Supporting Information

Introduction of Near to Far Infrared Range Direct Band Gap in Graphene: A First Principle Insight

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K point sampling: Total energy vs 'k' point sampling curve of a 5x5 graphene super cell is shown in figure S1. Total energy saturates around 8x8 k point sampling, based on this observation, 10x10 k point sapling was used in all the computations.
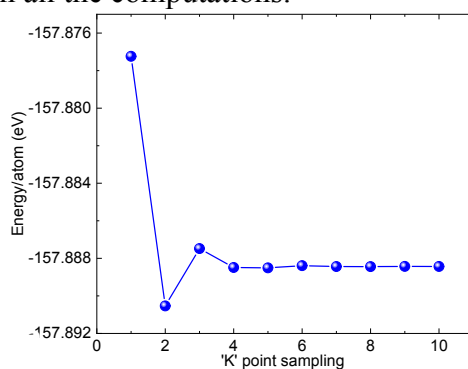

Figure S1: Total energy/ atom vs k point sampling curve of a 5x5 graphene super cell, computed using Local Density Approximation (LDA) functional.
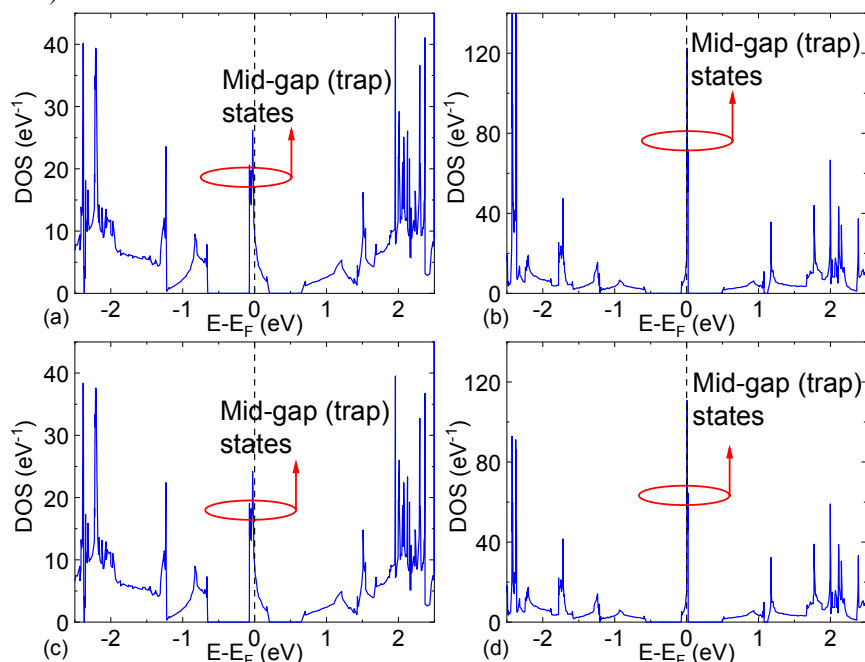

Figure S2: Density of states of 5x5 super cell of, (a) graphene with hydrogenated 1C vacancy, (b) graphene with fluorinated 1C vacancy. DOS of p-orbitals of all the carbon atoms in (c) graphene with hydrogenated 1C vacancy, (d) graphene with fluorinated 1C vacancy.

Density of States (DOS): Density of states of a 5x5 super cell each of hydrogenated (Fig. S2a) and fluorinated (Fig.S2b) graphene are compared with only p-orbitals DOS of all the carbon atoms in the corresponding super cells (Fig. S2c & S2d). Total trap state density near fermi level are same in total DOS and corresponding p-orbitals DOS of carbon atoms for hydrogenated (a, c) as well as fluorinated (b, d) graphene. Which tells that Mid-gap (trap) state densities near fermi level in the hydrogenated as well as fluorinated graphene are mainly due to contribution of p-orbitals of all the carbon atoms in the system.

Band Structure comparison: Energy optimized structures and band structures of 5x5 supercells of hydrogenated graphene and fluorinated graphene (Fig. S3a-d), computed using Perdew-Burke-Ernzerhof (PBE) form of Generalized Gradient Approximation (GGA) functional. Although, planar structure of fluorinated graphene is deformed to minimize the ring strain (Fig. S3b) which has not been captured by LDA in the manuscript. However, the computed band gaps are comparable with corresponding LDA functional (Fig. S3e).
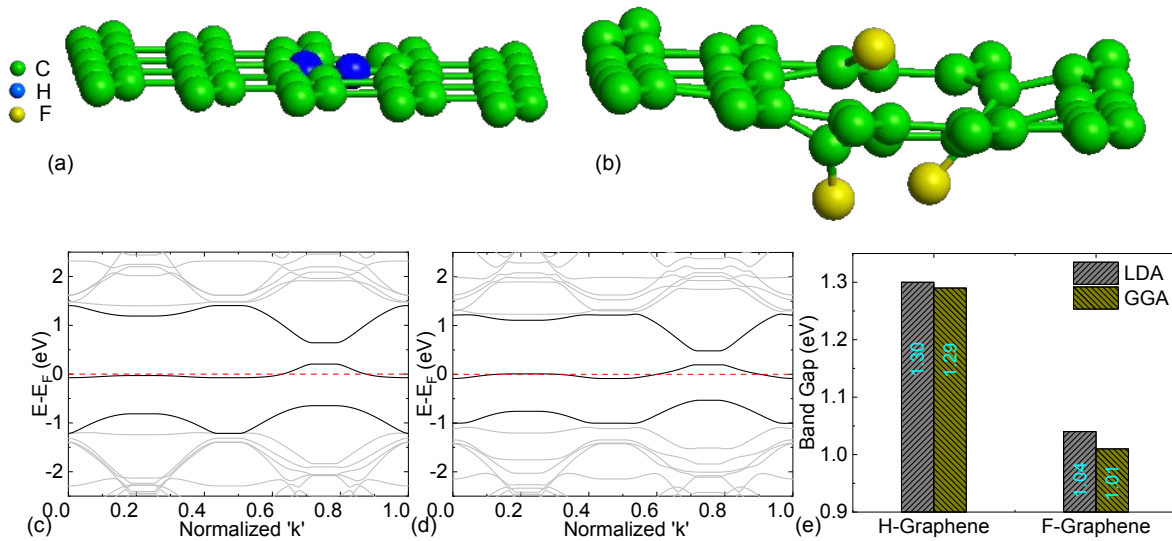

Figure S3: Tilted side view of (a) hydrogenated and (b) fluorinated one carbon vacancy of a 5x5 graphene super cell after optimization using PBE form of GGA functional. Band structures of 5x5 super cells of (c) H-graphene and (d) F-graphene, computed using Perdew-Burke-Ernzerhof (PBE) form of Generalized Gradient Approximation (GGA) functional. (e) Band gaps comparison with LDA functional.

7x7 super cells modules: Energy optimized structures of 7x7 super cells graphene which has hydrogenated or fluorinated carbon vacancy (Fig. S4).
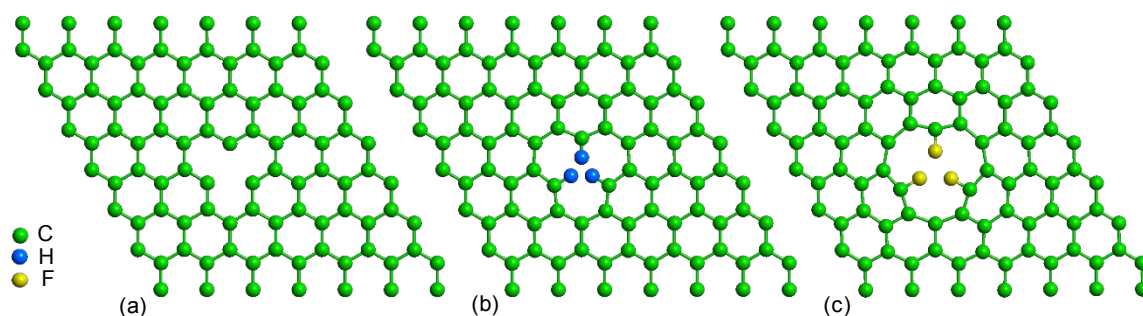
Figure S4: (a) 7x7 super cell of graphene with 1-C vacancy (b) hydrogenated 7x7 super cell of graphene at one carbon vacancy, (c) fluorinated 7x7 super cell of graphene at one carbon vacancy.

H_2 and F_2 near vacancy site of graphene: DFT optimization results show that when fluorine/hydrogen molecule approaches the vacancy site of graphene, its atoms have tendency of one to one bonding to unsaturated carbon atoms rather than changing hybridization of carbon and bonding together to the same carbon atom (Fig. S5).
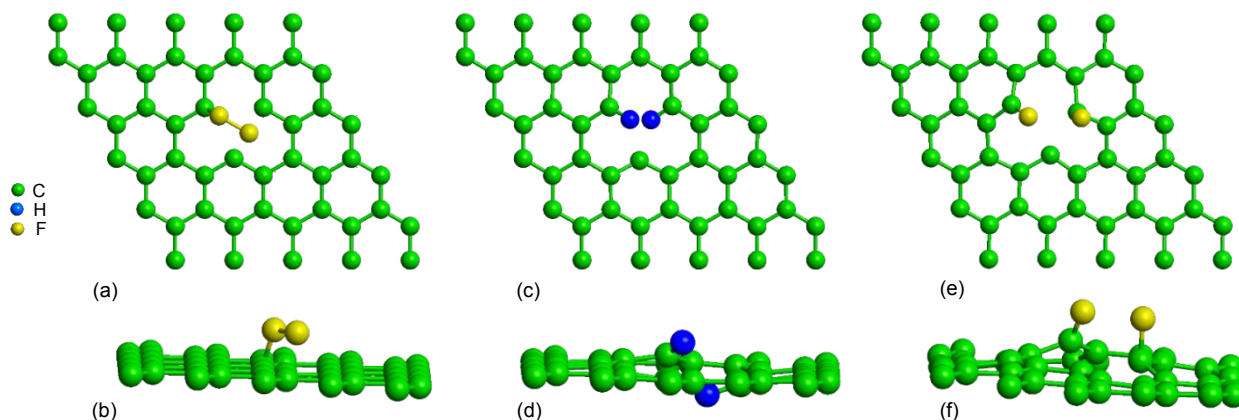

Figure S5: (a) top view and (b) tilted side view of fluorine molecule near vacancy site of a 5x5 graphene super cell before optimization. Similar module was created for hydrogen molecule as well. (c) top view and (d) tilted side view of energy optimized structure of hydrogen molecule near vacant site of graphene. (e) top view and (f) tilted side view of energy optimized structure of fluorine molecule near vacant site of graphene. The optimization study shows that H_2/F_2 has one to one bonding tendency to the unsaturated carbon atoms rather than bonding together with same carbon atom.

H-Graphene and F-Graphene with Oxygen: Hydrogenated and fluorinated graphene are relatively unreactive with oxygen unlike graphene with only vacancy. Energy optimized structure of the modules (Fig. S6) using Perdew-Burke-Ernzerhof (PBE) form of Generalized Gradient

Approximation (GGA) functional along with Grimme D2 van der Waals (vdW) correction confirm that oxygen is adsorbed over the graphene surfaces but doesn't dissociate hence will not degrade graphene near the hydrogenated or fluorinated sites.
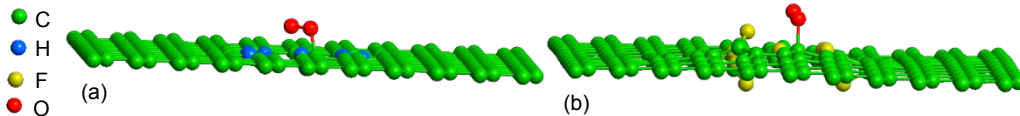
Figure S6: Energy optimized structures of 11x11 super cell (13 C vacancy) of, (a) hydrogenated graphene with an oxygen molecule, (b) fluorinated graphene with an oxygen molecule.

Chlorination of carbon vacancy: Chlorination of the vacant site in graphene doesn't give similar result as fluorination. Chlorination of the vacant site doesn't give one-to-one bonding with unsaturated carbons (Fig. S7a) like fluorination due to its multivalent property. Fermi level of the system, as shown in corresponding band structure (Fig. S7b), lies inside conduction band which makes the system metallic and hence not useful for bandgap-oriented applications. Effect of Bromine or Iodine are not studied but they can behave similar as chlorine due to their similar multivalent chemistry.
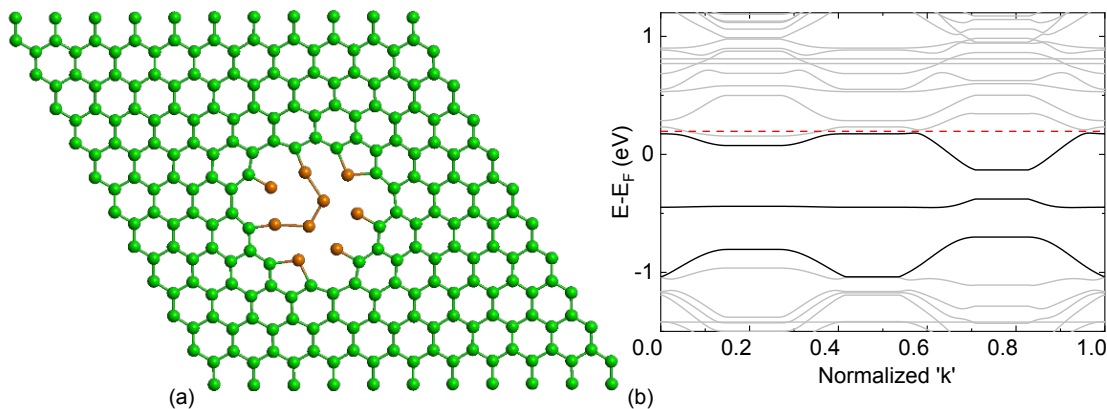

Figure S7: (a) Chlorinated 13-C vacancy of 11x11 graphene super cell (b) band structure of the chlorinated graphene.