Bandgap Engineering in Modified α-4 Graphyne via Chemical Functionalization and Strain Tuning

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Bandgap engineering in low-dimensional materials is crucial for tailoring their electronic properties to meet the demands of nanoelectronic and optoelectronic applications[1]. In this study, we propose and examine two complementary strategies to tune the bandgap of a modified α-4 graphyne structure(α-4'), namely chemical functionalization and mechanical strain, using first-principles density functional theory (DFT) calculations[2,3].

The base material is derived from pristine α-4' graphyne by removing two acetylenic linkers, followed by hydrogen passivation of the resulting undercoordinated carbon atoms, yielding a chemically stable 2D framework. First, we investigate chemical functionalization of this structure with hydrogen (H), fluorine (F), and chlorine (Cl) at two substitution levels: (i) complete functionalization at all carbon sites, and (ii) selective functionalization excluding the acetylenic (triple-bonded) carbon atoms. Band structure and density of states analyses reveal significant variations in electronic behavior(**Figure 1**). Selective hydrogenation produces a wide direct bandgap of 3.9 eV, which reduces to 2.8 eV upon complete hydrogenation. Fluorinated variants exhibit a narrowing of the gap from 3.2 eV to 2.6 eV with complete substitution. Selective chlorination yields an indirect gap of 3.1 eV, while full chlorination induces metallicity with complete gap closure. Thermodynamic analysis based on formation energies confirms the stability of all functionalized configurations, with fluorinated systems being the most stable.

In the second approach, we explore mechanical tuning by applying uniaxial strain to the unfunctionalized modified α-4 graphyne. The results indicate strain-induced transitions in the band structure, including bandgap opening, closing, and direct-to-indirect transitions, which depend on the magnitude and direction of the strain. The expansive strain caused a narrow bandgap (Figure 2), while the compressive strain maintained the Dirac cone. These findings underscore the structure's mechanical flexibility and electronic tunability[4].

This work establishes dual pathways for bandgap control in α-4' graphyne, offering valuable insight into designing tailored 2D materials for next-generation electronics, including semiconductors, sensors, and flexible devices.

Figures

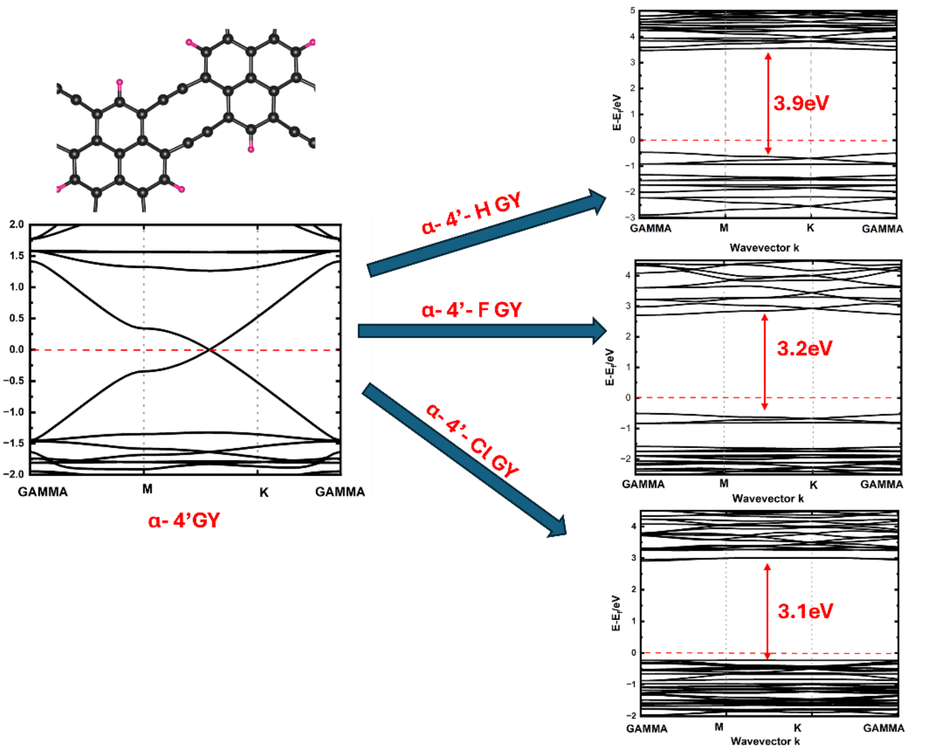

Figure 1: The band gap opening due to the chemical functionalization in α-4' graphyne

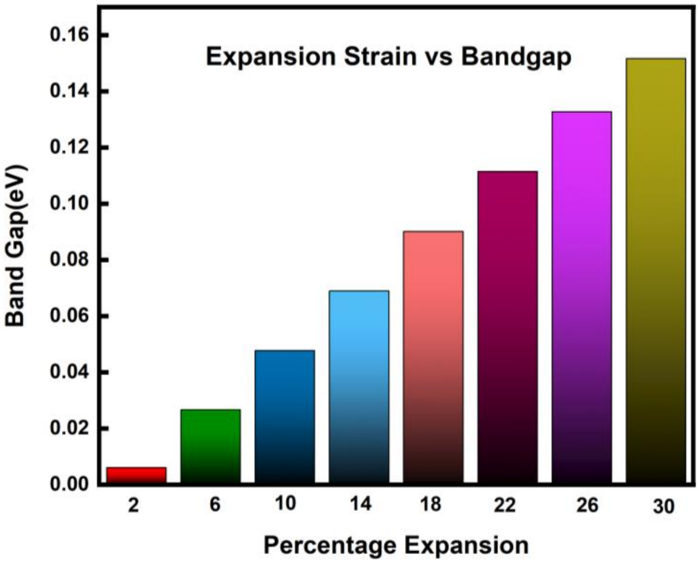

Figure 2: The effect of expansive strain on the electronic band structure of α-4' graphyne

References

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