Differential ionic interaction in graphene electrodes quantified by *in situ* Raman spectroscopy

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Understanding the chargepotential landscape at the graphene-liquid interface is crucial when working with graphene electrodes, extensively used nowadays for biosensing or energy storage applications, among others.

In this work we investigate the influence of ionic aqueous solutions on single layer graphene. Differently supported graphene electrodes were immersed in ionic solutions of increasing KCI concentration (at a constant pH). Impedance spectroscopy was used to calibrate the shift of the charge neutrality point of graphene with [KCI]. In parallel, chronoamperometric experiments and *in situ* Raman spectroscopy were performed to monitor the influence of the [KCI]. The change of the Fermi level in graphene was obtained from the shift of the energy of the G Raman band [1,2].

This study reveals an intriguing behaviour. Our data show that there is a shift of the Fermi level in graphene with [KCI], when the the graphene layer is supported on an insulating substrate. Such a shift, however, is not observed when graphene is on a conductive substrate.

By combining Raman and capacitance measurements on graphene electrodes we discuss the ion interaction and related charge induction mechanisms, which play a key role in the phenomena at the graphene-liquid interface, crucial for many applications such as sensors, energy storage, etc.

References

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Figure 1: Frequency shift of the G band of graphene (on different substrates) with [KCI]. Schematic representation of the charge balance of graphene depending on the substrate, $\sigma_{subs}+\sigma_{GR}+\sigma_{diff}=0$