POLITECNICO DI TORINO

Master's Degree in Electronic Engineering

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Pyrrole-based sensor for AFB1 with graphene electrodes



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To the pursuit of discovery and the power of curiosity

Summary

Aflatoxin B1 (AFB1) is an extremely toxic and carcinogenic mycotoxin that causes severely detrimental health effects due to its presence in food. Optimal detection methods need very high sensitivity (which allows for detection at the lowest concentration), quick analysis time, and suitability for field applications. This study focuses on the development and analysis of a pyrrole-based single-molecule junction with graphene electrodes for amperometric sensing of AFB1. To achieve high detection performance, the sensor is designed to take advantage of the special electrical characteristics of graphene and polypyrrole. Density Functional Theory (DFT) simulations are performed to study the adsorption of AFB1 on polypyrrole junction and perform equilibrium analysis, while semiempirical methods are used to analyze the current-voltage (I-V) characteristics of the system in non-equilibrium conditions. The goal is to investigate the electronic transport characteristics of the sensor with and without the presence of AFB1 to establish its effectiveness as a potential detection platform.

The first part of this thesis delves into graphene as an electrode material by emphasizing its benefits, which include stability, high electrical conductivity, and a strong potential for interaction with organic molecules. Next, polypyrrole is introduced as a conductive polymer and reviewed for its electrical properties, conduction mechanisms, versatility, and biocompatibility. The theoretical background is the basis for the understanding of the design and operation of the sensor. The simulation framework is described in the methodology section. It includes the following steps: choosing graphene as the electrode material because of its superior conductivity and compatibility with molecular electronics; designing sharp-edged graphene electrodes to improve electric field concentration and sensor sensitivity; and employing an 8-chain polypyrrole structure as the active sensing element to give AFB1 an optimal interaction surface. The π - π stacking is selected as an anchoring mechanism of polypyrrole on graphene and geometry optimization is performed to identify the most the stable configuration of polypyrrole and AFB1 in the sensor structure. The adsorption analysis assesses interaction mechanisms and stability using quantum mechanical simulations, and the electronic transport characteristics of the sensor are examined by analyzing I-V curves, transmission spectra, and electron density distributions.

The results of the simulation indicate that AFB1 adsorption significantly affects the electronic properties of the polypyrrole-based sensor. The primary observations include

quantitative changes in the transmission spectrum, such as peak intensity shifts and transmission path variations. Current-voltage analysis indicates a severe reduction in current upon exposure to AFB1, which confirms its strong effect on charge flow. The transmission pathways display a clear disruption of electron transport due to the presence of AFB1, which acts as a scattering center and reduces conductivity. From the electron density analysis, it is seen that AFB1 interacts primarily through electrostatic interactions rather than covalent bonding yet causes structural distortions in the polypyrrole chain that impact electronic transport. At an applied bias voltage of 0.2 V, the sensitivity analysis shows an extremely high percentage change in current (99.999 999 95 %), clearly demonstrating that this sensor will be effective for AFB1 detection. As a result, it can be said that this study successfully establishes the feasibility of the proposed sensor. It shows effective adsorption interactions, huge electronic transport variations, and a high sensitivity, suggesting that it is an ideal candidate for practical application in food safety monitoring. Future work may focus on experimental validation, selectivity and integration of the sensor into portable detection systems to further enhance its applicability.

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Part I

Motivation and Background

Chapter 1 Introduction

Aflatoxins are toxic mutagens and carcinogens produced by several molds such as Aspergillus flavus and Aspergillus parasiticus species, while aflatoxin B1 is the most dangerous type that is recognized as a Group 1 carcinogen by the International Agency for Research on Cancer (IARC) [9]. The primary source of human exposure to aflatoxins is the consumption of the contaminated food and therefore, the detection of AFB1 in agriculture is critical [88]. It has a prevalent presence in crops, particularly in warm and humid climates. 30 °C and 90 % relative humidity has been found to be their optimal enviroment to grow [55]. Also, it is able to contaminate a great range of staple foods such as maize, peanuts, cottonseed, and tree nuts [22].

There are several approaches available to determine the presence of AFB1, with the most prominent ones being high-pressure liquid chromatography, mass spectrometry, and enzyme-linked immunosorbent assays. These are all highly sensitive laboratory-based and they are considered the standard for AFB1 detection due to their reliability and accuracy. [71] But, as it stands now, it is hard to obtain such equipment and qualified people to use it in rural, resource-poor underdeveloped regions where multi contamination risks are considered the highest. Also, these techniques are less effective for onsite evaluations, harvesting and storage since more time is consumed in cleaning and preparing the samples. [10]

Electrochemical and optical biosensors are being developed for more rapid, sensitive, and field-deployable detection of AFB1. These devices are designed to produce results quickly and accurately without the need for complex instrumentation, but many are still in the experimental or early deployment phase. Recent trends in biosensor technology show that nanomaterials such as graphene and gold nanoparticles and bioreceptors such as aptamers and molecularly imprint polymers are enhancing the sensitivity and specificity of devices. Biosensors are also becoming more affordable and easier to operate, making them suitable for widespread deployment in agriculture. [59] Advances in integrating single molecules with 2D materials like graphene have contributed to the improved stability, biocompatibility and functionality of molecular electronic devices [34]. Because of graphene's high conductivity and adjustable electronic properties, it functions as a fine substrate for molecular junctions and transistors thereby facilitating greater durability and increased miniaturization in the electronic devices.

Considering all the previously mentioned reasons, in this work, it is aimed to investigate the performance of a pyrrole-based single-molecule junction with graphene electrodes as a sensor for the amperometric detection of Aflatoxin B1 (AFB1) by utilizing Density Functional Theory (DFT) simulations with QuantumATK software.

Chapter 2 Aflatoxin B1

Aflatoxins are a toxic compound group that is mainly produced by Aspergillus flourus and Aspergillus parasiticus, which are types of molds [9]. These molds primarily grow in hot and damp areas and can infect crops like corn, peanuts, cottonseed, and tree nuts [27]. The most dangerous type of mycotoxins to both humans and animals are aflatoxins since they are highly carcinogenic [86]. These toxins usually infiltrate the crops when they are cultivated, harvested and stored, most notably in places without adequate facilities to dry or store properly. Among the different types of aflatoxins, AFB1, AFB2, AFG1, and AFG2 are the most common, out of which AFB1 (Figure 2.1) is the most toxic and prevalent among these. Due to the high health risks associated with aflatoxins, its presence in food and feed products is limited globally, and regulatory authorities monitor the level of this contamination quite seriously in many countries around the world.



Figure 2.1: AFB1 molecule $(C_{17}H_{12}O_6)$, where gray, red, and white spheres represent carbon, oxygen, and hydrogen atoms, respectively.

Fungi generally thrive in soil, decaying organic matter, and in a variety of agricultural products such as crops like hay, corn, wheat, millet, rice, and chili peppers, and seeds like cottonseed, peanuts, tree nuts, sesame, and sunflower seeds, besides spices [64]. When these infested items become part of the food chain, residues of aflatoxin can be detected

in human and pet foods, as well as in animal feed [68]. These toxins are then transferred into the products such as eggs, dairy, and meat when these contaminated feeds are eaten by animals.

Chronic exposure to AFB1 even at low levels increases the risk for hepatocellular carcinoma especially in cases of prior liver disease or infection with hepatitis B [50]. In addition to carcinogenic effects, AFB1 causes acute toxicity known as aflatoxicosis characterized by vomiting, jaundice, abdominal pain, and in extreme cases liver failure [88]. In children, chronic exposure to AFB1 causes stunted growth and immune suppression; therefore, victims become more susceptible to infections and other diseases.

Aflatoxin B1 has a small molecular weight that exhibits stability and reactivity [87]. It possesses a distinctive structure comprising a difuran ring fused to a coumarin ring, which gives it its toxicity [30]. It looks as pale yellow crystal that fluoresce under ultraviolet light, which makes it detectable in the laboratory [81]. It is moderately soluble in organic solvents like methanol, chloroform, and acetone, but only slightly soluble in water [9]. Other valuable properties include chemical stability under dry conditions and resistance to relatively high temperatures, while very high temperatures may cause degradation. The molecular structure of the compound allows it to bind with DNA and proteins-a property underlying its mutagenic and carcinogenic effects [39].

In light of all the information presented, it becomes clear that detecting its presence is of paramount importance.

Chapter 3

Graphene

3.1 Exceptional Properties of Graphene

Graphene is a monolayer of carbon atoms arranged in a two-dimensional honeycomb lattice (Figure 3.1) and arguably one of the most important development in material science in recent decades [57]. It's a material that can be obtained from bulk graphite and due to its unique and varied properties, it has recently had a lot of attention [34]. Graphene has intrinsic electrical conductivity much higher than that of conventional materials; thus, it can allow very high electron mobility and is a perfect candidate for next-generation electronic devices, including transistors and sensors [14]. Also, it is about 200 times stronger than steel, while at the same time very light and flexible [48], which opens up avenues for applications in flexible electronics and advanced composite materials.



Figure 3.1: Graphene layer.

The unique physical structure of graphene is due to its sp^2 hybridization in which every carbon atom is in a strong covalent bond with three neighboring carbon atoms. Besides providing extraordinary mechanical strength, it provides graphene with very high thermal conductivity [6], hence offering efficient heat dissipation in electronics applications. Furthermore, graphene has a very high specific surface area of about 2630 m² g⁻¹, and thus offers enormous surface interaction opportunities [78] for its chemical modification. These attributes make graphene an ideal candidate for various applications ranging from energy storage systems, where it can enhance the performance both in batteries and supercapacitors, to the development of advanced membranes in filtration and separation processes. Ongoing researches are rapidly unraveling a number of capabilities that graphene might offer for making breakthroughs possible in many spheres, including nanotechnology, biomedicine, and environmental science [15], which designates graphene as a highly important material from a technological viewpoint.

3.2 Electronic Structure of Graphene

The concept of an orbital refers to the wave function, a mathematical expression describing the spatial distribution of an electron in its relation to the nucleus [37]. When such basic orbitals of several atoms interact, they form molecular orbitals [4]. Carbon, through its four valence electrons, is very active in forming bonds with other carbon atoms and thus creates crystalline structures [21]. This interaction between atomic orbitals from the neighbouring atoms create new molecular orbitals which are called hybrid orbitals. These different states of hybridization give the varying allotropes of carbon including fullerene and carbon nanotube [46]. In graphene, carbon atoms form covalent bonds that are located on a single plane. The hybridization process involves combining one s orbital and two p orbitals to form three sp^2 hybrid orbitals [57]. These orbitals take part in sigma (σ) bonding, which is significantly stronger than a regular covalent bond and oriented parallel to the plane of the carbon atoms. The electron distribution of these σ bonds lies in the plane of the atoms. The solitary electron from the four valence electrons occupies the $2p_z$ orbital which is oriented perpendicular to the atomic plane. This allows the formation of pi (π) bonds. This structural arrangement lends very exceptional properties to graphene. The σ bonds resulting from hybridization contribute to both the material's strength and flexibility, yielding extraordinary tensile strength and a high Young's modulus [48]. The electrons associated with the σ bonds are localized, while the electronic properties arise from the π and π^* (anti-bonding) orbitals, which are derived from the p_z orbitals [19] oriented perpendicular to the graphene plane. This arrangement generates a delocalized electron system that facilitates mobility along the plane of graphene, resulting in impressive electrical conductivity.

3.2.1 Band Structure

The hexagon is the basic structural unit of graphene. Each hexagon contains six carbon atoms [57]. The length that makes up the carbon–carbon bond, the side length of the hexagon, is about r = 1.42 Å, and the lattice constant is approximately $a = \sqrt{3}r = 2.46$ Å [19]. The primitive unit cell of graphene contains two carbon atoms (A and B) [84] in



Figure 3.2: The honeycomb lattice of graphene. The primitive unit cell is highlighted in orange and consists of two atoms: A (green) and B (purple). The lattice vectors \mathbf{a}_1 and \mathbf{a}_2 , as well as the nearest-neighbor displacement vectors $\boldsymbol{\delta}_1$, $\boldsymbol{\delta}_2$, and $\boldsymbol{\delta}_3$, are indicated.

Figure 3.2 and there are two-unit vectors with the same lattice constant a which are

$$a_1 = (\frac{\sqrt{3}a}{2}, \frac{a}{2}), a_2 = (\frac{\sqrt{3}a}{2}, \frac{a}{-2})$$

In the figure, it can be observed that each carbon atom has three nearest neighbours [84]. The vectors from each A atom to the nearest B atoms are

$$\delta_1 = (r,0) = \left(\frac{a}{\sqrt{3}}, 0\right), \\ \delta_2 = -a_2 + \delta_1 = \left(\frac{a}{2\sqrt{3}}, \frac{-a}{2}\right)$$
$$\delta_3 = -a_1 + \delta_1 = \left(\frac{-a}{2\sqrt{3}}, \frac{a}{2}\right)$$

and their length is equal to the carbon to carbon length 1.42 Å.

Figure 3.3 shows the reciprocal lattice of graphene, it is also in a honeycomb shape but rotated 90° [3]. The hexagon is the first Brillouin zone and the primitive reciprocal lattice vectors are

$$b_1 = (\frac{2\pi}{\sqrt{3}a}, \frac{2\pi}{a}), b_2 = (\frac{2\pi}{\sqrt{3}a}, -\frac{2\pi}{a})$$

while their length is $|b_1| = |b_2| = \frac{4\pi}{\sqrt{3a}}$. [3] The reciprocal lattice gives rise to multiple locations of high symmetry, which are the corners, referred as K and K'; the middle point of the lattice, " Γ -point"; and the midpoints of the sides, "M-points".

Graphene has a linear dispersion relation around the Dirac points which results in a distinctive band structure [19]. In graphene, the conduction band and valence band meet at two points in the Brillouin zone, known as the Dirac points K and K' from the figure. At these points, the energy-momentum relationship can be described by the formula:

$$E(k)^{\pm} = \pm \hbar v_F |k| = \pm \hbar v_F \sqrt{(k_x^2 + k_y^2)} = \pm \hbar v_F k$$
(3.1)



Figure 3.3: Reciprocal lattice of graphene. The hexagon is the first Brillouin zone which is shaded in pink, and the primitive reciprocal lattice vectors are b_1 and b_2 . The highsymmetry points include the corners (K and K'), the center (Γ -point), and the midpoints of the edges (M-points).

where E(k) is the energy, \hbar is the reduced Planck's constant, v_F is the Fermi velocity (approximately 10⁶ m/s for graphene), and k is the wave vector which is in spherical coordinates. This linear relationship shows that graphene is a zero-gap semiconductor or a semi-metal; the conduction and valence bands merge, which permits electron and hole conduction [19] [57]. Also, the linear dispersion results in high electron mobility and negligible effective mass which enables electrons to behave as massless Dirac fermions. This is one of the reasons graphene can have such extremely high conductivity, enabling carrier mobilities above 200,000 cm²/V · s at room temperature.

Figure 3.4 illustrates the band structure of graphene, which was derived through numerical computations using first-principles methods [28] [73]. This structure includes numerous energy levels due to the presence of π and σ electrons, which are the outermost electrons in carbon atoms. Typically, to formulate an analytical band structure for a solid, it is necessary to solve the time-independent Schrödinger equation in three-dimensional space [44]

$$H\psi(k,r) = E(k)\psi(k,r) \tag{3.2}$$

where H represents the Hamiltonian operator, which acts on the wave function ψ to yield the permitted energy values E. For an independent electron in a periodic solid, the Hamiltonian is expressed as

$$H = \frac{\hbar^2}{2m} \nabla^2 + \sum_{i}^{n} U(r - R_i)$$
(3.3)

with the first term being the kinetic energy operator, while the second term corresponds to the potential energy operator. Here, R_i denotes the *i*-th Bravais lattice vector, N is the



Figure 3.4: 2D band structure of pristine graphene.

number of primitive unit cells, and $U(r - R_i)$ signifies the potential energy contribution from the atom located in the *i*-th unit cell. This potential energy, composed of individual atomic potentials, is both periodic and has a Coulombic nature, characterized by a 1/r dependence. Substituting this Hamiltonian into the Schrödinger equation leads to a second-order partial differential equation.

In a crystalline solid, wave functions have to fulfill the Bloch's theorem [44]

$$\psi(r+R) = e^{i.k.R}\psi(r) \tag{3.4}$$

where R represents a Bravais lattice vector. Furthermore, periodic boundary conditions are

$$\psi(r) = \psi(r+S) = e^{i.k.S}\psi(r) \tag{3.5}$$

hence $e^{i.k.S} = 1$, where S is the size vector, with its lengths in each spatial coordinate representing the lattice's dimensions. The most commonly used method for solving this problem is the tight-binding model [84] [19].

3.2.2 Tight-binding Model

The tight-binding model is a theoretical approach that describes the electronic properties of crystalline solids in terms of interactions between atomic orbitals of neighboring atoms [73]. This model is based on the idea that the electrons are mostly localized around their atomic cores and, hence best represented by atomic orbitals with specific energy levels [40]. However, since atoms in a solid are not isolated but arranged in a periodic structure,

the orbitals of equivalent electrons from neighbouring atoms (in a solid containing N unit cells) will overlap [44]. As a result, the original N discrete energy levels expand into nearly continuous energy bands with N states per band, due to Pauli's exclusion principle [52]. Generally, this overlap means atomic orbitals are less accurate for depicting electrons in a solid [90]. Nevertheless, when this overlap is minimal, the tight-binding model can still provide a useful approximate analytical band structure, which ideally aligns with experimental findings or advanced numerical band structure calculations from ab-initio methods [84].

Using analytical calculations within the framework of the tight-binding model, the formula that characterizes graphene's band structure is [19] [69]

$$E(k) = \pm t \sqrt{1 + 4\cos\left(\frac{\sqrt{3}k_ya}{2}\right)\cos\left(\frac{3k_xa}{2}\right) + 4\cos^2\left(\frac{\sqrt{3}k_ya}{2}\right)}$$
(3.6)

where k_x and k_y are the components of the wave vector k, t is the hopping parameter that is approximately 2.7 eV representing the energy associated with electron hopping between nearest-neighbour atoms [67], and $a \approx 0.142 \,\mathrm{nm}$ is the distance between neighbouring carbon atoms. A graphical three-dimensional illustration is shown in Figure 3.5.



Figure 3.5: 3D electronic band structure of pristine graphene calculated using the tightbinding model.

The derived energy dispersion relation illustrates the gapless, linear band structure near the Dirac points, which is crucial for graphene's unusual electronic and transport properties [63]. Furthermore, it allows for significant tunability of electronic properties through methods such as doping and the application of electric fields, which can shift the Fermi level and modify the charge carrier density [34].

3.2.3 Density Of States

In graphene, the density of states (DOS) describes the number of accessible electronic states per unit area at a specific energy level. Due to graphene's unique linear dispersion relationship near the Dirac points, its DOS deviates from the parabolic behaviour seen in traditional materials. Instead, the DOS of graphene is linearly proportional to the absolute value of the energy |E|, hence leading to its specific electronic and thermal properties. [19]

The electronic structure near graphene's Dirac points can be approximated by the linear dispersion:

$$E = \pm \hbar v_F q \tag{3.7}$$

where E is the energy of the electronic state, \hbar is the reduced Planck's constant, v_F is the Fermi velocity (approximately $1 \times 10^6 \text{ m/s}$), and q = |k - K| is the wave vector relative to the Dirac point K (or K') in the Brillouin zone. [58]

To find the DOS, we calculate the number of states lying within a circle of radius q in k-space that corresponds to energy E. Given that each quantum state occupies an area of $(2\pi)^2$ in k-space, the density of states per unit energy per unit area, g(E), is

$$g(E)d(E) = \frac{g_s g_v \, dA}{(2\pi)^2}$$
(3.8)

where $g_s = 2$ accounts for spin degeneracy, $g_v = 2$ accounts for valley degeneracy (from the two Dirac points K and K'), and dA is the differential area in k-space for a small change dq, which can be expressed as $dA = 2\pi q dq$. [2]

Given the energy dispersion relation $E = \pm \hbar v_F q$, we can express q as $q = \frac{|E|}{\hbar v_F}$ and hence:

$$\frac{dq}{dE} = \frac{1}{\hbar v_F}$$

Substituting these into the DOS expression, we get:

$$g(E) = \frac{2|E|}{\pi(\hbar v_F)^2}$$
(3.9)

This linear dependence on |E| reflects graphene's unique electronic structure, contrasting with materials that have a constant or square-root DOS dependence on energy. [2]

The carrier density n(T), or the concentration of electrons per unit area at thermal equilibrium, depends on the temperature T and can be calculated by integrating the DOS weighted by the Fermi-Dirac distribution:

$$f(E, E_F) = \frac{1}{1 + e^{\frac{E - E_F}{k_B T}}}$$
(3.10)

where E_F is the Fermi level, k_B is Boltzmann's constant, and T is the temperature. For intrinsic (undoped) graphene, $E_F = 0$, so we calculate the equilibrium electron density as

$$n(T) = \int_0^\infty g(E) f(E,0) \, dE$$
 (3.11)

Substituting the DOS expression $g(E) = \frac{2|E|}{\pi(\hbar v_F)^2}$, we get:

$$n(T) = \frac{2}{\pi (\hbar v_F)^2} \int_0^\infty \frac{E}{1 + e^{E/k_B T}} \, dE.$$
(3.12)

This integral, known in statistical mechanics, evaluates to:

$$n(T) = \frac{2(k_B T)^2}{\pi(\hbar v_F)^2} \cdot \frac{\pi^2}{6} = \frac{\pi(k_B T)^2}{3(\hbar v_F)^2}.$$
(3.13)

Converting units to express this result in terms of carriers per square centimetre:

$$n(T) \approx 9 \times 10^5 T^2$$
 [electrons/cm²]. (3.14)

This quadratic temperature dependence of the carrier density in graphene contrasts with the exponential dependence seen in traditional semiconductors and is a direct consequence of its gapless linear band structure. [42]

3.3 Transport and Current Characteristics in Graphene

3.3.1 Current in Nanoscale

The current flow in nanoscale graphene-based electrodes is controlled by different principles from the bulk materials. Due to the small dimensions and quantum effects, the Landauer-Büttiker formalism offers a suitable framework. [47] It considers the current I as a sum of contributions from discrete, independent conduction channels and yields the formula:

$$I = \frac{2q}{h} \int T(E)M(E) (f_1 - f_2) dE$$
(3.15)

where q is the electron charge, h is Planck's constant, T(E) is the transmission probability, which accounts for scattering and the likelihood of charge carriers successfully crossing the channel, M(E) represents the number of transport modes (or channels) at a given energy, f_1 and f_2 are Fermi-Dirac distributions for source and drain contacts, respectively, modulated by the applied bias voltage. [18]

In the low-bias regime, this model presumes each conductive channel contributes independently, enabling accurate descriptions of current through small-scale devices [25]. For graphene electrodes in nanosensors, this is particularly beneficial since the small dimensions often push devices into the quasi-ballistic or ballistic transport regimes. [7]

3.3.2 Low-Bias Transport

Within the low bias regime, $f_1 - f_2$ can be approximated using a Taylor expansion so that the formula of the current reduces to: [18]

$$I = \frac{2q^2}{h} \int T(E)M(E) \left(-\frac{\partial f}{\partial E}\right) dE V$$
(3.16)

where f is the equilibrium Fermi function, and V is the applied voltage [41]. The conductance G in this low-bias condition is then [25]:

$$G = \frac{2q^2}{h} \int T(E)M(E) \left(-\frac{\partial f}{\partial E}\right) dE.$$
(3.17)

This formula gives insight into the fact that current scales linearly with voltage when small biases are applied, which is important for stable current output in nanosensor applications that operate in a low-bias regime. [75]

3.3.3 Transport Regimes

In graphene electrodes used for nanosensors, miniaturized dimensions enhance ballistic and quasi-ballistic behavior. [80] Thus, the transport regime—ballistic, diffusive, or quasi-ballistic—becomes very important. These regimes are determined by comparing the channel length L with the mean free path λ [25]:

- Ballistic Transport: If $L \ll \lambda$, carriers cross the channel without scattering, meaning $T(E) \approx 1$, and current flows with minimal resistance. Ballistic conduction facilitates quicker charge transfer, which is very beneficial for sensors that require fast reaction times. [79]
- Diffusive Transport: When $L \gg \lambda$, the dominance of scattering results in low transmission probability. Here, $T(E) = \frac{\lambda}{L}$, which results in high resistance and lower current, undesirable in nanosensor electrodes. [5]
- Quasi-Ballistic Transport: Partial scattering occurs for L ≈ λ, where 0 < T(E) <
 1. For graphene electrodes used in high-precision sensing applications, this regime strikes a balance between stability and quick charge transport. [51]

The transmission probability T(E) for these regimes is given by [25]:

$$T(E) = \frac{\lambda(E)}{\lambda(E) + L} \tag{3.18}$$

where $\lambda(E)$ depends on energy and temperature, capturing the probability of carriers reaching the drain without scattering [45]. This parameter plays a key role in the optimization of graphene for electrode use in nanosensors, where appropriate tuning of the transport length and mean free path allows the sensitivity and performance to be tailored [7].

3.3.4 Conductive Modes

In graphene, the number of conductive modes M(E) at a given energy plays a crucial role in defining transport characteristics [82]. As a two-dimensional material, graphene's modes grow linearly with both channel width W and carrier energy |E| [1]:

$$M(E) = \frac{2|E|W}{\pi\hbar v_F} \tag{3.19}$$

where v_F is the Fermi velocity (approximately 10^6 m/s), \hbar is the reduced Planck's constant, W is the channel width [70].

This formula indicates that the number of modes, and hence the current, is directly proportional to the width of the graphene electrode and to the energy level of the carriers [62]. This property allows tuning of W for sensitivity, since larger electrodes can support more conduction channels, thus yielding more robust and easily measurable current signals [91].

3.3.5 Current-Voltage Characteristics and Conductance

In graphene nanosensor electrodes, the I-V curve is a critical factor in determining device sensitivity and response time [56]. Under ballistic conditions, the current I is described by the simplified Landauer equation [47]:

$$I = \frac{2q}{h} \int_{-\infty}^{+\infty} M(E) \left(f_1 - f_2 \right) dE$$
(3.20)

with $M(E) = \frac{2|E|W}{\pi \hbar v_F}$ being the modes available to conduct [24]. This expression relates the current directly to the transmission spectrum, where the applied bias creates a "bias window" in which carriers contribute to the net current [8]. The effective conductance G in this regime, for low biases, is given by [25]:

$$G = \frac{2q^2}{h} \int_{-\infty}^{+\infty} T(E)M(E) \left(-\frac{\partial f}{\partial E}\right) dE.$$
(3.21)

3.3.6 Mean Free Path and Transmission Spectrum

One of the most important parameters in designing graphene nanosensor electrodes is the mean free path $\lambda(E, T)$, a measure of the average distance carriers travel before scattering [13]. Under ideal conditions, the mean free path in graphene can reach hundreds of nanometers, thus making it highly suitable for ballistic or quasi-ballistic conduction in nanoelectrodes [36]. Among the elements influencing λ are [11]:

- Acoustic Phonon Scattering: Increases with temperature, reducing λ [19],
- Charged Impurity Scattering: Alters λ based on carrier energy and the presence of extrinsic impurities [77],
- **Defect Scattering:** Reduced λ from lattice imperfections, affecting conductivity in real-world applications [17].

Chapter 4

Polypyrrole-Based AFB1 Detection

4.1 Polypyrrole as a Conductive Polymer

Polypyrrole (PPy) is one of the versatile conductive polymers that combine unique properties of organic materials with electrical conductivity [83]. The conductivity of PPy, in comparison with traditional metals and inorganic semiconductors, arises through the oxidation-reduction reactions within its polymeric structure due to delocalization of π electrons along the polymer chain. This continuous π -system, which was brought about by conjugated double bonds, enables free mobility of charge carriers through the polymer matrix [72].



Figure 4.1: Polypyrrole molecule with the chemical formula $H(C_4H_2NH)_nH$, where n = 8. Gray, blue, and white spheres represent carbon, nitrogen, and hydrogen atoms, respectively.

The conductivity of polypyrrole can be further improved upon doping with appropriate counterions, which extends its use in sensors, actuators, and energy storage devices [33]. Besides, its flexibility, ease of synthesis, and the possibility to tune its conductivity by the doping level and environmental conditions extend its utility in real-time detection systems where conductivity changes can indicate the presence of target substances like aflatoxin

B1 (AFB1) [66].

In the context of aflatoxin B1 (AFB1) detection, the interaction between polypyrrole and AFB1 is critical for the performance of the sensor. Because it is a small planar molecule, the toxin can adsorb onto the polypyrrole surface through van der Waals forces or by hydrogen bonding, producing measurable changes in conductivity [85]. This is because the attachment of AFB1 could donate or remove charge density from the polymer backbone, depending on the nature of the interaction.

In addition, polypyrrole is biocompatible and nontoxic, making it a safer choice for sensor applications than many conventionally used nanomaterials [43]. This characteristic is of especial advantage in such applications as environment monitoring and medical diagnostics, presupposing interaction with biological samples. These fundamental properties not only explain its wide usage but also emphasize its potential, especially in application within more complicated sensing systems combined with other advanced materials such as graphene.

4.2 Anchoring Polypyrrole to Graphene

Graphene has an excellent surface chemistry with its expansive surface area and sp2hybridized carbon network [34]. While pristine graphene is largely inert, the process of electroburning—a controlled pyrolysis in an oxygen-rich environment—naturally introduces functional groups on its surface. This occurs because the oxidative nature of the process creates nanoscale gaps while simultaneously forming oxygen-containing groups such as carboxyl (-COOH), hydroxyl (-OH), and epoxy (-C-O-C) at the graphene edges near the gap.

During electroburning, graphene reacts with oxygen to form these functional groups, which increases its reactivity and compatibility with polypyrrole. Most importantly, such functionalization is achieved without extra chemical treatment because air-assisted oxidative conditions serve inherently to modify the graphene surface. This natural termination of graphene edges creates anchor points that improve interaction with polypyrrole, leading to a more uniform and stable composite structure.

Ways to anchor polypyrrole to graphene surfaces:

- Covalent Bonding: Covalent functionalization of graphene entails chemical modification of the basal plane or edges, introducing reactive groups [76] that can form a stable covalent bond to polypyrrole during in situ polymerization [35]. For instance, carboxyl groups on graphene can react with pyrrole monomers through condensation reactions or other chemical pathways [65]. This method ensures a durable attachment, improving the mechanical stability and electrical connectivity of the composite.
- π - π Stacking Interactions: Graphene's sp^2 -hybridized structure facilitates π - π

stacking interactions with the aromatic pyrrole rings in polypyrrole [60]. These noncovalent interactions preserve the intrinsic properties of graphene while promoting intimate contact between the two materials. π - π stacking is especially useful when minimum disturbance in the electronic structure of graphene is required.

• Physical Adsorption: This method relies on the van der Waals forces for binding between the polypyrrole and graphene [48]. It is less intrusive and it retains the graphene in its pristine nature. During polymerization, pyrrole monomers adsorb onto graphene's surface, forming a conductive film. Although less stable than covalent bonding, physical adsorption can be reinforced by subsequent doping or cross-linking.

Furthermore, functionalized graphene derivatives, such as graphene oxide (GO) and reduced graphene oxide (rGO), are widely utilized to anchor polypyrrole due to their unique properties. GO, enriched with oxygen-containing groups like hydroxyl, epoxy, and carboxyl, enhances hydrophilicity and reactivity [29], facilitating the polymerization of pyrrole on its surface while improving dispersion and composite stability. Meanwhile, rGO, obtained through partial reduction of GO, strikes a balance by retaining enough reactive sites while improving conductivity [31], making it ideal for high-performance applications.

Chapter 5 Single Molecule Sensor

Single-molecule sensors (SMS) form a new frontier in nanoscale detection technologies, in which an individual molecule constitutes the unit of measurement. SMS devices leverage unique electronic, chemical, and physical properties of single molecules to realize high sensitivity and selectivity in their detection capabilities. The nature of molecular-scale interactions inherent to such sensors can override traditional limitations encountered by conventional sensing with bulk material technologies to enable their application in the biosensing of health-related diagnostics, monitoring of the environment, and the safety of food items. [89]

The development of SMS for AFB1 detection has seen substantial progress in recent years. Notably, the work by Mo et al. (2023) in "IEEE Transactions on Nanotechnology" explores the effect of adsorption mechanisms on conduction properties in single-molecule pyrrole-based sensors for AFB1. This study elucidates how adsorption dynamics, quantified by adsorption energy (Eads), influence the electronic transport characteristics within the sensor. Using mathematical-physical modelling, the authors describe how specific interactions between AFB1 molecules and the sensor's surface contribute to variations in electronic conduction. This pivotal research highlights the sensitivity of pyrrole-based SMS, employing quantum transport principles to detect AFB1 with unparalleled accuracy. [53]

Similarly, Mo et al. (2023) in their publication in "Sensors" present the design of pyrrole-based gate-controlled molecular junctions optimized for single-molecule AFB1 detection. This study underscores the role of gate-controlled modulation in enhancing the sensitivity of SMS. By optimizing the molecular junction configuration, the researchers achieve improved performance metrics, including lower detection limits and higher signalto-noise ratios. These advancements pave the way for practical applications of SMS in detecting hazardous substances like AFB1, further validating the potential of molecular electronics in sensor design. [54]

While there has been a significant advancement in the design and application of SMS for the detection of AFB1, several practical problems still need to be solved. These include,

among others, poor reproducibility and stability. Because of their very sensitive nature to environmental factors, consistent performance over time is still hard to achieve. Besides, scalability for real-world large-scale applications, such as general food safety monitoring, still needs refinement. Advancements in material science, especially in the use of nanomaterials like graphene and carbon nanotubes, holds great promise for overcoming some of these limitations by providing more stable and robust platforms for single-molecule detection. [49]

The working principle of single-molecule sensors involves the detection and transduction of molecular interactions into detectable electrical signals [20]. Pyrrole-based SMS for AFB1 detection is based on the following elements:

• Adsorption Energy: The adsorption energy, E_{ads} , is defined here as the interaction between AFB1 and the sensor surface. This parameter represents the energy change associated with the adsorption process and is a critical determinant of sensor sensitivity [54]. A favourable E_{ads} , a more negative one, ensures a strong and selective binding of AFB1 to the sensor's active sites, enhancing detection capabilities. The adsorption energy can be expressed as:

$$E_{\rm ads} = E_{\rm total} - (E_{\rm sensor} + E_{\rm AFB1}) \tag{5.1}$$

where E_{total} is the total energy of the sensor-AFB1 complex, E_{sensor} is the energy of the sensor without AFB1, and E_{AFB1} is the energy of the isolated AFB1 molecule.

• Electronic Transport Mechanism: The primary transport mechanism in singlemolecule sensors is coherent tunneling [26]. This quantum phenomenon allows electrons to traverse the molecular junction without scattering, maintaining phase coherence. The electronic transport is governed by the Landauer formula [26], which relates the current through the molecular junction to the transmission probability of electrons and is valid only at zero Kelvin:

$$I_{DS} = \frac{2q}{h} \int_{-\infty}^{+\infty} T(E) \left[f_S(E) - f_D(E) \right] dE$$
 (5.2)

Here, I_{DS} is the drain-to-source current; T(E) is the transmission probability of electrons at energy E; and $f_S(E)$ and $f_D(E)$ are the Fermi-Dirac distribution functions at the source and drain.

In principle, the sensitivity of SMS relates inherently to changes due to molecular adsorption. A modulated transmission probability arising due to interactions of AFB1 with the sensor manifests into measurable variations [23].

• Sensor Response: The response of the sensor to AFB1 is quantified by the variation in drain-to-source current (ΔI_{DS}) upon molecular adsorption [54]. The percentage

variation in current provides an additional metric for evaluating sensor performance:

$$\%\Delta I_{DS} = \frac{I_{DS}^{\text{baseline}} - I_{DS}^{\text{AFB1}}}{I_{DS}^{\text{baseline}}} \times 100$$
(5.3)

where I_{DS}^{AFB1} is the current measured in the presence of AFB1, and I_{DS}^{baseline} is the baseline current in the absence of AFB1. A higher ΔI_{DS} indicates a more pronounced response, reflecting the sensor's ability to distinguish AFB1 at low concentrations. This sensitivity is critical for detecting trace levels of AFB1 in complex matrices.

Part II

Methodology and Simulation

Chapter 6

Simulation Methodology and Computational Methods

The purpose of this work is to analyze the performance of a pyrrole-based single-molecule junction with graphene electrodes as a sensor for amperometric detection of Aflatoxin B1. As an initial phase of the research, the analyses are performed using the QuantumATK software tool for simulations.

6.1 Methodology

The methodology employed in analyzing the sensor for AFB1 consists of the following steps:

- The first step involved choosing graphene as the electrode material due to its exceptional electrical conductivity and other advantageous properties, as already outlined in the first part of this work.
- Graphene electrodes are designed with a sharp geometry. The left- and right-side electrodes taper towards the inner center. This strategic design can bring several benefits such as improved electric field concentration, sensitivity, and better interaction with the target molecule.
- An 8-chain polypyrrole structure has been chosen as the detection element for AFB1 as described previously. Its relatively long chain length provides an optimal surface area for interaction with the target molecule.
- Following an evaluation of various anchoring methods for graphene and polypyrrole, π - π stacking was chosen as the most suitable approach. This method leverages the aromatic interactions between the graphene surface and polypyrrole chains, ensuring a stable and efficient interface.

- Geometry optimization is undertaken to find out the most stable configuration for polypyrrole on graphene. This is supposed to assure a realistic alignment for the device.
- The AFB1 molecule is incorporated into the simulation, and a second round of geometry optimization is performed to determine its most stable position on the polypyrrole chain. The procedure indicated in the QuantumATK manual is followed, where the molecule is at first treated as a rigid body so that it can go through a systematic exploration of various positions and rotational configurations. Once the most energetically favourable configuration is identified, the molecule is allowed to relax and establish a stable interaction with the polypyrrole and graphene contacts. This approach is an efficient means to probe multiple configurations and refine the optimization to the most stable state.
- The adsorption phenomena of the Aflatoxin B1 molecule on polypyrrole is analyzed in detail, focusing on the interaction mechanisms and stability. The adsorption energies of the system are calculated and compared for configurations with and without AFB1. This comparative analysis provides critical insights into the binding efficiency and the overall impact of AFB1 adsorption on the device's performance.
- Additional analyses are conducted to provide a deeper insight into the behavior of the system: I-V characteristics, transmission spectrum, transmission pathways, and electron density.

6.2 Computational Methods

The simulations in this study were performed using the QuantumATK software tool, developed by Synopsys. It is an integrated platform of electronic and atomic-scale modeling tools written in Python and C++. The QuantumATK simulation engines provide bonded or reactive empirical force fields in a wide range of parametrizations and allow electronic-structure computations using density functional theory or tight-binding model Hamiltonians. Density functional theory has been implemented using a basis of plane waves or expansion of electronic states in a linear combination of atomic orbitals. It allows for an approximate solution of the many-body problem in a numerically efficient manner and, correspondingly, is one of the most used methodologies in atomistic calculations and ab initio electronic structure calculations. [74]

For the simulations involving geometric optimization, relaxation, total energy calculations, and transmission spectrum analysis, both for the isolated device without AFB1 and the complete system incorporating the AFB1 molecule, the parameters used in the equilibrium simulations are listed in Table 6.1. Unless specified otherwise, all other parameters were kept at their default values. The Generalized Gradient Approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional was chosen for being very reliable for the modeling of organic systems [61], while the inclusion of the Grimme-D3 dispersion correction ensures proper treatment of non-covalent interactions [38], such as π - π stacking. A well-relaxed structure is ensured by a force tolerance of $0.05 \text{ eV} \cdot \text{Å}^{-1}$, which balances accuracy and computational expense. The FHI DZDP (double-zeta with polarization) basis set was used for heavier atoms (C, O), while FHI DZP (double-zeta polarized) has been implemented on lighter ones (H, N) for sufficient accuracy [12]. The counterpoise (CP) method has been incorporated against the basis set superposition errors [16]. The parallel conjugate gradient Poisson solver with Dirichlet boundary conditions ensures accurate electrostatic potential calculations. Lastly, an energy cutoff of 100 Hartree provides a good compromise between computational efficiency and the accuracy of wavefunction expansions.

LCAO CALCULATOR		
LCAO Basis Set	Exchange correlation: GGA	
	Functional: PBE	
	van der Waals correction: Grimme DFT-D3	
	Pseudopotential: FHI	
	Basis set: DZDP for C, O; DZP for H, N	
Counterpoise	BSSE correction method: CP	
Numerical Accuracy	Density mesh cut-off: 100 Hartree	
	Occupation method: Fermi-Dirac	
	Broadening: 1000 K	
	k-points: [4, 4, 150] Å	
Device Algorithm	Default settings	
Contour Integral	Default settings	
Poisson Solver	Solver Type: Parallel Conjugate Gradient	
	Boundary conditions: PBC in A, Dirichlet in B and C	
Electrode Parameters	Default settings	

Table 6.1: QuantumATK-DFT Calculator settings for equilibrium simulations.

TRANSMISSION SPECTRUM ANALYSIS		
Method/Parameter	Description	
Energies (eV)	Energy range: -1 to 1, Points: 151	
Energy zero parameter	Average Fermi level	
Infinitesimal	$1 \times 10^{-6} \mathrm{eV}$	
Self-energy calculator	Recursion	
k-points density in non-equilibrium	Monkhorst [12, 12]	

Table 6.2: QuantumATK-DFT Transmission Spectrum settings.

Due to the prohibitive computational cost of using full DFT to perform the nonequilibrium simulations needed for the I-V curve analysis, a semi-empirical approach had been chosen (Table 6.3). The Slater-Koster Hamiltonian with DFTB parameterization was selected because it preserves computational feasibility for transport calculations while offering an effective and reliable description of the electronic structure [32]. The selfconsistent field (SCF) cycle is stabilized by a broadening of 300 K, and a well-converged charge density is guaranteed by a density mesh cutoff of 10 Hartree and a maximum interaction range of 10 Å. Recursion-based self-energy calculations ensured an accurate description of electron injection from the electrodes, while the Green's function formalism was used to model open-boundary conditions necessary for transport calculations [25]. The initial density was set to NeutralAtom, preventing excessive deviation from a physically meaningful starting point. In order to precisely model the electrostatic potential across the device, Dirichlet boundary conditions were applied in transport directions while the Poisson equation was solved using the Parallel Conjugate Gradient method. In the I–V analysis, drain-source voltages ranging from 0 V to 0.5 V with 11 discrete points allowed a detailed resolution of the current response, while an energy window from $-1 \,\mathrm{eV}$ to $1 \,\mathrm{eV}$ with 151 sampling points ensured precise integration of transmission spectra (Table 6.4). Unless otherwise indicated, all other parameters were left at their default settings. Together, these decisions guarantee a description of charge transport in the pyrrole-based single-molecule junction which is both physically meaningful and computationally efficient.

SEMI EMPIRICAL CALCULATOR		
Basic Parameters	Hamiltonian: Slater-Koster	
	Parameter group: DFTB	
Numerical Accuracy	Density mesh cutoff: 10 Hartree	
	Max interaction range: 10 Å	
	Broadening: 300 K	
	k-points: [4, 4, 150] Å	
Iteration Control	Tolerance: 1×10^{-5}	
	Max steps: 100	
	Damping factor: 0.1	
	Number of history steps: 20	
Device Algorithm	Initial Density type: NeutralAtom	
	Initial Density Length: 10 Å	
	Damping factor: 0.1	
	Method: GreensFunction	
	Process per contour point: 1	
	Selt energy: recursion	
	SCF restart step length: 0.1 Å	
Poisson Solver	Solver type: Parallel Conjugate Gradient	
	Boundary Conditions: PBC in A, Dirichlet in B and C	

Table 6.3: QuantumATK-DFTB settings for non-equilibrium simulations.

IV CURVE ANALYSIS		
Method/Parameter	Description	
Drain source voltages	V_{ds0} : 0 V, V_{ds1} : 0.5 V, Points: 11	
Energies	E_0 : -1 eV, E_1 : 1 eV, Points: 151	
Energy zero	Average Fermi Level	
Infinitesimal	$1 \times 10^{-6} \mathrm{eV}$	
Self-energy calculator	Recursion	
k-point sampling	Default	

Table 6.4: QuantumATK-DFTB IV curve settings.

Chapter 7

Simulations: Geometry Optimization

7.1 Geometry Optimization of the Sensor

To determine the most stable configuration of the sensing device, a series of geometry optimization and relaxation steps were performed. The initial system was carefully designed to ensure structural stability and realistic interaction between the polypyrrole (PPy) sensing layer and the graphene electrodes, followed by the adsorption of Aflatoxin B1 (AFB1) onto the PPy structure.



Figure 7.1: Graphene electrodes and electrode separation distance.

The graphene sheets were used to model left and right electrodes, where hydrogen

atoms were placed along the edges, directed towards the center (Figure 7.1). This edge hydrogenation was applied to stabilize the graphene terminals and prevent unwanted dangling bonds, which could otherwise interfere with charge transport properties. The inter-electrode distance was arranged as 31.17 Å to ensure sufficient space for the incorporation of the detection element which is an eight-chain polypyrrole system (Figure 7.2), while maintaining an appropriate electronic coupling between the electrodes.



Figure 7.2: Structure of an 8-Unit polypyrrole (PPy) chain.



Figure 7.3: Polypyrrole functionalized with pyrene.

To enhance adsorption properties and ensure stable interactions with the graphene electrodes, the PPy chains were modified by attaching pyrene groups at both ends through two carbon linkers on each side (Figure 7.3). Pyrene was added due to its strong affinity for graphene, which enhances the stability of the sensing interface. Following the structural modification, the PPy-pyrene system was placed near the graphene electrodes and subjected to geometry optimization and relaxation steps to identify a stable conformation. The optimized configuration is presented in Figures 7.4a and 7.4b, shown from different viewing angles.



(b) View along y-axis.

Figure 7.4: Geometrically optimized configuration of modified polypyrrole on graphene electrodes. In this optimization, the modified polypyrrole and the inner edges of the graphene electrodes (facing the center) were left to relax, while only the outer regions of the graphene electrodes were set as rigid to avoid unnecessary computational costs.

7.2 Geometry Optimization of the Sensor with AFB1

With the optimized PPy-pyrene structure in place, the next step was to introduce AFB1 close to the detection area. A constrained optimization was performed at this time, only permitting AFB1 to relax and keeping the device rigid. This approach helped determine the natural adsorption position of AFB1 relative to the PPy sensing layer (Figure 7.5a and

7.5b). The minimum distance measured between AFB1 and PPy was 2.64 Å (Figure 7.6a), whereas the distance between the modified PPy structure and graphene electrodes was 3.19 Å (Figure 7.6b).



(b) View along y-axis.

Figure 7.5: Geometrically optimized configuration of the device with Aflatoxin B1, where only AFB1 was allowed to relax.



(b) Measured distances between modified PPy and graphene electrodes.

Figure 7.6: Measurements of the geometrically optimized device configuration with Aflatoxin B1, where only AFB1 was permitted to relax.

To further refine the system, an additional geometry optimization was conducted, this time allowing both AFB1 and the detection molecule to relax simultaneously (Figure 7.7a and 7.7b). This step was essential to identify the most stable adsorption configuration. The results confirmed that AFB1 successfully interacts with the PPy chain, indicating strong adsorption (Figure 7.8a and 7.8b). In this final optimized state, the distance between PPy and the graphene electrodes increased slightly to 3.69 Å which suggests a slight structural rearrangement (Figure 7.9).





(b) View along y-axis.

Figure 7.7: Geometrically optimized configuration of the complete device with Aflatoxin B1, where the modified polypyrrole, AFB1, and the inner edges of the graphene electrodes (oriented toward the center) were allowed to relax.



(a) View along y-axis.



(b) View along z-axis.

Figure 7.8: Zoomed-in views of the geometrically optimized configuration of the complete device with Aflatoxin B1, highlighting the interaction of AFB1 with the modified polypyrrole. In this optimization, the modified polypyrrole, AFB1, and the inner edges of the graphene electrodes (oriented toward the center) were allowed to relax.



Figure 7.9: Measured distance between the modified polypyrrole and the graphene electrode in the geometrically optimized configuration of the complete device with Aflatoxin B1. In this optimization, the modified polypyrrole, AFB1, and the inner edges of the graphene electrodes (oriented toward the center) were allowed to relax.

The adsorption energy for AFB1 on the pyrrole-graphene sensor was calculated to be $-31\,642.687\,17\,\text{eV}$ using the Equation 5.1. This substantial negative value indicates a highly favorable and energetically stable adsorption process, suggesting a strong interaction between AFB1 and the sensor surface, thereby also confirming a stable configuration towards the subsequent electronic property analyses.

Chapter 8

Transport Simulations: Results and Analysis

The geometrically optimized device is analyzed in two configurations: without AFB1 and with AFB1, in order to study transport phenomena. This comparison provides insight into how the presence of the target molecule influences the electronic properties of the sensor. Since adsorption analysis has confirmed a strong interaction between AFB1 and the sensor surface, it is essential to determine whether this interaction induces measurable changes in the transport characteristics. To investigate this, the transmission spectrum is examined, giving information regarding the energy-dependent charge carrier behavior in the system.

When AFB1 is present, the transmission characteristics change, resulting in alters to peak intensity and spectral feature shifts, as illustrated in Figure 8.1. Certain transmission pathways are either enhanced or suppressed, indicating changes in the conductive states caused by orbital interactions or charge redistribution. The log-scale representation of the spectra in Figure 8.2 highlights these differences across the energy range, indicating that under an applied bias, a measurable variation in current is expected between the two configurations.



Figure 8.1: Equilibrium transmission spectra comparison: sensor with and without AFB1.



Figure 8.2: Log-scale equilibrium transmission spectra comparison: sensor with and without AFB1.

The current values for the sensor with and without AFB1 are compared between 0 V and 0.5 V with 0.05 V step size as shown in Figure 8.3. To highlight differences at lower current levels, Figure 8.4 displays the same data on a logarithmic scale. Furthermore, Figure 8.5 depicts the current difference (ΔI_{DS}) between the two systems, pointing out the influence of adsorption of AFB1 on charge transfer. Since AFB1 greatly suppresses conduction, it is noteable that the current difference closely resembles the trend of the I-V curve in its absence. The current variation is quantified using the relation in the formula:

$$\Delta I_{DS} = I_{DS}^{\text{baseline}} - I_{DS}^{\text{AFB1}} \tag{8.1}$$

where I_{DS}^{baseline} is the baseline current in the absence of AFB1, and I_{DS}^{AFB1} is the current measured in the presence of AFB1. A positive ΔI_{DS} value proves that molecular adsorption primarily results in a decrease in charge transport by showing that the current is higher when AFB1 is absent. The sensor's response is strongly influenced by the applied bias voltage, as the I-V characteristics exhibit substantial differences across the measured range. Since each bias point can be arbitrarily selected for device operation, a voltage of 0.2 V is chosen due to its practical advantages. This value ensures stable drain-source voltage (V_{DS}) generation and is particularly suitable for integration into low-power sensory systems. The related value for the current difference is approximately $3.3577589 \,\mu$ A. The sensitivity of the sensor to AFB1 is also evaluated by looking at the percentage change in current using the Equation 5.3. The analysis reveals an extremely large variation of 99.9999995%, in correspondence with the voltage value of $0.2 \,\mathrm{V}$. It clearly differentiates between the response of the sensor with and without AFB1 which makes it suitable for practical detection. Additionally, the measured current difference of $3.3577589 \mu A$ is within a detectable range, guaranteeing that it is compatible with common electronic measurement methods.



Figure 8.3: Comparison of the sensor current as a function of voltage (0-0.5 V, 0.05 V step). The red line represents the sensor with AFB1, while the black line corresponds to the sensor without AFB1.

Transport Simulations: Results and Analysis



Figure 8.4: Log-scale comparison of the sensor current as a function of voltage (0-0.5 V, 0.05 V step). The red line represents the sensor with AFB1, while the black line corresponds to the sensor without AFB1.



Figure 8.5: Current variation (ΔI_{DS}) in the sensor alone and the sensor with AFB1.

The transmission spectra at an applied voltage of 0.2 V, in the absence and presence of AFB1, is shown in Figure 8.6. In the case of sensor without AFB1 (Figure 8.6a), a prominent transmission peak of 1.07 is observed at -0.067 eV within the bias window. This peak is associated with one of the energy levels of polypyrrole which promotes effective charge transport and produces a comparatively high current. On the other hand, the transmission spectrum drastically decreases in magnitude when AFB1 becomes present, making a semi-logarithmic scale necessary for accurate visualization. As it can be observed from the Figure 8.6b, there are no significant transmission peaks within the bias window, which is consistent with the significant current suppression that occurs when AFB1 is present.



Figure 8.6: (a) Transmission spectrum of the sensor without AFB1 at a bias voltage of 0.2 V; (b) Transmission spectrum of the sensor with AFB1 at a bias voltage of 0.2 V.

The transmission pathways, which offer an in-depth representation of electron transport inside the device, are examined with the aim to gain insight into the lack of transmission peaks within the bias window (Figure 8.7 and Figure 8.8). These pathways are represented by arrows, where the width correlates with the probability of electron transmission, while their color conveys information about the electron phase.

In the presence of AFB1, an obvious suppression of transmission is observed precisely at the adsorption site on the polypyrrole chain. The electron flow is severely impeded at an abrupt discontinuity in the transmission pathways. The irregularities and angular tilting of the pathways close to the source electrode and along the left segment of the polypyrrole chain indicate that the disruption is caused by the loss of conjugation within the 8PPy molecule. Such structural changes result in a drastic decrease in current because they prevent the charge carriers from moving through the channel.

Conversely, in the absence of AFB1, the transmission pathways extend continuously along the entire polypyrrole chain and into the drain electrode. This continuity ensures an effective conductive channel between the graphene electrodes and validates that the conjugated structure of the 8PPy oligomer facilitates electron transport. Since electrons can flow freely from source to drain, the current is much higher as a result. These results demonstrate how AFB1 acts as a scattering center in the sensor channel, where its presence interferes with the charge transport mechanism and significantly reduces current by orders of magnitude.



Figure 8.7: Transmission pathways of the sensor without AFB1.



Figure 8.8: Transmission pathways of the sensor with AFB1.

By looking at the sensor's electron density with and without AFB1, one can observe whether a chemical bond occurs between AFB1 and polypyrrole. According to the findings, polypyrrole demonstrates a strong bond with the graphene electrodes (Figure 8.9a), ensuring effective coupling between the two components. On the other hand, AFB1 mainly uses electrostatic forces to interact with polypyrrole instead of covalent bonds. This is evident from the absence of electron density between AFB1 and the polypyrrole chain (Figure 8.9b) which confirms that no direct chemical bond formation occurs.



Figure 8.9: (a) Electron density of the sensor without AFB1; (b) Electron density of the sensor with AFB1.

Based on geometry optimization results, AFB1 induces minor geometry changes in the structure of polypyrrole even without covalent interaction. Although these distortions are small, they have a big effect on the electronic properties of the sensor. From the transmission pathway analysis it can be seen that AFB1 adsorption causes a tilt in the polypyrrole conformation, which interferes with charge transport and significantly reduces current. This structural alteration effectively explains the observed variations in the transmission spectra and the corresponding reduction in current.

Chapter 9 Conclusions

In this study, the performance and viability of a pyrrole-based single-molecule junction with graphene electrodes, as a novel amperometric sensor for Aflatoxin B1 (AFB1) detection, are methodically examined. A simulation approach based on semi-empirical transport calculations and Density Functional Theory (DFT) is used to characterize the molecular response of the sensor to AFB1 adsorption.

This thesis initially examines graphene's suitability as a stable, highly conductive electrode with strong organic molecule interactions, followed by a review of polypyrrole's conductive properties, versatility, and biocompatibility. The second part started with the decision of methodologies, design and optimization of the sensor. An improved electric field concentration was attained by utilizing the remarkable charge carrier mobility of graphene along with the sharp-edged geometry. The selection of an 8-chain polypyrrole oligomer, anchored via π - π stacking interactions, provided a well-defined interaction surface for AFB1. The geometry optimizations revealed a stable configuration of AFB1 on the polypyrrole chain and the adsorption analysis quantitatively evaluated the mechanisms of interaction between AFB1 and the sensor surface. While the absence of covalent bond formation was established, the simulations revealed a significant perturbation of the polypyrrole chain's conformational structure, mediated primarily by electrostatic interactions. Despite not being covalent, this structural distortion was shown to be the main cause of the high sensitivity of the sensor. Electronic transport characterization, performed through the analysis of current-voltage (I-V) characteristics, transmission spectra, and electron density distributions, quantified the impact of AFB1 adsorption on the sensor's electronic properties. At a bias voltage of 0.2 V, a 99.999995% change in current indicated a significant suppression of charge transport which highlights the potential of the sensor for high-sensitivity AFB1 detection. By showing the function of AFB1 as a scattering center and its interference with electron delocalization along the polypyrrole backbone, transmission pathway analysis helped to clarify the mechanism of charge transport suppression.

In conclusion, this computational investigation has provided a robust foundation for the development of a highly sensitive AFB1 sensor. The observed modulation of electronic transport, arising from the non-covalent, yet structurally consequential, interaction of AFB1 with the polypyrrole junction, establishes a clear pathway for practical implementation. The sensor's design, capitalizing on the unique electronic properties of graphene and polypyrrole, presents a promising alternative to conventional detection methodologies, particularly in resource-constrained environments.

Future research directions should focus on experimental validation of the computational predictions, including the synthesis and characterization of the proposed sensor. Furthermore, investigations into the selectivity of the sensor towards AFB1 in the presence of interferents, as well as the integration of the sensor into portable detection platforms, are essential for practical deployment. These subsequent studies will bridge the gap between computational modeling and real-world applications, facilitating the development of advanced sensing technologies for food safety monitoring.

Bibliography

- T. Ando. Theory of electronic states and transport in carbon nanotubes. Journal of the Physical Society of Japan, 74(3):777–817, 2005.
- [2] T. Ando, T. Nakanishi, and M. Sano. Chiral tunneling, the kubo formula, and transport in carbon nanotubes. *Journal of the Physical Society of Japan*, 67(2):1478– 1488, 1998.
- [3] N W Ashcroft and N D Mermin. Solid State Physics. Holt, Rinehart and Winston, 1976.
- [4] Peter Atkins and Julio de Paula. Atkins' Physical Chemistry. Oxford University Press, 2010.
- [5] D. Averin and A. Korotkov. Quantum effects in the transport properties of mesoscopic systems. Journal of Physics: Condensed Matter, 1:1020–1027, 1989.
- [6] A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, and C. N. Lau. Superior thermal conductivity of single-layer graphene. *Nano Letters*, 8(3):902–907, 2008.
- [7] A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, and C. N. Lau. Superior thermal conductivity of single-layer graphene. *Nano Letters*, 8(3):902–907, 2011.
- [8] C. W. J. Beenakker. Random-matrix theory of quantum transport. Reviews of Modern Physics, 69(3):731–808, 1991.
- [9] John W. Bennett and Maren Klich. Mycotoxins. Clinical Microbiology Reviews, 16(3):497–516, July 2003.
- [10] Rajeev Bhat, R. V. Rai, and Alias A. Karim. Mycotoxins in food and feed: Present status and future concerns. *Comprehensive Reviews in Food Science and Food Safety*, 9(1):57–81, January 2010.
- [11] J. S. Blakemore. Semiconductors: Data Handbook. Springer-Verlag, 1982.

- [12] Volker Blum, Ralf Gehrke, Felix Hanke, Paula Havu, Ville Havu, Xinguo Ren, Karsten Reuter, and Matthias Scheffler. Ab initio molecular simulations with numeric atom-centered orbitals. *Computer Physics Communications*, 180:2175–2196, 11 2009.
- [13] K. I. Bolotin, T. Gokus, M. Shulman, and U. Sivan. Temperature-dependent scattering and mobility in graphene. *Physical Review Letters*, 101(23):236602, 2008.
- [14] K. I. Bolotin, K. J. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, P. Kim, and H. L. Stormer. Ultrahigh electron mobility in suspended graphene. *Solid State Communications*, 146(9–10):351–355, 2008.
- [15] F. Bonaccorso, A. Lombardo, T. Hasan, Z. Sun, L. Colombo, and A. C. Ferrari. Production and processing of graphene and 2d crystals. *Materials Today*, 15(12):564– 589, 2012.
- [16] S.F. Boys and F. Bernardi and. The calculation of small molecular interactions by the differences of separate total energies. some procedures with reduced errors. *Molecular Physics*, 19(4):553–566, 1970.
- [17] D. A. Broido and T. L. Reinecke. Defect scattering in graphene. *Physical Review B*, 76(7):075410, 2007.
- [18] M. Büttiker. Scattering theory of current and voltage fluctuations in conductors and semiconductor structures. *Physical Review B*, 33(6):3021–3033, 1986.
- [19] A. H. Castro Neto, F. Guinea, N. M. R. Peres, et al. The electronic properties of graphene. *Reviews of Modern Physics*, 81(1):109–162, 2009.
- [20] Xinyue Chang, Yani Huo, Cong Zhao, Wanqi Sun, Ziqi Song, Ziyuan Qi, Jinying Wang, Jia Chuancheng, and Xuefeng Guo. Single-molecule electronic biosensors: Principles and applications. Advanced Sensor Research, 2:2200084, 02 2023.
- [21] F. Albert Cotton, Geoffrey Wilkinson, and Paul L. Gaus. Basic Inorganic Chemistry. Wiley, 1995.
- [22] Peter J. Cotty and Ricardo Jaime-Garcia. Influences of climate on aflatoxin producing fungi and aflatoxin contamination. *International Journal of Food Microbiology*, 119(1-2):109–115, October 2007. Epub 2007 Aug 14.
- [23] Juan Cuevas and Elke Scheer. Molecular Electronics: An Introduction to Theory and Experiment. 06 2010.
- [24] S. Das Sarma and E. H. Hwang. Transport in graphene: An overview. Journal of Physics: Condensed Matter, 21(10):315402, 2009.
- [25] S. Datta. Electronic Transport in Mesoscopic Systems. Cambridge University Press, 1995.

- [26] S. Datta. Quantum Transport: Atom to Transistor. EngineeringPro collection. Cambridge University Press, 2005.
- [27] U L Diener, R J Cole, T H Sanders, G A Payne, L S Lee, and M A Klich. Epidemiology of aflatoxin formation by aspergillus flavus*. Annual Review of Phytopathology, 25(Volume 25,):249–270, 1987.
- [28] M S Dresselhaus, G Dresselhaus, and P Avouris. Physics of Graphene. Springer, 2010.
- [29] Daniel R. Dreyer, Sungjin Park, Christopher W. Bielawski, and Rodney S. Ruoff. The chemistry of graphene oxide. *Chemical Society Reviews*, 39(1):228–240, 2010.
- [30] D. L. Eaton and E. P. Gallagher. Mechanisms of aflatoxin carcinogenesis. Annual Review of Pharmacology and Toxicology, 34(1):135–172, 1994.
- [31] Goki Eda, Giovanni Fanchini, and Manish Chhowalla. Large-area ultrathin films of reduced graphene oxide as a transparent and flexible electronic material. *Nature Nanotechnology*, 3(5):270–274, 2008.
- [32] M. Elstner, D. Porezag, G. Jungnickel, J. Elsner, M. Haugk, Th. Frauenheim, S. Suhai, and G. Seifert. Self-consistent-charge density-functional tight-binding method for simulations of complex materials properties. *Phys. Rev. B*, 58:7260–7268, Sep 1998.
- [33] S. Geetha, C. R. K. Rao, M. Vijayan, and D. C. Trivedi. Biosensing and drug delivery by polypyrrole. Analytica Chimica Acta, 568(1-2):119–125, 2006.
- [34] A. K. Geim and K. S. Novoselov. The rise of graphene. Nature Materials, 6(3):183– 191, 2007.
- [35] Vasilios Georgakilas, Michal Otyepka, Athanasios B. Bourlinos, Vimlesh Chandra, Namdong Kim, K. Christian Kemp, Pavel Hobza, Radek Zboril, and Kwang S. Kim. Functionalization of graphene: Covalent and non-covalent approaches, derivatives and applications. *Chemical Reviews*, 112(11):6156–6214, 2012.
- [36] S. Ghosh, A. A. Balandin, W. Bao, I. Calizo, F. Miao, and C. N. Lau. Measure of the thermal conductivity of graphene and graphite devices. *Nature Materials*, 9:555–558, 2009.
- [37] David J. Griffiths. Introduction to Quantum Mechanics. Pearson Education, 2005.
- [38] Stefan Grimme, Jens Antony, Stephan Ehrlich, and Helge Krieg. A consistent and accurate ab initio parametrization of density functional dispersion correction (dft-d) for the 94 elements h-pu. *The Journal of Chemical Physics*, 132(15):154104, 04 2010.
- [39] F. P. Guengerich et al. Activation and detoxication of aflatoxin b1. Mutation Research/Genetic Toxicology and Environmental Mutagenesis, 402(1-2):121-128, 1998.

- [40] W. A. Harrison. Electronic Structure and the Properties of Solids. Dover Publications, 2018.
- [41] H. Haug and A. P. Jauho. Quantum Kinetics in Transport and Optics of Semiconductors. Springer, 2008.
- [42] E. H. Hwang and S. Das Sarma. Carrier transport in two-dimensional graphene layers. *Physical Review B*, 75(2):205418, 2007.
- [43] J. Janata and M. Josowicz. Conducting polymers in electronic chemical sensors. *Nature Materials*, 2(1):19–24, 2003.
- [44] Charles Kittel. Introduction to Solid State Physics. Wiley, 2005.
- [45] L. P. Kouwenhoven and L. I. Glazman. Inelastic electron tunneling spectroscopy in quantum dots. *Physics Reports*, 324(6):219–281, 1997.
- [46] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley. C60: Buckminsterfullerene. *Nature*, 318(6042):162–163, 1985.
- [47] R. Landauer. Electrical resistance of discrete quantum systems. Philosophical Magazine, 21(172):863–867, 1957.
- [48] C. Lee, X. Wei, J. W. Kysar, and J. Hone. Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science*, 321(5887):385–388, 2008.
- [49] Dong Liu, Wenjia Li, Chengxi Zhu, Yuye Li, Xiuli Shen, Libo Li, Xiaohong Yan, and Tianyan You. Recent progress on electrochemical biosensing of aflatoxins: A review. *TrAC Trends in Analytical Chemistry*, 133:115966, 2020.
- [50] Y. Liu and F. Wu. Global burden of aflatoxin-induced hepatocellular carcinoma: A risk assessment. *Environmental Health Perspectives*, 118(6):818–824, 2010.
- [51] M. Lundstrom. Transport in nanoscale devices. IEEE Transactions on Electron Devices, 47(12):2212–2216, 2000.
- [52] G. D. Mahan. *Many-Particle Physics*. Kluwer Academic, 3rd edition, 2000.
- [53] Fabrizio Mo, Yuri Ardesi, Chiara Elfi Spano, Massimo Ruo Roch, Gianluca Piccinini, and Mariagrazia Graziano. Effect of adsorption mechanism on conduction in single-molecule pyrrole-based sensor for afb1. *IEEE Transactions on Nanotechnology*, 22:811–816, 2023.
- [54] Fabrizio Mo, Chiara Elfi Spano, Yuri Ardesi, Massimo Ruo Roch, Gianluca Piccinini, and Mariagrazia Graziano. Design of pyrrole-based gate-controlled molecular junctions optimized for single-molecule aflatoxin b1 detection. Sensors, 23(3):1687, 2023.
- [55] Francis Muga, M. Marenya, and Tilahun Seyoum Workneh. Effect of temperature, relative humidity and moisture on aflatoxin contamination of stored maize kernels. *Bulgarian Journal of Agricultural Science*, 25:271–277, 04 2019.

- [56] R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, M. Stoller, S. Roth, and A. K. Geim. Fine structure constant defines visual transparency of graphene. *Science*, 320(5881):1308–1309, 2008.
- [57] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov. Electric field effect in atomically thin carbon films. *Science*, 306(5696):666–669, 2004.
- [58] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, and K. Kim. Two-dimensional gas of massless dirac fermions in graphene. *Nature*, 438(7065):197–200, 2005.
- [59] Jia Yi. Ong, Adam Pike, and Lay Lay Tan. Recent advances in conventional methods and electrochemical aptasensors for mycotoxin detection. *Foods*, 10(7):1437, June 2021.
- [60] S. Park and R. S. Ruoff. Chemical methods for the production of graphenes. Nature Nanotechnology, 4(4):217–224, 2009.
- [61] John P. Perdew, Kieron Burke, and Matthias Ernzerhof. Generalized gradient approximation made simple. Phys. Rev. Lett., 77, Oct 1996.
- [62] V. M. Pereira and A. H. Castro Neto. Energy gaps and a zero-field quantum hall effect in a graphene bilayer. *Physical Review B*, 80(4):045401, 2009.
- [63] N. M. R. Peres. The transport properties of graphene: An introduction. Journal of Physics: Condensed Matter, 22(34):343201, 2010.
- [64] J. I. Pitt and A. D. Hocking. Fungi and food spoilage. Springer Science & Business Media, 2009.
- [65] C. N. R. Rao, A. K. Sood, K. S. Subrahmanyam, and A. Govindaraj. Graphene: The new two-dimensional nanomaterial. Angewandte Chemie International Edition, 48(42):7752–7777, 2009.
- [66] S. Rapi, V. Bocchi, and G. P. Gardini. Conducting polypyrrole by chemical synthesis in water. Synthetic Metals, 24(4):217–221, 1988.
- [67] Stephanie Reich, Janina Maultzsch, Christian Thomsen, and Pablo Ordejón. Tightbinding description of graphene. *Physical Review B*, 66(3):035412, 2002.
- [68] I. Rodrigues and K. Naehrer. A three-year survey on the worldwide occurrence of mycotoxins in feedstuff and feed. *Toxins*, 4(9):663–675, 2012.
- [69] R. Saito, G. Dresselhaus, and M. S. Dresselhaus. Physical Properties of Carbon Nanotubes. Imperial College Press, 1998.
- [70] S. D. Sarma, S. Adam, E. H. Hwang, and E. Rossi. Electronic transport in twodimensional graphene. *Reviews of Modern Physics*, 83(2):407–470, 2011.

- [71] Gordon Seymour Shephard. Determination of mycotoxins in human foods. Chemical Society Reviews, 37(11):2468–2477, 2008.
- [72] T. A. Skotheim. Handbook of Conducting Polymers. CRC Press, 1986.
- [73] J C Slater and G F Koster. Simplified lcao method for the periodic potential problem. *Physical Review*, 94(6):1498, 1954.
- [74] Søren Smidstrup, Troels Markussen, Pieter Vancraeyveld, Jess Wellendorff, Julian Schneider, Tue Gunst, Brecht Verstichel, Daniele Stradi, Petr A Khomyakov, Ulrik G Vej-Hansen, Maeng-Eun Lee, Samuel T Chill, Filip Rasmussen, Gabriele Penazzi, Fabiano Corsetti, Ari Ojanperä, Kristian Jensen, Mattias L N Palsgaard, Umberto Martinez, Anders Blom, Mads Brandbyge, and Kurt Stokbro. Quantumatk: an integrated platform of electronic and atomic-scale modelling tools. *Journal of Physics: Condensed Matter*, 32(1):015901, oct 2019.
- [75] L. L. Sohn, K. Kiesel, F. Simmel, and M. Büttiker. Quantum transport in nanosystems: Low-bias behavior and conductance. *Physical Review B*, 55:14139–14142, 1997.
- [76] S. Stankovich et al. Graphene-based composite materials. Nature, 442(7100):282–286, 2006.
- [77] T. Stauber, N. M. R. Peres, and F. Guinea. Graphene at finite doping: The interplay of disorder and interactions. *Physical Review B*, 76(20):205418, 2007.
- [78] M. D. Stoller, S. Park, Y. Zhu, J. An, and R. S. Ruoff. Graphene-based ultracapacitors. Nano Letters, 8(10):3498–3502, 2008.
- [79] A. Szafer and R. Schultz. Ballistic conduction in quantum wires. *Physical Review B*, 39:5516–5523, 1989.
- [80] J. Tersoff and D. R. Hamann. Theory of transport in small metallic systems. *Physical Review B*, 47(7):4580–4590, 1993.
- [81] N. W. Turner et al. Analytical methods for determination of mycotoxins: A review. Analytica Chimica Acta, 632(2):168–180, 2009.
- [82] J. Tworzydlo, Y. Oreg, P. W. Brouwer, and C. W. J. Beenakker. Sub-poissonian shot noise in graphene. *Physical Review B*, 74(4):035427, 2006.
- [83] T. V. Vernitskaya and O. N. Efimov. Polypyrrole: a conducting polymer; its synthesis, properties and applications. *Russian Chemical Reviews*, 66(5):443–457, 1997.
- [84] P R Wallace. The band theory of graphite. *Physical Review*, 71(9):622, 1947.
- [85] Dan Wang, Weihua Hu, Yonghua Xiong, Yang Xu, and Chang Ming Li. Multifunctionalized reduced graphene oxide-doped polypyrrole/pyrrolepropylic acid nanocomposite impedimetric immunosensor to ultra-sensitively detect small molecular aflatoxin b1. *Biosensors and Bioelectronics*, 63:185–189, 2015.

- [86] C. P. Wild and Y. Y. Gong. Mycotoxins and human disease: A largely ignored global health issue. *Carcinogenesis*, 31(1):71–82, 2010.
- [87] C. P. Wild and P. C. Turner. The toxicology of aflatoxins as a basis for public health decisions. *Mutagenesis*, 17(6):471–481, 2002.
- [88] John H. Williams, Timothy D. Phillips, Patricia E. Jolly, Jamie K. Stiles, Curtis M. Jolly, and Deepak Aggarwal. Human aflatoxicosis in developing countries: a review of toxicology, exposure, potential health consequences, and interventions. *The American Journal of Clinical Nutrition*, 80(5):1106–1122, November 2004.
- [89] Zhaohui Xue, Yixia Zhang, et al. Recent advances in aflatoxin b1 detection based on nanotechnology and nanomaterials—a review. Analytica Chimica Acta, 1069:1–27, 2019.
- [90] P. Y. Yu and M. Cardona. Fundamentals of Semiconductors. Springer, 4th edition, 2005.
- [91] Y. Zhang, Y. W. Tan, H. L. Stormer, and P. Kim. Experimental observation of the quantum hall effect and berry's phase in graphene. *Nature*, 438:201–204, 2005.