

Graphene band structure engineering by surface functionalization

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Abstract — We have employed first-principles density-functional calculations to study the electronic characteristics of covalently functionalized graphene by metal-bis-arene chemistry. It is shown that the M-bis-arene (M=Ti, V, Cr, Mn, Fe) functionalization leads to an opening in the band gap of graphene (up to 0.81eV for the Cr derivative), and as a result, transforms it from a semi-metal to a semiconductor. The $M[\eta^6\text{-(arene)}_2]$ -induced gap is attributed to the modification of the π -conjugation that depends on the concentration of bis-arene. This approach offers a means of tailoring the band structure of graphene and potentially its applications for future electronic devices.

I. INTRODUCTION

Graphene represents an ideal example of a nano-material and as such, continues to draw immense interest because of its unusual electronic and spin properties resulting from a simple structure composed of a single layer of carbon atoms arranged in a 2-dimensional honey-comb pattern [1]. These properties, including ballistic carrier transport and quantum Hall effect, make it a promising candidate as a building block of future nanoelectronic devices and as a possible replacement for silicon [2, 3]. In spite of graphene's amazing properties, there are some obstacles that need to be overcome before it can be considered as a viable candidate to replace silicon. The main barrier is absence of a bandgap. Therefore, producing a band gap is probably one of the most important challenges that need to be addressed before it can ultimately enable practical applications ranging from digital electronics to infrared nanophotonics.

Several methods have been proposed to functionalize graphene in such way that the adduct interacts with the conjugated π -system of graphene locally disturbing the conjugation and opening an energy gap. However present methods of functionalization usually create a lot of scattering centers, which diminish electron mobility.

Therefore, our objective is to identify molecules, when covalently bonded to graphene, can break its conical band structure and open up an energy gap even at low concentrations. To achieve this goal, we have examined electronic structure of metal-bis-arene (MBA) functionalized graphene and report below our results based on first-principle density-functional calculations. It is shown that the MBA covalently binds at the π -conjugation of graphene and changes the electronic properties from metallic to semiconducting. We also show that the energy gap can be tuned by adjusting the number of bound MBA adducts.

II. RESULTS AND DISCUSSION

The calculations were conducted within the framework of the DFT theory as implemented in the DMol₃ package [4]. The generalized gradient approximation (GGA) in BLYP exchange-correlation parameterization was used for both final geometry optimization and band structure calculation.

A 6x6 graphene supercell with a vacuum space of 11.5Å normal to graphene plane was used. To pursue the effect of adduct concentration on the electronic structures, we have considered two configurations: by adding one or four MBA molecules onto a 6 x 6 rhombus cell, respectively. The cell constitutes 72 carbon atoms of graphene and 1 metal, 6 carbon, and 6 hydrogen atoms of each MBA molecule.

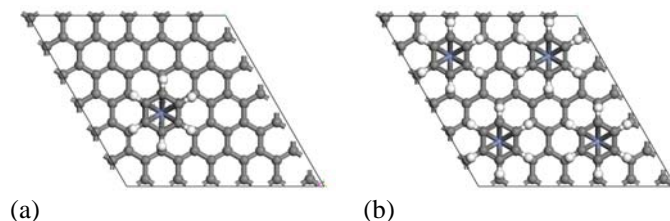


Fig. 1 Ball-and-stick presentation of optimized structures of MBA-functionalized graphene (top view) with one (a) and four (b) MBA adducts per 6x6 graphene supercell.

Geometry optimization convergence criterion was satisfied when the total energy change was less than of $3 \cdot 10^{-5}$ Ha. Only one k-point (Gamma) was used throughout the calculations since the distance between neighbouring k-points was only 0.077 1/Å due to a large supercell choice. For the band structure computation the k-path selected was Γ -M-K- Γ , with 24, 20, and 40 k-points on each segment correspondingly.

We undertook a study of the bis-arene functionalized graphene for the following 3d-metals: Ti, V, Cr, Mn, Fe in different geometrical configurations. It was found that MBA produced very strong bonds with the graphene sheet. Binding energy of Cr-MBA found by extrapolating to 0 K of the binding energies obtained by the Hess's law for different values of thermal occupancy smearing was 455.41 kJ/mol, which is about 25 kJ/mol per electron, indicating strong bonding and presenting an evidence for real existence of such compounds.

The bonding to an "infinite" graphene sheet changes the structural features with respect to the free $M[\eta^6\text{-(arene)}_2]$

molecule. General trends in the bonding lengths demonstrate the following features: the M-C(graphene) bond lengths remain about 3% longer than the one in the free molecule; M-C(arene) bonds, however, remain almost unchanged with respect to the free molecules for Ti-Cr metals and become about 3% shorter for Mn and Fe. The graphene-metal interaction in the haptic functionalization has direct consequences for electronic properties of graphene. As previously reported, functionalization of graphene with radical (primarily hydrogen, epoxide, and nitrene) groups locally disrupt the planarity of the graphene sheet, changing local hybridization from sp^2 to sp^3 [5-7], which induces a sp^3 -type defect-like state near the Fermi level. In our case, however, the graphene sheet is not distorted in the z -direction and thus no re-hybridization of carbon atoms occur. The local bonding configuration is, however, significantly affected by the electronic structure of the functionalizing atom, and especially its d-electrons that were found to lie close to the Fermi level.

The calculated band structures for CrBA-functionalized graphene are compared with pristine graphene in Figure 2. It is readily observable that after the haptic functionalization the linear dispersion law of pristine graphene at the Dirac point is entirely broken, so that the functionalized structure is converted to a direct band gap semiconductor.

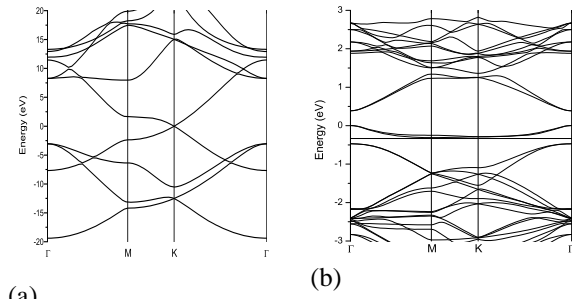


Fig. 2 Calculated band structures for pristine graphene (a), one single molecule CrBA functionalized graphene (b)

Energy gaps for other central metal atoms of the functionalizing MBA molecules and for different adduct concentrations are represented in table 1:

Metal atom	Ti	V	Cr	Mn	Fe
# valence electrons	16	17	18	19	20
Eg (1 molecule) (eV)	0.4082	0.1088	0.3809	0.2993	0
Eg (4 molecule) (eV)	0.3265	0.7891	0.8163	0	0.4907

Table 1 Electronic configuration of the metal atoms in the MBA, and the corresponding energy gap opening in the MBA-Gr as the result of functionalization.

As the analysis of the density of states calculated for different atoms and projected on different angular momenta demonstrates, a system of pure (with no π -admixture) localized d-bands of the metal is located between the π - and π^* -bands of graphene, preventing them from crossing. These d-bands cause strong repulsion and are responsible for the opening of the gap now between the bands produced by the metal. The fact that the band gap strongly depends on

the nature of the functionalizing metal atom confirms our idea about the importance of the number of d-electrons or the modification of the band structure. Both occupied and empty d-levels of the metal form flat bands close to the top of the valence band.

II. CONCLUSIONS.

We have studied the electronic characteristics of MBA-functionalized graphene and have shown that the metal-bis-arene adducts mainly preserve the sp^2 hybridization network of the carbons on graphene away from the functionalizing groups. The π -conjugation of graphene near the Fermi level is greatly disturbed by the π -backbonding process, caused by the d-orbitals of the metal atom in the functionalizing molecule, which leads to opening of a substantial band gap dependent upon the adduct concentration and number of the occupied d-orbitals. The electronic structure of the functionalizing metal in the MBA molecules allows the possible of controlled modification of both the band gap itself and the position of the Fermi level with respect to the “d-impurity” levels and native graphene bands. Such dependence of the electronic properties on the type of functionalizing metal suggests a novel tunable approach for the “band engineering” of graphene. Our findings on the nature of MBA-functionalization induced band gap provide useful guidelines for enabling flexibility and optimization of graphene-based nanodevices.

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