

Molecular Characterization and DNA-sensing using Graphene Electrochemical Devices under Illumination*

Pedro Alpuim, Edgar Pinzón, Laís C. Lopes, Telma Domingues, Jérôme Borme, Erika Godoy, M. Manuela M. Raposo, Paulo R. Bueno

Abstract— In the AC-electrochemical mode, the signal of quantum capacitance (C_q) of individual graphene channels was resolved as a function of a superimposed DC bias potential through electrochemical impedance spectroscopy (EIS). This capacitive response was used to study the electronic states of push-pull molecules immobilized on the graphene surface in the dark and under visible illumination in the 400 to 580 nm range. The same technique will be further used in the molecular detection of target DNA by functionalizing the graphene surface with complementary probe-DNA and monitoring the C_q -minimum (Dirac point) changes for different target-DNA concentrations in the dark and under visible illumination.

Since its isolating in 2004 by Geim and Novoselov, graphene, a monolayer of carbon atoms arranged in a honeycomb-type hexagonal lattice, has revolutionized solid-state physics and material science because of its unique electrical and electronic properties, such as its ambipolar transport and relativistic electron dynamics close to the electroneutrality point.¹ These properties converted this 2D material into different applications' platforms, particularly optoelectronics and biosensing.

Therefore, experimental approaches that allow access to its electronic structure quickly and straightforwardly are required to advance in developing technologies based on graphene quantum properties. In this sense, electrical perturbation-based methodologies, considered non-destructive, enable access to graphene's electron density-of-states (DOS) by measuring electrical properties in mild experimental conditions.² For instance, in the graphene field-effect transistor setups, with three contacts, source (S), drain (D), and gate (G), from the measuring of the graphene channel current between S and D as a function of the DC bias potential imposed between the S and G, it is possible to resolve a V-shaped transfer curve, which is characteristic of the graphene ambipolar behavior.^{3,4}

It has recently been demonstrated that graphene electronic DOS can be resolved using an electrochemical setup by experimentally measuring its quantum capacitance (C_q) response through electrochemical impedance spectroscopy (EIS) measurements.⁵ The latter is supported by the proportionality relation between both properties, C_q and DOS, when plotted as a function of energy:

$$C_q (eV) = e^2 \text{DOS} (eV) \quad (1)$$

where e and eV correspond to the electron charge and energy, respectively. Therefore, it is possible to access the graphene DOS when measuring its C_q -response experimentally.⁵ Another exciting characteristic of graphene is the possibility to use its surface as a playground to immobilize and excite inorganic and organic molecules whose quantum states may couple with the graphene DOS. Among the principal forms of anchoring molecules onto the graphene surface is their modification with a π -conjugated side chain, prompting a non-covalent π - π interaction with graphene. This approach lends itself to different applications in biosensors, supercapacitors, and solar cells, in which these organic molecules are π - π stacked over graphene.⁶

Furthermore, the immobilization of molecular systems with electron donor – π bridge – acceptor structure, which are known as push-pull molecules⁷ (see Figure 1), over graphene allows us to explore the phenomenon of electronic coupling of the quantum states of both systems through measurement of C_q -response of the coupled system. In this line, we present a device comprising 20 graphene functionalized channels per chip (each channel with dimensions $L=25 \mu\text{m}$ and $W=81 \mu\text{m}$) that can be operated in an electrochemical mode to characterize the electronic structure of push-pull molecules immobilized over graphene through the C_q -response of this later. Because this type of molecule strongly absorbs visible light and graphene is a potent photoluminescence quencher at short distances,⁸ we decided to repeat the electrochemical

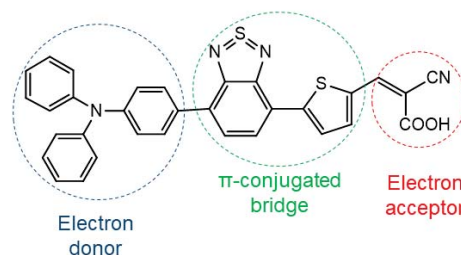


Figure 1. Chemical structure of the push-pull molecule 2-cyano-3-(5'-(7''-(4'''-diphenylamino)phenyl)benzo[c][1,2,5]thiadiazol-4''-yl) thiophen-2'-yl) acetic acid (DTTA).

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P. Alpuim (pedro.alpuim.us@ inl.int), T. Domingues and J. Borme are with the International Iberian Nanotechnology Laboratory (INL), Av. Mestre José Veiga, Braga, Portugal.

E. Pinzón, L. Lopes, E. Godoy and P. Bueno are with the Instituto de Química, Universidade Estadual Paulista (UNESP), Araraquara, Brazil

M.M.M Raposo is with the Centro de Química da Universidade do Minho, Braga, Portugal.

P. Alpuim and T. Domingues are also affiliated with the Centro de Física da Universidade do Minho, Braga, Portugal.

experiences in the dark and under illumination in a range of visible wavelengths and compare the results.

The graphene electronic structure was first resolved in the dark, as shown in Figure 2, in which the characteristic V-shaped C_q -response was observed as a function of energy (black curve). Then, graphene channels were modified with the push-pull molecule DTTA, depicted in Figure 1, by incubating them in a solution of this molecule (1 mM DTTA in DMF) for 4 hours.

The EIS characterization obtained in the dark after modification is also presented in Figure 2 (red curve), where significant changes were observed in the graphene C_q -response, such as the decrease in the C_q magnitude,

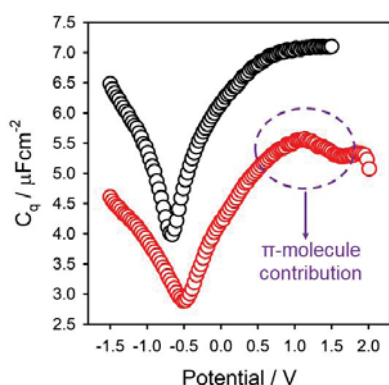


Figure 2. Quantum capacitance (C_q) as a function of the DC potential obtained via EIS for (a) graphene channel and (b) this modified with the DTTA molecule through π - π stacking. EIS measurements in phosphor buffer solution (PBS) were performed in the low-frequency range.

displacement of the C_q -minimum and rise of a new contribution between 0.5 and 2.0 V, which was not observed for the pristine graphene. Therefore, these changes electrochemically demonstrate the graphene surface modification with the DDTA molecule and the electronic interaction between the energy states of both systems.

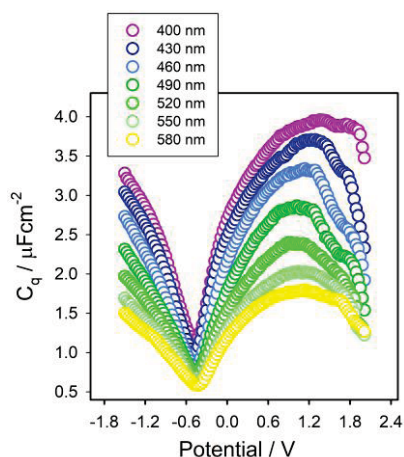


Figure 3. Quantum capacitance (C_q) response was obtained for an individual graphene channel modified with the DTTA molecule under visible-light illumination of different wavelengths. All measurements were performed in PBS at the equilibrium frequency (117.6 Hz)

Next, we repeated the measurements under illumination using a monochromator to select visible light of different wavelengths. Figure 3 presents the behavior of the C_q attained

for wavelengths ranging from 400 to 580 nm, in which the most remarkable changes in the C_q magnitude were observed approximately in the same potential window where the molecule's contribution appeared in the dark. A non-radiative resonance energy transfer mechanism between the graphene electronic states and the photon-excited electron in the molecule is proposed to explain the relaxation of the excited DDTA molecule through the graphene DOS; in other words, the electronic coupling of graphene's and the molecule's density-of-states.

By plotting the maximum value of C_q obtained for each wavelength as a function of this latter and comparing this response with the DTTA molecule visible absorption spectrum in solution (not shown), it is possible to conclude that the C_q follows a sigmoidal behavior where its inflection point corresponds to the absorption maximum. This correspondence suggests that the optical absorbance of the DTTA molecule⁸ can be monitored through the C_q -response of graphene. Accordingly, graphene can be considered a platform to electronically and optically characterize molecular systems by immobilizing them on the graphene surface and measuring their properties through time-dependent electrochemical approaches such as EIS.

Finally, considering that the carboxylic acid group present in the DTTA structure can be used to bind receptor-biomolecules via amide bond covalently, the DTTA-graphene coupled system modified with probe-DNA will be tested as a biosensing interface for detecting target-DNA (tDNA) with a complementary oligonucleotide sequence for hybridization. Preliminary data showed a linear response in the dark as a function of the tDNA concentration in solution when using the C_q -response as a transduction signal. In addition, the biosensing experiments will also be performed under illumination, expecting a greater sensitivity due to the additional charge separation generated by the photoexcitation.⁹

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