SERS on Functionalized Silver Nanostructures: Towards the Detection of Single Molecules in Hot Spots

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The optical properties of metallic Nanoparticles have a big scientific and technological importance. Such properties are determined by the Localized Surface Plasmons (LSP) the nanoparticles (NPs) support, which strongly depend on the NPs size and shape. The resonant excitation of the LSP leads to enormous enhancement of the electromagnetic field in close proximity of the NPs which originates a very important enhancement in the cross sections of SERS technique (Surface Enhanced Raman Scattering). This is the reason of the high sensitivity of this technique which, together with its ability to provide accurate structural information, makes it suitable to be employed as a molecular sensing technique. The possibility of controlling the LSP, tailoring the NPs morphology, pushes ahead the investigation of new methods of production of metallic NPs. Besides, they can be functionalized to improve their properties and increase their selectivity, consequently enlarging their applications.

In general the molecules active in SERS show some affinity for the metal resulting in the necessary approach to the surface. However many other molecules, whose trace detection is of great interest, do not present this affinity and their SERS signal is not detectable. The important environmental contaminants polycyclic aromatic hydrocarbons (PAHs) belong to the last group of molecules. Nonetheless it has been shown that by modifying properly the chemical properties of the metal surface it is possible to augment drastically the approaching of these pollutants to the metallic substrate [1-3], then their SERS sensing being feasible.

At the same time it is generally accepted that the possibility of single molecule detection (SMD) depends on the existence of interparticle gaps where the main part of the electromagnetic field intensification occurs [4,5]. One usually refers to these special regions of the metallic surface as *hot spots* (HS). Aggregated colloids are the main source for SMD [6] but the fabrication of such HS escapes from the experimental control in macro conditions. Thus, the molecules adsorbed on the metal surface may effectively play a crucial role in the formation of these HS [7,8].

We have employed three Viologen Dications (VGD), specifically paraquat (PQ), diquat (DQ) and lucigenin (LG), for the functionalization of silver colloidal nanoparticles (Ag NPs). VGD are able both to form charge transfer (CT) complexes with electron donor species such as PAHs [9] and interact strongly with the metal surface. In particular their bifunctional nature makes them able to induce the formation of HS. Thus VGD act simultaneously as HS builders and as molecular hosts in the detection of analytes to the highly sensitive region of the so-formed HS. The three VGD considered were selected because of their different structure regarding the extension of the aromatic part and the position of N atoms included.

The LG functionalization provided the most powerful VGD-NPs sensor system: we have reported the SERS detection of pyrene (PYR) down to nanomoles through spectra obtained employing the colloidal suspension (macro Raman) and in the zeptomol regime for spectra products of single aggregate of NPs (micro Raman). Furthermore we concluded that the LG-

NPs sensor system presents the ability to improve at the same time its stability (increased CT contribution and tighter bridging between LG and the two silver particle constituting the dimer) when interacting with the target molecule PYR.

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