Abstract

In the first part of the Thesis, a new type of active system for SERS and SERRS of hydrophobic molecules, namely a 3-dimensional (3D) nanosponge aggregate with incorporated hydrophobic molecules has been developed, and tested by fullerene C_{60} and hydrophobic free-base tetraphenylporfine (H_2TPP). The SERS and SERRS (surface enhanced /resonance/ Raman scattering) limits of detection (LODs) of C_{60} at four excitation wavelengths spanning the visible spectral region were found to be by one order of magnitude lower than in the reference system, which mimics the previously reported ways of utilization of Ag nanosponges as substrates for SERS and SERRS. The superiority of the newly developed sample is attributed to the efficient localization of the hydrophobic molecules into hot spots in 2D fractal aggregates of Ag nanoparticles (NPs). Diprotonation of H_2TPP during the procedure using HCl as the preaggregation agent has been eliminated by employment of NaCl. On the other hand, investigation of the mechanism of H_2TPP protonation during the former preparation procedure opened a possibility to employ Ag nanosponge aggregate as nanoreactor.

In the second part of the Thesis, 2D assemblies of AgNPs were found to be better substrates for SERS of single layer graphene (SLG) than the 3D ones. In particular, the 2D assembly of Ag NPs modified by ethanethiolate spacer deposited on SLG on glass enabled to obtain SERS of unperturbed SLG. By inversion of the preparation procedure, AgNPs array/SLG hybrid systems were prepared, and a weak negative doping of SLG by Ag NPs was revealed by SERS spectral probing.

In the third part, the last mentioned hybrid system was employed as a platform for assembling of AgNPs arrays/SLG/H_2Pc (ML) [H_2Pc = free base phthalocyanine, ML = monolayer] hybrid system for investigation of the mechanism of combined surface- and graphene-enhanced Raman scattering (SERS+GERS) of a monolayer of planar aromatic molecule, namely H_2Pc. By micro-Raman spectral probing of the hybrid sample as well as of the appropriate reference systems at 5 excitation wavelengths, SERS, GERS and SERS + GERS enhanced factors and SERS + GERS excitation profiles of H_2Pc spectral bands were determined. Two mechanisms of GERS, in particular (i) modification of the position and localization of the Q_y (0,1) electronic transition in the visible region and (ii) a charge transfer from Fermi level of SLG (positioned at -4.4 eV) to LUMO of H_2Pc and their additive operation with the electromagnetic mechanism of SERS were established.