Summary of Thesis in Electronic Engineering
Politecnico di Torino

Graphene-based sensor of aflatoxin molecule: a simulation-based investigation

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Introduction and research context

Aflatoxins are a group of mycotoxins produced by fungi and molds. They contaminate a large group of agricultural products such as rice, cocoa, walnuts, hazelnuts... They are also present in animal feed and animal-derived products such as milk and cheese. They are very dangerous to human health, they can cause serious poisoning and even cancer. The most widespread and harmful is aflatoxin B1. Today, for the identification of this molecule it is necessary to resort to specialized laboratories with high instrumentation costs, high costs of specialized personnel and long response times to the analyses. It thus becomes important to be able to create a sensor capable of being quick in responding to analyses, with low production costs, which can also be used by non-specialised personnel, which can be used in the various stages of production and marketing of agricultural products and which is reusable. Graphene with its particular properties together with molecular electronics is an excellent candidate for this task. Graphene is composed of a single layer of carbon atoms bonded via covalent bonds to form a honeycomb hexagonal structure. Its electronic band structure, linear near Fermi levels, is able to detect small changes in electronic properties. The bonds created by the carbon atoms leave the p_z orbitals free to interact with the individual external molecules. Also it being made from a single layer of atoms it has a high surface area to volume ratio.

Project Goals

In this context, in my thesis work I investigated graphene as a possible sensor for the molecule of aflatoxin B1 (AFB1). In the first part I verified the adsorption of the molecule on the graphene layer. I analyzed various geometric positions and calculated the adsorption energies, to find the most stable geometric configuration. In the second part I analyzed graphene as a sensor by investigating the sensitivity and selectivity properties. I did the analysis through simulations with the software tool QuantumWise ToolKit (ATK) by Synopsys and with Density functional Theory (DFT) method.

Results

For the adsorption phase, I took a graphene layer of 40 exagons. I analyzed eight different geometric positions of aflatoxin and graphene. In all configurations, I placed the AFB1 at an initial minimum distance of about 2 Å from the graphene. Then I allowed the system to relax unconstrained to reach the most stable configuration. I calculated the adsorption energies through the formula:

$$E_{ADS} = E_{GR+AFB1} - (E_{GR} + E_{AFB1}) \qquad (1)$$

Configuration 1 is the most stable with an adsorption energy of $-112.4508\,\mathrm{kJ/mol}$. (Table 1)

Configuration	E_{ADS} (kJ/mol)
1	-112.4508
2	-109.9585
3	-103.6685
4	-102.8059
5	-32.3996
6	-46.7020
7	-48.8199
8	-32.5058

Table 1: Adsorption energies of the eight configurations

Then I did a further study regarding the adsorption site of aflatoxin on graphene, to see its influence on the adsorption energy. I took configuration 1 and I moved the aflatoxin to three different graphene sites: above a carbon atom, above a bond between two carbon atoms, on the center of a hexagon. The result is that there isn't a significant variation in the adsorption energy with respect to the adsorption site. The variation between the

three positions is negligible. In conclusion I can say that the aflatoxin molecule binds to graphene. In the first four configurations analyzed, the interactions are quite strong. The adsorption energy strongly depends on the relative orientation between AFB1 and graphene while it is almost independent of the adsorption site.

Then I moved on to investigating graphene as a sensor. I used a graphene layer of 91 hexagons in the central part so that the aflatoxin was affected as little as possible by the edges of the graphene and the electrodes. The electrodes are also in graphene. Then I calculated the current change in the device with and without the aflatoxin molecule. In the graph we see the trend of the two currents.(Figure 1)

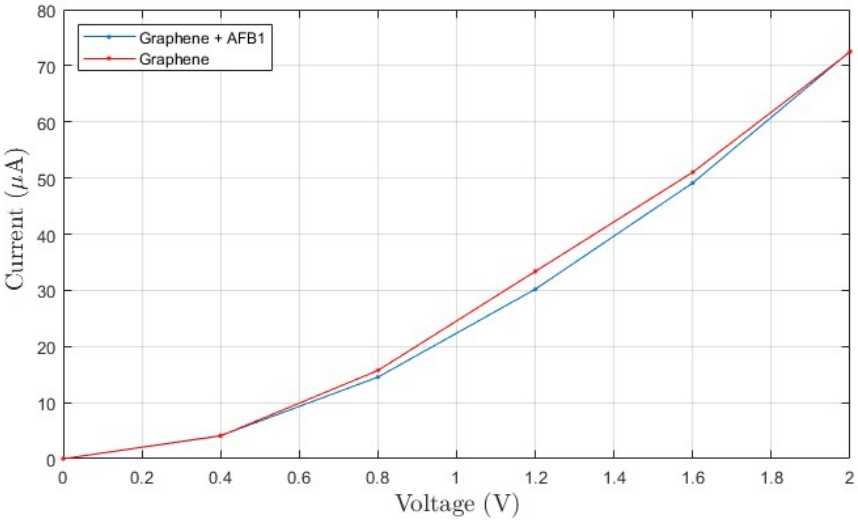

Figure 1: Comparison between the current in the graphene and the current in the graphene + AFB1 in configuration 1

There is a peak in the current difference in correspondence with the voltage of 1.2 V. That means there is a high sensitivity of the sensor to aflatoxin in this bias point. The corresponding current difference value is 3.167 µA. From the analysis of the percentage variation of the current, a maximum percentage variation of 10,48 % can be seen, always in correspondence with the voltage value of 1.2 V. This bias value has the greatest current difference both in absolute value and in percentage, obtaining the best response from the sensor. It is the point of greatest sensitivity. The analysis Transmission Pathways and Eigenstates Transmission show the presence of scattering phenomena responsible for the current reduction in the presence of the molecule, which behaves as a scattering center for the electrons that are transmitted from source to drain. The reason for this scattering may be an electron repulsion between the orbitals of graphene and aflatoxin.

As previously done with configuration 1 of aflatoxin B1, I studied the trend of the current also in correspondence with configuration 2 of aflatoxin. The trend of the current is very similar to that obtained with the first configuration. In configuration 2 the current is generally slightly higher than that in configuration 1, but the difference is small. At a voltage of 1.2 V, the current in the second configuration is 0,656 µA greater than that in the first configuration. This bias point (1.2 V) is also confirmed for this second configuration as the point of greatest sensitivity for the aflatoxin B1 molecule.

The next step, to approach the simulation of a real sensor, I simulated a finished graphene layer also in the transverse direction, passivating the remaining free carbon atoms along the edges of the graphene. I used the same device as previously, so that the results were comparable, with the only difference being the passivation of the edges. It can be seen that the presence of aflatoxin also in this case leads to a reduction of the current in the device up to about 1.3 V where instead there is a change in behavior. At 1.2 V there is a maximum in the current difference which is 2.079 µA.

Finally, to be such, a sensor must not only guarantee sensitivity with respect to the target molecule, but also selectivity with respect to all the molecules that can be found in the working environment. Selectivity is the property of detecting the target molecule and minimizing the sensitivity with respect to other molecules, at a given bias voltage. To investigate this property in the graphene sensor I analyzed its behavior with respect to some other molecules. I investigated the behavior of graphene with respect to some molecules that could be present in a solution: H_2O, Na_2 HPO_4, NaCl, KCl. I analyzed the adsorption of molecules on graphene. I calculated the adsorption energy to find the most stable configurations. Then I calculate the currents. In the figures (2) and (3) it is possible to see the trends of the currents and the zoom around the polarization point of 1.2 V, the point of maximum sensitivity. In all cases there is an increase in current comparared to

graphene with aflatoxin at 1.2 V. The molecule of NaCl increases of 2.37 µA, H_2O increases of 0.461 µA and KCl increses of 0.046 µA. So even if the selectivity with respect to other molecules such as NaCl is present, graphene as a sensor for the aflatoxin molecule has problems in the selectivity with respect to H_2O and a KCl, for the molecules I analyzed.

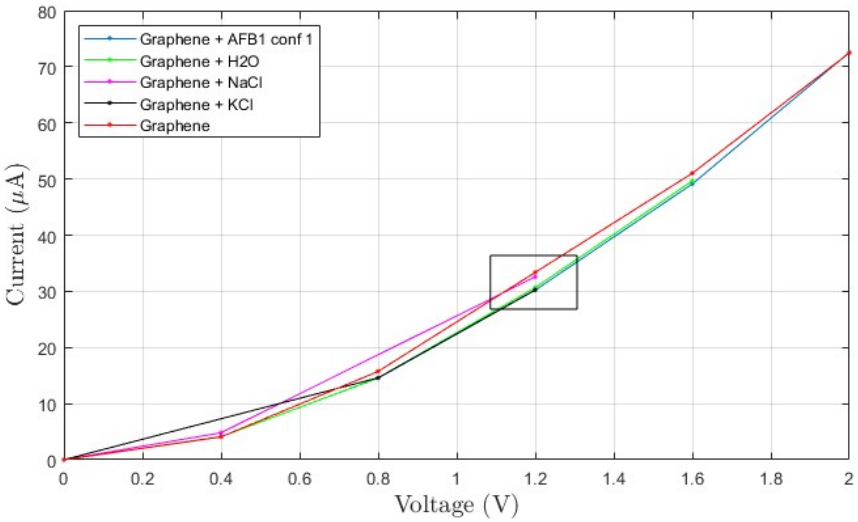

Figure 2: Current in Graphene + AFB1 in configuration 1, Graphene + H_2O, Graphene + NaCl, Graphene + KCl, Graphene.

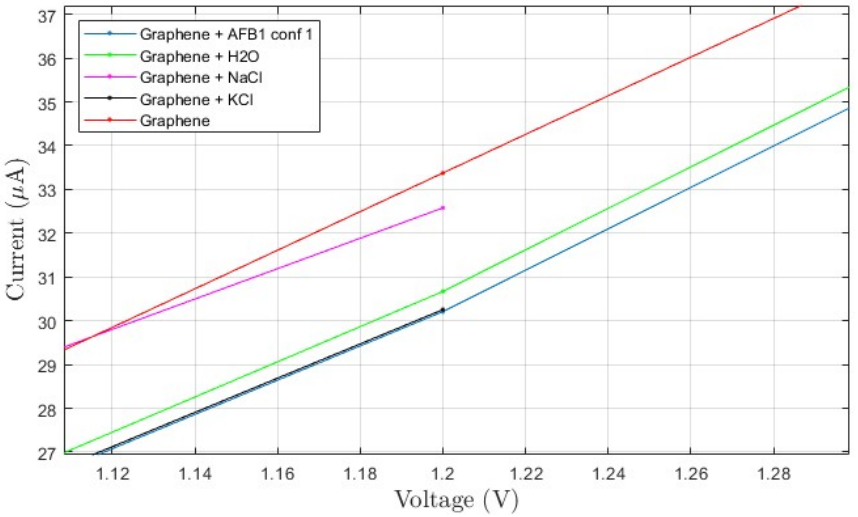

Figure 3: Zoom of the current around the voltage of 1.2 V for Graphene + AFB1 in configuration 1, Graphene + H_2O, Graphene + NaCl, Graphene + KCl, Graphene.

Conclusions and Future Works

In conclusion, graphene is able to detect a single molecule of aflatoxin B1. The bias point of maximum sensitivity is 1.2 V at which we have a current difference of 3.167 µA. On the other hand, there are problems regarding selectivity especially for H_2O and KCl.

Future work could try to improve the selectivity of graphene. For example, by heating the sensor, molecules with lower adsorption energy than AFB1 should interact with graphene for a short time compared to aflatoxin (this could be the case of H_2O). Instead, in the case of KCl, one could think a buffer with only H_2O and NaCl, without KCl. Also one could think of exploiting the kinetic energy of the molecules through a flow, verifying whether with certain speeds the adsorption of AFB1 is obtained and not that of the other molecules. The general idea to improve the selectivity may be to supply from the outside the energy to the molecules which decreases their adsorption on the graphene compared to that of AFB1. Other future works could investigate functionalized graphene, to try to obtain good sensitivity and at the same time the necessary selectivity.