

A study of the "background" in SERS (Surface Enhanced Raman Scattering) spectra.

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Abstract

The Raman spectrum enhancement can be obtained by using the surface plasmon resonance of a metal nanoparticle, this effect is known as SERS. In this work we present a study about the relationship between the background seen in the SERS spectra and the shape of the silver nanoparticle used to enhance the Raman signal.

Key words:

SERS, background, nanoparticle.

Introduction

SERS is an enhancement effect of the Raman spectrum of a molecule which is adsorbed on the surface of a metal nanoparticle, typically gold, silver and copper. There are two mechanisms that are responsible for the enhancement of the Raman signal: the chemical (CE) and the electromagnetic (EM) mechanisms. Between these mechanisms, EM is more pronounced with a greater contribution to the increase in the Raman intensities of a given molecule. Such mechanism is related to localized surface plasmon (SP) excitations on a metal nanoparticle surface. Surface plasmon consists in modes of collective oscillation of the free electrons on the surface of the nanoparticle (NP),^{1,2} and the resonant excitation of these modes depends, among other factors, on the NP's shape. The SP excitation leads to an increased local electric field in the vicinity of the metal surface, resulting therefore, in the enhancement of the electromagnetic radiation experienced by the molecule adsorbed on the NP. The purpose of this work is to analyze the relationship between the Raman spectrum enhancement and the shape of the NP.

Results and Discussion

The SERS spectra were obtained using a brilliant green (BG) solution of concentration 10^{-8} mol L⁻¹. The samples were prepared by depositing the silver nanospheres (AgNPs) or nanocubes (AgNPc) over a silicon slab, on which it was deposited an aliquot of the BG solution that were then left to dry at room temperature. The spectra were obtained in mapping form, 2500 spectra per analysis, using a laser of 633 nm as exciting radiation. Due to the large amount of spectra, the SERS mapping data were analyzed in terms of multivariate curve resolution by alternating least squares (MCR-ALS) and the pure components of the data matrix are presented in Image 1B, for the AgNPs and 1C, for the AgNPc. Image 1A shows a BEM (Boundary Element Method) simulation for the scattering spectrum for dimers of nanoparticles laid on silicon slabs. The region inside the frame in Image 1A represents the region on the electromagnetic spectrum (ES) observed in SERS spectra, from 633 to 725 nm (which corresponds to the range of 0 to 2000 cm⁻¹ in Raman shift). Based on the analysis of the spectra presented in Image 1, one can notice that the enhancement of Raman signal was more effective when AgNPc were used, that happened, possibly, because of

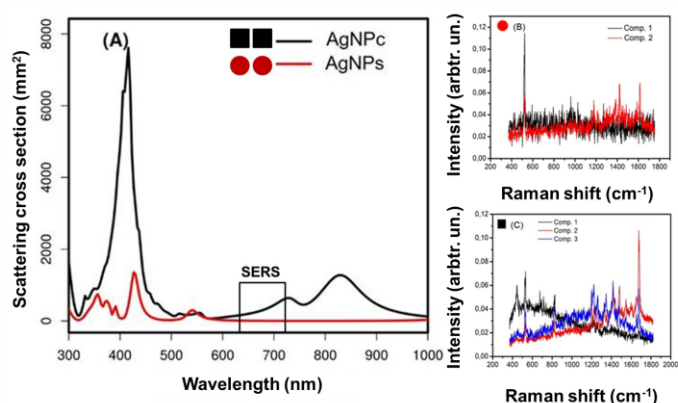


Image 1. BEM simulation for the scattering spectrum for dimers of AgNPs and AgNPc (A) and pure components for BG using AgNPs (B) and AgNPc (C).

the scattering profile shown in Image 1A. In the ES region in which the SERS spectra were obtained, AgNPc are closer to the plasmon resonance than AgNPs. For AgNPc it can also be observed backgrounds in the experimental spectra that show a correlation with the preferential enhancement of the Raman bands. The observation of backgrounds and appreciable enhancement for the AgNPc to detriment of the AgNPs indicates a strong contribution of EM mechanism to the enhancement of Raman signal and correlates the shape of the NP with the background.

Conclusions

The distinct backgrounds observed for AgNPc indicate the formation of different kinds of aggregates in the sample, while the absence of background and low enhancement for AgNPs can be explained by the region of ES in which the experiments were made, far from the SP resonance. The data presented in this work indicate a correlation between the shape of the NP and the observation of a background in the SERS spectra.

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