Organic and Metallo-organic Doping of Graphene

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Accurate control of the carrier concentration is of fundamental importance to the application of any material in semiconductor devices. In order to study changes to the carrier concentration in graphene ab initio calculations have been employed to study the doping efficiencies, binding energies and changes in electronic properties of graphene upon adsorption of TTF, DDQ and cobaltocene molecules. We have used the local density approximation (LDA) to obtain the molecular binding energies and have employed the Hirshfeld charge partitioning method to calculate the charge transfer. Spin polarised calculations were used for the open shell molecule cobaltocene and we explored the effects of different adsorption sites. It was found that TTF and cobaltocene both act as n-type dopants with high binding energies and doping efficiencies of 0.24 and 0.41 electrons/molecule transferred respectively. DDQ acts an effective p-type dopant with a high binding energy of 1.2 eV and a doping efficiency of 0.33 electrons/molecule transferred from graphene to the DDQ molecule. Molecular doping using large organic molecules offers an attractive path to permanently modify the electronic properties of graphene while introducing minimal structural defects.

Computational method

• DFT calculations completed using the DMol³ code.
• The Local Density Approximation (LDA) functional of Vosko, Wilk and Nusair (VWN), which has been shown to perform well for a number of weakly bound systems such as graphite, has been employed here.
• Hirshfeld charge partitioning method has been used to determine the charge transfer.
• The graphene layer is modelled using a 6 x 6 unit cell (Figure 1) and the binding energy, doping efficiency and density of states calculated for each of the molecules in the adsorption sites shown below.

DDQ adsorption

• DDQ (2,3-dichloro-5,6-dicyano-p-benzoquinone) is an organic p-type dopant.
• Chemical formula: C8H4Cl2N2O2 (Figure 3a).
• Very high electron affinity (4.8 eV) similar to the work function of graphene (4.6 eV).
• Effective p-type dopant: 0.33 e/molecule, Fermi level shifted downwards by 0.34 eV (Figure 3c).
• Binding energy: 1.2 eV/molecule, forms a stable charge transfer complex with graphene due to strong π–π stacking.
• LUMO lies just below Fermi energy of graphene (Figure 3d).

Cobaltocene adsorption

• Metallocene (sandwich molecule) with chemical formula: Co(C5H5)2 (Figure 4a).
• Optimum adsorption geometry with the cyclopentadienyl ring above a bond site.
• Very low ionisation potential: 3.8 eV.
• Binding energy: 0.87 eV.
• Strongly n-doping: 0.41 e/molecule.
• Highest occupied molecular orbital (HOMO) becomes delocalised upon adsorption (Figure 4b).
• Band structure remains linear close to the K point (Figure 4d).

References

2. F. L. Hirshfeld, Theoretica chimica acta, 44, 129 (1977)