

ULTRA-HIGH SENSITIVE DETECTION WITH SURFACE-ENHANCED RAMAN SPECTROSCOPY

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Abstract. Ultra-high sensitive detection is a technological and scientific challenge with implications in different disciplines from medicine to national security and the military industry. Although there are many ways to achieve high sensitivity, one driven force towards technological developments is the possibility to obtain an extremely high performance in an inexpensive and easy way. In this regard, we report in this contribution a way to implement plasmonic nano-particles used in surface-enhanced Raman spectroscopy sensing with a sensitive better than commercial products tested under the same conditions. For testing purposes, we use different organic molecules from ultra-thin layers to monolayers formed by self-assembly. Our results show the possibility to produce highly-sensitive sensors in an inexpensive and efficient way.

Introduction. The highest possible sensitivity of any chemical detector is that of a single-molecule detection¹. Such high sensitivity can be achieved with surface-enhanced Raman spectroscopy (SERS). This method allows the chemical identification of different analyzes ranging from biomarkers for cancer detection to pesticides and other environmental pollutants. However, in addition to the Raman spectrometer that nowadays can be available even as portable handheld devices, another critical component of SERS concerns the plasmonic nanostructures that are directly responsible for the Raman signal amplification. In this work, we aim at demonstrating experimentally and with computer simulations that single crystalline nanoparticles made from Ag salts can be used as highly efficient SERS substrates. We show the generality of our concept by the environmentally-friendly and inexpensive fabrication of plasmonic nanostructures from household materials.

Experimental methods

Sample fabrication: Ag nanocrystals were obtained by electrochemical reduction of Ag in a AgNO₃ aqueous dispersion, as energy source we used household cells, including with natural electrolytes and solar cells. Metal film on nano spheres, a commercial substrate (Klarite) and a blank piece of silicon were used as reference systems of enhancement.

Raman spectra were obtained in the back-scattering configuration using a LabRam HR800 and 514.7 nm excitation. The samples were simultaneously coated with a 2 nm layer of cobalt phthalocyanine (CoPc) by organic molecular beam epitaxy under ultra-high vacuum.

Results and discussion

Fig.1a shows the Raman spectra acquired from different substrates including the metal films on nano spheres, a Si substrate, and a commercial SERS sample (Klarite). The comparison of the main C=C vibration enhancement from the CoPc molecule² with peak intensity located at 1535 cm⁻¹ is shown in Fig.1b. It is clear that the highest degree of enhancement is not for the commercial sample but for the Ag or even Al home-made substrates. Typically, the plasmonic enhancement of the Raman signal can be as high as 10⁸ orders of magnitude. In our case we find a lower signal enhancement which can be related to the higher thickness of the layer as to the analyte concentrations used in single molecule detection. The scanning electron microscopy images and atomic force microscopy observations of the samples providing the highest enhancement reveal the presence of a high density of nano-junction made by two or more nanoparticle close together. These regions of the sample make the so-called hotspots responsible of the high signal amplification³. The simulation results for different nanoparticle configurations demonstrate the high signal amplification at the hotspots.

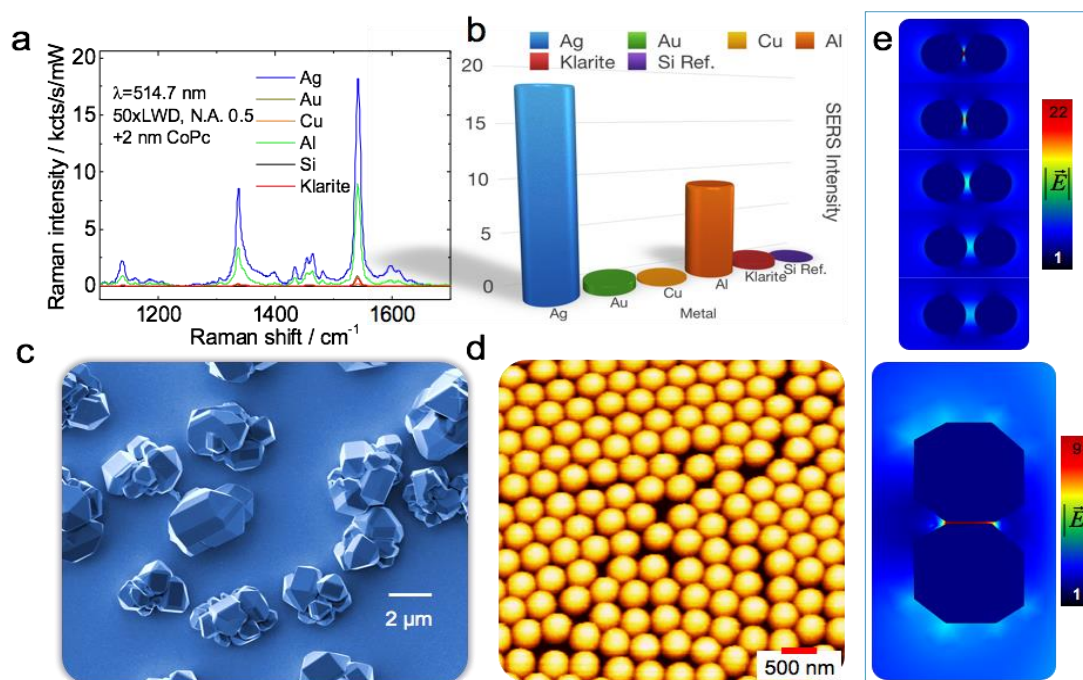


Figure 1: a) Raman spectra from ultra thin layers of cobalt phthalocyanine. Different substrate materials have been investigated including a commercial substrate (Klarite). b) Comparison chart of the enhancement obtained from different materials. c) Scanning electron microscopy image of the Ag substrate producing the highest signal enhancement. d) Atomic force microscopy image from a self-assembled monolayer polystyrene spheres used as template for metal deposition. e) Illustration of the finite element method simulation results of different nanoparticle configurations, Top: Au nanospheres 50 nm radius at distances from top to bottom of: 2, 5, 10, 15, and 20 nm. Bottom: Two octahedra nanoparticles showing the larger enhancement area as compared to the nanospheres. In all cases the excitation electromagnetic wave has a wavelength of 532 nm, with electric field polarized along the axis joining the two nanoparticles.

Summary

We present the first systematic experimental and computer simulation results for the most versatile, ultra-sensitive, and inexpensive implementation of plasmonic sensors based on SERS. We anticipate the exploitation of our research in technological applications such as detectors to clinical applications in early diagnosis detection from advanced clinics to developing countries thanks to the cost-efficient nature our fabrication method.

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