Density of states of adsorbed sulphur atoms on pristine and defective graphene layers.

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Abstract. The density of states for adsorbed sulphur atom on a graphene layer system is discussed for pristine graphene layer and for mono and divacancies on the graphene layer. To our knowledge this is the first time that an entire adsorption of the sulphur atom is reported at the plane of the carbon atoms, when there is a pair of closer vacancies at the graphene layer.

Introduction
The adsorption of sulphur atoms on a graphene layer and on mono and divacancies on the graphene layer is discussed showing how the changes on the electronic density of states are. The most important result is the fact that due to the presence of sulphur atoms, there are many available states beyond the Fermi level. This change promises new possibilities about adsorption or capture of some other pollutants atoms or molecules. A brief resume for pristine graphene layer and of one and two carbon vacancies on the graphene layer is given. Then the adsorption of one or two sulphur atoms on those systems is given with a comparison and discussion of their electronic densities of states. One work about this class of study explores simultaneous doping of the graphene layer with S and N atoms, for example [1]. Also several factors could be studied about the performance of a sulfur graphene composite cathode material [2]; this was applied in a lithium-sulfur battery. Also the adsorption of molecules such as NO, NO₂ or O₂ were studied theoretically over S-doped graphene [3]. It is expected that this kind of novel systems could be used as gas sensors for those or other polluting gases. Even more close to this work it was found an article about hydrogen sulfide adsorption on defective graphene [4]. The adsorption is studied as a function of the carbon vacancy concentration. There is covalent binding between the S atom of the hydrogen sulfide molecule and the three closer carbon atoms around the graphene vacancy. In a very recently accepted paper [5], there is a DFT study for H₂O₂ adsorption and activation on a graphene surface (formed by 73 C atoms), when this is doped with different atoms such as N, B, S, Pd, Pt, Au, Ag and Cu. The Gaussian calculation includes 21 H atoms around an equal amount of the more external C atoms of the graphene layer.

1. Pristine graphene layer.
The computer free code Quantum espresso is used to do the computer calculations. A 4x4 graphene layer (32 carbon atoms) with cell parameter a = 4.6117 a.u. [6] was used to build the initial pristine graphene layer. The pseudopotentials used for the calculations were c.fhi.UPF and S.pz-van_ak.UPF.

For the optimized cell parameter, the total energy, (E_{tot}) was -365.58814088 Ry, with Fermi energy -1.4977 eV. It was enough to use 25 a.u. for the distance between graphene layers. The calculated DOS (electronic density of states), figure 2, shows the known result: DOS at the Fermi level is zero.
2. Sulphur atom above one carbon atom on pristine graphene layer.
To begin the study of the interaction of sulphur atoms with the graphene layer, only one sulphur atom was placed above one of the carbon atoms of the pristine graphene layer. The relaxation of the system show that S atom was adsorbed 2.1938 Å above the C atom of the graphene layer with adsorption energy of -1.73 eV. Figure 1 shows the studied system. The corresponding DOS is shown on figure 2. Due to the S-C bond, there are now a few available electronic states above the Fermi state.

![Relaxed system formed by one sulphur atom adsorbed above one carbon atom of the graphene layer](image1)

Figure 1. Relaxed system formed by one sulphur atom adsorbed above one carbon atom of the graphene layer, (left panel). Double carbon vacancy with a pair of adsorbed sulphur atoms, (right panel). Sulphur atoms have bigger size than carbon atoms in this and other figures.

![Density of electronic states for pristine graphene](image2)
![Density of electronic states for sulphur adsorbed above one carbon atom](image3)

Figure 2. a) Density of electronic states for pristine graphene, Fermi energy = -1.533 eV; b) Density of electronic states for a sulphur atom adsorbed above one of the carbon atoms of pristine graphene, Fermi energy = -1.4818 eV.

3. Adsorption of one S atom above the center of one hexagonal cavity of the graphene layer.
Compared with the relaxation of a single S atom above a C atom, it was hoped that one sulphur atom could be adsorbed to a closer distance due to the space at the center of the hexagonal cavity. But contrary to the expected, the S atom remains 2.833 Å above the center of the cavity and the adsorption energy for S atom is only -0.625 eV, much less than -1.73 eV for the adsorption above a C atom. The first panel on figure 3 shows the density of states of a sulphur atom adsorbed above one of the hexagonal cavities of pristine graphene layer. For this case there are even more available states above the Fermi level, compared to the sulphur adsorption above one carbon atom.

4. Sulphur atom above one carbon vacancy graphene layer.
The design of one or two carbon vacancies on the graphene layer, follows very nearly the same as was done before [7], for the BN layer. Here are given only some details. After extracting one or two carbon
atoms from the pristine graphene layer, one has to completely relax the defective carbon structure and obtain the relaxed total energy. One compares those energies with that obtained for the pristine graphene layer. For example, for the unrelaxed and relaxed energies of formation of a single vacancy for the graphene supercell, we obtained the energies 0.6150 and 0.5978 Ry [8]. DOS for one carbon vacancy graphene layer is shown on figure 3, panel b. There is a relative maximum value for DOS at the Fermi level, at -1.9274 eV. Again, there are electronic available states beyond the Fermi level. Besides here it is not shown a figure for the final configuration when only one sulphur atom is relaxed above the one carbon vacancy graphene layer, the final configuration is very nearly the same as figure 3 of reference [4]. In that case the hydrogen atoms of the hydrogen sulfide molecule are repelled by the defective graphene layer and form one hydrogen molecule above the sulphur atom and the carbon atoms of the vacancy graphene layer. The S atom makes protrude bonds out of the graphene plane, with the three closer carbon atoms of the vacancy. The hydrogen molecule remains above the sulphur atom.

5. Adsorption of S atom at a double carbon vacancy site.
Relaxing one sulphur atom above the center of a double carbon vacancy, created when two closer carbon atoms are omitted in the pristine graphene layer gives an interesting configuration. There are two pentagonal and two hexagonal cavities around the adsorbed sulphur atom that is almost entirely adsorbed on the same plane of the carbon atoms (see figure 5). Besides there is a distortion of the carbon atoms around the S atom, the changes are in such a way that in the final configuration the S atom makes bonds with four carbons atoms, the nearest to sulphur atom. The electron density of states goes beyond the Fermi energy level, localized at -1.4719 eV. This is shown on figure 4. To obtain that result, first it was necessary to do a scf (self-consistent-calculation), followed by an nscf (non-self-consistent-calculation), the dos (density of states) calculation and finally the calculation of the pdos (projected density of states). The same sequence of calculations was done for the different studied configurations. The final z coordinate of the sulphur atom was 0.165 Å and some of the carbon atoms around the S atom have z coordinates around 0.11 Å; that is why it can be said that the S atom is adsorbed nearly at the same plane of the carbon atoms of the defective graphene layer. It was thought that due to the bonding of the sulphur atom with four carbon atoms the DOS could be different as that obtained in figure 4. It was believed that necessarily at the Fermi level the DOS could have values far from zero. This was a non-expected result.

![DOS](https://via.placeholder.com/150)

Figure 3. a) Density of electronic states of a sulphur atom adsorbed above one of the hexagonal cavities of pristine graphene layer, Fermi energy = -2.3157 eV; b) Density of electronic states created by a lonely carbon vacancy on the graphene layer, Fermi energy = -1.9274 eV.
7. Adsorption of two S atoms at a double carbon vacancy site.
Two S atoms were relaxed above a pair of carbon vacancies that correspond to two opposite carbon atoms at one of the hexagonal cavities in the pristine graphene layer. Besides the distance between the carbon vacancies, there was not enough space to allow the complete adsorption of both S atoms at the graphene layer. The final configuration, (second panel of figure 1), is a very symmetrical one. The S atoms stay a little above a distorted graphene layer.

![Figure 4](image1.png)

**Figure 4.** Density of states for one sulphur atom adsorbed at the center of a double carbon vacancy, Fermi energy = -1.4719 eV. The corresponding system is shown on figure 5.

![Figure 5](image2.png)

**Figure 5.** Adsorption of a sulphur atom at the center of the carbon double vacancy. There are two opposite pentagonal and two hexagonal cavities around the S atom.

8. Conclusions.
Results were obtained with Quantum espresso computer code, with ultrasoft pseudopotential S.pz-van_ak.UPF for sulphur atom and LDA (local density approximation) pseudopotential and c.fhi, for carbon atoms. This pseudopotential was used before to study the hydrogen molecule adsorption both, on a graphene layer [6] and on the (5, 5) and (6, 6) carbon nanotubes [9]. Cutoff energies as high as 80 Ry were used in the scf and ns cf calculations. Other configurations for the adsorption of the sulphur atom on the pristine and defective graphene layer were studied. For an entire pristine graphene layer, it is impossible that some sulphur atom could be at the plane of the carbon atoms of the graphene layer. There is not enough space in the hexagonal cavity to find one sulphur atom at its centre or near that point. In some configurations the sulphur atom remains some distance above the centre of the hexagonal cavity or above of one of the carbon atoms. Some of the explored configurations considered simultaneous adsorption on both sides of the graphene layer, above and below the same point or different points of the layer.

Taking into account the results given here and other configurations in which S-C bonding breaks the bidimensionality of graphene layer, can be used not only to modify but even control or regulate electronic and other kind of properties of these and similar systems.

Taking into account similar results [1-5], those obtained with colleagues [6, 9], those reported previously [7], and the reported in this work, allows to propose that the defective graphene layer, and in particular the double vacancy, as shown here can be used to capture, retain and storage not only sulphur atoms. Because for this kind of application it is not necessary a high quality of graphitic material, the cost of this one to capture and storage different kind of molecules or atoms as sulphur atoms for example, it could be a non-expensive one in contrast with other applications.
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