PÔSTER - RESUMO - SENSORES E BIOSSENSORES

THEORETICAL DESIGN OF CARBON DOT AND POLYPYRROLE NANOCOMPOSITES FOR CHEMICAL SENSING: A FIRST-PRINCIPLES STUDY

Augusto Cisconi Deienno (a.deienno@unesp.br)

Augusto Batagin Neto (a.batagin@unesp.br)

Graphene quantum dots (CQDs) functionalized with conjugated polymers have emerged as promising platforms for chemical sensing due to their tunable electronic and optical properties [1]. In this work, a systematic theoretical investigation was conducted to elucidate how successive chemical functionalization and polymerization modulate the electronic structure and gas-sensing response of CQD-based nanocomposites. Pristine zig-zag graphene nanoflakes were progressively functionalized with carboxylic groups, followed by anchoring of 2-(1H-pyrrol-1-yl)ethan-1-amine ligands (PETN), which were subsequently polymerized into polypyrrole-decorated structures (CQDnPPy). Geometry optimizations and electronic-structure calculations were performed within the density functional theory framework (DFT/B3LYP/6-31G(d)), while optical properties and photoinduced charge-transfer processes were evaluated using TD-DFT, including the long-range-corrected wB97X-D functional [2]. Local reactivity was assessed via condensed-to-atoms Fukui indices (CAFI) [3], and sulfur dioxide (SO2) adsorption was investigated at the most reactive sites. Born-Oppenheimer molecular dynamics (BOMD) simulations were conducted using density-functional-based tight binding (DFTB) and extended tight binding (xTB) approaches [4] to assess cluster stability. The results reveal that

carboxylation induces uniform stabilization of the frontier orbitals without significantly altering the band-gap, whereas PETN anchoring shifts orbital energies upward through inductive effects. In contrast, polymerization into PPy networks produces pronounced band-gap narrowing driven by HOMO destabilization and enhanced p-conjugation. CAFI analyses indicate that only polymerized CQDnPPy systems exhibit electrophilic reactive sites on the polymer chains, highlighting the crucial role of PPy formation in sensing activity. SO2 adsorption perturbs frontier orbital energies and introduces analyte-derived states near the conduction band, consistent with electron-trapping behavior and reduced electronic mobility. The complexes exhibit binding energies and recovery times consistent with reversible physisorption suitable for sensing applications, as further supported by BOMD simulations. TD-DFT analyses reveal analyte-induced charge-transfer excitations dominated by PPy-to-analyte transitions mediated by pyrrole bridge units, which are expected to modulate photoluminescence and exciton dynamics. Overall, the results demonstrate that controlled PPy polymerization on CQDs creates electronically responsive adsorption centers and enables efficient analyte-induced charge trapping, establishing CQD-PPy nanocomposites as promising candidates for sensitive optoelectronic SO2 sensors.

Acknowledgements. The authors gratefully acknowledge the São Paulo Research Foundation (FAPESP) for financial support (grants 2025/27044-5 and 2025/09784-1) and the National Council for Scientific and Technological Development (CNPq) for funding (grants 408449/2024-1 and 305002/2025-2). This study was also financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001.

References:

[1] N. Naidek, A.J.G. Zarbin, E.S. Orth, J. Polym. Sci. Part Polym. Chem. 56 (2018) 579–588. DOI: 10.1002/pola.28944.

[2] J.-D. Chai, M. Head-Gordon, Phys. Chem. Chem. Phys., 10 (2008) 6615–6620. DOI: 10.1039/B810189B.

[3] W. Yang, W.J. Mortier, J. Am. Chem. Soc. 108 (1986) 5708–5711. DOI: 10.1021/ja00279a008

[4] F. Spiegelman, N. Tarrat, J. Cuny, L. Dontot, E. Posenitskiy, C. Martí, A. Simon, M. Rapacioli, Adv. Phys. X 5 (2020) 1710252. DOI: 10.1080/23746149.2019.1710252.

Palavras-chave: graphene quantum dots; polypyrrole; gas sensing; so2 adsorption; nanocomposite; dft.