PÔSTER - RESUMO - SENSORES E BIOSSENSORES

AB INITIO INVESTIGATION OF GAS ADSORPTION ON Γ-GRAPHYNE: ELECTRONIC STRUCTURE MODULATION AND POTENTIAL APPLICATIONS IN SENSING

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Two-dimensional (2D) carbon allotropes have emerged as highly promising platforms for next-generation gas-sensing technologies, primarily due to their large surface-to-volume ratios, tunable electronic properties, and structural versatility [1,2]. Gamma-Graphyne, characterized by a mixed sp^2/sp hybridization arising from the periodic insertion of acetylenic linkages (–C=C–) into a graphene-like hexagonal lattice, possesses an intrinsic semiconducting band gap (~0.5 eV) combined with high carrier mobility, rendering it particularly suitable for chemiresistive sensing applications [3,4]. We report a comprehensive first-principles investigation of the adsorption of four environmentally and industrially relevant molecules — CH4, CO, CS2, and Cl2 — on a pristine Gamma-graphyne monolayer, employing Density Functional Theory (DFT) with van der Waals dispersion corrections (GGA-PBE+vdW) as implemented in PWSCF [5]. Adsorption was systematically evaluated at four high-symmetry sites (H1: center of the sp^2 hexagonal ring, H2: center of the sp–sp^2 cavity, T1: sp^2 carbon, T2: sp carbon of the acetylenic bond), considering multiple molecular orientations and initial molecule–surface separations of approximately 3.0 Å and 1.5 Å. All systems were fully relaxed without geometric constraints, and electronic properties were characterized through band-gap

analysis and projected density of states (PDOS) calculations. The results establish a well-defined sensitivity hierarchy: Cl2 » CS2 ˜ CO » CH4. CH4 exhibits exclusively weak physisorption (E_ad = -0.25 to -0.27 eV) with negligible band-gap modulation (~2%), indicating that effective methane detection would require surface functionalization or heteroatom doping. CS2 and CO physisorb preferentially at ring sites (H1/H2) with moderate adsorption energies (-0.26 to -0.33 eV) and band-gap variations below 2%, chemisorbed configurations at T1/T2 sites yield significant band-gap reductions (~11–13%) but are thermodynamically prohibited (E_ad > 0). In contrast, Cl2 undergoes thermodynamically favorable dissociative chemisorption at the T2 site (E_ad = -0.42 eV), with formation of covalent C–Cl bonds (d = 1.78 Å) and substantial elongation of the Cl–Cl distance from 2.01 Å to 2.88 Å. The Cl2_near_T1 configuration induces the largest electronic perturbation observed in this study, reducing the band gap from 0.50 eV to 0.37 eV (-27.18%) — a modulation exceeding those reported for graphene (<5%) and transition metal dichalcogenides (10–15%) [6]. PDOS analysis confirms that Cl2 is the sole adsorbate contributing directly to frontier states (valence band maximum and conduction band minimum), corroborating its exceptional sensing potential. These findings position pristine Gamma-graphyne as a selective and intrinsically sensitive platform for Cl2 detection, with direct applicability to industrial safety monitoring, water treatment facilities, and environmental sensing systems.

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Palavras-chave: gamma-graphyne; gas sensing; density functional theory; van der waals corrections; chlorine (cl2).