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On the formation of ternary metallic-dielectric multicore-shell nanoparticles by inert-gas condensation method

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HIGHLIGHTS

- Preparation of FeAg multicores NPs with Si shell by inert-gas-condensation method.
- The size of NPs is increased by increasing their residence time in the aggregation zone.
- Thicker Si shell improves protection against oxidation and inhibits NPs aggregation.
- The increment of Si thickness induces an additional red-shift light absorption band.
- Mechanism of formation based on the physico-chemical properties of Fe, Ag and Si.

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ABSTRACT

Magneto-plasmonic hybrid nanoparticles (HNPs) are promising for a large number for dual magneto-optical bioapplications. Gas-phase techniques offer a good alternative to chemical routes for the generation of tailored HNPs. Here, we present a novel method to synthesize ternary HNPs composed of multiple dumbbell-like FeAg cores encapsulated by an amorphous Si shell. The method involves a simultaneous sputtering of Fe, Ag and Si targets under controlled conditions. We demonstrate that the morphology and the size of the HNPs can be modulated by tuning experimental parameters such as the energy and the cooling rate, or the collision and coalescence processes experienced by the HNPs during their formation. We find that by increasing the residence time of the HNPs in the aggregation zone, we increase both the size of the HNPs, and the thickness of the Si shell. HNPs exhibit ferromagnetic behavior and show an enhanced, red-shifted, light absorption band due to the strong near-field coupling between the Ag cores and the Si shell. A mechanism of formation of these HNPs is suggested, combining the physico-chemical properties of the materials (Fe, Ag, Si) with the experimental conditions.

1. Introduction

Due to their unique physical and chemical properties, multifunctional hybrid NPs that contain components with both magnetic and optical properties have emerged as attractive candidates for advanced biomedical applications, such as multimodal imaging, targeted drug delivery, and magnetic hyperthermia. In particular, dumbbell-like nanoparticles composed of magnetite (Fe_3O_4) and Au or Ag, are attractive because of their biocompatibility, plasmonic activity, and magnetic properties [1–7]. A broad range of techniques in chemistry and physics has been explored for the preparation of such multicomponent nanoparticles. Further details of synthesis, properties, and applications of dumbbell-like nanoparticles can be found in several review articles [1,8,9].

In the last decade, physical vapor deposition techniques have emerged as versatile methods for the production of hybrid inorganic nanoparticles. However, only a few attempts have been made to produce heterogeneous, dumbbell-shaped multicomponent nanoparticles [10,11], other than the widely reported core/shell nanoparticles [12,13]. In light of the present work, it is noteworthy to mention reports of the preparation of Fe-rich-core/Si-rich-shell nanoparticles using double glow discharge sources [14,15]. A recent study by Elsukova et al. [16], reported the behavior of AgFe

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HNPs prepared by magnetron sputtering with subsequent in-flight annealing, and demonstrated the instability of these HNPs under atmospheric conditions.

Further research and development of heterogeneous, dumbbell-like nanoparticles is needed to control their synthesis and to improve their resistance to degradation and aggregation. In order to use high-moment magnetic core materials such as Fe and Co, a stabilizer that does not affect their solid-state properties (especially magnetic and optical) is required to prevent agglomeration and degradation.

In this work, we present a one-step novel method to synthesize ternary magneto-plasmonic nanoparticles composed of multiple Fe–Ag cores encapsulated by a Si shell as a potential tool for magneto-optical bioapplications. This method is based on the co-sputtering of Ag, Fe and Si independent targets under controlled conditions of pressure and powers. The Si shell provides three advantages: i) it maintains a fixed spatial configuration between the multiple cores; ii) it prevents Fe cores from oxidizing; iii) it inhibits nanoparticle aggregation. Moreover, these hybrid nanoparticles show an enhanced, red-shifted, light absorption band due to the strong near-field coupling between the Ag cores and the Si shell.

For this purpose, the experimental conditions were adjusted and combined with the physico-chemical properties of the materials, to modulate the morphology and size of the HNPs. Transmission electron microscopy (TEM), including high-resolution imaging (HRTEM), scanning transmission electron microscopy (STEM), and electron energy loss spectroscopy (EELS), were used to examine nanoparticle morphology, structure, and composition. X-ray photoelectron spectroscopy (XPS) was used to study the oxidation behavior of the Si shell and Fe core. Magnetization measurements were carried out to evaluate the magnetic behavior of the HNPs. The optical response of the HNPs throughout the visible region is presented. Finally, we suggest a mechanism for the formation of these HNPs, based on the combination of the experimental conditions and the physico-chemical properties of the materials (miscibility and surface energy).

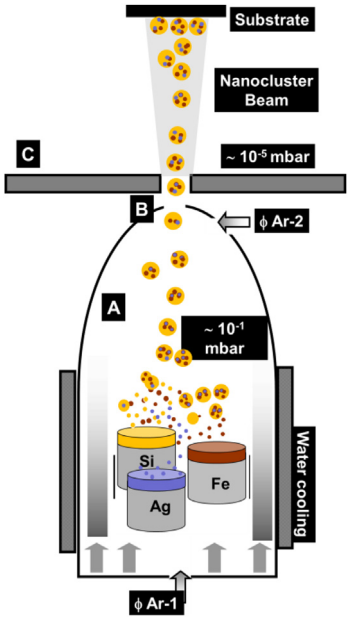

Fig. 1. Sketch of the nanoparticle source used in this study. (A) indicates the aggregation zone where the three (Ag, Si, and Fe) targets are DC co-sputtered in an Ar atmosphere. Working pressure is ~10^{-1} mbar. (C) shows the main chamber where nanoparticles are deposited on substrates. The pressure is maintained at ~10^{-5} mbar. The nanoparticles are extracted and accelerated by the differential pressure between the aggregation zone (A) and the deposition chamber (C) through the aperture (B).

2. Experimental section

The NPs synthesis technique used in this work is based on the condensation of an atomic vapor produced by sputtering multiple targets at high pressure (Fig. 1). Briefly, during the deposition process, targets are DC sputtered in an Ar atmosphere (~10^{-1} mbar working pressure) and a saturated vapor of metal atoms is

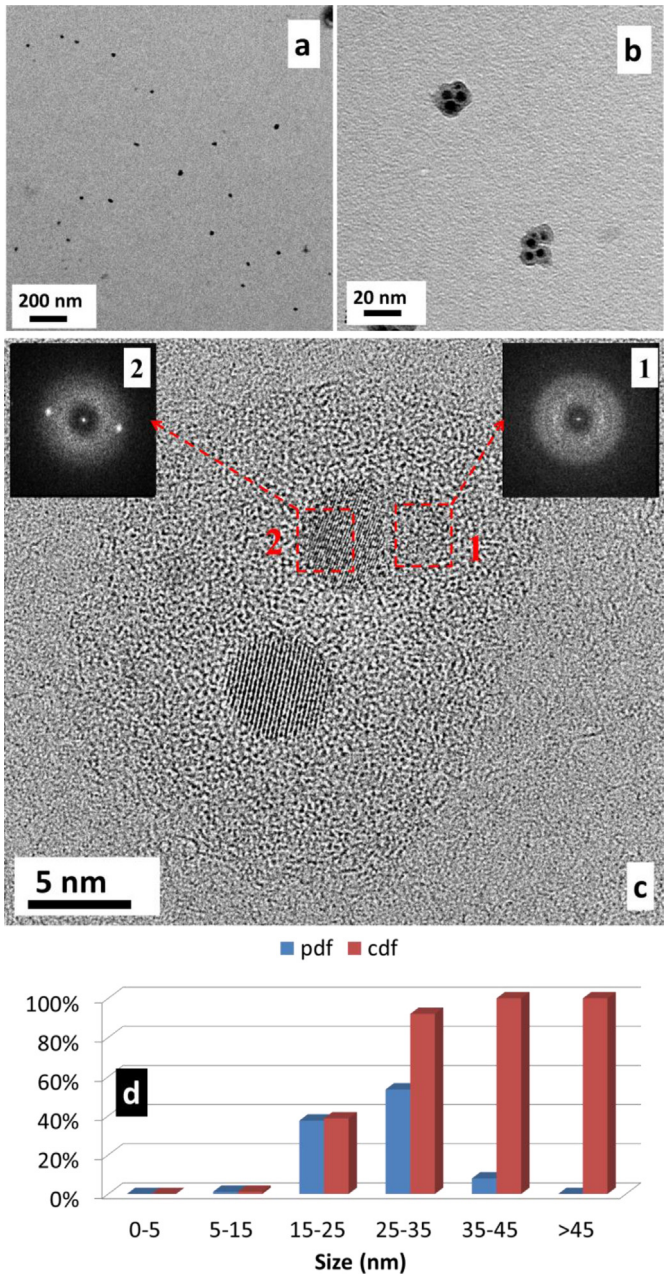

Fig. 2. Low magnification TEM images showing (a) the distribution, and (b) the multicore-shell morphology of HNPs-1. (c) High resolution TEM (HRTEM) image of two-core HNPs showing the differences in contrast within the dumbbell-like core and the Si amorphous shell. Insets show the FFT patterns corresponding to regions 1 and 2. The d-spacing measured from the pattern 2 corresponds to the d-spacing of the {111} planes of fcc Ag. The FFT pattern 1 demonstrates the amorphous structure of Fe. (d) Size probability distribution function (pdf) and cumulative distribution function (cdf) of HNPs-1.