Bifunctional Fe₃O₄/Ag nanoparticles obtained by two-step laser ablation in pure water

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ABSTRACT

Hypothesis: Bimetallic nanoparticles made of iron oxide and Ag could be fabricated by pulsed laser ablation of iron and silver targets in pure water by a two-step route. These nanoparticles could exhibit both magnetic and plasmonic properties.

Experiments: Bimetallic nanoparticles were fabricated by using a focused Nd:YAG nanosecond laser source emitting a 1064 nm wavelength radiation and characterized with z-potential, Dynamic Light Scattering (DLS), UV–vis absorption, Transmission Electron Microscopy (TEM), High Resolution TEM (HRTEM), Energy Dispersive X-ray Spectrometry (EDX), and Selected Area Electron Diffraction (SAED). The magnetic character of the nanoparticles was ascertained by observing attraction by a magnet and complete removing from the water environment, while their SERS (surface-enhanced Raman scattering) response was checked by decorating them with 2,2’-bipyridine as molecular reporter and performing Raman tests with green (514.5 nm) and far-red (785 nm) excitation wavelengths.

Findings: The observed magnetic attraction was due to magnetite (Fe₃O₄), the only ferromagnetic iron oxide form evidenced by the characterization tests in the aqueous colloidal system, where silver nanoparticles were also embedded. UV–vis and SERS spectra confirmed the presence of nanostructured silver as plasmonic constituent of the fabricated metal nanoparticles.

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1. Introduction

Binary metal nanoparticles offer potential applications in the fields of nanotechnology, environmental research, biomedicine
and heterogeneous catalysis [1–6]. These applications are often related to the Raman signal amplification of the adsorbed molecules by SERS (surface-enhanced Raman scattering) effect [7], due to the collective oscillations of free electrons on the nanostructured surface of noble metals excited by an incident radiation, known as localized surface plasmons. Plasmonic nanoparticles constituted by silver, gold or copper are commonly used as biosensors, drug delivery, SERS or fluorescence markers. In addition, they possess also an intrinsic biological activity. Indeed, the direct assumption by humans of silver or gold nanoparticles in proper doses has been demonstrated a highly biocompatible countermeasure to various inflammatory or infective diseases, as indicated by the huge number of market available products in form of colloidal solutions. Thus, these nanoparticles are per se biocompatible functional nanoplatforms, but their potential applications can be strongly implemented by adding complementary functionalities, like magnetic properties. For instance, in biomedicine they are exploited as diagnostic agents in magnetic resonance imaging (MRI), but also to generate hyperthermia through the application of locally intense alternating magnetic fields [8,9]. Actually, the fabrication of nanosized objects with both magnetic and plasmonic properties can open new perspectives in nanomedicine, where the use of theranostic nanoparticles, that is with both diagnostic and therapeutic potentials, is a demanding issue [10,11]. Here, we present the synthesis and characterization of Fe3O4/Ag nanoparticles obtained by two-step laser ablation of iron and silver targets in pure water, in order to obtain colloidal suspensions with magnetic properties, along with spectral tests demonstrating their SERS activity. Silver is by far the most suitable metal to provide SERS intensification, apart from marked anti-bacterial, anti-fungal and anti-inflammatory activities [12–15], as previously said. Fe3O4 magnetic nanoparticles present good biocompatibility and low toxicity [16–18] and are therefore widely used in biomedical applications. Recently, Fe3O4/Ag nanoparticles have been employed for catalytic purposes [19] as well as in biomedical research [20]. However, these nanocomposites are usually prepared by following chemical routes [21–25], with consequent issues due to the presence of surfactants, organic stabilizers, reducing agents and reduction by-products. Moreover, the interference of such molecules in SERS measurements can impair the detection of the analytes of interest. The laser ablation in pure water adopted in the present work represents a suitable method to bypass the above purity problems, and has been successfully adopted to fabricate magnetic nanoparticles (see, for instance, Ref. [26]), but very few works are reported aimed at fabricating with the same technique bimetallic nanoparticles with both magnetic and plasmonic characteristics. Very recently, Amendola et al. [27] prepared iron-doped silver nanoparticles by laser ablation in ethanol starting from a bulk bimetallic FeAg target. However, our method is quite different in both preparation and results: (a) the magnetic properties of our colloidal samples are ensured by the formation of magnetite (Fe3O4) by two-step laser ablation in pure water; (b) no organic stabilizer or surfactant is added, whereas the Amendola’s laser-generated nanoparticles were mixed with a solution of thiolated polyethylene glycol (PEG) and EDTA; (c) our entire colloidal samples undergo magnetic attraction, whereas in the Amendola’s sample a magnetic fraction had to be separated from a non-magnetic fraction.

2. Materials and methods

Iron (0.25-mm thickness, 99.99% purity) and silver (0.5-mm thickness, 99.9% purity) plates were purchased from Aldrich. Colloidal suspensions were prepared by laser ablation of iron and silver targets in deionized water (18.2 MΩ cm @ 25 °C) and characterized within two hours from the preparation. Laser ablation of iron and silver targets was performed with the fundamental wavelength (1064 nm) of a Q-switched Nd:YAG laser (Quanta System G90-10: rep. rate 10 Hz, pulse width at FWHM of 10 ns). The laser pulse energy was set at 20 mJ/pulse, corresponding to 200 mW average power, focusing the laser light into a laser spot of approximately 1-mm diameter and corresponding fluence of 2.5 J/cm2. The target plate was fixed at the bottom of a glass vessel filled with ~6 ml of liquid (height above the target: 2 cm). The irradiation time of the metal targets was about 20 min. To minimize effects due to crater formation in the metal targets, the glass vessel was manually rotated and translated, stopping the ablation process every three minutes. The laser pulse entered the vessel from above, thus impinging perpendicularly onto the target.

ζ-potential and Dynamic Light Scattering (DLS) analysis were performed with a Zetasizer Nano ZS90, Malvern Instruments. The temperature was fixed at 25 °C. Particle size measurements, obtained by Dynamic Light Scattering, ranges from 0.3 nm (diameter) to 5 μm, using 90° scattering optics.

UV–visible absorption spectra of the colloidal suspensions were obtained in the 200–800 nm region by using a Cary 5 Varian spectrophotometer.

TEM (Transmission Electron Microscopy) and HRTEM (High-Resolution Transmission Electron Microscopy) images were obtained after dipping carbon-coated Cu grids in the colloidal suspensions. Microscopic measurements, EDX (Energy Dispersive X-ray Spectrometry) analysis and SAED (Selected Area Electron Diffraction) patterns were performed with a Jeol 2010 instrument operating at 200 kV with 1.9 Å resolution, and equipped with a microanalytic system EDS Link ISIS EDX.

Micro-Raman spectra of metal nanoparticles deposited on aluminium plate were measured by a Renishaw RM2000 instrument, equipped with a diode laser emitting at 785 nm. Sample irradiation was accomplished by using the 50x microscope objective of a Leica Microscope DMLS. The backscattered Raman signal was fed into the monochromator through 40 μm slits and detected by an air-cooled CCD (2.5 cm−1 per pixel) filtered by a double holographic notch filters system. Spectra were calibrated with respect to a silicon wafer at 520 cm−1.

SERS spectra of the colloidal sample obtained by two-step Fe/Ag ablation after addition of 2,2'-bipyridine (Aldrich, purity > 99%) in 10−4 M concentration were measured by using the 514.5-nm line of a Coherent Argon ion laser, a Jobin-Yvon HG25 monochromator.

Fig. 1. FeAg colloidal sample, as obtained by two-step laser ablation (A), after application of magnetic field (B) and after successive removing of the magnet (C).
equipped with a cooled RCA-C31034A photomultiplier and a data acquisition facility. To reduce the thermal effects due to the laser light, a defocused beam with low power (50 mW) was used for irradiating the colloidal samples. Power density measurements were performed with a power meter instrument (model 362; Scientech, Boulder, CO, USA) giving $\pm 5\%$ accuracy in the 300–1000 nm spectral range.

3. Results and discussion

3.1. Colloidal stability

The colloids prepared only by iron ablation are unstable, exhibiting a slightly positive $\zeta$-potential (2.73 mV), and completely collapse after few hours. The colloidal stability gets better after the subsequent silver ablation. Indeed, the $\zeta$-potential goes to strongly negative values (~26.7 mV), due to adsorption on the silver surface of anions deriving from the aqueous solution, as well as in the case of silver colloids obtained by laser ablation [28]. In this situation, bimetallic colloids remain stable for several days. In the Supplementary Material, the $\zeta$-potential data are reported, as obtained by the Malvern instrument.

3.2. UV–visible absorption spectra

The colloidal sample obtained by double laser ablation of an iron target and then of a silver target (hereafter called FeAg colloid) totally collapses by applying a magnetic field (see Fig. 1), as well as the colloid consisting of only iron (hereafter called Fe colloid).

Fig. 2. UV-visible absorption spectra of the Fe (A) and FeAg (B) colloids (OPL = 2 mm).

The UV–vis absorption spectra of the Fe colloid (spectrum A) and of the FeAg colloid (spectrum B) are reported in Fig. 2. For the Fe sample, the spectrum shows a trend compatible with that expected for nanoparticles of ferromagnetic magnetite ($\text{Fe}_3\text{O}_4$) [29]. After the subsequent laser ablation of silver, the FeAg colloid shows also the typical plasmon band of spheroidal silver nanoparticles around 400 nm. Upon the application of an external magnetic field, the colloidal suspension becomes colorless and, correspondingly, the UV–vis spectral features completely disappear. This confirms the metal nanoparticles possess a magnetic response and can be totally removed from the aqueous medium.

3.3. Raman spectra

The Raman spectra of the colloidal nanoparticles obtained by laser ablation of iron in water, deposited on an aluminium plate, have been recorded in different points of the dried film, as shown in Fig. 3. The typical Raman band of magnetite ($\text{Fe}_3\text{O}_4$) occurs at

![Fig. 3. Raman spectra of the Fe colloid deposited on aluminium plate for different points of the dry film.](image)

![Fig. 4. Low-magnification TEM micrographs of the Fe and FeAg colloids deposited on carbon-coated Cu grids.](image)
665 cm$^{-1}$, in agreement with the results reported in the literature [30,31]; the Raman band of maghemite ($\gamma$-Fe$_2$O$_3$) around 720 cm$^{-1}$ [32] is not appreciably observed, even if the oxidation of magnetite to maghemite, which is also ferromagnetic, is likely to occur [33,34]. The typical Raman bands of hematite ($\alpha$-Fe$_2$O$_3$) [35], which is the most stable form of ferric oxide, that should occur at 292, 411, 612 cm$^{-1}$, are completely absent. The same Raman band at 665 cm$^{-1}$ is also found in the nanoparticles of the FeAg colloidal sample, without the presence of other bands.

3.4. TEM, HRTEM, EDX, SAED measurements

For both Fe and FeAg colloids the TEM images at low magnifications (Fig. 4) show a remarkable dimensional heterogeneity, with the presence of low-crystallinity material with mucilaginous aspect (low-contrast matrix) and of metal nanoparticles (black spheres) with sizes varying from 10 nm up to 250 nm in diameter. In the FeAg colloid such particles are more electron-dense and present in a larger amount.

For Fe colloidal sample the SAED electron diffraction and the EDX analysis (Fig. 5) indicate that both nanospheres and low-contrast matrix are made up of Fe oxide as magnetite (Fe$_3$O$_4$). The left figure shows a HRTEM image of the low-crystalline material with nanocrystals with diameters ranging from 20 nm to a few nm (few lattice fringes). In the same image, granules without lattice planes are observed, to be considered amorphous or with unfavorable orientations. In the SAED diffraction pattern, shown in the upper right panel, the measured interplanar distances

![TEM micrograph of a metal nanoparticle in the Fe colloid (left panel), along with SAED (top-right panel) and EDX (low-right panel) analyses.](image1)

![TEM micrograph of the FeAg colloid showing Ag nanoparticles embedded in low-contrast matrix (top-left panel), along with EDX (low panel) and SAED (top-right panel) analyses.](image2)
are corresponding to the planes (2 2 0), (3 1 1), (4 0 0), (4 4 0) and (5 1 1) of magnetite.

SAED diffraction and EDX analysis of the FeAg colloidal sample (Fig. 6) indicate larger nanocrystals composed of silver; magnetite is present as both nanocrystals and fine-grained matrix with low crystallinity. The Ag nanocrystals are characterized by lamellar nanostructures due to the presence of polysynthetic twinning formations.

3.5. SERS activity

The presence of the surface plasmon bands of nanosized silver particles, observed in the absorption spectra of the FeAg colloid (Fig. 2), points to a SERS activity of this bimetallic system. In order to find confirmation to this hypothesis, we have checked the SERS response of the FeAg colloid by excitation with both green-light (514.5 nm) and red-light (785 nm) laser lines. Strong SERS signals are obtained in the presence of 2,2’-bipyridine (bpy) in 10^{-4} M concentration, after addition of 10^{-3} M NaCl. The presence of coadsorbed chloride anions in the colloidal suspension is necessary for the SERS-activation of the silver nanoparticles obtained by laser ablation, as recently verified [28]. By excitation with the 514.5-nm laser line, the observed SERS bands are corresponding to two different forms of adsorbed bpy, as reported in the literature [36]. One of these forms is usually observed in Ag colloids without chloride activation [37], as shown in Fig. 7 (lower trace), with strong bands at 767, 1010, 1060 and 1304 cm^{-1}. The other one, characterized by SERS bands at 660, 1024, 1320 and 1490 cm^{-1}, is typical of the charge transfer (CT) complex [38], whose CT transition is resonant with the green-light exciting radiation [39]. The bimetallic nanoparticles deposited as dry film on aluminium plate show very strong Raman bands that all correspond to the charge-transfer complex.

The dry film is SERS-active also by excitation with the far-red line (785 nm wavelength) of the microRaman instrument (Fig. 8). In this case, we observe the SERS bands of the species usually adsorbed on silver, because there is not Raman resonance for the charge transfer complex, with relative intensities varying from point to point. The SERS activity by excitation at 785 nm may be due to the presence of coadsorbed chloride ions that activate both electromagnetic and chemical enhancement even in the NIR region [40–42]. This activation could be related to the formation of large metal aggregates in the deposited dry film, as shown in Fig. 9.

4. Conclusions

In summary, we have reported on the production of bimetallic nanoparticles possessing both magnetic and plasmonic characteristics in colloidal suspension by a two-step laser ablation of iron and silver in pure water. These nanoparticles have the following properties:

1. They are stable for some days in colloidal suspension and exhibit magnetic properties;
2. Colloidal silver is intimately linked to the ferromagnetic material; indeed, all the metal nanoparticles can be completely separated from the water host with a magnet;
3. Magnetite (Fe_{3}O_{4}) is the sole magnetic material present in the colloidal solution, because no evidence of other iron oxide (maghemite or hematite) has been found;
4. In addition to magnetic properties, the bimetallic colloidal nanoparticles also exhibit strong SERS activity by using laser excitation with green-light radiation (514.5 nm), as well as with far-red-light radiation (785 nm).

Moreover, it is worth to underline that magnetite appears in the form of both spheroidal nanoparticles with crystalline structure and low-crystallinity matrix with mucilaginous texture, which is able to incorporate the silver nanoparticles. These latter exhibit very good SERS activity even by excitation in the far-red spectral region.
region, that is close to the transparency window of the human tissues (around 800 nm wavelength), a clear advantage in view of their application as optical tracers for in vivo biological application. This paves the way to the use of these bifunctional metal nanoplatforms in theranostic medical applications, by exploiting their magnetic and plasmonic properties.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcis.2016.08.040.

References