Electronic interactions at the graphene interface: the effect of substrate and the media

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Graphene possesses a unique combination of electronic and chemical properties, which makes it particularly suitable for developing electrochemical devices for biomedical applications. Due to its aspect ratio, i.e. large surface exposure for a minimal thickness, graphene is widely used in a number of biological sensing devices, where it is in direct contact with an aqueous electrolyte containing ions and molecules of different nature. Previous works concerning bidimensional (2D) materials-based sensors reveal extremely large dispersions regarding graphene's sensitivity to specific analytes. Such differences are not well understood and may be attributed to intrinsic (eg. related to the graphene quality) and/or extrinsic (eg. the nature of the substrate or the presence of absorbed charges) factors. Thus, understanding the interaction of this 2D material with the aqueous medium and the way charges in the solution may screen those in graphene, is crucial. In this work, we explore how the graphene/electrolyte interface is affected by a combination of factors: substrate, medium (eg. pH, ionic strength) and altered surface chemistry (absorbed charge), providing a more profound understanding of the physicochemical interfacial phenomena. To this end, spectroscopic techniques such as Raman and Electrochemical Impedance were used. We demonstrate that Raman enables addressing charge carriers in graphene supported on conductive or insulating substrates; as well as being an indirect measurement of the adsorbed charge in graphene [1]. Complementary, from impedance spectroscopy we obtain information about the capacitance dependence with the parameters of study: substrate nature, pH, ionic concentration and applied voltage [2]. Additionally, theoretical simulations help in understanding the effect of involved phenomena as the type of the adsorbed charge and the graphene/substrate coupling. Our results have unveiled an intriguing effect of the graphene´s close environment on the carrier modulation of graphene, which have revealed the need for uncovering a strategy to place a controlled adsorbed charge on top of graphene, precious information for numerous applications involving graphene-liquid interfaces.

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FIGURES

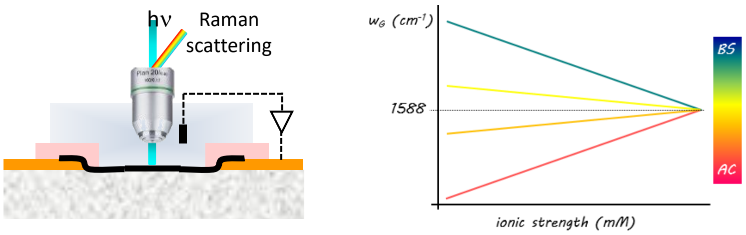

Figure 1: Left) Schematic lateral view of the graphene electrode device for in situ Raman characterization. Right) Fermi Level modulation (i.e. LO phonon energy) with the ionic strength at different pH.