Study of advanced nanostructures for SERS effect in μ-Raman Spectroscopy

The spectroscopy is a branch of physics that studies, interprets, and analyses the composition of a substance thanks to an electromagnetic radiation [1]. The spectroscopy techniques give useful and complementary information in different fields of research. For example spectroscopy is extensively applied in astronomy, geochemistry, biology, biodiagnostics and material science. There are a lot of different types of spectroscopy but all of them are based on the fact that the matter under analysis is able to absorb or emit energy when excited under right conditions. One of the most important and used types of spectroscopy is vibrational spectroscopy that allows to extract information of the matter analysed. Infrared and Raman spectroscopy are the most prominent exponents of this technique. Both are non-destructive tools that provide to give information about the molecular composition, structure and interactions of the compounds under analysis. One of the main exciting challenges for these techniques is their application in biology, material science and related disciplines, in view of characterizing different materials and systems under working conditions. Infrared spectroscopy is strongly limited in biological applications due to its very sensitive detection of the vibrations of water. In fact in most of the cases the signal of the analyte may be hidden by the strong signal of water. Raman spectroscopy could be a valid alternative to infrared spectroscopy because of its lowsensitivity to water. But most of the analytes have a very low Raman cross-section, that strongly limits the use of this technique to specific cases [2]. This problem was partially reduced with the discovery of the SERS effect, which takes advantage of localized plasmon resonances excited by the interaction of a laser source with metallic nanostructures to achieve a huge enhancement of the Raman signal [3]. Unfortunately the SERS effect obtained by metallic systems is often affected by several drawbacks. The main one is related to the dissipation of the increased electric field through radiative [4] and non-radiative (heat) [5] channels. For the analysis of non-biological systems this is not a huge problem, but during the analysis of biological analytes the dissipation can significantly alter their structure. Analogous effects can also originate from the chemical conjugation of the biological analytes with colloidal nanoparticles used as SERS-active substrates [2]. These negative aspect of the metallic SERS Raman spectroscopy are unavoidable and lead to the denaturation of the biological analytes even causing its degradation or the passivation of their reactive moieties. So that the world of research is moving to the development of new materials and analysis methodologies based on semiconductors where is possible to enhance the local electromagnetic field caused by the interaction of a light source with the surface plamons of matter avoiding the drawbacks of metallic SERS.

The aim of my research would be an investigation new non-metallic systems in order to know if they are able to induce a SERS effect in Raman spectroscopy avoiding the drawbacks of the metallic systems. I will study new semiconductors and check their possibility to induce a SERS effect, but also I will study already known SERS semiconductor materials (Si, SiO2, TiO2,…) under new morphology or for new applications. The study of the SERS effect regarding non-metallic nanoparticles and nanostructures started in 1988 [6] but is only in recent years that the importance of these systems has been realized, so that is going to be a hot topic in the field of Raman spectroscopy. During the last two decades a lot of different semiconductors have been studied in order to investigate if they were suitable for producing a useful enhancement in Raman spectroscopy. For example the NASA in 2010 [7] exploiting the whispering gallery modes through the use of 5μm-diameter SiO2 spheres was able to detect biological probes and now this robust sensor with a consistent response is installed in their robots for planetary analysis in situ. Another noteworthy research group is CCNY where Lombardi is studying unconventional semi-conductive systems (ZnS, CdTe, CdSe, ZnSe…) obtaining outstanding results in enhancing the signal of biological analytes up to 4 orders of magnitude [8]. Also the University of Brescia [2, 9, 10, 11] thanks to the Chemistry for Technology Laboratory is active in this research field we have developed a SiO2-TiO2 core-shell μ-system (T-Rex) with the capacity to increase the output of the titana anatase of the shell and the signal of an analyte present on its surface. T-Rex can be used for further experiments since it is one of the best non-metallic SERS sensor.

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