

Organic and Metallo-organic Doping of Graphene

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Control of the carrier concentration is of utmost importance for graphene's application as an electronic material and in understanding of its properties. Using *ab initio* density functional theory calculations we have investigated the adsorption of organic (TTF, DDQ and F2-HCNQ) and metallo-organic molecules (cobaltocene and ferrocene) on graphene. We have discovered that the doping mechanism is not a simple one and that the open or closed shell natures of the molecules or their ionisation potentials do not always imply strong doping. Molecular doping is explained in terms of the density of states and hybridisation of the band structure of graphene with these adsorbed molecules along with the delocalisation of the HOMO and LUMO wavefunctions.

Metallocenes such as cobaltocene and ferrocene are sandwich compounds in which a divalent metal ion is sandwiched between two cyclopentadienyl rings. Ferrocene has 18 valence electrons which is considered to be the most stable configuration for metallocene compounds, hence it possesses a relatively high ionisation potential of 6.3 eV. However, cobaltocene has 19 valence electrons and a very low ionisation potential of 3.8 eV, making it an ideal candidate as a dopant for graphene. We find that the doping effect from ferrocene is very weak, with a charge transfer of only ca. 0.03 e/molecule, suggesting doping by an inductive effect rather than a true doping mechanism while the n-type doping from cobaltocene is an order of magnitude higher at 0.31 e/molecule. The delocalisation of the HOMO wavefunction of cobaltocene is shown in Figure 1.

Tetrathiafulvalene (TTF, $\text{H}_2\text{C}_2\text{S}_2\text{C}_2$) is a well known sulfur containing planar organic molecule which has shown promising results in the doping of carbon nanotubes^[1]. The adsorption of TTF results in n-type doping of 0.16 e/molecule and a relatively large binding energy of 0.72 eV, consistent with $\pi - \pi$ stacking between graphene and the TTF molecule. The adsorption of TTF also results in the opening of a modest bandgap in graphene (Figure 2). P-type doping of graphene by organic molecules is also possible using compounds such as DDQ (2,3-dichloro-5,6-dicyano-p-benzoquinone) and F2-HCNQ (3,6-difluoro-2,5,7,7,8,8-hexacyanoquinodimethane). Both of these molecules have a relatively high electron affinity of -4.86 eV and -4.7 eV respectively, comparable to the work function of graphene^[2] (≈ 4.6 eV), implying they should act as effective p-type dopants. Our calculations show DDQ results in a p-type doping of 0.32 e/molecule while F2-HCNQ accepts 0.77 e/molecule. The adsorption of F2-HCNQ also results in a 0.7 eV shift of the Fermi energy into the conduction band as shown in Figure 3.

References

- [1] Jing Lu *et al.* Phys. Rev. Lett. **93**, 116804 (2004)
[2] Filleter, T. *et al.* Appl. Phys. Lett. (2008), **93**, 133117

Figures

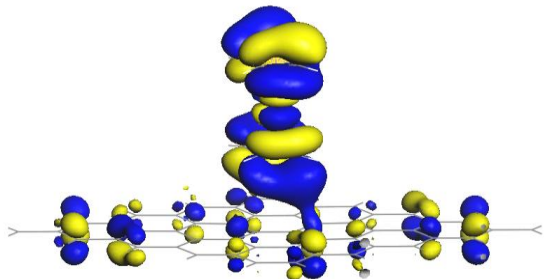


Figure 1: Delocalisation of the HOMO of cobaltocene upon adsorption on a graphene layer.

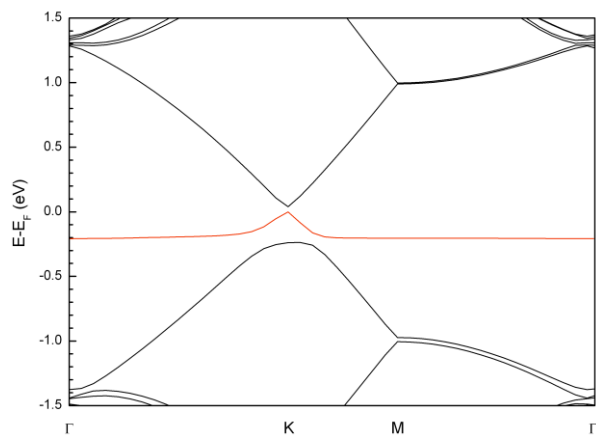


Figure 2: Band structure of graphene with an adsorbed TTF molecule, TTF impurity band shown in red.

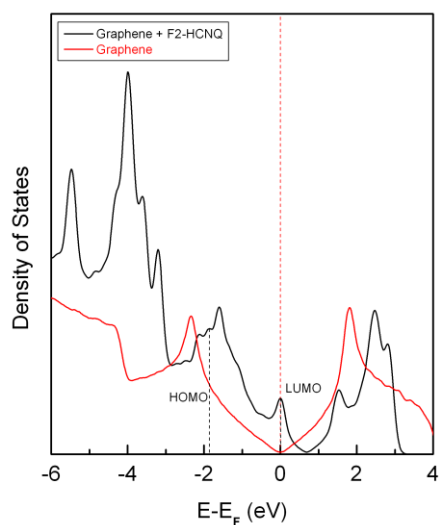


Figure 3: Density of states of graphene with an adsorbed F2-HCNQ molecule, DOS of graphene alone shown in red and graphene with an adsorbed F2-HCNQ shown in black.