

ELECTRONIC PROPERTIES OF GRAPHENE OXIDE IN THE PRESENCE OF CELLULOSE CHAINS: A DENSITY FUNCTIONAL THEORY APPROACH

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The effect of cellulose chains on the electronic properties of graphene oxide sheets has been studied using the density functional theory. The results show that graphene oxide sheets with insulating and semiconducting properties behave as semiconductors in the presence of cellulose chains. The large energy band gap of graphene oxide sheets decreases by increasing the number of adsorbed cellulose chains. The results provide a new insight into hybrid materials, with higher performance, to be used in emerging nanoelectronic devices.

Keywords: cellulose chain, graphene oxide, energy band gap, density functional theory

INTRODUCTION

Graphene is a two-dimensional honeycomb lattice of C atoms. It has become one of the most studied materials of the last decade due to its exceptional electrical, mechanical and thermal properties.^{1,2} Owing to its novel structure and special properties, graphene is used in many applications, ranging from electronics to optics, sensors and energy storage systems.^{1,2} The absence of the band gap in graphene is one of its main problems, which limits the actual applications of graphene. In order to solve this problem, several methods, including doping, applying electric field, functionalization and cutting graphene into ribbons, have been developed.³⁻¹⁰ For instance, the addition of O atoms to the C framework of graphene is a method that is often used to open the band gap.^{9,10} The first product of chemical functionalization of graphene layers by O functional groups is called graphene oxide (GO). GO is a monolayer of graphene with various oxygen functional groups, such as hydroxyl, epoxy, carbonyl and carboxyl groups.^{11,12} The unique properties of GO make it an attractive material for applications in sensors, catalysis, composites, transparent paper-like materials and nanoelectromechanical systems.

Due to the presence of O functionalities, GO can easily disperse in organic solvents, water and different matrices. This is a major benefit when combining the material with polymer or ceramic matrices to enhance their mechanical and electrical properties.^{11,12} Recently, it was reported that nanomaterials prepared by hybridizing a two-dimensional GO sheet and one-dimensional nanofibrilled cellulose are much stronger than materials made solely from one of the two building blocks.¹¹⁻¹⁴ The improvement in the mechanical properties of GO sheets with nanocellulose motivated us to study the effect of cellulose addition on the electrical properties of GO.

With respect to its electrical conductivity, GO functions as an electrical insulator.^{9,15} As an ideal structure would be an allotrope of carbon with a good band gap value, the reduction of the energy band gap of GO is important. In the present work, engineering the energy band gap and consequently the electrical conductivity of GO sheets by adsorption of cellulose chains has been studied using the density functional theory (DFT).

EXPERIMENTAL

All DFT calculations were performed using the generalized gradient approximation (GGA) for the exchange-correlation functional proposed by Perdew, Burke and Ernzerhof (PBE).¹⁶ The OpenMX 3.8 code¹⁷ was employed to calculate the structural and electronic properties. The energy cutoff was set to 100 Ry. The van der Waals interactions between the adsorbed molecules and the sheets were described by Grimme's method.¹⁸ All

atomic structural models were fully relaxed as long as the atomic forces were lower than 0.001 eV/Å. For calculations of electronic band structures and density of states (DOS), 11 k-points were assumed along each high symmetry lines in the Brillouin zone.

Supercells of GO sheets were considered as host materials for the adsorption of cellulose chains. Periodic boundary conditions were applied to the supercells. A vacuum width of 20 Å was constructed for eliminating the interaction between adjacent images of supercells.

RESULTS AND DISCUSSION

In the present simulations, two models for GO sheets are investigated. Figure 1 shows the atomic structure of a fully oxidized graphene sheet named model I. In this model, each O atom forms an epoxy functional group with two C atoms, alternating above and below the graphene sheet, thereby minimizing the Coulomb repulsion.^{19,20} As shown in Figure 1, the GO model I exhibits a buckling structure. The effects of this buckling are balanced by the alternating O atoms coverage and so this structure is considerably more stable than that with O atoms coverage only on one side of the graphene sheet.^{19,20} We have considered that a supercell contains 32 C and 16 O atoms in the present work. Here, the C:O ratio is 2:1. The optimized atomic bond lengths are listed in Table 1. The electronic band structure and DOS of the GO model I are presented in Figure 2. The large energy band gap of 4.74 eV between the bottom of the conduction band and the top of the valence band indicates the insulating property of the GO model I. Our results are in good agreement with those of a previous study, which predicted that the GO is a wide band gap insulator.¹⁹ The energy band gap of the GO model I was estimated to be 4.09, 6.85 and 6.50 eV from PBE-GGA, PBE0 and B3LYP hybrid functional, respectively.¹⁹

Table 1
Optimized bond lengths of GO sheets (Å)

Bond	Model I	Model II
C1-C2	1.42	1.45
C2-C3	1.45	1.46
C4-C5		1.50
C-O	1.45	1.45
C-OH		1.46

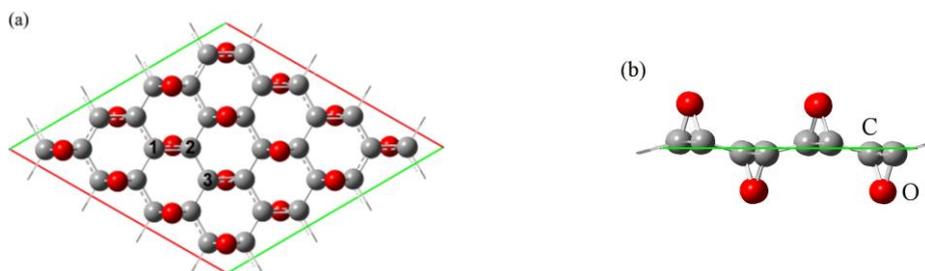


Figure 1: (a) Top and (b) side views of GO model I

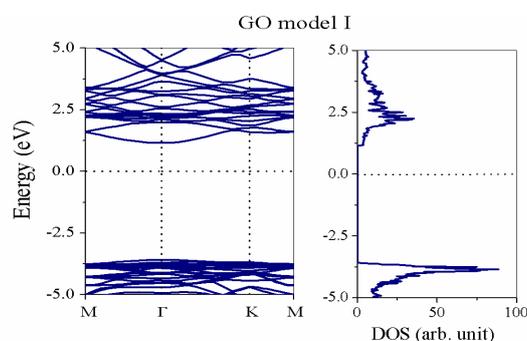


Figure 2: Electronic band structure and DOS of GO model I

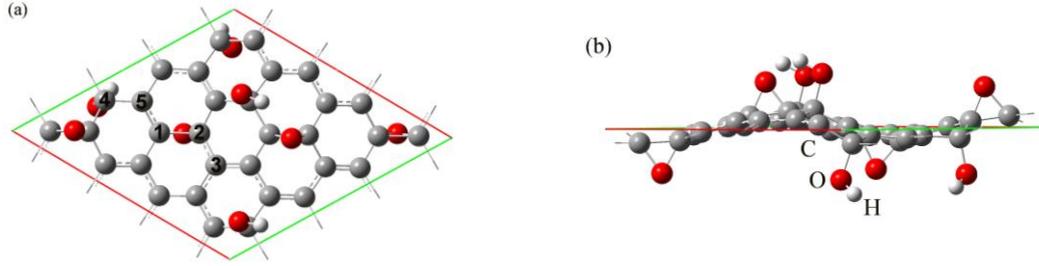


Figure 3: (a) Top and (b) side views of GO model II

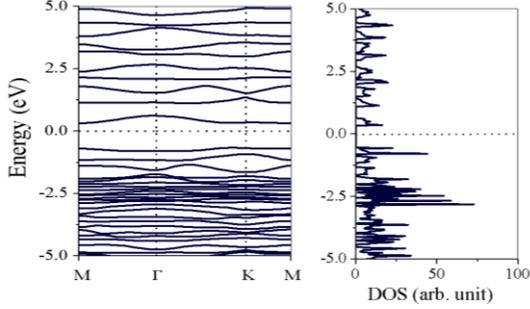


Figure 4: Electronic band structure and DOS of GO model II

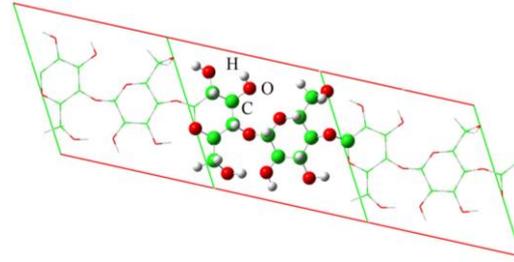


Figure 5: Atomic structure of a cellulose chain

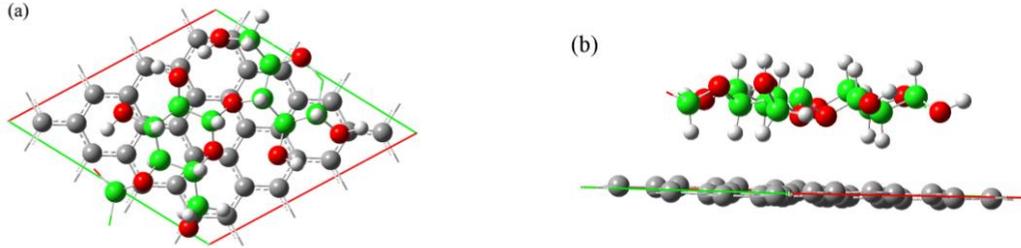


Figure 6: (a) Top and (b) side views of adsorbed cellulose chain on GO model II

A supercell of GO containing 32 C, 8 O and 4 H atoms has been also studied (Fig. 3). This sheet has a C:O ratio of 4:1. In the atomic structures of the GO model II, one epoxy and one hydroxyl group per 8 C atoms are distributed randomly on both sides of the graphene sheet. The electronic band structure and DOS of this model of GO are plotted in Figure 4. Here, an energy band gap of 0.99 eV indicates the semiconducting properties of the GO model II. It was shown that removing a selected number of O atoms from the fully oxidized graphene sheet was accompanied by a reduction of the energy band gap.^{19,21} As expected, the energy band gap of the GO model II was smaller than that of the GO model I.

The atomic structure of cellulose was taken from X-ray and neutron fiber diffraction experiments.²²⁻²⁵ A chain of cellulose was cleaved from bulk cellulose (Fig. 5). In each supercell, two cellobiose units ($C_6H_{10}O_5$)₂ were placed.

It was found that cellulose chains prefer to locate parallel to the surface of GO sheets. As an example, the most stable adsorption configuration of cellulose on the GO sheet model II is presented in Figure 6. To evaluate the stability of the structures, binding energy was calculated:

$$E_b = E_{sheet+cellulose} - (E_{sheet} + E_{cellulose}) \quad (1)$$

where $E_{sheet+cellulose}$ is the total energy of the GO sheet with adsorbed cellulose chains, E_{sheet} and $E_{cellulose}$ denote total energies of the isolated GO sheet and cellulose chain, respectively.

The negative values of the binding energy reveal stable structures. The binding energies of the most stable structures are -0.9 and -0.6 eV for the GO sheets model I and model II, respectively. A more negative value of binding energy indicates a stronger interaction between the chain and the sheet. For the GO model I, the binding strength is found to be stronger than for the GO model II. This is attributed to the hydrogen bond density, which has an important role in the binding strength between the GO sheet and the cellulose chain. Systematic molecular dynamics modeling was performed to provide quantitative evidence of the effect of hydrogen bond density.¹² The results confirmed that

there is a cascade of formation, breaking and reformation of hydrogen bonding between the GO sheet and the cellulose chain, which defines the strength of the binding between them.¹² The hydrogen bond can form between the sheet and the chain only when one hydroxyl groups from the cellulose chain comes in close contact with the hydroxyl or oxygen groups of the GO sheets (*i.e.* –OH to –OH or –OH to –O). The abundant oxygen groups in the GO model I can significantly increase the number of hydrogen bonds and consequently the binding strength between the GO sheets and the cellulose chain.

To understand the effect of cellulose chains on the electronic properties of GO sheets, the electronic band structures and DOS of these sheets with adsorbed cellulose chains were calculated. As seen in Figure 7 and Figure 8, the adsorption of cellulose chains on the GO sheets causes the appearance of additional states in the forbidden energy region between the conduction and valence bands. The GO sheets model I and model II with adsorbed cellulose chains behave as semiconductors with energy band gaps of 1.35 and 0.35 eV, respectively. A comparison between the energy band gaps of the GO sheets before and after cellulose adsorption indicates that the band gaps decrease with the adsorption of cellulose chains. The ability of band gap engineering through the encapsulation of cellulose into carbon nanotubes was investigated in a previous study.²⁵ It was found that the energy band gap of carbon nanotubes with semiconducting properties decreased as a result of the encapsulation of cellulose into them.²⁵ Hence, cellulose adsorption is an effective method to change the electronic properties of carbon based nanostructures.

In order to study the effect of the number of adsorbed cellulose chains on the energy band gaps of GO sheets, two cellulose chains were considered above and below the sheets. As an example, two cellulose chains adsorbed in each supercell of the GO model I are shown in Figure 9.

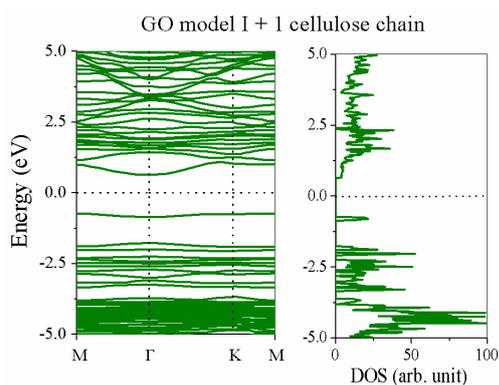


Figure 7: Electronic band structure and DOS of GO model I with adsorbed cellulose chain

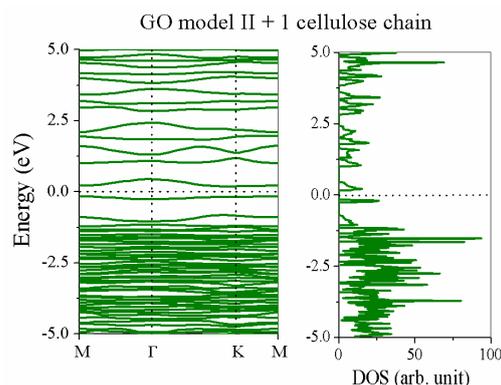


Figure 8: Electronic band structure and DOS of GO model II with adsorbed cellulose chain

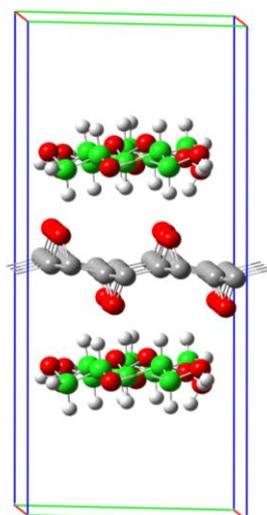


Figure 9: Side view of two cellulose chains adsorbed on GO model I

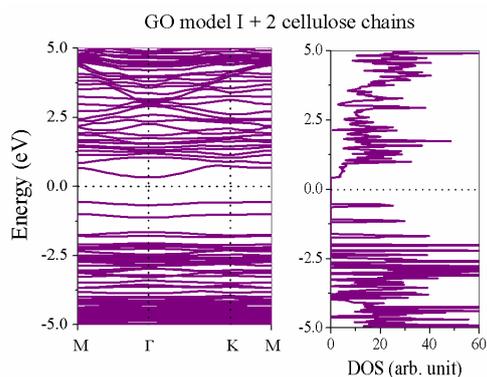


Figure 10: Electronic band structure and DOS of GO model I with 2 cellulose chains

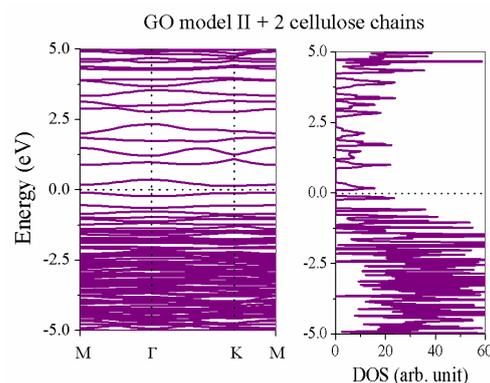


Figure 11: Electronic band structure and DOS of GO model II with 2 cellulose chains

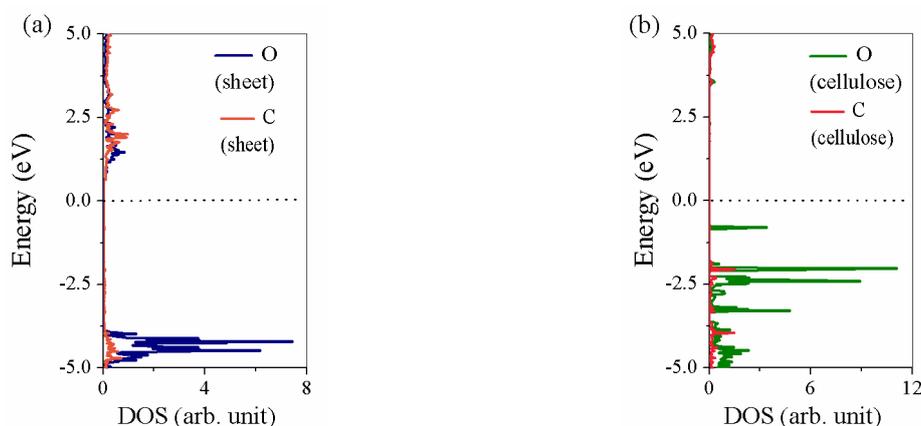


Figure 12: Partial DOS of GO model I with adsorbed cellulose chain

The electronic band structures and DOS of the GO model I and model II in the presence of two cellulose chains are plotted in Figure 10 and Figure 11, respectively. Here, the number of states and DOS peaks around the Fermi level increases by increasing the number of adsorbed cellulose chains. The calculated energy band gaps of the GO model I and model II in the presence of two cellulose chains are 0.89 and 0.23 eV, respectively. It means the energy band gaps of GO sheets decrease by increasing the number of cellulose chains.

Partial DOS was studied to identify the contribution of cellulose chains. As an example, partial DOS of C and O atoms for the adsorption systems of cellulose chains and the GO model I is shown in Figure 12. It is observed that DOS peaks below the Fermi energy (between 0 and -2.7 eV) are mainly formed by the O and C atoms of the cellulose chains. The results clarify the main role of cellulose chains on the electronic properties of GO sheets.

CONCLUSION

In the present project, changing the energy band gap of GO sheets by adsorption of cellulose chains was investigated using the density functional theory. The GO sheets showed semiconducting properties in the presence of cellulose chains. The energy band gap of the GO sheets decreased as a result of cellulose adsorption on their surface. The results provided a way to change the electronic properties of GO sheets. Hybrid materials made from GO sheets and cellulose chains have potential applications in future nanoelectromechanical devices.

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