

TUNING THE STRUCTURAL AND OPTICAL PROPERTIES OF GOLD/SILVER NANOALLOYS PREPARED BY LASER ABLATION IN LIQUIDS FOR ULTRA-SENSITIVE SPECTROSCOPY AND OPTICAL TRAPPING

E. MESSINA,^a L. D'URSO,^{a*} C. SATRIANO,^a E. FAZIO,^b M. G. DONATO,^c B. FAZIO,^c
C. D'ANDREA,^c O. M. MARAGÓ,^c P. G. GUCCIARDI,^c G. COMPAGNINI,^a AND F. NERI^b

ABSTRACT. The plasmon resonance of metallic Au/Ag alloys in the colloidal state was tuned from 400 nm to 500 nm using a laser irradiated technique, performed directly in the liquid state. Interesting optical nonlinearities, trapping effects and spectroscopic enhancements were detected as function of gold concentration in the nanoalloys. In particular a reduction of the limiting threshold was observed by increasing the gold amount. The SERS activity of the Au/Ag alloys was tested in liquid and in solid state in presence of linear carbon chains as probe molecules. The dependence of the increased Raman signals on the nanoparticle Au/Ag atomic ratio is presented and discussed. Finally preliminary studies and prospects for optical and Raman tweezers experiments are discussed.

1. Introduction

In these last years noble metal nanoparticles (NMNPs) have been largely studied because of their light confinement effects at the nanoscale as well as size-and-shape dependent optical properties. Thanks to these interesting features, NMNPs have attracted great attention in several fields, including optoelectronics, plasmonics and biomedicine. For instance, much effort has been devoted recently to the assembly of noble-metal nanoparticles with the aim of enabling novel methods for the detection of biomolecules via surface-enhanced Raman spectroscopy (SERS) or to improve the nonlinear optical response of specific materials[1, 2]. Nanostructures with well defined plasmonic properties and engineered surface functionalities can be obtained by various approaches. Among them, pulsed laser ablation (PLA) in water allows the synthesis of extremely stable metal colloids[3, 4, 5], ensuring the formation of contaminant-free nanostructures and the absence of by-products.

In this work, we describe a systematic study of the effects of the ablation parameters and re-irradiation treatments on PLA Au/Ag colloids properties using different spectroscopic techniques. Moreover we discuss some crucial aspects for applications in spectroscopy and optical trapping.

2. Experimental

Colloidal solutions of metallic Ag and Au were separately produced by PLA in Millipore water, using three harmonics (1064, 532 and 355 nm) outputs of a Nd:YAG laser operating at 10Hz (see more details about the preparation procedure in [4, 5]). In a second step, we mixed the Au and Ag colloids at the volume ratio of 20/80, 50/50 and 80/20. The as mixed solutions were irradiated with the same laser source at constant power density ($0.2\text{J}/\text{cm}^2$) and at different irradiation times. To test the presence of nanoalloys, optical transmittance spectra were acquired with a double beam spectrophotometer in the 200 to 900 nm wavelength range. The sample structural and morphological characteristics were investigated by Atomic Force Microscopy (AFM), depositing in air at room temperature some drops of the colloids onto suitable substrates.

The chemical composition was investigated by X-ray Photoelectron spectroscopy (XPS). Spectra were acquired using a system equipped with an Al K- α source (1486.6 eV) and a concentric analyzer. SERS spectra were excited by the 514.5 nm and the 632.8 nm radiation of an Ar ion and a He-Ne lasers, analyzed by a Jobin Yvon 450 mm focal length monochromator equipped with a CCD detector cooled at 77 K. A macro-configuration was used in order to avoid heating effects of the samples. Polyynes (sp-hybridized linear carbon chains) were employed as probe molecules in order to test the SERS activity of produced samples.

In order to directly probe the spectroscopic properties of individual colloids in solution, we integrated Raman spectroscopy with optical trapping[9, 10, 11], realizing a Raman optical tweezers[2, 6, 9] (ROT). In our set-up (see Fig.2a for a simplified sketch) the same light, generated by a He-Ne (Melles Griot 05-LHP-991, 633nm, P=9mW) at 633nm, is used for trapping and Raman excitation. The laser beam is reflected by an aluminum mirror towards an edge filter (Semrock LP02-633RU-25, band pass 641-1427.4nm, transition width $<150\text{cm}^{-1}$). Thus it is sent towards a $100\times$ oil immersion objective (NA= 1.3) focusing the light on a diffraction limited spot. This ensures stable trapping at laser power of about 1-2 mW. The colloidal dispersion is loaded in a chamber (75 micro-litres volume) mounted on a piezostage (Physics Instruments, P-517.3CL). The backscattered light passes through the edge filter, used for Rayleigh scattering removal, and is subsequently focused by a 50mm lens onto a Jobin-Yvon Triax 190 spectrometer (190mm focal length) equipped with a 1200 l/mm grating blazed at 650nm. An avalanche photodiode (Perkin Elmer SPCM-AQRH-16) is used for light detection. Raman spectra are typically acquired with integration times of 0.1-1sec.

The third-order nonlinear optical properties were determined by the Z-scan method, a sensitive technique to measure both nonlinear absorption and nonlinear refraction response, simultaneously. A nanosecond Nd:YAG laser ($\lambda = 532\text{nm}$) with a pulse duration of 5 ns and a repetition rate of 10Hz was used as the laser source. Details about the z-scan techniques and the procedure adopted to analyze the experimental data are presented in [7, 8].

3. Results and Discussion

Figure 1 reports UV-vis spectra of two sets of Au/Ag colloidal nanoalloys (namely Sample A and B) obtained at different gold molar fraction. In the same figure spectra of the

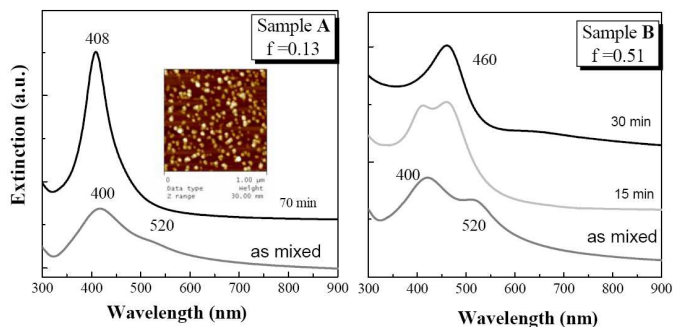


Figure 1. Optical properties for sample A and B irradiated with $0.2 J/cm^2$ at different irradiation time as shown on the lines labels. The gold molar fraction f is reported in both figures. In the inset of the figure on the left the AFM image of Au/Ag sample is also shown.

as-mixed Au and Ag colloids are shown for comparison. As-mixed samples presented double localized surface plasmon resonance (LSPR) peaks, positioned at 400 and 532 nm, indicating respectively the presence of pure Ag and Au structures. After irradiation, the spectral properties drastically change: a unique LSPR band is visible and its position is given for the specific alloy composition. Molar fractions (f) of 0.13 and 0.51 were calculated from the plasmon resonance position for the A and B samples, respectively. These values are in good agreement with the results from XPS analysis, obtained considering the Ag 3d and the Au 4f core signals. The typical morphology of the as deposited nanoalloy is observed by AFM microscopy (see the inset in Fig. 1). The structures appear to be nearly spherical with average sizes of 20nm in radius.

3.1. SERS and Optical Trapping. The plasmonic properties of the Au-Ag nanoalloys make them potentially suited for SERS studies. SERS spectra of all produced samples were recorded after the interaction of metallic nanoparticles with polyynes (linear carbon chains) in solution and in solid state, after a drop cast of a polyyne-water dispersion on a as-prepared Au-Ag SER substrate (see Fig.2b, black line). A different enhancement of the sp-hybridized carbon vibrational signals ($1700-2100cm^{-1}$) was observed varying the chemical composition in the alloys and the laser excitation wavelength. Individual aggregates of gold nanoparticles in solutions were also characterized by Raman tweezers experiments. Exciting at wavelengths red-shifted with respect to the plasmon resonance of the aggregates, both an efficient trapping and excitation of SERS signal is simultaneously obtained. In fig. 2b is shown a typical SERS spectrum of polyynes (red line) obtained on an individual trapped aggregate of gold nanoparticles and polyynes.

3.2. Non-linear optical properties. The optical limiting efficiency of the samples was investigated by means of nonlinear transmittance measurements as a function of the input fluence, to determine the limiting threshold. Figure 2c shows a clear optical limiting performance of the Au, Ag and Au/Ag colloids. The vertical lines in the figure indicate the approximate fluence at which the normalized transmission begins to deviate from linearity.

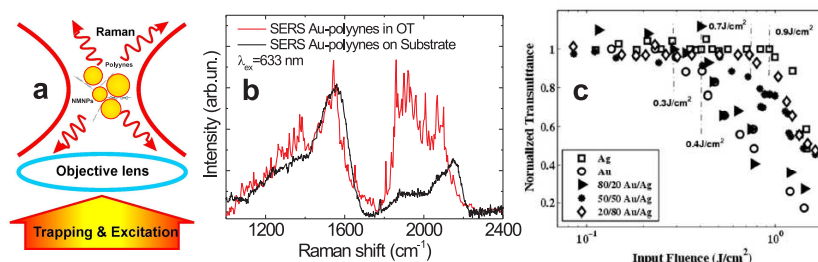


Figure 2. (a) Sketch of the Raman tweezers: optical trapping and Raman spectroscopy are performed with the same laser (633nm, He-Ne laser). The Raman signal from the linear carbon chains (polyynes) adsorbed on the trapped aggregate is collected through the same objective used for trapping (oil immersion, NA=1.3). (b) SERS spectrum on gold aggregates and polyynes samples drop cast on a substrate (black line) and on an individual trapped aggregate. Laser power is about 1-2 mW in both cases. The left region of the spectrum, $1100\text{-}1500\text{cm}^{-1}$, is attributed to sp^2 -hybridized carbon, while the region between $1700\text{-}2100\text{cm}^{-1}$ is related to the sp -hybridization of the polyynes. (c) Nonlinear optical limiting performance of the samples towards 532nm laser light.

The fluence value corresponding to the onset of optical limiting (optical limiting threshold) decreases upon increasing the Au/Ag volume ratio: from 0.9J/cm^2 for the Ag colloids down to 0.3J/cm^2 for the Au ones. No significant effects was observed after the annealing treatments. In conclusion, we are able to synthesize contaminant-free Au-Ag nanostructures with tunable plasmon resonances suitable for optical trapping, SERS and non linear optics applications. Interesting optical nonlinearities, trapping effects and spectroscopic enhancement were studied as function of gold concentration in the nanoalloys.

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- ^a Università degli Studi di Catania
Dipartimento di Scienze Chimiche
I-95125 Catania, Italy
- ^b Università degli Studi di Messina
Dipartimento di Fisica della Materia e Ingegneria Elettronica
I-98166 Messina, Italy
- ^c CNR-IPCF, Istituto per i Processi Chimico-Fisici
Consiglio Nazionale delle Ricerche
I-98158 Messina, Italy
- * To whom correspondence should be addressed | Email: ldurso@unict.it

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