

Fluorinated Graphene: A Stable Large-Gap Graphene Derivative Investigated by Scanning Tunneling Microscopy

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We present the first atomic-resolution microscopic and spectroscopic study of monolayer fluorinated graphene films. Graphene grown by chemical vapor deposition on polycrystalline copper foil is fluorinated by XeF₂ gas and characterized by x-ray photoelectron spectroscopy (XPS), Raman spectroscopy, scanning tunneling microscopy (STM), and scanning tunneling spectroscopy (STS). We directly measure the atomic and electronic structures of planar-sheet graphene fluoride, probe its stability under electron bombardment and thermal annealing, and elucidate interaction between the copper substrate and fluorinated graphene overlayer. We discover that fluorinated graphene C₆F retains a planar structure, exhibits a large band gap, and remains stable under electron bombardment and mild thermal annealing below 500°C.

While graphene has attracted a great deal of scientific interest, its inherent semi-metallic nature limits opportunities for this material in digital logic and microelectronics. In response, several techniques have been developed for modulation of the graphene band gap, including the patterning of nanometer-scale graphene ribbons and graphene hydrogenation. Fluorinated graphene offers unique advantages over these alternatives, as it lacks electronic edge states, and unlike hydrogenated graphene (graphane),¹ exhibits thermodynamic stability and high resistivity.^{2,3,4}

Bulk fluorinated graphite exists in several forms and has been studied extensively. However, monolayer fluorinated graphene has been isolated only recently,^{2,3,4} and very little is known of its structure, stability, and electronic properties, particularly in the case of planar-sheet graphene fluorides.

Like graphite fluoride, graphene fluorides exist in both planar-sheet and puckered-sheet configurations. In the puckered-sheet case, carbon atoms are fully *sp*³ hybridized and covalently bound with fluorine, buckling the carbon skeleton, opening a large (>3 eV) energy gap, and leading to stable (CF)_n or (C₂F)_n. This material can be exfoliated to produce few-layer and monolayer puckered-sheet graphene fluoride.^{3,4} However, reduction is generally destructive to the graphene skeleton, undermining one important goal of graphene functionalization.² In contrast, planar-sheet graphite fluorides (C_xF), synthesized near room temperature, exhibit ionic (x>20) or semi-covalent (x≤4) bonding and preserve the planar graphitic structure, yet are found to have a sizable energy gap (0–3 eV) that depends on fluorine concentration.

In this work, planar-sheet graphene fluoride is synthesized from monolayer graphene films grown on copper foil.⁵ Post-fluorination Raman spectroscopy of the D and D' bands shows increased *sp*³ hybridization on the foil. As indicated by XPS (Figure 1) and STM, XeF₂ fluorination produces ~C₄F, which after a 10 min vacuum anneal at 500°C approaches ~C₆F (locally) to ~C₁₂F (globally). The annealing process drives adsorbates and ionically-bound fluorine from the graphene, resulting in an energetically stable, atomically resolved fluorinated graphene lattice.

On high symmetry faces of polycrystalline copper the energy band structure (Figure 2) of fluorinated graphene is found to be consistent with theoretical predictions and spatially invariant across the graphene lattice. Although the observed band structure is predominantly that of fluorinated graphene, a copper surface state is often visible near –0.4 eV, an effect consistent with graphene on Cu(111).⁶

Structurally, the fluorine lattice is hexagonal with an inter-fluorine spacing of 6.0 Å (Figure 3). Despite semi-covalent C-F bonding the planarity of the graphene basal plane is preserved, following topographic modulation in the underlying copper substrate, and offering potential for future lithographic reduction of planar-sheet graphene fluoride.

References

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Figures

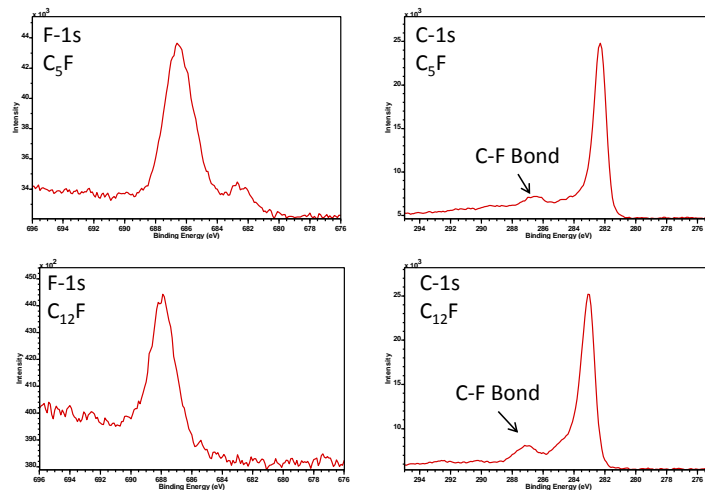


Figure 1: X-ray photoelectron spectroscopy of fluorinated graphene, consistent with semi-covalent carbon-fluorine bonding both before and after annealing. While XPS indicates a reduced fluorine concentration after anneal ($C_{12}F$ versus C_5F initially), the presence of a C-1s peak at 287 eV and F-1s peak at 688 eV suggest strong C-F bonding in both cases, indicating that remaining carbon-fluorine bonds are semi-covalent. (a) F-1s transition before annealing. (b) C-1s transition before annealing. (c) F-1s transition after annealing. (d) C-1s transition after annealing.

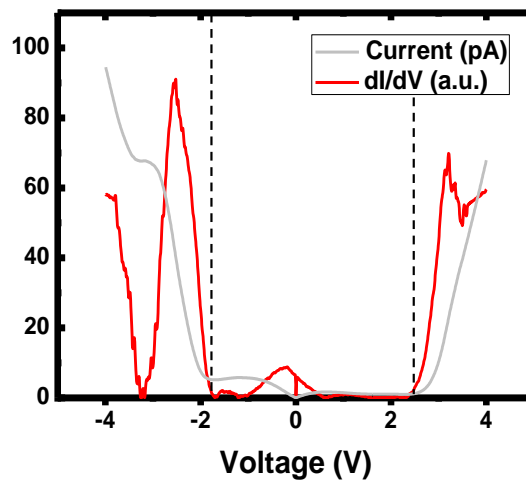


Figure 2: Scanning tunneling spectroscopy of fluorinated graphene on copper. Absolute value of current and dI/dV for graphene fluoride/copper system. Note the copper surface state near the Fermi level and the graphene fluoride band structure beyond $\pm 2V$. Energy gap is larger than anticipated due to band bending resulting from charging in the graphene fluoride overlayer.

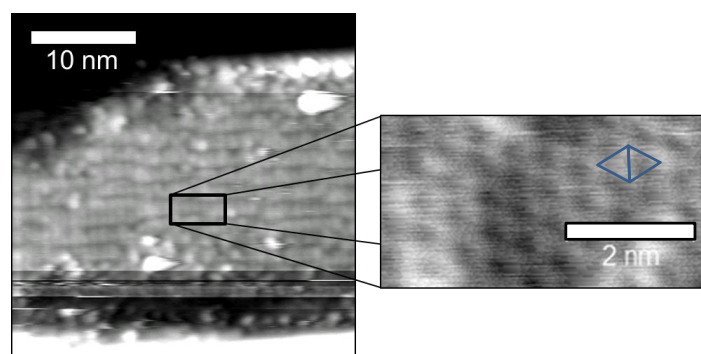


Figure 3: Atomic-resolution imaging of the graphene fluoride overlayer, exhibiting a hexagonal fluorine lattice with inter-fluorine spacing of 6.0\AA . This spatial locality is further evidence for semi-covalent fluorine-carbon bonding.