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

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Abstract

Multilayered structures composed by Single Layer Graphene (SLG), silver nanoparticles and polydimethylsiloxane membranes were used as SERS substrates for the analysis of porphyrins and hemoproteins (e.g. Myoglobin). The transfer process of SLG from its Cu growth substrate to the Ag-decorated polydimethylsiloxane membrane was optimized. A Limit of Detection (LOD) of 10^{-8} M was found for ethanolic solutions of Rhodamine 6G and the efficient detection of porphyrins and Myoglobin, adsorbed on SLG surface, was achieved. This study evidenced the potentialities of plasmonic graphene-based chips for biosensing.

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Keywords: "Surface Enhanced Raman Scattering; graphene-silver nanostructures; porphyrins; PDMS; biosensor"

1. Introduction

Surface-Enhanced Raman Scattering (SERS) spectroscopy is a powerful technique which can be applied for high-sensitive label-free detection of biomolecules. In addition to nanostructured noble metals, dielectrics/semiconductors have emerged as potential SERS-active substrates [1, 2]. Among them, graphene has been recently exploited in combination with Au/Ag nanoparticles (NPs), showing a noticeable Raman-enhanced signal of the adsorbates. Here we report on the SERS analysis of Hemin (H), Protoporphyrin IX (PRPIX) and Myoglobin (MYO), adsorbed through non-covalent strong π-π interactions [3] on Single Layer Graphene (SLG), transferred on an elastomeric support (polydimethylsiloxane, PDMS) decorated by Ag NPs.

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2. Experimental, Results and Discussion

The synthesis of the Ag on PDMS membranes were performed by d.c. sputtering [2]. The SLG was obtained on Cu substrate by CVD deposition. The SLG transfer was performed as it follows: i) liquid PMMA spinning on SLG surface; ii) Cu support removal in a $FeCl_3$ aqueous solution; iii) PMMA layer dissolution in acetone after the coupling of the SLG/PMMA membrane to the Ag-PDMS. A SLG/PDMS substrate without Ag NPs was also prepared for sake of comparison. The SLG surface was incubated with Rh6G ethanolic solutions (10^{-12}-10^{-7} M, 5µl) and then dried to assess the LOD. H ($5x10^{-3}$ M, in NaOH (0.1 M)/EtOH (1:1)), PRPIX ($5x10^{-3}$ M, in DMF/EtOH (1:1)) and MYO (1 mg/ml, in PBS) were incubated on the SLG and analyzed by SERS spectroscopy with excitation at 514.5 nm, after rinsing. The transferred SLG shows a good quality in terms of graphene typical Raman features (# in Fig1a-b). Both SLG/Ag/PDMS and SLG/PDMS chips were analyzed after H (Fig1a) and PRPIX (Fig 1b) adsorption. The porphyrins Raman modes (green and brown vertical lines, for H and PRPIX, respectively) are quite intense in the case of SLG/Ag/PDMS samples, where the synergic Raman enhancement due to the SLG and Ag NPs is evident. For the samples fabricated without Ag NPs, only weak vibrational modes of PRPIX are detectable. The spectra, acquired after the MYO adsorption [3] on the SLG, confirm the higher enhancement efficiency of the chip embedding the Ag NPs. Moreover, MYO, adsorbed on porphyrins (especially PRPIX) already interacting by stacking with the SLG surface (dark blue curve in Fig.1b), shows higher peaks intensity, thus suggesting that the inner (naturally embedded in myoglobin) and the outer (adsorbed on surface) porphyrins are π–π interacting. A LOD of 10^{-8} M for Rh6G, used as probe molecule, was experimentally verified for the SLG/Ag/PDMS chip.

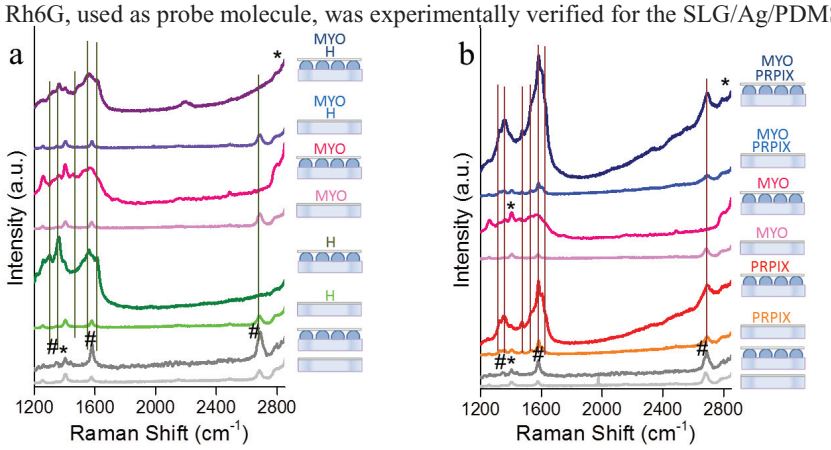

Fig. 1. SERS analysis on (a) H and MYO, adsorbed on SLG/AgNPs/PDMS and SLG/PDMS and (b) PRPIX and MYO, adsorbed on SLG/AgNPs/PDMS and SLG/PDMS. SLG peaks are marked with # and PDMS peaks are marked with *.

3. Conclusion

The successful porphyrin-mediated adsorption of biomolecules was proved by SERS analysis by means of SLG/AgNPs/PDMS substrates, demonstrating that porphyrins can be used as functional molecules for plasmonic graphene-based biosensing and highlighting its potential integration in optofluidic chips.

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