Detection of Alzheimer Disease Markers by High Performance Plasmonic Silver Nanostars

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Abstract

The manufacture of nanoparticles (NPs) with metallic plasmonic properties, displaying advanced spectroscopic applications is one of the tasks of our research Group. In fact, shape control of metal nanostructures is a promising strategy to tailor their physical and chemical properties. A variety of metal nanostructures with well-defined morphology have been obtained e.g. spheres, triangle, cubes, octahedrons, rods, and plates. Recently, metal nanostructures with complex three dimensional (3D) surface morphology, which are often referred to as nanoflowers or nanostars in literature, have received considerable attention due to their excellent performance as SERS (Surface Enhanced Raman Scattering) substrates.[1]

Further, for a metal nanostar, the hybridization of plasmons of the core and tips could dramatically increase the excitation cross section and the electromagnetic field enhancements of the tip plasmons, which results in better SERS performance.[2]

The main purpose of our work is the fabrication of nanoscopic systems leading to high electromagnetic field intensifications. The strategy for obtaining these systems has been the preparation of anisotropic NPs with special morphologies leading to high field enhancement, as triangular nanoprisms and nanostars. Progress has been made in a very special way to develop protocols for the preparation of silver nano-shaped nanoparticles, which were not prepared so far in silver.

These nanoparticles have a larger number of advantages in relation to gold, since Ag is more efficient in SERS, because of the greater intensification factor, and because of their wider range of activity, as the Ag NPs exhibit plasmon resonances in the visible spectrum and the near-infrared. In addition, the protocols of preparation of Ag nanostars were aimed at avoiding the use of surfactants, which are normally used in the preparation of Au nanostars, since these substances prevent the approach of the analyte to the surface, thus decreasing the efficiency of these systems in spectroscopy. In this work we describe the one-step colloid synthesis of silver nanostars and their characterization by spectroscopic and microscopic techniques (Extinction spectroscopy, SERS, TEM and SEF).
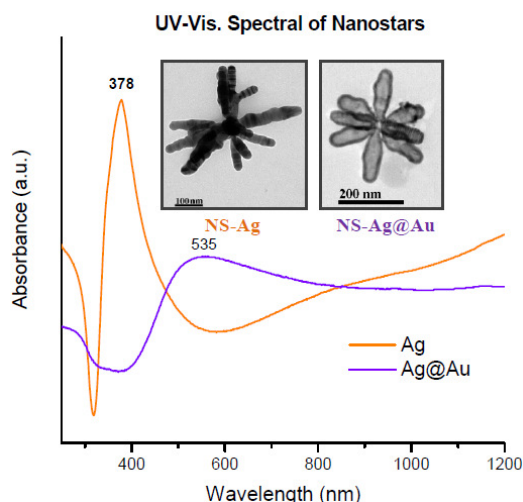
Figure 1: Extinction spectra and TEM (inset) images of NS-Ag and NS-Ag@Au nanoparticles.

Two nanostar types have been fabricated. One of them by synthesis in one step of chemical reduction of nitrate silver solution with neutral hydroxylamine (NS-Ag). The second one, by synthesis in two steps adding gold solution to the first Ag nanostars and reducing with citrate at 1% at 100ºC (NS-Ag@Au).

Figure 1 shows the TEM images (inset) and the extinction spectra of both colloids. In particular, the NS-Ag@Au nanoparticles have a thin uniform shell of gold coating the silver core. Extinction spectra of these nanoparticles show a big background at high wavelengths indicating a high size and shape distribution with many different numbers of tips, in both cases. The extinction peak about 535 nm in the case of NS-Ag@Au is indicative the presence of gold shell in the nanoparticles.

In order to test these nanostar morphologies as plasmon surfaces, Congo Red (CR) and Thioflavine (ThT) dyes were characterized by vibrational spectroscopy (IR, Raman, SERS) and SEF. CR and ThT are used as histological dyes for staining the peptide β-amyloid, which is a pathologically aggregated form of protein and found in some human diseases including Alzheimer and prion diseases.[3, 4]

Figure 2 shows the SERS spectra of RC and ThT obtained using NS-Ag and NS-Ag@Au as SERS substrates. As can be seen, intense SERS bands of both RC and ThT were obtained in the fabricated nanostars. However, the intensity was higher when using NS-Ag@Au. In addition, the SERS enhancement is much higher in the case of RC. The higher activity of the latter nanoparticles is attributed to the higher extinction of light occurring on NS-Ag@Au due to the better match of the extinction plasmon with the exciting laser. Moreover, the larger SERS intensity obtained for RC can be explained on the basis of the higher resonance effect obtained for this dye at the 532 nm excitation.
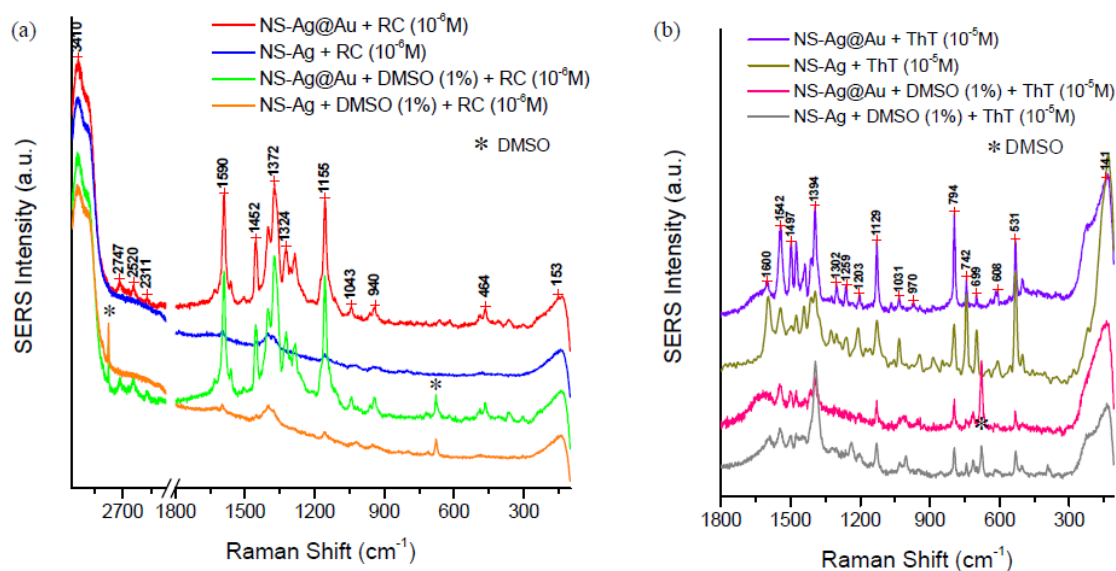

Figure 2: SERS spectra with NS-Ag and NS-Ag@Au without aggregation for (a) RC and (b) ThT. λexc. = 532 nm. Spectra normalized to the water band.

References
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