Graphene-Metal Nanostructures as Surface Enhanced Raman Scattering Substrates for Biosensing

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During the past decades, surface-enhanced Raman scattering (SERS) spectroscopy attracted much attention for the high-sensitive label-free detection in the field of materials science, biophysics, medical diagnostics and molecular biology. SERS effect is known to be ascribed to both the enhancement of the electromagnetic (EM) fields localized at the edges of metallic particles (mostly noble metals such as Au and Ag) after excitation of surface plasmons at resonance conditions and a chemical enhancement attribute d to a charge-transfer (CT) process based on the transfer of an electron from an excited metal state to a vibrational level within the target molecule [1]. In addition to noble metals, dielectrics/semiconductors have emerged as potential SERS-active substrates. In particular, GaP nanoparticles (NPs), InAs/GaAs quantum dots, Si and Ge nanowires/nanotubes, ZnO nanocrystals, NiO, Cu_2O, TiO_2 and graphene exhibited SERS effects in absence of plasmonic enhancement, taking advantage of CT mechanisms.

In particular, the graphene-enhanced Raman scattering (GERS), discovered in 2010 [2], is supposed to be related to a chemical effect without any involvement of the EM mechanism. However, by covering the metal nanoparticles (Au/Ag) with graphene or graphene derivatives [3], some problems concerning conventional metal-based SERS substrate have been overcome, and noticeable Raman-enhanced signals of the adsorbate were obtained, taking advantages of the synergy between EM and CT enhancements [4].
In this work, we report on the coupling of Au NPs (obtained by colloidal synthesis) and Ag NPs (obtained by Ag sputtering) with single layer graphene (SLG) sheets obtained by CVD on Cu substrates.

The Raman Limit of Detection of a Ag NPs/SLG/Cu substrate in presence of Rhodamine 6G, used as a probe molecule, is discussed and compared with results previously obtained on some optimized Ag nanostructures in resonant SERS regime [1,5].

Beside this study, the transfer of the graphene-metallic NPs complex from the pristine Cu substrate to an elastomeric support (PDMS) [6] is presented as an alternative SERS substrate.

Protoporphyrin IX, a molecule able to exploit non-covalent strong π-π interactions [7] by forming a stacking complex with SL-graphene surface, is analysed in terms of GERS/SERS spectroscopy on optimized SL-Graphene/NPs/PDMS substrates. This molecule is characterized by a macrocyclic structure contained in hemoproteins such as hemoglobin and myoglobin. As the structure contains carboxylic terminations, it can be further derivatized with biomolecules and used as functional linker with respect to receptors (e.g., antibodies or amino modified ss-DNA) for biosensing aims. The results are discussed in view of a potential integration of plasmonic graphene-based biosensors in optofluidic chips [8].

References

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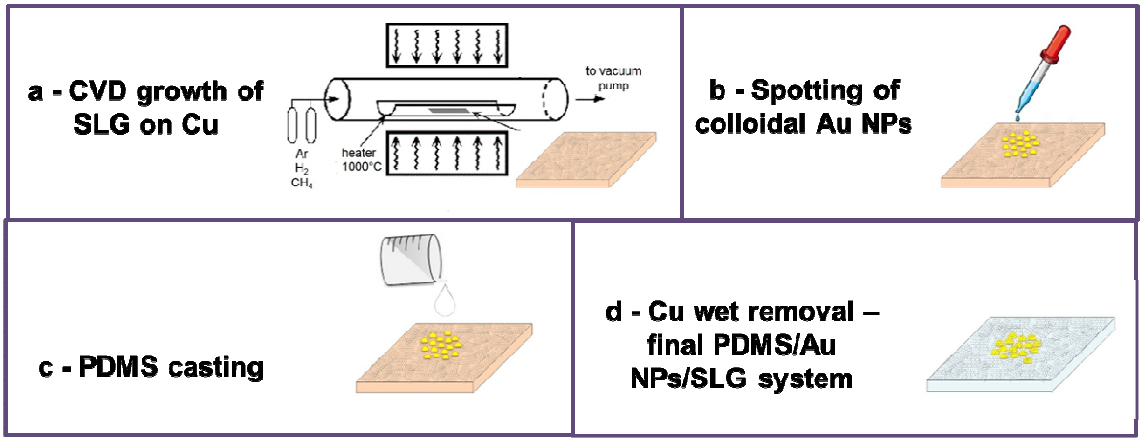

Figure 1: Scheme of transfer of SLG/Au-NPs complex from Cu to PDMS substrate.

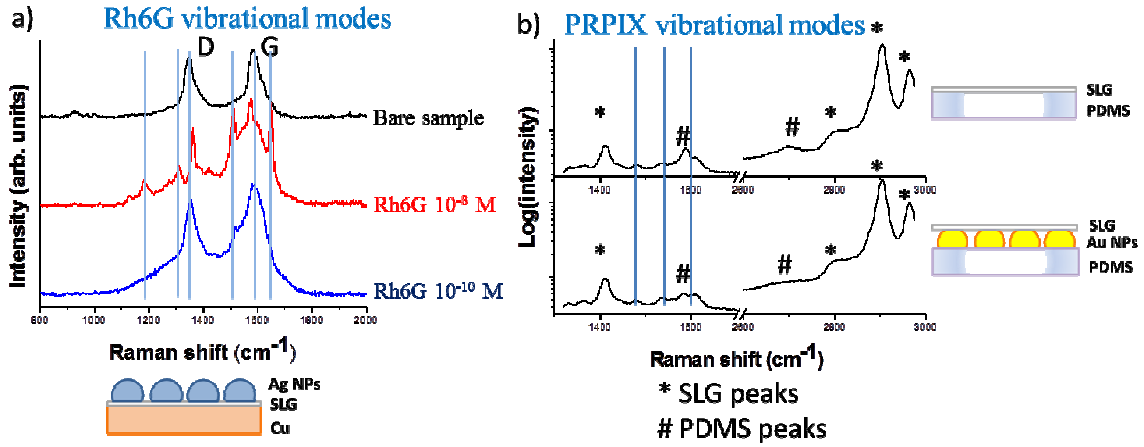

Figure 2: a) Rh6G Spectra; b) PRPIX Spectra