



Determination of the structure and composition of Au-Ag bimetallic spherical nanoparticles using single particle ICP-MS measurements performed with normal and high temporal resolution

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ARTICLE INFO

Keywords:

Bimetallic nanoparticles

Core-shell

Alloy

Gold

Silver

Inductively coupled plasma mass spectrometry

ABSTRACT

In this study, the information that can be obtained by combining normal and high resolution single particle ICP-MS (spICP-MS) measurements for spherical bimetallic nanoparticles (BNPs) was assessed. One commercial certified core-shell Au-Ag nanoparticle and three newly synthesized and fully characterized homogenous alloy Au-Ag nanoparticle batches of different composition were used in the experiments as BNP samples. By scrutinizing the high resolution spICP-MS signal time profiles, it was revealed that the width of the signal peak linearly correlates with the diameter of nanoparticles. It was also observed that the width of the peak for same-size nanoparticles is always significantly larger for Au than for Ag. It was also found that it can be reliably determined whether a BNP is of homogeneous alloy or core-shell structure and that, in the case of the latter, the core comprises of which element. We also assessed the performance of several ICP-MS based analytical methods in the analysis of the quantitative composition of bimetallic nanoparticles. Out of the three methods (normal resolution spICP-MS, direct NP nebulization with solution-mode ICP-MS, and solution-mode ICP-MS after the acid dissolution of the nanoparticles), the best accuracy and precision was achieved by spICP-MS. This method allows the determination of the composition with less than 10% relative inaccuracy and better than 3% precision. The analysis is fast and only requires the usual standard colloids for size calibration. Combining the results from both quantitative and structural analyses, the core diameter and shell thickness of core-shell particles can also be calculated.

1. Introduction

Bimetallic nanoparticles (BNPs) have appealingly tunable magnetic, catalytic and optical properties, therefore they have been designed and synthesized in great numbers for novel application areas in recent years [1–3]. Synthesis routes via various chemical reactions (e.g. co-reduction, thermal processing, seeded-growth, galvanic replacement), physical methods (e.g. spark discharge, laser ablation, atomic layer deposition) and „green”/biological approaches (based on plants or microbes) have been equally proposed and are in use, as described in recent reviews covering this area [4–7]. Among all BNPs, the noble metal-containing types are particularly popular [2].

A wide range of applications of BNPs relies on their tunable magnetic properties, controllable by the quality of elements, their concentration ratio, distribution and geometry (structure). Many works demonstrated that the presence of a noble metal in the BNP leads to high magnetic anisotropy, high saturation magnetization and coercivity. These features enable engineering applications such as the fabrication of microwave absorbers or magnetic recording media, and biomedical applications including contrast enhancing in diagnostic magnetic resonance imaging (MRI) and magnetically directed drug delivery (e.g. chemotherapeutic agents can be attached to or encapsulated in magnetic NPs) [8,9].

Another important BNP application area is catalysis. The in-

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roduction of a second metal into a catalytic nanomaterial structure can bring better catalytic activity, selectivity and stability, afforded by the opportunity for catalytic fine-tuning relying on bimetallic complementarity and synergisms. Cost-savings can also be realized by reducing the amount of more expensive metals (e.g. platinum group elements) typically used in catalysts [2,3,5]. In addition, some BNP catalysts have been proved to undergo a reversible change in the surface composition and chemical state during surface chemical reactions, based on which the concept of „smart” catalysts was also proposed [10].

Core-shell BNP structures have been shown to offer unique optical properties inaccessible by monometallic NPs, such as strong and wide, tunable absorption bands not only in the UV–Vis [11], but also in the NIR range, which can be exploited in plasmonic applications [12]. For example, Au–Pd and Au–Ag core–shell NPs showed greatly improved (e.g. 50000-fold) surface-enhanced Raman scattering (SERS) activity compared to that of their monometallic core alone. In addition, surface plasmon resonance (SPR) peaks of Au–Ag nanocages with controllable pores were found to change with the size and location of the pores [8].

BNPs have already proved their usefulness in several biomedical applications too. These include therapeutic uses such as local hyperthermic treatment and targeted drug delivery for cancer, or diagnostic uses, such as contrast enhancing in MRI imaging [9]. Last, but not least, BNPs can also be used in sensor assemblies by exploiting their advantageous features as catalytic or optical characteristics in order to boost the selectivity and sensitivity of optical and electrochemical sensors [13–15].

The morphological and compositional characterization of zero dimensional nanocomposites or BNPs are traditionally done by a combination of methods including electron microscopy (TEM, SEM-EDS), X-ray diffraction (XRD), UV–Vis spectroscopy, X-ray photoelectron spectroscopy (XPS), or atomic spectroscopy following dissolution [16,17]. Single particle, or particle-mode, inductively coupled plasma mass spectrometry (spICP-MS) is an emerging, versatile and high-throughput nanoparticle (NP) characterization technique. In this technique, ICP-MS spectrometers are used in the time-resolved mode for the measurement of dilute nanodispersions. Each detected NP produces a narrow signal peak (a few hundred μ s in duration) with a height that is proportional to the mass of the analyte in the NP. The dwell time (or integration time) is typically in the 5–10 ms range in order to minimize the occurrence of signal peak overlaps. By the statistical evaluation of the signal time profiles, information can be obtained about not only the elemental (isotopic) composition of the NPs, but also their characteristic size and distribution, as well as the particle concentration. The measurement only takes about 100 s. For monometallic NPs, typical size detection limits range from 10 to 30 nm [18–21]. Recently, quadrupole ICP-MS instruments with 100 μ s or less dwell times („high resolution”) became available commercially (e.g. Perkin Elmer NexION). Although the introduction of high resolution spICP-MS (HR-spICP-MS) does provide new possibilities and certain advantages, such as offering dual-element detection capability, lowered spectral backgrounds and resolution of particle peak profiles, but it also seems to generate new drawbacks, e.g. increased split-particle events and decreased sensitivity [22–24]. Nevertheless, high time resolution in spICP-MS definitely provides a promising and interesting tool for the optimization of spICP-MS analysis and for obtaining more information about the nanoparticles.

The goal of the present study was to assess the capabilities of the combination of normal and high time resolution ICP-MS measurements for the characterization of the elemental composition and structure of bimetallic nanoparticles. The experiments were performed on spherically shaped, homogeneously and core-shell structured Au–Ag alloy nanoparticles, prepared by chemical synthesis for the purposes of the present study.

Table 1
ICP-MS instrumental settings and conditions.

Parameter/device	NexION350	Agilent 7700x
RF power	1400 W	1550 W
Plasma gas flow rate	16.0 L/min	15.0 L/min
Carrier gas flow rate	1.05 L/min	1.05 L/min
Plasma sampling depth	4 mm	10 mm
Dwell time in TRA mode	20 μ s	6 ms
Acquisition time in TRA mode	100 s	100 s
Nebulizer	MicroMist	MicroMist
Spray chamber	Cyclonic	Scott double-pass
Isotopes monitored	^{107}Ag , ^{197}Au	

2. Experimentals

2.1. ICP-MS instrumentation and data evaluation

Two ICP-MS instruments were used in the experiments. Normal resolution spICP-MS and solution-mode ICP-MS measurements were performed on an Agilent 7700x type instrument (University of Szeged, Szeged, Hungary), whereas HR-spICP-MS measurements were all carried out on a Perkin Elmer NexION 350 instrument (University of Natural Resources and Life Sciences, Vienna, Austria). NP data was always collected in the time-resolved analysis (TRA) mode. On the NexION 350, the Syngistix Nano Application Module was also used. The instrumental settings and conditions are summarized in Table 1.

HR-spICP-MS measurements on the NexION 350 produced millions of data during the acquisition time. Thus pre-processing of the collected data was necessary prior to the statistical evaluation. For this purpose, we developed and used a macro-based program, written in Visual Basic for Applications (Microsoft, USA). This program counted individual particle events in the dataset and calculated the transit time of their ion cloud. Particle discrimination was based on the condition that a particle peak should be preceded and followed by at least three datapoints with zero signal. The transit time was then calculated as the product of the number of data points in that event and the dwell time. The total particle signal for a given NP detection event was obtained as the sum of time-resolved signals in that event.

The data processing for spICP-MS measurements with normal (6 ms) time resolution and the statistical evaluation of all spICP-MS data was performed in Origin 8.5 (OriginLab, USA). Data evaluation in spICP-MS typically involves the plotting of signal histograms (counts vs. frequency diagrams). For Agilent 7700x TRA data, we use background correction by subtracting the mode of the background peak (fittable by a Poisson function) from the mode of particle peak (fittable by a log-normal function). The TRA data output by the NexION software has no background. All histogram operations were carried out using unit bin sizes.

2.2. Materials and methods

For spICP-MS size calibration purposes, a series of standard PELCO NanoXact nano-dispersions containing tannic acid capped gold and silver NPs obtained from Ted Pella (Redding, California, USA) were used. The certified size of the gold NPs used were 28.8, 39.3, 61.3 and 75.4 nm, whereas the diameter of the silver NPs were 43.4, 59.0, 82.1 and 95.7 nm. Sodium citrate stabilized, silver-shelled gold nanospheres with 79.0 nm diameter (51.0 nm core diameter and 14.0 nm shell thickness) were obtained from NanoComposix (San Diego, USA).

Gold-silver alloy nanoparticles - with 40:60, 60:40 and 80:20 M ratios - have been synthesized with the combination of co-reduction of gold and silver salts and seeded growth methodology [25]. The composition of alloy nanoparticles was controlled by changing the ratio of Au and Ag precursor salts. Stabilization of the particles was achieved by sodium citrate that also acted as a reducing agent during the synthesis.

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