Laser Ablation in Liquids as a Versatile Approach for the Synthesis of Hybrid Nanoparticles with Plasmonic and Magneto-Plasmonic SERS Applications

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***Abstract*— The synthesis of nanomaterials with tunable optical and magnetic properties is essential for applications in nanomedicine, sensing, and bioimaging. This work explores Laser Ablation in Liquid (LASiS) as a clean and efficient method for producing hybrid nanoparticles for use as SERS (Surface-Enhanced Raman Spectroscopy) substrates. We synthesize and characterize two types of hybrid nanoparticles: metallic Au-Ag alloys and core-shell Au-Fe(oxide) structures. The study demonstrates how LASiS enables the engineering of nanomaterials with enhanced properties for electric field amplification in vibrational spectroscopy, highlighting its potential as a versatile tool for nanobiophotonics applications through a unified experimental approach.**

***Keywords*— magneto-plasmonics, nanoparticles, laser ablation, SERS, biophotonics**

I. INTRODUCTION

Multifunctional plasmonic and hybrid nanomaterials have become central to modern materials science due to their rich optical, magnetic, and catalytic properties. Among these, magneto-plasmonic (MP) nanostructures — materials that simultaneously exhibit plasmonic and magnetic phenomena — as well as bimetallic plasmonic hybrids composed of noble metals such as gold (Au) and silver (Ag), have enabled novel applications in diverse fields ranging from biomedicine and molecular sensing to catalysis and energy conversion [1].

MP nanomaterials are typically designed by integrating plasmonic metals such as Au, Ag, and Cu with magnetic components like 3d transition metals and their oxides, resulting in systems that exhibit both localized surface plasmon resonance (LSPR) and magnetic responsiveness [2]. These materials have attracted attention for their ability to interact with light at the nanoscale while also being manipulated using magnetic fields, enabling control over particle positioning and concentration [3–5] — a feature particularly valuable for biomedical imaging, drug delivery, and surface-enhanced vibrational spectroscopy.

On the other hand, non-magnetic hybrid nanoparticles (NP), such as Au–Ag nanostructures, are well known for their tunable plasmonic properties [1]. In these systems, LSPR can be modulated by controlling size, shape, and composition, allowing precise adjustment of optical responses across the visible and near-infrared ranges [6–8]. Alloyed and core–shell Au–Ag NP, for example, have shown superior performance in optical sensing and photothermal conversion, especially when high sensitivity or spectral tunability is desired [7]. In this context, investigating both MP and bimetallic plasmonic nanoparticles is important to advance our understanding of how nanoscale structure may influence enhancement mechanisms such as those involved in surface-enhanced Raman spectroscopy (SERS) [7–8,10]. By exploiting both electromagnetic enhancement from plasmonic components and the spatial concentration of nanoparticles induced by magnetic fields, these materials open new avenues for detecting trace analytes and complex biomolecules. In this work, we report the synthesis of multifunctional nanostructures via laser ablation in liquid (LASiS), including both magneto-plasmonic core–shell Au–Fe(oxide) [2, 9, 16, 17] nanoparticles and plasmonic Au–Ag hybrids [1, 7]. We investigate their structural and optical properties and demonstrate their effectiveness as substrates for SERS [15–18] in detecting biologically relevant molecules, such as urea and thiourea, in aqueous environments.

II. EXPERIMENTAL

Both hybrid nanoparticles were synthesized via LASiS in aqueous media using distinct configurations and each colloid was ablated until reaching an optical density (OD) of 1.0. For the Au-Ag alloy NP, a two-step protocol was employed: (i) separate generation of Au and Ag colloids using a fiber laser operating at 1064 nm (400 ns; 0.5 mJ; 50 kHz); (ii) mixture of the colloids followed by further irradiation with a Nd:YAG laser at 532 nm (5 ns; 100 mJ; 10 Hz), promoting alloy formation. For the Au–Fe(oxide) core-shell nanoparticles, the strategy involved the initial ablation of a gold target in water using the fiber laser, followed by the ablation of an iron target immersed in the previously synthesized Au colloid, leading to stable hybrid nanostructures stabilized by iron oxide.

III. RESULTS AND DISCUSSION

The graph in Fig. 1(a) shows the UV-Vis extinction spectrum of the Au–Ag alloy colloid over different ablation times. Their distinctiveness lies in the ability to precisely control the surface plasmon resonance (SPR), which arises from the collective oscillation of conduction electrons in partially filled electronic shells [1]. For Au and Ag NP, the plasmon peaks are centered at 530 nm and 400 nm, respectively. After varying the ablation time of the Au–Ag NP mixture in a 1:1 ratio, the resulting change in particle size led to a shift in the localized surface plasmon resonance (LSPR) frequency. The appearance of dipole plasmon absorption bands situated between the LSPR peaks of individual Au and Ag NP indicates the formation of bimetallic structures due to plasmon decoupling of Au and Ag NP [1].

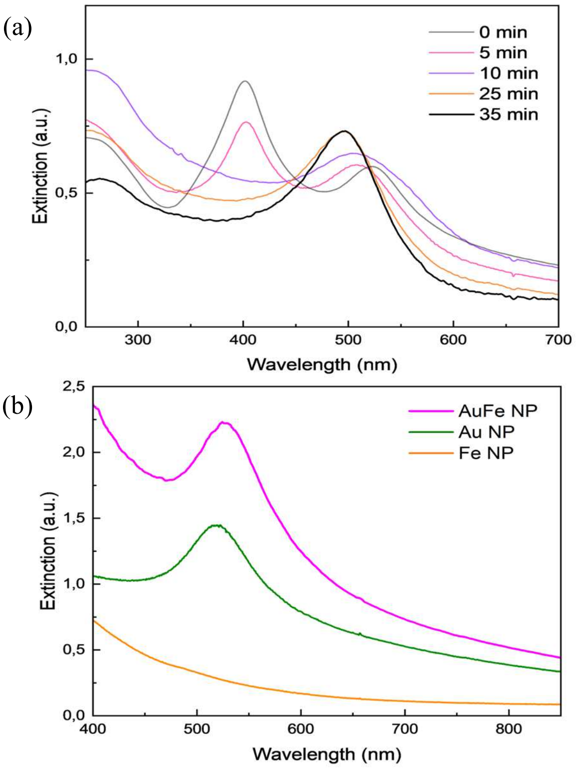

Fig. 1. UV-Vis extinction spectrum of the (a) Au–Ag alloy colloid over different ablation times and (b) Au, Fe and Au-Fe nanoparticles.

For Au NP and Au–Fe NP, the feature plasmon peak at 520 nm is visible in Fig. 1(b), whereas for Fe NP, we observe intense extinction starting below 400 nm. Since the laser ablation process was conducted in water, oxidation is expected to occur during the ablation of the iron target, leading to the formation of iron oxide nanoparticles, specifically Au–Fe(oxide), with Fe_2O_3 being a likely product [16-18].

The size and morphology of the Au-Ag alloy and Au-Fe nanoparticles were characterized by Dynamic Light Scattering (DLS) and Transmission Electron Microscopy (TEM). Au-Ag NP exhibited a narrow size distribution, with a mean hydrodynamic diameter ranging from 4 to 30 nm. as shown in Fig. 2(a). TEM images showed predominantly spherical particles of approximately 10 nm with homogeneous contrast and well-defined contours, consistent with an alloyed or core–shell structure. In contrast, Au–Fe nanoparticles displayed broader size distributions in DLS (5–500 nm), attributed to magnetic dipolar interactions and aggregation. TEM revealed that either a core-shell or core-satellite [9] structure was formed, although further investigations should be carried out, with morphologies with average diameters ranging from 5 nm (Au) to 80 nm (Fe), with 20% size dispersion of about 35 nm and iron oxide shells of 10 nm, confirming the formation of magnetically induced clusters, as shown in Fig. 2(b).

In SERS tests, Au–Ag alloy nanoparticles demonstrated high performance as signal-enhancing substrates, especially for urea and thiourea, by forming effective plasmonic hotspots. Signal enhancement was directly related to the efficient surface plasmon resonance of homogeneously mixed domains.

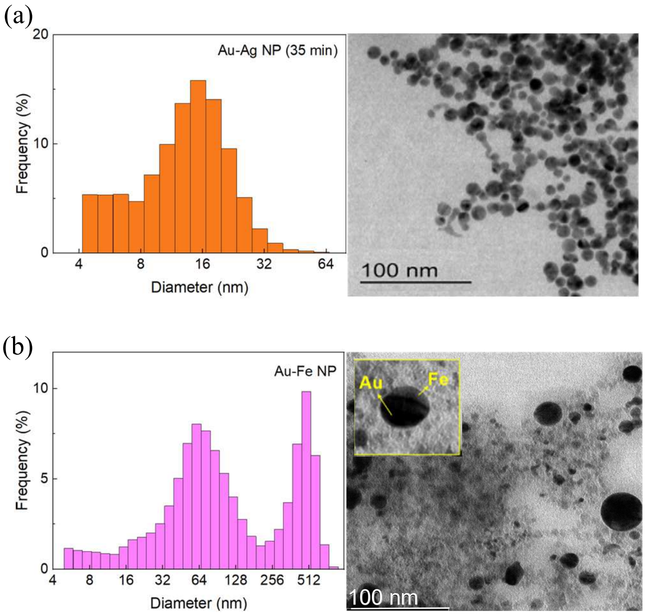

Fig. 2. (a) DLS and TEM characterization of Au–Ag nanoparticles showing narrow size distribution and spherical morphology. (b) DLS and TEM images of spherical Au-Fe NPs. Inset: dark areas related to Au and light areas is associated with the presence of Fe.

In turn, Au–Fe(oxide) nanoparticles combine plasmonic behavior with magnetic responsiveness, enabling external manipulation and potential reuse — an asset in bioseparation protocols [2]. SERS experiments confirmed sensitivity to thiourea and urea, reinforcing their suitability for biological detection.

Under the experimental conditions used to acquire the SERS spectra (top spectrum in Fig. 3(b)), no Raman signal was detected in the absence of nanoparticles, clearly indicating plasmonic enhancement and the occurrence of the SERS effect. Since thiourea differs from urea by substitution of an oxygen atom with a sulfur atom, their vibrational fingerprints are similar. However, the strongest peak (N–C–N bond stretch) shifted in both Raman and SERS spectra. Interestingly, NH_2 stretching vibrations appear more prominently in the spectrum obtained with Au–Fe NP, suggesting strong interaction with the sulfur atom. In contrast, Au–Ag NP yielded sharper signals, reflecting their greater uniformity and stronger plasmonic activity.

Both types of hybrid nanoparticles exhibited optical stability over months and reproducible Raman signal enhancement, highlighting their potential for real-time molecular sensing in biomedical diagnostics, environmental monitoring, and in vivo imaging.

IV. CONCLUSIONS

This study highlights LASiS as a powerful technique for producing pure, controllable, and functional hybrid nanoparticles without chemical reagents or complex purification steps [10]. The presented approaches demonstrate the flexibility of laser ablation in generating materials with plasmonic and magneto-plasmonic properties, with proven efficiency in SERS-based applications. Our results position laser ablation as a promising route for the design of nanomaterials targeting nanobiophotonics, enabling the development of sensitive, selective, and integrable platforms for biomedical systems.

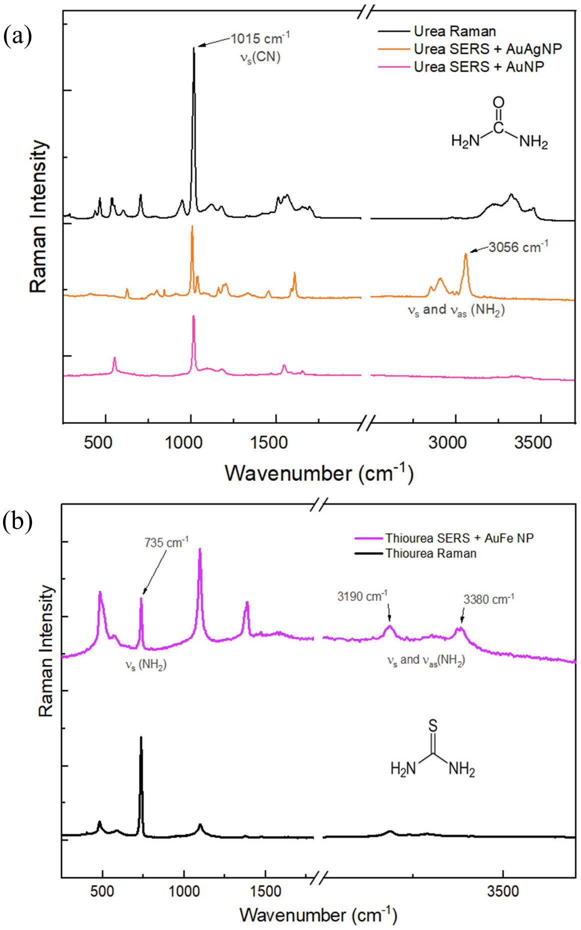

Fig. 3. Raman and SERS spectra of analytes. Raman spectra were acquired from bulk samples, while SERS spectra were obtained by mixing 1 µL of 10 mM analyte with nanoparticle colloids: (a) Urea with Au–Ag NP. (b) Thiourea with Au–Fe(oxide) NP.

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