

Building plasmonic hot spots in Ag nanoparticles by using bifunctional viologens

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During the last years new experiments have renewed the interest for the surface-enhanced techniques, such as the possible detection of a single molecule (SMD) by surface-enhanced Raman scattering (SERS)[1]. SMD is possible because the intensification of the EM field does not occur homogeneously on the whole metallic substrate. In fact, it is widely accepted that the main part of the electromagnetic field intensification occurs in special regions of the metallic surface called hot spots (HS) [2]. In particular, interparticle gaps are good candidates to behave as HS, where the distance and the excitation wavelength play an important role [3]. The number of interparticle junctions acting as HS can be increased by adsorption on the surface of bifunctional molecules [4].

In the work presented here we proposed to go further in the fabrication of HS, by using molecules providing a double function: (1) inducing the formation of HS, by virtue of their bifunctional nature and their ability to interact strongly with the surface, and (2) acting as molecular hosts in the detection of analytes promoting their approach to these so-formed highly sensitive regions. To accomplish this objective, we have employed viologen dications (VGD). VGD gather several properties of interest to fulfil the above purposes: they are electron acceptors [5], thus able to interact strongly with the metal surface; and besides, they are able to form CT complexes with electron donor species such as polycyclic aromatic hydrocarbons (PAHs), a group of pollutant compounds with a marked carcinogenous activity, which trace detection is nowadays of much importance.

Viologen dications can create highly sensitive and selective hot spots in junctions of silver nanoparticles, which can be followed in macroscopic samples by means of the plasmon absorption of these nanoparticles in suspension. The method was applied in the case of detection of pyrene (a PAH pollutant), confirming the great ability of viologens, mainly Lucigenin, in the increasing of the sensitivity and selectivity of SERS technique as both hot spot inducers and host molecules.

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