Tailoring the size and shape of a new type of Silver Nanostars with outstanding plasmonic properties

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Abstract
Branched metal nanoparticles (NPs) such as nanostars and nanoflowers are exciting plasmonic and catalytic platforms on account of their often large surface areas, multiple high angle edges, and sharp tips [1]. The small radius of curvature of sharp tips can concentrate electromagnetic fields at these features of Au and Ag nanostructures to achieve high sensitivity in plasmon-enhanced surface spectroscopy [2]. Also, through size controlled syntheses of branched metal nanoparticles, the extinction features of their localized surface plasmon resonance (LSPR) can be tuned. The fabrication of silver nanostars (AgNS) should be of high interest in spectroscopy and, therefore, in the optical detection field, due to the better optical properties of this metal in comparison to gold, taking into account the LSPR properties of each metal. In addition, AgNPs displays higher SERS enhancement factors (EF) in comparison to gold ones [3]. In this work, a reduction in two steps method, using hydroxylamine and citrate to obtain AgNS is reported. This method can be modulated to give rise to NPs of different morphological features, the diameter, as well as the length and the tip width of arms. The Principal Component Analysis (PCA) was used to identify the morphological features in 24 samples and to correlate them to the different experimental conditions employed in their fabrication.

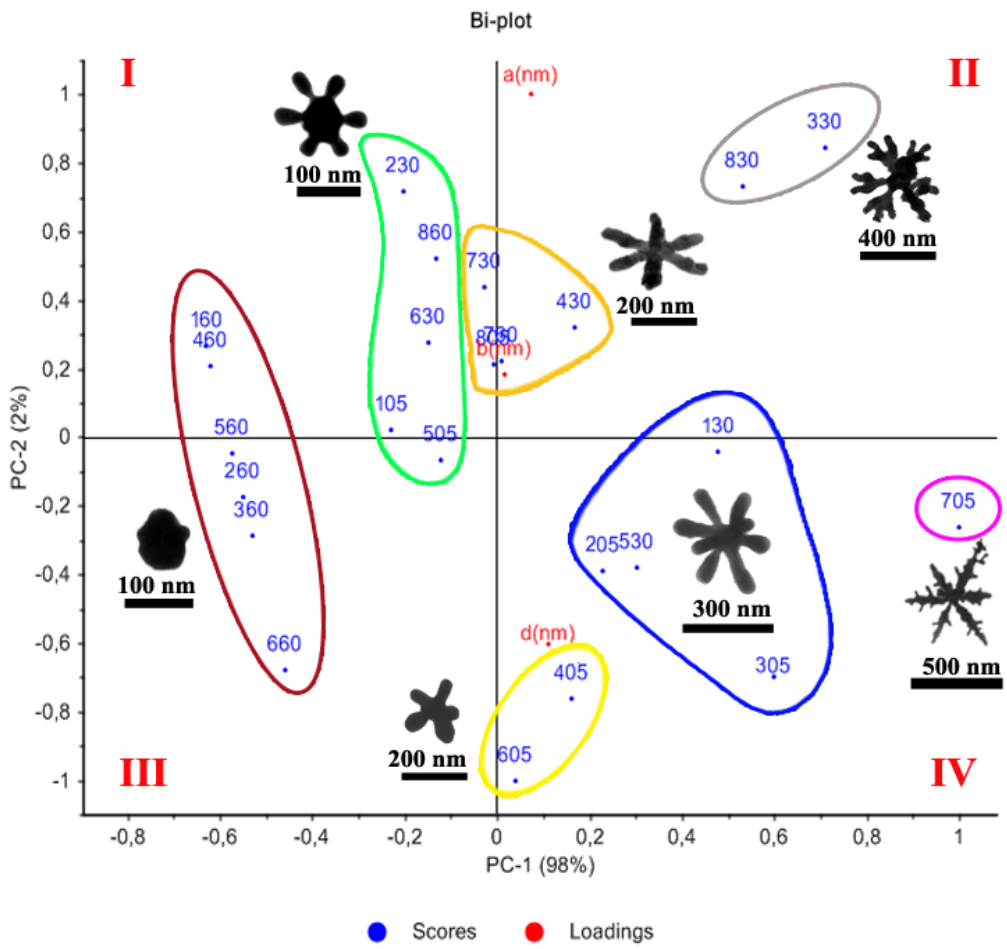

Figure 1: PCA graphic of scores and loadings of data obtained from morphological features of 24 AgNS samples. Loadings: d-diameter, a-arm length and b-tip width. Scores: 24 samples of AgNS obtained by different experimental conditions.

The oxidation-reduction method described in reference [3] was used to fabricate 24 samples, but changing the values of the experimental conditions. A colloidal suspension of AgNS was prepared by chemical reduction of Ag^+ in two steps using as reduction agent a neutral hydroxylamine solution (HA) in a first step and a citrate solution (CIT) in the second one. The combination of these two reduction agents affords the necessary conditions to induce the growth of the spiked and the stabilization of nanoparticles. The resulting NPs were characterized by Transmission Electron Microscopy (TEM) and extinction spectra. Finally, the morphological features derived from the TEM analysis were used to carry out the corresponding PCA study.

TEM images corresponding to 24 AgNS samples were analyzed by PCA with the ImageJ software to obtain the diameter (*d*), arm length (*a*) and tip width (*b*) data of nanostars. As can be seen, Figure 1 shows that the data can be classified in seven groups formed by samples with similar features depending of: size (bigger or smaller), type of arm (longer or shorter) and type of tip (spiky or rounded). As can be seen from Figure 1, *d* and *a* are the most influencing parameters on the NPs morphology, because they are placed far away from the center. This indicate a significant separation of NPs into larger ones (on the right side, sample 705), and the smaller ones (left side, samples 160, 260, 360, 460, 560 and 660). The extinction and surface-enhanced Raman scattering (SERS) spectra were measured from all these samples and the enhanced factors were calculated from the SERS spectra using thiophenol as probe molecule.

References

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