Large-scale nano-structured templates for enhancing fluorescence and Raman spectroscopy

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In recent years potential applications of metallic nanoparticles as an efficient source of light, heat and energetic electrons at the nanoscale regime attract a lot of attention and lead to their extensive study. The collective oscillations of electrons in metal nanoparticles as a result of electromagnetic interaction with light, or so called nanoparticles' plasmon resonances, can be tuned by altering their size, shape, surrounding medium and even their assemblies or spatial arrangement. Their unique light interaction and recent advances in their syntheses and application paved the way toward their use in chemical, biological and therapeutics fields. Their strong interaction with light (absorption, scattering and electromagnetic field confinement) found application in sensing, detection and enhanced spectroscopy, particularly as a nanoantenna to enhance luminescence, fluorescence and Raman scattering signals [1,2,3].

Here we present our attempts to design and fabricate nano-structured templates. We used two different facile bottom-up approaches for preparation of plasmonic templates. The templates were prepared by charge driven assemblies of nanoparticles on different functionalized surfaces. Later these structures were modified by LBL (layer-by-layer) and seeded growth methods to alter the interparticle distance of nanoparticles and enhance their ability in enhancing fluorescence and surface enhance Raman spectroscopy.

The LBL method was applied in order to provide a well-defined distance between the fluorescent dye layer and the gold nanoparticles arrays [4,5]. We investigated the plasmon-enhanced fluorescence of single array and double arrays of gold nanoparticles. A maximum of a 99-fold increase in the fluorescence intensity of the dye layer sandwiched between two gold nanoparticle arrays is found. The interaction of the dye layer with the plasmonic system causes a spectral shift in the emission spectrum and a decrease of fluorescence lifetimes in presence of nanoparticle arrays. However the lifetime increased with increasing distance between the dye and gold nanoparticle arrays.

Several templates were fabricated by seeded-growth method to study a Raman active Nile-blue A fluorophore. Applying the growing steps led to increase of nanoparticles size and change of their interparticle distance. We observed a noticeable enhancement (averaged over the sample) due to the tuning of the nanoparticles' plasmon with the excitation laser line at optimal growth step. These nanostructures were further investigated by scanning electron microscopy and UV-Vis. By applying 4 and 5 steps of growing, we observed a plasmon resonance red shifted to the NIR and the aggregation of the closest neighbors into larger and more elongated particles via the SEM micrographs (Figure1). Preliminary attempts were also done on flexible substrates by applying a mechanical stress for plasmonic-tuning.

References

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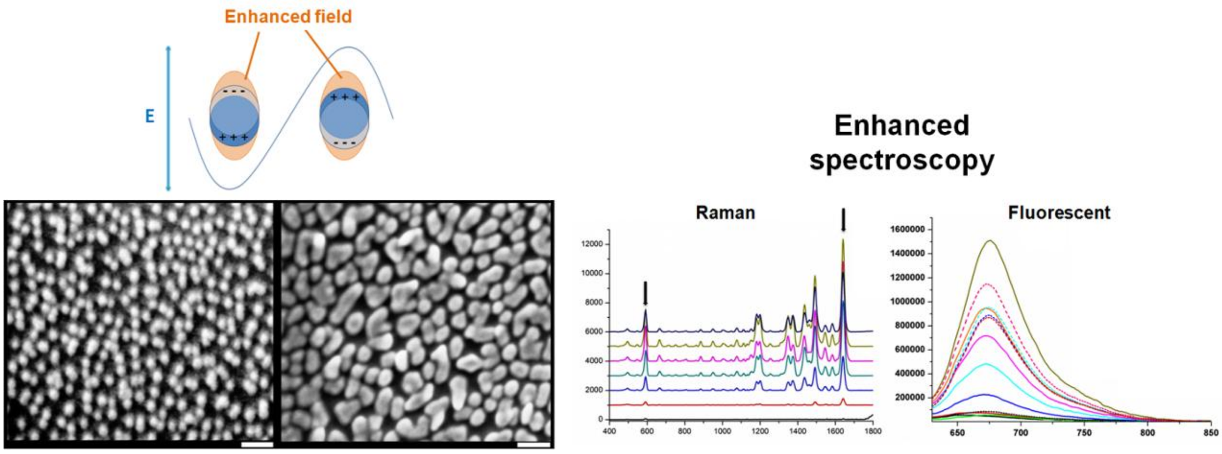

Figure1: Top left: Scheme of field enhancement as a result of plasmon resonances. Bottom left: The SEM micrograph of SERS templates without growth (left) and after fifth growth (right, scale bar 100 nm). Bottom right: The enhanced Raman and fluorescence spectra of large-scale templates.