



Electron energy loss spectrum of graphane from first-principles calculations



H. Nejati, M. Dadsetani*

Department of Physics, University of Lorestan, Khorramabad, Iran

ARTICLE INFO

Article history:

Received 26 March 2014

Received in revised form 3 June 2014

Accepted 11 June 2014

Available online 25 June 2014

Keywords:

Hydrogenated graphene

Chair

Tricycle

ELNES

Core-hole approximation

FP-LAPW

Density functional theory

ABSTRACT

In this study, the energy loss near edge structure (ELNES) of carbon atoms in chair and tricycle conformers of hydrogenated graphene, namely 'graphane', has been calculated in the density functional theory using FP-LAPW method, and then, it has been compared with that of graphite and graphene. Using ELNES from chair conformer, the carbon K-edge was found to have a few main features including electron transition from 1s orbital of carbon atom to π^* , σ^* , and a hybridization of these two states. The first feature in tricycle conformer, however, has contributions of both π^* and σ^* states. The comparison of ELNES and the unoccupied density of states in each structure also justifies this. The energy difference between π^* and σ^* features of graphane conformers was decreased relative to it in graphite and graphene. Since the inclusion of core-holes and super-cells is essential for accurate reproduction of features in graphite and graphene, it may be essential as well for the ELNES spectra of graphane conformers.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Graphene (Novoselov et al., 2004), a single sheet of graphite, is a two-dimensional carbon material consisting of a monolayer of carbon atoms in a honeycomb lattice. This material exhibits many unusual properties in relevant areas of physics, chemistry and material science (Geim and Novoselov, 2007; Katsnelson, 2007; Castro Neto et al., 2009) such as the high electrical conductivity, the optical transparency and the half quantized quantum Hall effect, etc.

Graphane, a fully hydrogenated graphene sheet, which is a covalently bonded hydrocarbon, was theoretically proposed by Sofo et al. (2007), and it was synthesized in the laboratory by Elias et al. (2009). Some various interesting properties of graphene including insulating wide band gap (Sofo et al., 2007; Boukhvalov et al., 2008) and magnetization by partial dehydrogenation of the sheet (Neek-Amal and Peeters, 2011) were reported. Experimentally, adsorption of hydrogen on graphene was indeed observed to result in a gap opening in the electron states (Elias et al., 2009). Therefore, the adsorption of hydrogen turns the highly conductive graphene into insulating graphane, as theoretical predictions show (Sofo et al., 2007; Boukhvalov et al., 2008). However, the exact value of the band

gap is still unknown. The thermal contraction effect and the heat capacity of graphane are larger than those of graphene (Neek-Amal and Peeters, 2011). Six possible conformers of this hydrocarbon were reported, known as 'chair', 'boat-1', 'boat-2', 'stirrup', 'twist-boat', and 'tricycle', for the connection of the hydrogen atoms to up- and down-side of carbon atoms in a honeycomb lattice (Sofo et al., 2007; Samarakoon and Wang, 2009; Flores et al., 2009; Chaoyu et al., 2012; Wen et al., 2011). The chair conformer is the most stable, and the tricycle conformer is the second one (Chaoyu et al., 2012). Other physical properties of graphane conformers are under study.

Energy loss near edge structure (ELNES) spectroscopy, which is often performed within a TEM (Egerton, 1996), is a routine technique to detect and measure the electronic structure of materials. Since ELNES originates from the electron transition from a core orbital to unoccupied bands, spectral features of the ELNES reflect the partial density of states of unoccupied bands, and it can provide information on the atomic arrangements, electronic structures, and the chemical bonding of an objective atom in the materials (Botton et al., 1996; Mizoguchi et al., 2003, 2004). Despite the fact that DFT is not intended for the calculation of electronically excited states, the calculation of ELNES and the low-loss spectra with the DFT works pretty well (Rez et al., 1995). Among a variety of codes available for DFT calculations, in addition to the pseudopotential CASTEP code (Segall et al., 2002), the FP-LAPW+lo code WIEN2k (Blaha et al., 2001) has been successfully applied to EELS calculations of many different materials (Holec et al., 2008; Keast et al.,

* Corresponding author. Tel.: +98 6616200192; fax: +98 6616200192.

E-mail addresses: dadsetani.m@lu.ac.ir, dadsetani.m@yahoo.com (M. Dadsetani).

2003; McCullocha et al., 2012; Luitz et al., 2001). WIEN2k elegantly uses a number of approximations to find sensible results of ELNES although it explicitly calculates valence electronic states (Hébert et al., 2003). Using the WIEN2k code leads to highly accurate results for ELNES, specially carbon K-edges in the carbon materials (Dadsetani et al., 2010; Titantah et al., 2004; Titantah and Lamoen, 2005). It should be mentioned that another choice for excited state calculations is the Exciting-code (Anon., 2014) which recently has attained considerable successes. While the Exciting-code is also a full-potential all-electron package implementing the families of LAPW methods, it is based on a different theory. Its particular focus is on excited states within both the many-body perturbation theory (MBPT) (Møller and Plesset, 1934) and the time-dependent density functional theory (TDDFT) (Runge and Gross, 1984). The core loss calculation has not been yet implemented in the Exciting-code.

Low-loss spectra of hydrogenated graphene for different hydrogen coverage and different corrugation angles have been calculated by Bangert et al. (2010) using the WIEN2k-code. It has been shown that hydrogenated graphene exhibits a π -plasmon peak at 4.7 eV. Bangert et al. showed the evolution of π -plasmon in fully hydrogenated graphene with increasing corrugation angle. Like graphene, the flat hydrogenated graphene (angle 90°) possesses a π -plasmon. The π -plasmon diminishes for a corrugation angle of 99° , and it nearly disappears for corrugation angles larger than 107.8° . An additional peak at 6–7 eV emerges at the end of a pure σ -plasmon, which establishes sp^3 character in corrugated graphene when all bonds are used. The core loss spectroscopy of hydrogenated graphene, to be sure, is still unknown. In this work, using first-principles simulations, ELNES spectra of two more stable conformers of fully hydrogenated graphene, chair and tricycle, have been calculated. In order to compare and check the results, the ELNES spectra of graphite and graphene have also been calculated.

In this article, first we pointed to the ab initio calculation method. Then, we presented theoretical estimations for the effect of hydrogenation on the structural and electrical properties of the graphene layer. Afterwards, we calculated the energy loss near edge structure of graphane and finally we compared ELNES of hydrogenated graphene to graphite and graphene.

2. Computational details

2.1. Calculation parameters

The calculations presented in this work are based on the FP-LAPW method in which no shape approximation on potential or the electronic charge density is made. The calculations of structural and electronic properties have been done relativistically. We used the WIEN2k (Blaha et al., 2001) implementation of the method, which allows inclusion of local orbitals in the basis, improving upon linearization and enabling consistent treatment of the semicore and valence states in an energy window, hence ensuring proper orthogonality. In independent particle Kohn–Sham DFT, the exchange–correlation potential within the GGA was calculated by means of the scheme of Perdew et al. (1996) for all spectra. The interstitial plane wave vector cut off K_{Max} was chosen in a way that converging $R_{\text{MT}}K_{\text{Max}}$ of total energy, charge density and atomic forces equals 8 for the ground state. Since the use of super-cell increases the volume of calculations, and given the presence of very light materials like hydrogen, a smaller value of $R_{\text{MT}}K_{\text{Max}}$ (5.0) for core-hole super-cell calculations is sufficient (http://www.wien2k.at/reg_user/faq/rmt.html). The maximum l quantum number for the wavefunction expansion inside the atomic sphere was confined to $l_{\text{max}} = 12$. The G_{max} parameter was taken to be 18 Bohr^{-1} . Brillouin zone (BZ) integrations within self-consistency cycles were performed via a tetrahedron

method containing 24 k -points in the irreducible BZ of all structures. It corresponds to a mesh with dimensions $9 \times 9 \times 2$ for graphite, $14 \times 14 \times 1$ for graphene and chair, and $1 \times 5 \times 15$ for tricycle structures, respectively. Crystal lattices and atomic positions of chair and tricycle conformers of graphane are fully optimized up to the residual force on every atom less than 1 mRyd/a.u. In order to neglect any interlayer interactions, we set the distance 15 \AA between hydrocarbon layers.

Although there are different studies on the energy gap of chair, there is no experimental report of it. Moreover, the lack of an exact calculation of energy gap of tricycle reveals the need for knowledge of energy gap values of graphane conformers through a precise method. Therefore, the many body G_0W_0 approximation (Hedin, 1965) implemented in Exciting-code was used to calculate the exact values of chair and tricycle band gaps. It should be noted that while G_0W_0 changes the band structures, these changes do not in general improve the calculation of spectra and G_0W_0 data are not typically used for XANES or ELNES modeling.

2.2. The spectra method

In a band structure, the ELNES is calculated within the first Born approximation with the assumption that the incoming and outgoing fast electrons are plane waves with wave vectors \vec{k}_i and \vec{k}_f . The double differential scattering cross section (DDSCS) for the inelastic electron scattering is given by (Bethe, 1930):

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E}(E, \mathbf{q}) = \left[\frac{4\gamma^2}{a_0^2 q^4} \right] \frac{k_f}{k_i} \sum_{i,f} |\langle f | e^{i\vec{q}\cdot\vec{r}} | i \rangle|^2 \delta(E - E_f + E_i) \quad (1)$$

where $\vec{q} = \vec{k}_i - \vec{k}_f$ is the momentum transfer, a_0 is the Bohr radius, E is the energy loss, and $\gamma = \sqrt{1 - \beta^2}$ is the relativistic factor. The summation is done over all occupied initial and unoccupied final one-electron states. The initial state is the ground state of the target electron and the final state is the state occupied by the target electron in the conduction band after interaction. Eq. (1) can be recast in terms of the unoccupied density of states, $\chi(E)$. With some approximation (Nelhiebel et al., 1999), we can write:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E}(E, \mathbf{q}) = \sum_{l_f} |M_{l_f}(E, \mathbf{q})|^2 \chi_{l_f}(E) \quad (2)$$

which is a sum of transitions to final states of l_f -character (s, p, d, \dots). $M_{l_f}(\mathbf{q}, E)$ is a smooth and slowly decaying function of energy loss, representing the overall shape of the edge, in a way that variations in DDSCS represent the energy dependence of the densities of states (DOS) above the Fermi level. To simulate the energy loss near the edge structure, we used the TELNES3 program (Blaha et al., 2001), a modified version of TELNES (Nelhiebel et al., 1999), which involves the fully relativistic effects, and which is a part of the WIEN2k program.

Since the core-hole left by the excited electron locally changes the potential, and therefore, influencing the electron density, it serves as a perturbation, so the valence and conduction states can be contracted and shifted. The projected density of states is changed, and the overall shape of the spectrum can be strongly modified, in a way that it may even lead to excitonic peaks in the ELNES. The core-hole calculations have been carried out by the reduction of the occupancy of the core level corresponding to the observed edge. In order to avoid renormalization problems, the missing charge is added to the unit cell as a uniform background charge. In order to avoid the interaction among neighboring core-holes, we used super-cell structures. This approach including the DFT, the super-cell, and the core-hole, namely, “Final State Rule” (FSR) (Jorissen, 2007), was used for all spectra. This rule states that the calculation is done via Fermi’s golden rule with final states being

Download English Version:

<https://daneshyari.com/en/article/1588837>

Download Persian Version:

<https://daneshyari.com/article/1588837>

[Daneshyari.com](https://daneshyari.com)