AB INITIO STUDY OF GRAPHENE INTERACTION WITH O$_2$, O, AND O$^-$

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A systematic *ab initio* (DFT-GGA) study of adsorption of various oxygen species on graphene has been performed in order to find out general trends and provide a good starting point to analyze the oxidation of more complex carbon materials. Particular attention was paid to finding an appropriate supercell model. According to our findings, atomic O is characterized by stable adsorption on graphene and very strong adsorption on defective graphene. On the other hand, O$_2$ does not adsorb on graphene and is allowed to diffuse freely to the defect, where it is expected to dissociate into two strongly adsorbed O atoms. The obtained results were compared with available theoretical data in the literature and good agreement was achieved.

Keywords: grapheme; adsorption; density functional theory; oxidation

ИСТРАЖУВАЊЕ *AB INITIO* НА ИНТЕРАКЦИЈАТА НА ГРАФЕН СО О$_2$, О, И О$^-$

Извршено е систематско истражување *ab initio* (DFT-GGA) на атсорпцијата на различни кислородни видови врз графен со цел да се откријат општите трендови што можат да послужат како појдовна основа за анализа на оксидацијата на покомплексни јаглеродни материјали. Посебно внимание е посветено на откривање соодветен модел на суперќелија. Нашите сознанија укажуваат дека атомскиот О се карактеризира со стабилна атсорпција врз графен и многу силна атсорпција на графен со дефекти. Од друга страна, О$_2$ не се атсорбира на графен, но е овозможено слободно да дифундира во дефектите каде што се очекува да дисоцира во два силно атсорбирани атоми на О. Добиените резултати беа споредени со теоретските податоци што се на располагање во литературата при што е добиено задоволувачко совпаѓање.

Клучни зборови: графен; атсорпција; теорија на функционалот на густина; оксидација

1. INTRODUCTION

Oxidation of carbon materials has been the subject of many studies. A detailed understanding of the oxidation mechanism, as well as its dependence on experimental conditions, is of considerable interest for industrial applications [1]. Consequently, many *ab initio* studies considering various aspects of oxygen interaction with different carbon materials, mainly graphene models, have been performed [2–5]. Radović and Bockrath [2] pre-

sented an extensive study of the chemical nature of graphene edges and its influence on stability and magnetic properties. Mehmood et al. [4] studied the adsorption of atomic and molecular oxygen on periodic graphene with different defects using the Density Functional Theory (DFT) method. Sun and Fabris [5] investigated the interaction between atomic O and graphene clusters in order to determine mechanisms of oxidative unzipping and cutting of graphene. *Ab initio* studies of graphene are of particular interest when explaining and

predicting the behavior of more complex carbon materials under particular oxidizing conditions. As a first step, a consoledation of state-of-the-art knowledge is needed, including a systematic DFT study of the basic behavior of various oxygen species on graphene surface, which is, despite numerous studies considering various particular aspects of the system, still lacking.

The goal of this work was to establish an appropriate theoretical model to investigate the interaction of oxygen species with graphene as the simplest carbon material, point to some general trends, and provide a good starting point for further studies of more complex materials and processes.

2. THEORETICAL BACKGROUND

Periodic DFT calculations were performed using *PWscf* code of the Quantum ESPRESSO [6] distribution. Vanderbilt ultrasoft pseudopotentials [7] under the generalized gradient approximation – Perdew Burke Erzenhorf (GGA-PBE) level [8] were used to improve convergence. A plane wave basis set with a kinetic energy cutoff of 28 Ry was used to model valence electrons. For automatic k-point sampling, a Monkhorst-Pack grid [9] was used. The calculated graphene lattice constant was 2.47 Å, which is in good agreement with previous literature data (e.g. [10]). At this level, only spin-restricted calculations were considered, which is sufficient as far as general trends are of primary interest. Details of the supercell dimensions and symmetry are considered in the "Results and Discussion" section. In all cases, graphene was modeled as a single-layer slab and the system was fully relaxed. In the case of anion adsorption, an electron was added to the system and the charge was compensated by the uniform positive background, as implemented in Quantum ESPRESSO. Adsorption energies were calculated according to a common principle as the difference between the total energy of the final product and the sum of the total energies of substrate and adsorbate. The projection density of states was calculated using *projwfc.x* code, as implemented in Quantum ESPRESSO.

3. RESULTS AND DISCUSSION

Due to the rather complex symmetry of graphene, a systematic investigation of the dependence of the energetics of oxygen interaction with the surface on various supercell parameters could be the subject of a separate study. Here, we have chosen two different supercell models for initial evaluation: 1) a 2 × 2 cell with automatic sampling of 4 × 4 × 1 k-points and 12 Å of vacuum; and 2) a 3 × 3 cell with automatic sampling of 6 × 6 × 1 k-points and 25 Å of vacuum. In order to verify the validity of the model, the projected densities of states (PDOS) in the GGA-PBE approximation were calculated for comparison with the literature data. Supercell model units with the corresponding PDOSs are shown in Figure 1.

In addition, the adsorption energy of the oxygen atom at the bridge site was calculated for both cell models. It was –1.94 and –1.91 eV for bigger and smaller cell respectively, indicating that there was essentially no difference between the two cell models with regard to the consideration of oxygen adsorption energetics. On the other hand, in the case of a bigger 3 × 3 supercell, better agreement with the literature data is achieved in view of the position of the PDOS minimum around the Fermi level [11]. Moreover, a bigger cell has advantages when modeling graphene defects. For these reasons, despite the minimal dependence of the oxygen adsorption energy on cell size, a bigger cell was found to be more suitable for our purposes and was taken for further calculations.

In further work, the adsorption of chosen oxygen species, O, O_2, and O^-, on graphene (G) and monovacancy defect graphene (MV DG) has been analyzed and compared to existing literature data. To model MV DG, one C-atom was removed from the graphene cell, and the structure was optimized again. The most illustrative equilibrium adsorption geometries of oxygen species investigated in this work (preferred adsorption sites only) are shown in Figure 2.

Corresponding adsorption energies and surface-to-adsorbate distances compared to available literature data, as well as thermodynamic diffusion barriers, are shown in Table 1. Thermodynamic diffusion barriers are obtained from the energy difference between the adsorption of a species at the preferred (most stable) site and the neighboring site with the next highest stability.

Our results show reasonably good agreement with literature data, obeying the same general trends. Slightly lower values of adsorption energies compared to [4], where a similar model was employed, may be attributed to spin-restriction in our case, since oxygen triplet states are generally considered to take part in the interaction with graphene [3].
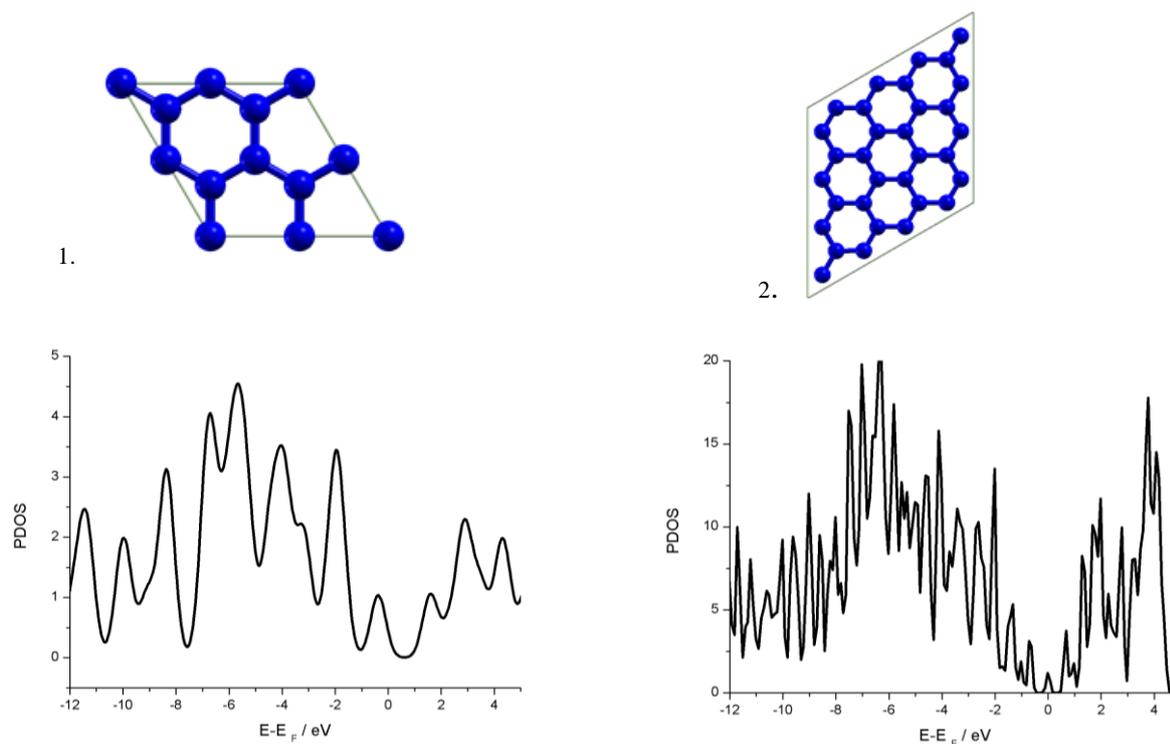
Fig. 1. Analyzed graphene supercell models (top) and corresponding calculated PDOSs (bottom).
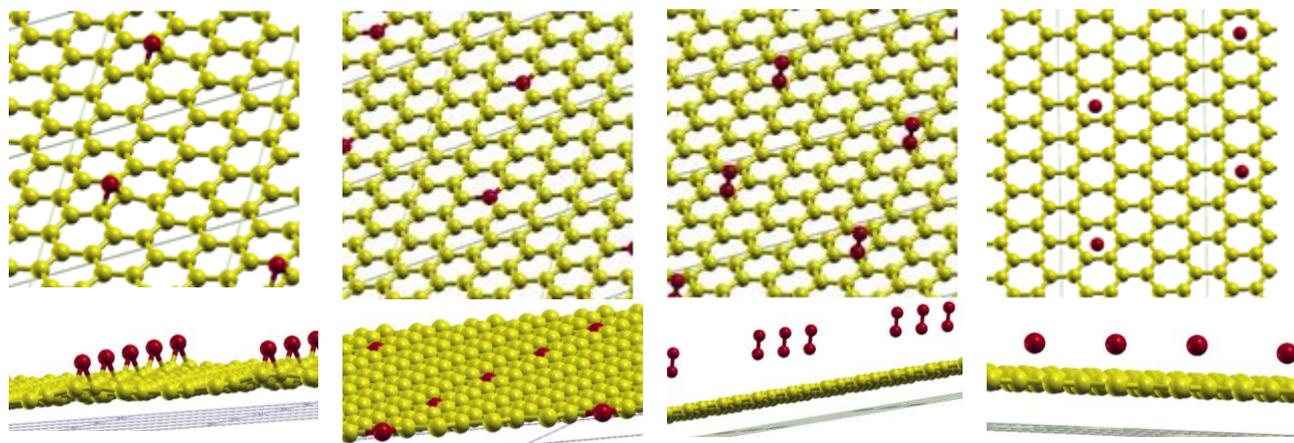All energies are shown referred to the Fermi level.

Fig. 2. Equilibrium adsorption geometries, from left to right respectively: atomic O on G, atomic O on MV DG, O₂ on G, and O⁻ on G. A crosscut view is given above, and the corresponding side view is shown below, in order to accentuate the differences in surface-to-adsorbate distances.

According to the summarized results, atomic oxygen exhibits intermediately strong adsorption on G while the thermodynamic diffusion barrier of 0.75 eV promises fairly slow diffusion of O, at least at room temperature. Adsorption on MV DG is much stronger, in good agreement with expectations [4]. Quite different behavior on G is observed for molecular oxygen. With no stable adsorption site and no diffusion barrier, it is able to "float" over the surface until it is caught by an appropriate defect. At MV DG, adsorption is, however, strong enough to provide energy for the dissociation of O₂ into two O atoms. Finally, we also looked at the oxygen anion O⁻, since, in principle, it could appear as an intermediate in particular oxidation processes at appropriate temperatures. Moreover, it could serve as a first-approximation model system for various species containing partially negative oxygen. Its adsorption on G is stable, although weaker than in the case of atomic O, but the corresponding diffusion is considerably facilitated in comparison to atomic O. On MV DG, adsorption of O⁻ is also

weaker than that of atomic O, and the diffusion barrier is correspondingly lower (details in Table 1). In short, the expected reactivity of O^- towards both

G and MV DG is somewhere between those of atomic and molecular oxygen.

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Adsorption energy (E_{ads}), geometry, and diffusion of oxygen species on G and MV DG: comparison of our results with literature data

System	E_{ads}/eV (preferred site)	Adsorbate–surface distance (Å)	Diffusion barrier / eV	Source
O on G	−1.94 (bridge) −2.40 (bridge) −4.79 (bridge)	1.69	0.75 (top-bridge-top)	Our work Ref [5] Ref [12]
O on MV DG	−6.95 (vacancy) −8.37	0.01	2.42 (over bridge)	Our work Ref [5]
O_2 on G	+0.01 (bridge) −0.04 −0.005	2.96	0	Our work Ref [5] Ref [3]
O_2 on MV DG	−14.67 (dissociated)	/	/	Ref [5]
O^- on G	−0.96 (bridge)	1.44	0.06 (top-bridge-top)	Our work
O^- on MV DG	−5.60 (vacancy)	0.01	1.61 (over bridge)	Our work

4. CONCLUSION

In this work, we established a theoretical model to investigate the interaction of oxygen species with graphene and monovacancy defect graphene surfaces through a comparison between our results and available literature data, paying special attention to general trends and the differences and similarities between these oxygen species. The obtained results are of importance for further *ab initio* simulations and discussions considering the behavior of oxygen-containing species interacting with more complex carbon materials under various oxidizing conditions.

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