Doctoral Dissertation
Doctoral Program in Material Science and Technology (36th Cycle)

Nanostructured Materials for Ultrasensitive Detection of Contaminants in Water

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Raman spectroscopy is a versatile and non-destructive technique for qualitative and quantitative chemical analysis, applicable to both gas, solid, and liquid samples. Despite its advantages, the intrinsic weakness of Raman scattering, occurring only for a small fraction of scattered photons (around 1 out of 10^7), has limited its widespread use. To address this, Fleischmann introduced surface-enhanced Raman scattering (SERS), utilizing metal nanoparticles to enhance the Raman signal significantly through localized plasmonic resonance phenomena.
This thesis explores diverse methods for preparing Surface-Enhanced Raman Spectroscopy (SERS) sensors, ranging from direct chemical synthesis of metal nanoparticles to the metal-thin film deposition on nanostructured substrates. It also addresses the challenge of identifying the most versatile and repeatable method, considering sensing conditions and target applications. The first chapter contains a review of the optical properties of metals and the principles of SERS.

In the second chapter, direct chemical synthesis of SERS substrates is performed using optimized process parameters determined through a Monte Carlo simulation. This approach aims to maximize the SERS signal intensity for a certain Raman band at a given excitation wavelength determined *a priori*. The starting point for this optimization is modeling the optical response of a nanoparticle array by computing the integral of the electrical field square modulus over a gold dimer surface. Such calculation was performed by varying the center-to-center distance, observing that the maximum SERS signal is achieved for a value of, e.g., 60 nm. Subsequently, a three-body interaction model applied to a Monte Carlo simulation was used to determine the deposition

conditions and to select optimal gold nanoseeds for the fabrication of the device (10 nm). The resulting sensor demonstrated a limit of detection (LOD) of 0.33 nM for skatole in water at an excitation wavelength of 785 nm.

In the third chapter, we report an innovative technique involving vapor-phase chemical dewetting for synthesizing silver nanoparticles, showcasing versatility in diverse applications such as SERS detection Rhodamine-6G and hard masking for silicon etching of nanostructures. This approach, based on the exposure of a thin film to hot water or acid vapor, is a valid alternative to thermal or laser treatments to induce dewetting in the spinodal regime, due to its lower cost and the possibility of working on heat-sensitive substrates. A thorough investigation was conducted to assess if the exposure to the vapor could lead to the formation of silver compounds, thus affecting both the optical and chemical properties of the nanoparticles. Both Energy Dispersion Spectroscopy (EDS) and X-ray photoelectron Spectroscopy (EDS) were used to that extent, concluding no massive reaction of the silver occurred, but a very thin oxidized layer formed on the particle's outer surface. Prepared nanoparticles were directly used as a sensor for the SERS detection of Rhodamine 6G at an excitation wavelength of 532 nm, demonstrating an excellent LOD as low as $1.9\ 10^{-11}$ M.
The dewetted silver nanoparticles also demonstrated very high stability during plasma etching in a fluorine (CF_4) atmosphere. They were, therefore, employed as masks for silicon etching, allowing for the fabrication of a pillar-like nanostructure with a maximum depth of more than 350 nm. Depositing a 40 nm conformal silver thin film on the obtained nanopillars allowed us to obtain a structural coloring of the silicon substrate where the color can be tuned by changing the etching time and, thus, the pillar height.

The fourth chapter discusses the preparation of SERS sensors by depositing thin films on nanostructured substrates, demonstrating exceptional sensitivity in detecting solid contaminants such as nanoplastics. In particular, a soda-lime glass nanostructure is created by dry etching using a copper nanoparticle as a shadow mask and coated with a variable gold or silver thin film thickness. The nanoparticle mask was obtained by inducing the dewetting of a copper ultra-thin film via exposure to a nanosecond pulsed laser. The silver-coated thin film was tested for the detection of 4-mercaptobenzoic acid in a 1 μM water solution, comparing the normalized SERS intensity of such a sensor with the one obtained under the same condition on a silver flat thin film. The nanostructure sensor showed an enhancement factor of 176 times higher than the flat film, confirming the fundamental role of the nanostructuring in enabling the SERS detection of molecular contaminants. On the other hand, the gold-coated device was successfully employed to detect 100 nm polystyrene nanoparticles in water, exhibiting a record limit of detection of 0.68 ng mL^{-1}, almost three orders of magnitudes better than the current state of the art. This relevant result set the path for the development of a novel category of sensor for the detection and quantification of nanoplastic pollution.

The choice of gold as a coating metal was confirmed by BEM simulation and was dictated by the need to perform the Raman measurement with an excitation wavelength of 633 nm, as the green laser induced some fluorescence of the PS, making it difficult to identify its characteristic peaks.

The fifth chapter emphasizes the importance of analytical software tools for the advanced processing of microscope images to ease the comprehensive characterization of micro and nanostructured surfaces. In particular, the chapter introduces two innovative tools developed in this thesis's work for the tridimensional reconstruction of surfaces at the micro- and nano-meter scale.

The first tool performs a tridimensional surface reconstruction by integrating the surface gradient calculated from the four-quadrant backscattered electron detector signal in a scanning electron microscope (SEM). Such reconstruction is also further improved by employing some regularization methods that have been validated against some AFM measurements by comparing the different obtained power spectrum densities (PSD).

The second tool is based on an extended depth of field (DoF) approach, which allows for the SEM characterization of samples that show ultra-high aspect ratio features. This technique allows us to obtain enhanced DoF images (potentially a few mm) and a tridimensional surface reconstruction conserving the highest resolution of the SEM at all depths.

In the last chapter, we summarize the main achievements of this thesis's work and discuss future perspectives stemming from them for advancing SERS technology and its applications.