Au atoms aggregate and form nuclei; then metallic nuclei aggregate to form mesoparticles in a process called particle-mediated growth; finally, Au atoms deposit onto the mesoparticle defining the final morphology of the mesoparticle. The final phase is called overgrowth and can be chemically controlled so that the resulting morphology can be tuned.

The preparation of magnetite microparticles of controlled surface morphology and internal structure has also been recently reported [11]. The authors proposed a particle-mediated growth mechanism which shares similarities with the one proposed for metallic mesoparticles: under appropriate conditions, nuclei are formed and then aggregate, while the morphology and size of the particles is defined during the overgrowth (in this phase, Ostwald ripening can also take place and modify the internal structure of the particle; this process is not possible for metallic mesocrystals).

Few studies have focused on the formation of mesoparticles composed by two dissimilar materials, such as magnetite and gold [12–15]. Moreover, a microscopic characterization of their internal structure has never been carried out and the mechanism of formation has not been properly discussed. In this paper, we present the preparation of magnetite and gold mesoparticles with tunable morphology, characterize their surface morphology and internal structure by scanning electron microscopy (SEM) and focused ion beam (FIB), and propose a particle-mediated growth mechanism of formation of mesoparticles.

2. Experimental

2.1. Synthesis of the mesoparticles

A co-precipitation method was used to obtain Fe_3O_4. 12 g of $FeCl_3.6H_2O$ were dissolved in 75 ml of deionized water and 6 g of $FeCl_2.4H_2O$ dissolved in 25 ml of deionized water was added. 25 ml of concentrated ammonium hydroxide was dropped into the iron solution with stirring. A black precipitate was obtained and washed four times with the aid of a permanent magnet. Then, 30 mg of Fe_3O_4 were added to 80 ml of a solution of toluene containing 3.5 mM of oleic acid and c mM of oleylamine, with $c = 1.2$, 2.4 and 24 mM and redispersed with ultrasonic agitation.

Four different types of mesoparticles were prepared. For the synthesis of the Type I and II particles, a solution of gold in toluene was obtained by dissolving 0.13 mmol of Au from $KAuCl_4.xH_2O$ (49% Au, Aldrich) in 20 ml of 2-propanol and then added to 100 ml of toluene.

For synthesis of Type III and Type IV particles, a solution of 0.13 mmol of $KAuCl_4.xH_2O$ (49% Au, Aldrich) in 40 ml of water was extracted with 100 ml of 1.5 mM solution of tetraoctylammonium bromide.

In all cases, the magnetic dispersion was added to the organic gold solution and 5.9 mM of hydroquinone dissolved in 20 ml of 2-propanol were added.

Mesoparticles were obtained after 12 h of reaction. Particles were collected with a permanent magnet and washed with toluene and 2-propanol and dried under vacuum.

2.2. Microscopic characterization

The structure of the Type I and Type III particles was characterized with a FEI Helios Nanolab 650 Scanning Electron Microscope/Focused Ion Beam (FIB/SEM) dual system. For 3D reconstruction of Type I mesoparticles, a set of high resolution SEM images was obtained from equally spaced FIB cross sections in an automated process. The images were then aligned and color segmented with an image processing software, and the volumes were rendered. In the sample preparations, a protective Pt layer of about 1–2 μm was deposited before ion beam milling. To study the particle structure by scanning transmission electron microscopy (STEM), thin lamellae of the sample were extracted and attached in-situ to a TEM half-grid by FIB milling and Pt deposition. The lamella was then thinned and polished to a final thickness of about 50 nm, suitable for STEM imaging. Electron diffraction images were taken with a Philips CM200 TEM microscope.

3. Results

Magnetite–gold mesoparticles have been prepared by the reduction of $AuCl_4^-$ in a dispersion of magnetite nanoparticles stabilized by oleylamine and oleic acid. Hydroquinone has been used as a reducing agent. Fig. 1 shows SEM images of mesoparticles prepared under different conditions. The morphology of the synthesized magnetite–gold mesoparticles could be controlled by the concentration of oleylamine and TOAB. Roughly spherical mesoparticles were obtained when an oleylamine concentration of 1.2 mM was used in the absence of TOAB (Type I particles). When the concentration of oleylamine was increased up to 2.4 mM in the absence of TOAB, mesoparticles with small gold protuberances of about 30 nm in the surface (Type II particles) were obtained. The presence of TOAB has a strong effect in the morphology of the mesoparticles. When an oleylamine concentration of 2.4 mM and a TOAB concentration of 1.5 mM were used, mesoparticles with a flower-like morphology were obtained (Type III particles), showing large pyramidal protuberances of gold. When the concentration of oleylamine was increased to 24 mM, keeping the TOAB concentration at 1.5 mM, nearly spherical mesoparticles with thin gold thorns were obtained (Type IV particles).

From these results, it is clear that oleylamine and TOAB play a key role in the fine tuning of the morphology of the mesoparticles. Oleylamine, in the absence of TOAB, promotes the formation of protuberances, as can be seen comparing Type I and Type II particles, where the oleylamine concentration was increased approximately four times. When TOAB is present in the synthesis media, the mesoparticles develop large protuberances, pyramidal at low TOAB concentrations corresponding to Type III particles and thorn-like at high TOAB concentrations corresponding to Type IV particles. In fact, the morphology of the prepared mesoparticles can be continuously varied among the structures shown in Fig. 1 by controlling the concentration of oleylamine and TOAB in the reaction media. (See supplementary information.)

It is worth noting that no free magnetite nanoparticles could be seen in these images. Since these mesoparticles presented a superparamagnetic behavior similar to that found for magnetite nanoparticles, it can be concluded that magnetite nanoparticles were present in the interior of the mesoparticles. In order to elucidate the question of the presence of the magnetite nanoparticles, as well as the internal structure of the mesoparticles, focused ion beam was used to progressively remove slices of a single mesoparticle, while the resulting sliced mesoparticle was observed by scanning electron microscopy (see Fig. 2).

It must be noted that internal structure of whole gold–magnetite mesoparticles could not be studied by TEM, because the presence