UNIVERSIDADE FEDERAL DO ABC (UFABC)

Programa de Pós-Graduação em Nanociências e Materiais Avançados (PPG-NMA)

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First-Principles and Molecular Dynamics Study of Topological Strain and Functionalization in 2D Carbon Allotropes for Hydrogen Evolution Catalysis

Pré-projeto de pesquisa apresentado ao Comitê de Seleção do PPG-NMA da Universidade Federal do ABC como requisito para ingresso no curso de Mestrado.

Orientador: Prof. Dr. Pedro A. S. Autreto
Linha de Pesquisa: Modelagem e Simulação de Nanomateriais

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1. Introduction and Justification

The discovery and isolation of carbon-based two-dimensional (2D) materials have revolutionized condensed matter physics and catalyst design. Pristine graphene, characterized by its hexagonal network with sp^2 hybridization, exhibits exceptional electronic and thermal properties. However, from the perspective of surface chemistry and electrocatalysis, its planar framework and restricted out-of-plane p_z orbital distribution render it thermodynamically inert [1, 2]. Breaking the resonant delocalized π symmetry to chemisorb an intermediate species, such as an atomic hydrogen intermediate (H^*) in the Hydrogen Evolution Reaction (HER), requires a prohibitive activation energy. This results in a highly endothermic Gibbs free energy of adsorption (ΔG_{H^*}) far from the thermoneutral ideal ($\Delta G_{H^*} \approx 0.0$ eV) [1, 2].

To overcome these limitations, structural topology engineering emerges as a powerful theoretical strategy. Recently, several **2D carbon allotropes** composed of non-hexagonal rings (such as 4-, 5-, 7-, and 8-membered polygons) have been proposed in the literature, including PHOTH-graphene, phagraphene, and the phographene family [2–5]. These highly frustrated topologies impose severe angular strain, microscopically altering bond lengths and breaking the bipartite sublattice symmetry typical of pristine graphene. Fundamental works indicate that these topological arrangements destabilize the spatial symmetry required to protect Dirac fermions, inducing continuous metallic signatures and highly active, localized p_z orbitals at specific topological nodes or sites, which are critical for optimizing adsorbate binding in electrocatalysis [1–4]. Unlike pristine graphene, which requires artificial defects to activate its inert basal plane, these allotropes feature intrinsic active sites arising from their specific ring topologies, thereby offering clean yet highly reactive surfaces for hydrogen adsorption [2, 5].

In this mechanistic context, the localized angular distortion ($\Delta\theta$) induced by nonhexagonal rings acts as a thermodynamic driving force. The local transition from a planar, delocalized sp^2 network to a partial sp^3 like hybridization during hydrogen chemisorption helps to partially release the inherent geometric stress stored within these frustrated topological nodes [2]. Then, this structural relaxation dynamically offsets the energetic penalty of adsorbing a hydrogen atom (H^*), shifting the Gibbs free energy of adsorption (ΔG_{H^*}) closer to the thermoneutral ideal [2].

Evaluating these inherent topological strain mechanisms in non-hexagonal carbon allotropes, specifically how localized angular strain modulates p_z band centers alongside transition metal anchoring strategies (*Single-Atom Catalysts* – SACs) is a key strategy for designing efficient electrocatalysts [2]. This approach builds upon the SAC methodologies already implemented by the candidate and Prof. Autreto's research group on monolayers, such as our collaborative work in the 2D $CrCl_3$ layer [6], which demonstrated how transition metal (Co, Fe, Ni) functionalization selectively activates the inert basal plane by optimizing intermediate binding. Consequently, this proposal aligns with the computational modeling initiatives on 2D carbon allotropes directed by **Prof. Dr. Pedro A. S. Autreto** at PPG-NMA [7]. By synthesizing the candidate's experience in Density Functional Theory (DFT) with the structural and

electronic exploration of newly predicted 2D carbon networks, this project aims to overcome the thermodynamic limitations of traditional planar catalysts [2, 3].

2. Objectives

2.1. General Objective

Investigate, through first-principles calculations, the stability and the electronic, mechanical, and catalytic properties of pure and functionalized 2D carbon allotropes, to determine their potential as efficient electrocatalysts for the HER.

2.2. Specific Objectives

- Evaluate the fundamental electronic structure of the selected 2D carbon allotropes (e.g., with non-hexagonal rings) using the Vienna *Ab initio* Simulation Package (VASP) and SIESTA.
- Map localized covalency and sublattice symmetry breaking utilizing Maximally Localized Wannier Functions (MLWFs), Quantum Theory of Atoms in Molecules (QTAIM), and spatial charge partitioning.
- Quantify the direction-dependent mechanical anisotropy and large-scale thermal stability under electrochemical conditions.
- Calculate hydrogen adsorption barriers and Gibbs free energies (ΔG_{H^*}) across non-equivalent topological sites to identify active sites approaching the thermoneutral ideal ($\Delta G_{\mathrm{H}^*} \approx 0.0$ eV).
- Investigate the thermodynamic and electronic impacts of constructing SACs via transition metal doping at defect sites.
- Evaluate bonding and antibonding orbital hybridization using COHP and ICOHP analyses via the LOBSTER (Local Orbital Basis Suite Towards Electronic-Structure Reconstruction) program.

3. Methodology

The project will synergistically combine DFT and classical MD simulations. DFT calculations will be conducted using VASP [8] and SIESTA [9] with a linear combination of atomic orbitals (LCAO) basis set. Screened hybrid functionals, specifically HSE06, will be employed to resolve electronic phase ambiguities and accurately predict bandgaps and distorted Dirac cones [3, 10, 11]. In VASP, core-valence interactions will be treated via the Projector Augmented Wave (PAW) method with a plane-wave kinetic energy cutoff of 500 eV and a Gamma-centered k-point grid converged to 10^{-6} eV for electronic self-consistency. Plane-wave eigenstates will be projected onto MLWFs, and QTAIM charge partitioning will be used to identify reactive anchoring sites by tracking charge redistribution induced by intrinsic topological frustration [12, 13].

Dynamical and thermal stability will be validated through density functional perturbation theory (DFPT) phonon mapping via *Phonopy* and Ab Initio Molecular Dynamics (AIMD). The

AIMD simulations will span 10 ps at 300 K and 500 K in the canonical (NVT) ensemble to confirm that thermal fluctuations do not trigger structural collapse. Large-scale MD simulations will be performed in LAMMPS (*Large-scale Atomic/Molecular Massively Parallel Simulator*) [14] using the ReaxFF potential [15–17] to capture bond-breaking and bond-forming events. Structural equilibration of the carbon framework will be performed under isothermal-isobaric (NPT) conditions (298 K, 1 atm) using a Nosé-Hoover thermostat and barostat. To prevent energy drifts, a strict 0.25 fs integration timestep and the charge equilibration (QEq) method will be applied. Mechanochemical coupling will be explored through uniaxial and biaxial tensile loading along the armchair and zigzag orientations. This will evaluate how localized topological features, intrinsic defects, and hydrogen-induced chemical strain act as stress concentrators, compromising the ultimate tensile strength, Young's modulus, and fracture toughness via hydrogen embrittlement [18]. Finally, hydrogen recombination kinetics at high coverage will be modeled in the canonical (NVT) ensemble. Cluster and site-occupancy analyses will map the liquid-like surface diffusion of adsorbed hydrogen (H^*) around non-hexagonal topological defects acting as proton sinks, resolving transition state barriers for the Volmer–Tafel and Volmer–Heyrovsky pathways [19].

Electrocatalytic modeling of SACs and non-hexagonal defect sites will be conducted. This will apply Proton-Coupled Electron Transfer (PCET) theory to evaluate the thermodynamic driving forces of the Volmer, Heyrovsky, or Tafel reaction pathways [2, 20]. The free energy of adsorption (ΔG_{H^*}) will be derived according to the Sabatier principle, incorporating Zero-Point Energy (ZPE) and entropic corrections. For SACs, this involves modulating the d-band and p_z band centers of the catalyst to optimize the local coordination environment alongside local structural nonplanarity, then enhancing electrocatalytic performance [2, 21]. Finally, COHP and ICOHP analyses will be performed via the LOBSTER program. This will determine how the filling of antibonding orbital states dictates the binding strength of adsorbates like hydrogen [22, 23].

4. Project Timeline

The project is structured to be executed over the standard 24 months of the Master's program:

- **Months 1–6:** Coursework. Structural convergence tests, phonon validation (DFPT), and classical MD runs (LAMMPS) to assess the mechanical stability of pristine and functionalized allotropes.
- **Months 7–12:** Electronic structure determination (VASP HSE06, SIESTA LCAO) and MLWF mapping. Adsorption energy (ΔG_{H^*}) calculations at different topological rings.
- **Months 13–18:** Evaluation of SACs under network constraints, AIMD dynamics, and LAMMPS mechanical runs. COHP analysis using LOBSTER. Writing and submission of the first manuscript.
- **Months 19–24:** Completion of data analyses, writing, qualification exam, and defense of the Master's thesis at UFABC.

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