Molecular linkage of plasmonic nanoparticles in colloidal suspensions for enhanced pollutant sensing

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Linear α,ω-dithiols with aliphatic nature have been used in this work as linkers to control the aggregation of silver nanoparticles and to induce the formation of interparticle gaps. The interest of these gaps resides in the well-known fact that when plasmonic surfaces are within a close distance, their plasmon modes couple[1]. This event affects the electromagnetic field distribution in a manner that a drastic enhancement occurs in the gaps leading to the creation of *hot spots*. As a result, the optical response of substances situated inside the hot spots is strongly increased, which is highly valuable for their use in surface-enhanced spectroscopies. In this work we present a study of the formation and the characterization of the gaps formed by using dithiols of different lengths, where both thiol groups are connected by a linear aliphatic chain with 6, 8 and 10 CH_2 groups. This characterization was done by using plasmon resonance and transmission electron microscopy (TEM). The Surface-Enhanced Raman Scattering (SERS) technique was employed in the investigation of the adsorption of these dithiols on the metal surface by analysing key structural spectral markers of the adsorption, metal coordination, orientation, ordering and interfacial packing of these molecules on surfaces of silver and gold NPs[2]. The fingerprint character of SERS spectra, the propension rules of SERS[3] and the high sensitivity of this technique make this study possible even at the very low concentration of dithiols sufficient to induce the NPs linking. Dithiol-linked nanoparticles were employed as sensors in the detection of the pesticides aldrin, dieldrin, endosulfan and linden at very low concentrations, taking advantage of the high affinity of these pollutants for aliphatic-like membranes. The sensing ability of these substrates was optimized by varying the surface coverage of dithiols. Finally, the adsorption of pesticides on the functionalized metal surfaces was studied by obtaining the adsorption isotherms, which provided the affinity constant and the linearity curve to relate the SERS intensity to the pollutant concentration. According to the results, the functionalization with dithiols induces the formation of chain-like aggregates where the hot spots are localized in the interparticle gaps induced by the multi-layered adsorption of dithiols, which in turn are able to link the pesticide molecules (Figure 1).

References

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Figure 1: Detection of pesticide molecules (aldrin) by insertion into interparticle gaps induced by nanoparticle linking with dithiols.