Abstract

A systematic chemical and spectroscopic approach to evaluation of the effect of single-layer graphene (SLG) on Raman spectra of free-base phthalocyanine (H_2Pc) in glass/SLG/H_2Pc hybrid systems has been developed. By a combination of electronic absorption spectra, Raman spectra at five excitation wavelengths (532, 633, 647, 785 and 830 nm) and excitation profiles of H_2Pc Raman spectral bands, the constitution of the three prepared hybrid sysems has been established in the following manner: Hybrid system I comprises probably a bilayer of H_2Pc molecules, system VI approximately a monolayer of H_2Pc, and system X a slightly reorganized monolayer of H_2Pc molecules. Micro-Raman spectral mapping of all three hybrid systems yielded H_2Pc spectral bands (together with the SLG spectral bands) at all five excitation wavelengths. By contrast, for all three HOPG/H_2Pc reference systems (HOPG = highly oriented pyrolytic graphite), prepared by the same procedure as the corresponding samples, H_2Pc signal was detected only at 633 and 647 nm excitations. A selective increase of normalized Raman intensities of H_2Pc spectral bands for the glass/SLG/H_2Pc monolayer hybrid systems at 830 nm was revealed on the basis of a mutual comparison of Raman excitation profiles of all three samples of glass/SLG/H_2Pc hybrid systems. This excitation was found to mach the calculated difference between the Fermi level of SLG and lowest unoccupied molecular orbital (LUMO) of H_2Pc, and the intensity growth was attributed to the mechanism of GERS (graphene-enhanced Raman scattering) based on a photo-induced charge transfer. Operation of the second GERS enhancement mechanism at 647 and 633 nm excitations was revealed and attributed to favorable changes in electronic absorption spectra of H_2Pc caused probably by a weak interaction between Fermi level of SLG and highest occupied molecular orbital (HOMO) of H_2Pc. The latter mechanism was at least approximately quantitatively evaluated, yielding GERS enhancement factors 13-33 for 633 nm and 6-27 for 647 nm. Free-base phthalocyanine has proved to be a very well suited molecule for the study of GERS, namely due to its planar aromatic character and D_{2h} symmetry, as well as because of the positions of its HOMO and LUMO, that is, below and above the Fermi level of SLG, respectively.

Keywords: free-base phthalocyanine, single-layer graphene, Raman spectroscopy, graphene-enhanced Raman scattering, H_2Pc, SLG, GERS