# On the role of silver nanoparticles shape for SERS of Rhodamine

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***Abstract*— This work shows the photoinduced shape conversion of spherical silver nanoparticles produced by laser ablation in liquids. A combination of blue and white LEDs was used as light source for the shape conversion. Photoconversion also used hydrogen peroxide as oxidizing agent of nanoparticles under different sodium citrate capping conditions. Rhodamine 6G was the molecule probe for assessing the influence of shape conversion in the efficiency of surface enhanced Raman scattering.**

***Keywords— plasmonics, optical spectroscopy, photoconversion***

## I. INTRODUCTION

Nanotechnology has a variety of definitions that can focus on different nuances like production, characterization, applications, new properties and functional organization of materials by controlling its shape and size at nanoscale. The common feature is the nanoscale, i.e., dimensions within the range from 1 to 100 nm. Such novel class of materials present outstanding and unique properties not comparable to the same materials in macroscopic scale. The dramatic change in the physicochemical properties of nanomaterials is a direct result from the increase in the ratio of surface atoms to bulk atoms, leading to an increase in the surface area of the nanomaterial. Additionally, the decreased dimensions lead to changes in the energy levels of the system, imparting new electromagnetic properties to nanoscale materials [1].

There are two basic routes to realize nanostructures: the bottom-up (sometimes referenced as chemical) and top-down (or physical). While the former relies on chemical reactions for grouping smaller constituents into more elaborated (but still at nanoscale) structures, the later obtains the nanometric elements from macroscopic materials. An example of the top-down route is the ablation of metals in liquid medium by employing high-energy pulses of lasers, a technique known as Laser Ablation in Liquids (LAL) [2]. Such technique can produce, e.g., a colloidal suspension of metallic nanoparticles (NPs) with a statistical distribution of sizes from a variety of metals like Gold, Silver or Cooper.

The size, shape and electrical charge of nanoparticles constitute a key set of parameters that will define its properties. Several techniques are employed to tailor the NPs characteristics, like photoirradiation and capping of NPs with ions from salts as sodium citrate. The latter acts as a surfactant, stabilizing the colloid, but also helps the growth of NPs as reducing agent [3], [4].

The possibility of exciting localized surface plasmons resonances (LSPR) by optical fields in metallic NPs, generating high local electromagnetic fields, opens the possibility of employing such structures as electromagnetic enhancers. This effect can be explored in the sensing field for Surface Enhanced Raman Spectroscopy (SERS), in which the Raman scattering of an analyte is intensified (physical nature) in the proximities of the NP. Additional enhancement, of chemical nature, can also contribute to SERS when the analyte is adsorbed on the NP surface [5]. As the maximization of the Raman signals rely on the resonance between the LSPR bands and the incident light, methods for tuning the NPs resonances are of interest.

In this sense, Photoinduced Shape Conversion (PISC) of spherical metallic NPs consists in an import tool for matching the resonances. For Silver nanoparticles (AgNPs), PISC can be accomplished in a plasmonic-mediated reaction where the constituents are $Ag^+$, sodium citrate, small plasmonic "seeds" (2 – 4 nm diameter) and visible light. The oxidation of Ag can be obtained at expenses of $O_2$ molecules present in the colloid [6].

Prismatic AgNPs were obtained by PISC from AgNPs synthesized by bottom-up route [7]. After 12 hours of monochromatic illumination with a sodium lamp ($\lambda$=589 nm) the colloid color changed from yellow to blue. TEM images showed a non-monodisperse size distribution of prisms, also resulting in multi-bands in the UV-VIS extinction spectrum. SERS spectrum of Rhodamine 6G (R6G) showed a higher enhancement for prismatic nanoparticles than for spherical nanoparticles, when KBr was added to the colloid.

If PISC is carried out at dichromatic illumination a monodisperse distribution of prisms can be achieved instead, provided that dipole resonances of nanoparticles (394 nm for Ag nanospheres, 610 nm and 650 nm for type I nanoprisms) are not excited [8]. Independently whether monochromatic or dichromatic excitation illumination is employed for PISC, extinction bands associated with non-spherical nanoparticles can be found from approximately 470 nm up to 1065 nm.

This work shows the photoinduced shape conversion of spherical silver nanoparticles by employing hydrogen peroxide as oxidizing agent of nanoparticles under different capping conditions. The influence of shape conversion in the efficiency of surface enhanced Raman scattering was probed by using Rhodamine 6G as analyte.

## II. METHODOLOGY

Silver NPs were produced by LAL of a silver plate (99.9%, CAS: 6440-22, Sigma Aldrich®) using the focused beam of a Nd:YAG laser (New Wave Tempest 20) operating at 532 nm with a frequency of 10 Hz, pulses of 3-5 ns and energies per pulse of 12 and 17 mJ. The ablation time was fixed in 20 minutes with the laser beam focused on the silver target with a 15 cm focal length lens. The target was positioned at the bottom of a Becker with 10 mL solution (0.1 and 0.3) of dehydrated sodium citrate (Biotec®

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