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Functionalization-Driven Modulation of Charge Transport in Graphene: An Atomistic Insight into Electrochemical Interfaces

Filipe Camargo Dalmatti Alves Lima[1], Rafael N. P. Colombo[2], Wanderlã L. Scopel[3], Frank N. Crespilho[2], Rodrigo G. Amorim[4]

[1]*Federal Institute of Education, Science, and Technology of São Paulo, Campus Matão, SP, Brazil*

[2]*São Carlos Institute of Chemistry, University of São Paulo, SP, Brazil*

[3]*Department of Physics, Federal University of Espírito Santo (UFES), Vitória, ES, Brazil*

[4]*Institute of Chemistry, Federal Fluminense University (UFF), Volta Redonda, RJ, Brazil*

e-mail address: fdlima@ifsp.edu.br

As electrochemical sensors and energy systems push toward higher sensitivity and efficiency, understanding how chemical modifications affect charge transport at the atomic scale becomes essential. Graphene, with its tunable surface chemistry and exceptional conductivity, presents both an opportunity and a challenge when introducing functional groups and structural defects.[1] Here, we present an atomistic theoretical study of graphene modified with 4-carboxyphenyl (4CP) groups and nanopores, as a model system relevant to Electric Electrochemical Vertical Devices (EEVDs). Using a quantum transport simulation framework combining density functional theory (DFT) and the non-equilibrium Green's function (NEGF) formalism, we calculated energy-resolved transmission spectra, local current densities, projected densities of states (PDOS), and binding energies for multiple configurations, including pristine graphene (GR), nanoporous graphene (GRP), and 4CP-functionalized surfaces (GR-4CP and GRP-4CP).

Our results show that 4CP preferentially adsorbs near nanopore edges, with site 1 exhibiting the strongest binding energy (−2.85 eV). However, this functionalization leads to a conductance drop of up to 35% in specific energy windows near the Fermi level. Position-dependent simulations (sites 1–5) reveal that adsorption at sites 1 and 3 causes the largest suppression in in-plane electron transmission. At −0.5 eV, sensitivity values exceeded 20%, aligning with electrochemical impedance observations in functionalized systems. Local current (LC) projections and wavefunction analyses indicate spatial redistribution of current pathways around the defect sites, with anisotropic current densities and localized states forming at 4CP adsorption zones. Interestingly, at −1.0 eV, functionalized systems showed enhanced local currents relative to pristine GRP, highlighting energy-dependent conductance recovery via molecular states.

PDOS analysis further confirms hybridization between molecular orbitals and graphene's π-system, especially at −1.6 eV and around the Fermi level. These electronic features are consistent with scanning tunneling spectroscopy profiles and help explain the trade-off between enhanced heterogeneous electron transfer (HET) and reduced in-plane conductivity upon functionalization.

These simulations reveal that covalent functionalization—specifically via 4-carboxyphenyl groups—produces stronger and more localized changes in charge transport than structural defects such as nanopores. Unlike vacancy-induced electronic disorder, functional groups selectively reconfigure electronic pathways, generate directional current anisotropy, and hybridize with graphene's π-system in energy-specific regions. This effect highlights that molecular functionalization is not merely equivalent to introducing defects, instead, it offers a tunable approach to control charge transport at the atomic level. Our findings link microscopic theory and experimental observations, offering insight into the design of graphene-based electrochemical platforms with optimized trade-offs between in-plane conductivity and out-of-plane electron transfer.

References:

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