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Morphological and compositional characteristics of bimetallic core@shell nanoparticles revealed by MEIS

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ABSTRACT

In this paper we report the application of a suitable methodology to study the morphology, structure and composition of core@shell nanoparticles (NPs) systems with polydispersity in the shell thickness, with subnanometer resolution and good sampling. Through the combination of Medium Energy Ion Scattering with Transmission Electron Microscopy, we perform a systematic investigation on core@shell Au@Ag NPs synthesized by an original wet chemical method. For samples synthesized with baths of different $AgNO_3$ concentrations, the present approach allowed us to determine the NP's Ag shell thicknesses distribution of about a few nanometers around the Au core.

1. Introduction

The particular optical properties of colloidal metallic nanoparticles (NPs) have been applied on glass technologies for thousands of years in the human history. Particularly, the use of NPs composed by gold and silver in glasses has been noticed since the Roman era [1]. Nowadays, bimetallic NPs still are of immense interest from both, the scientific and the technological points of view, since their physical properties can be controlled by tuning the NP characteristics such as size, shape, composition, crystallinity and surface properties. Bimetallic core@shell NPs form an important class of nanostructures whose applications are linked to catalysis, cancer immunotherapy, hydrogen fuel-cell devices and plasmonics among others [2–10]. In these systems, each NP has a multicomponent nature and its parameters can be individually tuned to manipulate the desired properties accordingly with a specific application. For example, the control of Ag shell thickness in Au@Ag NPs systems allows the tuning and enhancement of the Ag resistance to oxidation, which is important for the development of plasmonic sensors [8]. Irrespective to the wide variety of synthetic procedures available in literature [11,12], the formation mechanisms of core@shell NPs and even single-component NPs have been much less investigated. Therefore, the understanding of how several synthesis parameters operate is limited and so is the control over the characteristics of the NPs. The mechanistic studies require an accurate characterization of the properties of the produced NPs as a function of the synthesis conditions in order to unravel the physicochemical processes involved in their formation. A reliable characterization is necessary to precisely determine the relations between the structure of the NPs and their particular properties. Therefore, the developments of suitable techniques which allow the investigation of the NPs morphology, structure and composition with subnanometric resolution and good sampling, is a mandatory requirement [13]. Within this context, UV–Vis spectroscopy has been successfully employed to qualitatively characterize Au@Ag NPs owing to their plasmonic properties [14–16]. However, the quantitative morphological and compositional characterization by this technique has not been informed. Mainly, the difficulties for obtaining data about the morphology and the composition of NPs from UV–Vis are due to the need for a theoretical modeling of

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the spectra. Furthermore, Transmission Electron Microscopy (TEM) is the most commonly used technique for the study of the morphology and composition of Au@Ag NPs since the NPs can be individually analyzed and no modeling is needed. Conventional TEM, High Resolution TEM (HRTEM) and Scanning TEM with High-Angle Annular Dark-Field (STEM-HAADF) imaging in combination with Energy Dispersive X-ray Spectroscopy (EDS) technique have been successfully applied to resolve individual Au@Ag NPs shape, sizes of the Au core and the Ag shell as precisely identify well as their local composition [2,7–9,17–19]. However, a poor sampling is normally achieved since the analysis is usually performed only over tens to a few thousands of NPs. This restricts the TEM statistical analysis to samples that are nearly-monodisperse since, if the sample is polydisperse, the analysis would be unreliable. As a consequence, synthesis protocols which drive to polydisperse samples are limited to a merely qualitative analysis by the conventional techniques. With the lack of information, conclusions about the factors which contributes to a decreasing of sample quality may be lost and, also, the underlying mechanisms. The Medium Energy Ion Scattering (MEIS) technique, on the other hand, typically probes a sample area of about 10^8 times higher than TEM [20–22]. In addition, its use to analyze nanostructured systems has drawn great attention due to its potential as a tool for the characterization of the shape, size, local composition and stoichiometry of NPs systems [23–26]. Particularly on core@shell NPs, it has been recently demonstrated that MEIS is a powerful technique to investigate their compositional and morphological properties, such as the size of the core, thickness of the shell, as well as their local compositions with sub-nanometer resolution [27,22,26,28]. In addition, the recent development of the PowerMEIS software has expanded the possibilities of using MEIS, allowing to simulate and model MEIS spectra of any kind of nanostructured system, of any kind of shape, composition and spatial distribution [20,21,22,29,30].

In the present work we have extended the application of MEIS to a systematic investigation of the morphological and compositional properties of Au@Ag NPs which are polydisperse in both, morphology and composition. The Au@Ag NPs were produced by chemical reduction of water soluble metal salts precursors in a seed-mediated approach. Through the TEM observations, the typical average NPs sizes and shapes were obtained, which allowed the definition of a geometrical model to be used as an input for the MEIS analysis with PowerMEIS. The local compositional and morphological parameters were later refined. Following this procedure, the size distribution of the seed Au NPs was obtained; the formation of single Ag NPs in addition to a Ag layer on the Au NPs were identified, and the Ag shell thickness and its dispersion were determined.

2. Experimental

Au NPs seeds synthesis (s112): 1 mL of 0.1 M $NaBH_4$ ice cold solution was added under vigorous stirring into 50 mL of 0.2 mM $HAuCl_4$ and 2 mM HAc (Acetic Acid) aqueous solution heated up to 90 °C. The heating was kept for 30 min until reaction was complete. The Au NPs obtained are named hereafter as “seeds” or “gold seeds”.

Au@Ag NPs synthesis: core@shell NPs were synthesized by using a seed mediated approach, where gold seeds are added into reactive solutions (baths) for the silver deposition to take place. A typical bath is a solution containing $AgNO_3$ and a mild reducing agent in acid pH values. In this work the baths were formed by a 0.5 mM NH_3/2 mM HAc buffer (pH $\sim$ 6), 0.1 mM Hydroquinone (H_2Q) and variable $AgNO_3$ concentration: 0.02 mM (s113), 0.03 mM (s114) and 0.04 mM (s115). In these solutions nucleation of Ag NPs does not occur for at least a few hours as the spectroscopic evidence suggests.

In all cases, core@shell NPs were obtained by adding 0.1 mL of the gold seed suspension into 10 mL of the bath under stirring. The reaction was complete after approximately 2 h, after which stage no significant changes were detected in the spectroscopic signal.

Routine characterization: The extinction spectra of the NPs where recorded using a Shimadzu UV-1200 spectrometer with a 1 cm quartz cell at room temperature. For the morphological characterization, several Transmission Electron Microscopy (TEM) measurements were taken in a JEM-JEOL 1120 microscope employing an 80 kV accelerating voltage. TEM samples were prepared without any purification treatment by seeding many drops of the colloidal solutions onto a Formvar-carbon-covered cooper grid and evaporating the water in air at room temperature.

MEIS characterization: The MEIS measurements were performed using a 151.9 keV He^+ beam from the 500 kV electrostatic accelerator at the Ion Implantation Laboratory, Institute of Physics – UFRGS. The samples were mounted in a 3-axis goniometer inside the analysis chamber kept under a pressure of about 10^{-7} mbar. Typical beam current was less than 15 nA. The normal incidence was used and backscattered He^+ ions emerging from the target were analyzed using a Toroidal Electrostatic Analyzer (TEA) mounted at 120° with respect to the beam direction. At the top end of the TEA a set of two microchannel plates coupled to a position-sensitive detector allows each ion to be energy- and angle-analyzed leading to 2-D spectra. The TEA angular aperture is 24° and each angle bin corresponds to 0.08°. The overall energy resolution of the system is 500 eV. Details of the data analysis are described in Refs. [20,21,22,29,28]. The ion scattering intensities were analyzed by using the PowerMEIS program [29]. This software calculates the ion scattering intensities as a function of the backscattering energy and angle. For this purpose, the sample is discretized in space by using 3D matrices, where each matrix element stands for specific composition, stoichiometry and density of the material. In this way the set of NPs was generated with specific shapes, size and pair correlation function. The PowerMEIS program can handle any geometric shape, size distribution, and density of the nanostructures. It also accounts for the asymmetry of the energy loss-distribution due to the backscattering collision and also multiple scattering effects.

MEIS samples preparation: Si/SiO_2 wafers were functionalized with APTES (3-Aminopropyltriethoxysilane) in order to improve the binding of NPs to the surface. The Si/SiO_2 functionalized wafers were prepared by immersion in ethanol and ultrasonication during 2 h, then the wafers were immersed in a toluene 1% APTES solution by 30 min. After, the wafers were rinsed with ethanol and milli-Q water. To bind NPs to the substrate surface, the functionalized wafers were immersed by 24 h in the NPs solutions; finally they were washed with milli-Q water and dried at room temperature before the MEIS measurements. The samples' morphology was characterized by atomic force microscopy (AFM) using a Bruker-Innova system in tapping mode at air. The topological images were processed with the WSxM 5.0 software [31]. The AFM images indicate that NPs are attached in an homogenous distribution onto the surface with very little aggregation (see Fig. S1 on the Supporting Information).

3. Results and discussion

Fig. 1a shows a typical TEM image of the sample containing Au NPs seeds whereas in Fig. 1b is shown its size distribution. The NPs appear to be small spheres with a narrow size distribution, with radius of (3.5 ± 0.6) nm.

Fig. 2a shows the extinction spectra corresponding to Au@Ag NPs obtained by varying the baths' $AgNO_3$ content (lines blue, green and black). If compared this spectra with those of the seeds NPs (red line), the Surface Plasmon Resonance (SPR) peak associated to