IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

Analysis of energy gap opening in graphene oxide

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2014 J. Phys.: Conf. Ser. 526 012003

(http://iopscience.iop.org/1742-6596/526/1/012003)

View the table of contents for this issue, or go to the journal homepage for more

Download details:

IP Address: 79.70.242.31
This content was downloaded on 01/04/2016 at 21:58

Please note that terms and conditions apply.

4th Workshop on Theory, Modelling and Computational Methods for Semiconductors IOP Publishing
Journal of Physics: Conference Series **526** (2014) 012003 doi:10.1088/1742-6596/526/1/012003

Analysis of energy gap opening in graphene oxide

Mark Lundie[1], **Željko Šljivančanin**[2] **and Stanko Tomić**[1]
[1] Joule Physics Laboratory, University of Salford, UK
[2] Vinća Institute of Nuclear Sciences, University of Belgrade, Serbia

E-mail: `s.tomic@salford.ac.uk`

Abstract. The utilisation of graphene structures as photonics materials mandates that an optically active electronic energy gap be formed. Opening of a gap in graphene has been demonstrated by functionalisation with H, F, or O atoms, while experimental observations of graphene oxide have hinted at interesting optical properties, with the potential for absorption of visible light. As such, our analysis is focused on O functionalisation of graphene. We present results from extensive *ab initio* and hybrid DFT calculations, demonstrating the creation of an optically active gap.

1. Introduction

Graphene, owing to its many unique and novel properties, has drawn considerable attention at the prospect that it can be applied to composite materials and next generation nanoelectronics and photonics devices [1]. Unfortunately, the lack of electronic energy gap presents an obstacle to the latter of these applications [2]. Efforts to open a gap in graphene based materials have thus been the subject of much research in recent years.

The electronic structure of pristine graphene in the vicinity of the Fermi level is driven by a 2D network of sp^2-hybridised π bonds. Disruption of this network by surface adsorption of suitable atoms, among other methods, can be achieved, potentially leading to the formation of an energy gap. This has been shown theoretically and validated experimentally for graphene functionalised with atomic hydrogen [3–5], flourine [6], and oxygen [7, 8].

Experimental observations of graphene oxide (GO) have highlighted some interesting optical properties [9]. For example, in aqueous suspension, measurements reveal strong optical absorption in the ultraviolet (UV) [10]. Of key interest is the observation that absorption peaks are shifted toward the visible range with the reduction of the level of oxidation [11].

We investigate the optical properties of epoxy-functionalised graphene by means of *ab intio* and hybrid density functional theory (DFT) calculations. Our results show that this functionalisation opens a wide and optically active band gap.

2. Methodology

Structural calculations are performed using DFT at the generalised gradient approximation (GGA) level of theory, with the well-known PBE functional. These are initially carried out using the GPAW [12] code, an implementation of the projector augmented wave (PAW) method, and subsequently repeated with a plane wave (PW) basis set using CASTEP [13]. In order to make quantitative prediction of electronic and optical properties, the hybrid PBE0 and B3LYP functionals are used for the calculation of these. To make this practical, as well as to allow the use

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd

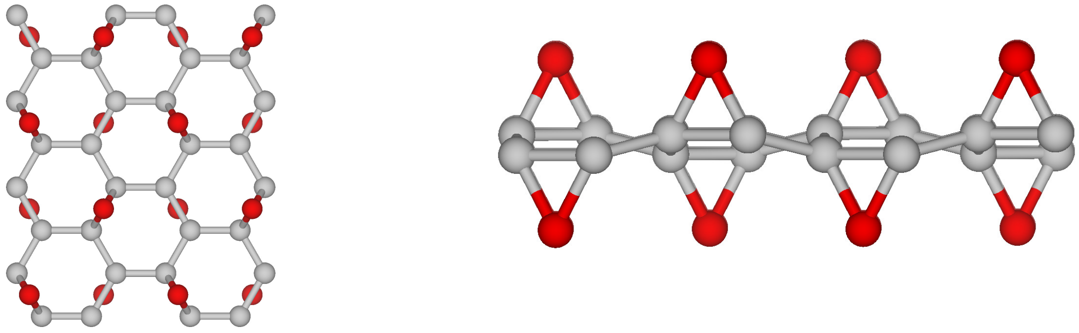
of an all-electron basis set, the CRYSTAL [14, 15] code, in which Bloch functions are constructed from localised Gaussian type orbitals (GTOs), is used for the majority of this study.

To find a suitable GTO basis set, the geometry of clean and partially oxidised graphene cells is relaxed and the bond lengths and binding energies compared to those calculated using PAW and PW basis sets. The most suitable is found to be the Dunning correlation-consistent cc-pCVDZ set [16]. For carbon, adjustment of the most diffuse orbital is required, while for oxygen, the original set is used without modification. Bond lengths are found to be within 0.1 Å and binding energies within 0.01 eV of calculations from the other methods.

Calculations are performed using a rectangular unit cell containing 8 C atoms and 4 O atoms. The geometry is relaxed and structural parameters calculated using the PBE functional [17]. The relaxed geometry is then used as input for band structure calculations using the PBE0 and B3LYP hybrid functionals [18–20].

3. Results and discussion

Fig. 1(a) shows the most stable configuration of fully oxidised graphene [21]. Each O adatom forms an epoxy functional group with two C atoms, alternating above and below the graphene lattice, thereby minimising Coulomb repulsion.



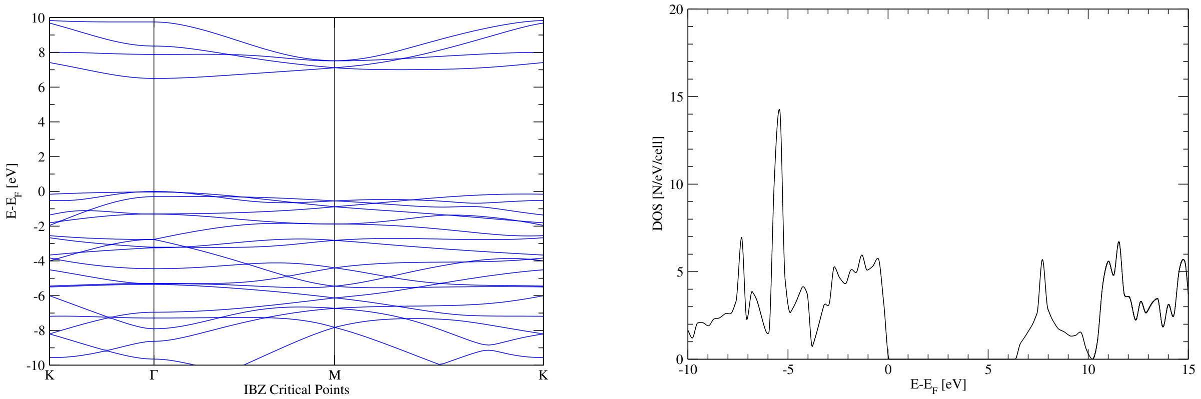
(a) Input.

(b) Optimised.

Figure 1. Surface supercell.

The resultant strain from the formation of sp^3-hybridised bonds between the C and O $2p_z$ orbitals causes vertical displacement of the C atoms from their 2D hexagonal lattice sites, as shown in Fig. 1(b). The binding energy per O adatom, calculated relative to the energy of a free O atom, is 3.38 eV, which indicates the structure to be highly stable. The mean C-O bond length is 0.15 Å, while the C atoms are displaced vertically by 0.16 Å relative to their positions in the honeycomb lattice of graphene. The sp^2 to sp^3 bond rehybridisation also causes substantial changes to the band structure, depicted in Fig. 2(a), in comparison to that of pristine graphene. This, along with the total density of states plotted in Fig. 2(b), clearly identify fully oxidised graphene to be an insulator, with a band gap of 6.50 eV, as calculated using B3LYP. As can be expected, the gap predicted by pure *ab initio* theory, using the PBE functional, is much smaller at 4.09 eV. The effective masses along the direction $\Gamma \rightarrow$ M are predicted as $m_e^* = 1.36\ m_0$ and $m_h^* = 0.56\ m_0$, and along $\Gamma \rightarrow$ K as $m_e^* = 0.40\ m_0$ and $m_h^* = 0.44\ m_0$.

Normalised dipole matrix elements are presented in Table 1, showing the fundamental gap to be optically active. Hybrid functionals again predict dramatically different values to those



(a) Band structure.

(b) Total density of states.

Figure 2. Band structure and density of states.

from pure *ab initio* theory. These values (from hybrid functionals) are $\sim 1/3$ of those for the direct gap bulk zincblende semiconductors, an indication of strong absorption of UV light. For example, GaAs has dipole matrix elements $p_x = p_y = p_z = 9.69$ eV Å.

Functional	p_x [eV Å]	p_y [eV Å]	p_z [eV Å]
B3LYP	3.66	0.00	0.00
PBE0	3.88	0.00	0.00

Table 1. Dipole matrix elements.

Acknowledgments

The authors acknowledge the Royal Society of London for the grants “Functionalized Graphene for Solar Cell Devices: Insight from Ab Initio Theory” and “High Performance Computing in Modelling of Innovative Photo-Voltaic Devices.” The authors also thank Barry Searle & Leonardo Bernasconi for useful discussions. Mark Lundie acknowledges the University of Salford for the award of Graduate Teaching Studentship. Željko Šljivančanin acknowledges financial support from the Serbian Ministry of Education and Science under grant no. 171033 and from the COST Action CM1104.

References

[1] Novoselov K, Geim A, Morozov S, Jiang D, Zhang Y, Dubonos S, Grigorieva I and Firsov A 2004 *Science* **306** 666–669

[2] Bonaccorso F, Sun Z, Hasan T and Ferrari A C 2010 *Nat. Photonics* **4** 611–622

[3] Balog R, Jørgensen B, Wells J, Lægsgaard E, Hofmann P, Besenbacher F and Hornekr L 2009 *J. Am. Chem. Soc.* **131** 8744–8745

[4] Balog R, Jørgensen B, Nilsson L, Andersen M, Rienks E, Bianchi M, Fanetti M, Laegsgaard E, Baraldi A, Lizzit S, Šljivancanin Ž, Besenbacher F, Hammer B, Pedersen T G, Hofmann P and Hornekaer L 2010 *Nat. Mater.* **9** 315–319

[5] Balog R, Andersen M, Jørgensen B, Šljivancanin Ž, Hammer B, Baraldi A, Larciprete R, Hofmann P, Hornekr L and Lizzit S 2013 *ACS Nano* **7** 3823–3832

[6] Nair R R, Ren W, Jalil R, Riaz I, Kravets V G, Britnell L, Blake P, Schedin F, Mayorov A S, Yuan S, Katsnelson M I, Cheng H M, Strupinski W, Bulusheva L G, Okotrub A V, Grigorieva I V, Grigorenko A N, Novoselov K S and Geim A K 2010 *Small* **6** 2877–2884

[7] Vinogradov N A, Schulte K, Ng M L, Mikkelsen A, Lundgren E, Martensson N and Preobrajenski A B 2011 *J. Phys. Chem. C* **115** 9568–9577

[8] Larciprete R, Fabris S, Sun T, Lacovig P, Baraldi A and Lizzit S 2011 *J. Am. Chem. Soc.* **133** 17315–17321

[9] Niyogi S, Bekyarova E, Itkis M, McWilliams J, Hamon M and Haddon R 2006 *J. Am. Chem. Soc.* **128** 7720–7721

[10] Eda G, Lin Y Y, Mattevi C, Yamaguchi H, Chen H A, Chen I S, Chen C W and Chhowalla M 2010 *Adv. Mater.* **22** 505

[11] Kong C Y, Song W L, Meziani M J, Tackett K N, Cao L, Farr A J, Anderson A and Sun Y P 2012 *J. Supercrit. Fluids* **61** 206–211

[12] Enkovaara J, Rostgaard C, Mortensen J J, Chen J, Duak M, Ferrighi L, Gavnholt J, Glinsvad C, Haikola V, Hansen H A, Kristoffersen H H, Kuisma M, Larsen A H, Lehtovaara L, Ljungberg M, Lopez-Acevedo O, Moses P G, Ojanen J, Olsen T, Petzold V, Romero N A, Stausholm-Mller J, Strange M, Tritsaris G A, Vanin M, Walter M, Hammer B, Hkkinen H, Madsen G K H, Nieminen R M, Nrskov J K, Puska M, Rantala T T, Schitz J, Thygesen K S and Jacobsen K W 2010 *J. Phys.: Condens. Matter* **22** 253202

[13] Clark S J, Segall M D, Pickard C J, Hasnip P J, Probert M J, Refson K and Payne M C 2005 *Z. Kristallogr.* **220** 567–570

[14] Bush I J, Tomić S, Searle B G, Mallia G, Bailey C L, Montanari B, Bernasconi L, Carr J M and Harrison N M 2011 *Proc. R. Soc. A* **467** 2112–2126

[15] Dovesi R, Saunders V R, Roetti C, Orlando R, Zicovich-Wilson C, Pascale F, Civalleri B, Doll K, Harrison N M, Bush I J, D'Arco P and Llunell M 2009 *CRYSTAL 09 Manual*

[16] Dunning T H 1989 *J. Chem. Phys.* **90** 1007–1023

[17] Perdew J P 1985 *Int. J. Quantum Chem.* **28** 497–523

[18] Perdew J P, Ernzerhof M and Burke K 1996 *J. Chem. Phys.* **105** 9982–9985

[19] Becke A D 1993 *J. Chem. Phys.* **98** 1372–1377

[20] Tomić S, Montanari B and Harrison N M 2008 *Physica E* **40** 2125–2127

[21] Šljivančanin Ž, Milošević A S, Popović Z S and Vukajlović F R 2013 *CARBON* **54** 482–488