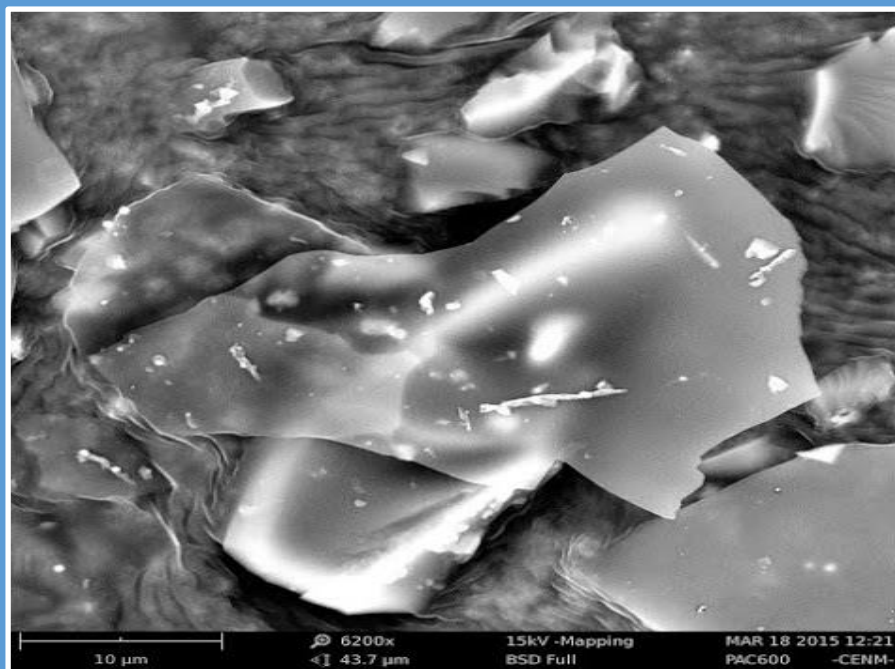


PhD. Dissertation

TRANSPORT MECHANISMS STUDY IN GRAPHITE OXIDE PLATELETS OBTAINED FROM BAMBOO FOR POSSIBLE APPLICATIONS IN ELECTRONIC



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UNIVERSIDAD DEL VALLE - Colombia

Transport mechanisms study in graphite oxide platelets obtained from bamboo for possible applications in electronic

Dissertation

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Cali – May 2018

To God, my wife, sons, mother, father, parents and friends.

Acknowledgements

Scientific mentors Pedro Prieto Pulido, Dr. Rer. Nat.; Hernando Ariza Calderón, PhD; and Katherine Gross, PhD. Also, international scientific mentors Christoph J. Brabec, Prof. Dr. and José Dario Perea, PhD(c) at i-MEET of the Friedrich Alexander Universität (FAU) Erlangen – Nürnberg, Germany; Ricardo Ibarra at Instituto de Nanociencia de Aragón, Universidad de Zaragoza, Spain. Moreover, members of the Thin Film Group at Universidad del Valle and Optoelectronic Group at Universidad del Quindío, Colombia; and co-workers Narly Andrea Echeverry Montoya, Tech. Edward Alexander Montoya Franco, Chem. Rafael Arias Niquepa, M. Sc. at Organic Materials Lab and Diego Javier Sanchez Trujillo, M. Sc. at Photoreflectance Lab of the Interdisciplinary Sciences Institute at the Universidad del Quindío. As well as, members of Physics Department of the Universidad del Valle and Electronic Instrumentation Technology Program at the Universidad del Quindío.

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Abstract

Graphite oxide (GO) is an interesting candidate for electronic applications, hence, important efforts have been dedicated to both large-scale and low-cost GO production as an intermediate in graphene production. At the same time, research efforts are aimed at identifying the role of defects, impurities, and disorder in the thermal, electrical, and magnetic properties of GO platelets for future electronic applications. Given the high interest in the fabrication, basic properties, and application of carbon-based materials, for first time, this work introduces a new and cost-effective method for the synthesis of GO platelets by using bamboo pyrolygneous acid (BPA) as source material, along with the basic study of its thermal, electrical, and magnetic transport mechanisms and discussion of future applications of these basic mechanisms in advanced electronics of sensors and devices. The GO-BPA samples were synthesized by using the double-thermal decomposition (DTD) method in a pyrolysis system under controlled temperature and nitrogen atmosphere, for carbonization temperatures (T_{CA}) from 673 to 973 K, and obtained from bamboo because of its high growth and production rates (approx. 3-5 years), good carbonization yield (28% - 17%), good abundance in the tropical region (1600 species, 67% Asia and Oceania, 30% America, and 3% Africa) and because the waste products from the bamboo industry are considered around 30% (approx. 1500 uses). We found that increased T_{CA} and decreased carbonization yield, varying from 28% to 18% determined by weight difference method, increased the graphite conversion (carbon presence) in the range from 83% to 95% and decreased oxygen coverage from 17% to 5%, measured by X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray spectroscopy (EDS) techniques and associated to the multifunctional oxide desorption through thermal decomposition effects.

Morphological, structural, elemental, thermal, electrical, and magnetic properties were studied by using high-resolution transmission electron microscopy (HR-TEM), transmission electron microscopy (TEM), electron diffraction (ED), scanning electron microscopy (SEM), X-ray diffraction (XRD), energy electron loss spectroscopy (EELS), X-ray photoelectron spectroscopy (XPS), EDS, Raman spectroscopy (RS), Fourier transform infrared (FTIR), current-voltage (I-V) curves, magnetic force microscopy (MFM), and vibrating sample magnetometer (VSM) as techniques in GO-BPA samples obtained for different T_{CA} . Identification of the GO structure in GO-BPA samples was carried out by using different characterizations via HR-TEM, TEM, ED, XRD, EELS, XPS, EDS, RS, and FTIR techniques. We found that GO-BPA samples exhibit stacking disorder as polycrystalline material with lateral dimensions of 5 - 100 μm and thicknesses below 100 nm as nanoplatelets, confirmed by HR-TEM, TEM, ED, and SEM. From the core-loss spectra, the sp^2 fraction ($\text{sp}^2 / (\text{sp}^2 + \text{sp}^3)$) was derived and is equal to 87% and 66% for the samples prepared at 973 and 673 K, respectively, and present crystalline order of short-medium range, determined by EELS. The structural behavior shows that increased T_{CA} decreased interplanar d-spacing and the average carbon-to-carbon bond length, which is identified through XRD and is attributed to desorption of some organic compounds and multifunctional oxides by thermal decomposition effects.

In the vibrational or thermal behavior at room temperature, it was found that increased T_{CA} increases the conversion to graphite, the density of boundary defects from 5.0×10^{-4} to $6.0 \times 10^{-4} \text{ cm}^{-2}$, which agrees with values reported in the range of 4.9×10^{-4} and $5.3 \times 10^{-4} \text{ cm}^{-2}$ for reduced graphene oxide material, which also increases the desorption of some organic compounds, multifunctional oxides, and the phononic response, as established by Raman and FTIR spectroscopies. We investigated temperature dependence on the frequency modes and line widths in the Raman spectra of GO-BPA samples and these were described by using a linear model based on net anharmonicity and thermal expansion contributions and no-linear model, the so-called Bose-Einstein model based on phonon-phonon interactions mechanism, respectively. It was found that increased temperature and increased I_D/I_G ratio possibly associated to the increased density of the boundary defects by net anharmonicity effect, and decreased Raman in-plane crystal size from 1.9 to 1.3 nm are possibly due to thermal expansion behavior. Temperature dependence on relaxation time was determined from Raman line width versus temperature and we found that the main transport mechanisms were attributed to phonon-defects and phonon-impurity interactions at temperatures from 95 to 190 K, and phonon-phonon interaction for temperatures from 190 to 325 K. These results were identified by using Raman spectroscopy. The functional groups at 3426, 2927–2850, 2350, 1680, 1590, 1435–1370, 1157, and 1066 cm^{-1} were attributed to O–H, C–H, CO_2 , C=O, C=C, C–H, C–O–C, and C–O bonds, respectively, and identified by using FTIR spectroscopy.

To determine the electrical properties from I-V curves of single GO-BPA nanoplatelets, these were contacted by Pt nanowires deposited through focused-ion and electron-beam-induced deposition techniques (FEBID/FIBID). At room temperature, electrical conductivity increased by two orders of magnitude as oxygen content decreased from 17% to 5%, reaching a value of $2.3 \times 10^3 \text{ Sm}^{-1}$ at the lowest oxygen content (from $6.3 \times 10^1 \text{ Sm}^{-1}$ at 17% oxygen coverage); we estimated the oxygen coverage dependence on the band-gap energy (E_g) in the single GO-BPA nanoplatelets, finding that increased oxygen coverage and increased E_g varied from 0.11 to 0.30 eV as a narrow band gap semiconductor, and this behavior can be described by charge carrier-impurity scattering mechanism as a main electrical transport mechanism. These behaviors were corroborated by using density functional theory (DFT) as computational simulation and considering the graphene oxide approximated molecular model proposed in this work. Temperature dependence on electrical conductivity reveals a semiconductor transport behavior, described by Mott's three-dimensional variable range hopping (3D-VRH) mechanism. Temperature dependence on the band gap energy was determined from electrical characterization in a single GO-BPA nanoplatelet at 5% oxygen coverage, finding that $E_g(T)$ can be described by Varshni's phenomenological expression, as expected for a semiconductor material, obtaining the Varshni coefficients of $E_g(0 \text{ K}) = 0.292 \text{ eV}$, $\alpha = 6.70 \times 10^{-4} \text{ eV/K}$ and $\beta = 34 \text{ K}$, which agree with the order of magnitude of the Varshni coefficients reported for other narrow band gap semiconductors, like InAs ($E_g(0 \text{ K}) = 0.417 \text{ eV}$, $\alpha = 2.76 \times 10^{-4} \text{ eV/K}$, and $\beta = 93 \text{ K}$), and InSb ($E_g(0 \text{ K}) = 0.235 \text{ eV}$, $\alpha = 3.90 \times 10^{-4} \text{ eV/K}$, and $\beta = 140 \text{ K}$).

Ferromagnetism (FM) order at room temperature induced by the density of boundary defects was observed in GO-BPA samples for different carbonization temperatures. We found that increased T_{CA} increases saturation magnetization by one order of magnitude from 2×10^{-3} to $3.9 \times 10^{-2} \text{ emu/g}$, attributed to increased density of boundary defects from $5.0 \times$

10^{-4} to $6.0 \times 10^{-4} \text{ cm}^{-2}$, and decreased remanence magnetization by one order of magnitude from 1.8×10^{-3} to $9.0 \times 10^{-4} \text{ emu/g}$, and the coercive field from 83 to 5.2 Oe, both associated to crystal size varying from 1.9 to 1.3 nm, as measured by VSM, MFM, Raman spectroscopy and observed via HR-TEM techniques. All these magnetic results agree with the same values reported for RGO material, as expected for a ferromagnetic soft material.

Correlations among transport mechanisms in GO-BPA samples were demonstrated via magneto-resistance (MR) experiments, taken at different temperatures from 100 to 400 K, finding that charge-carrier transport can be influenced by the 3D-VHR mechanism, as corroborated via electrical characterization. The temperature variations can be affected by thermal transport via phonon-defects and phonon-impurity at low temperatures (95 - 190 K) and phonon-phonon interaction mechanism at high temperatures (190 - 325 K), as obtained by vibrational characterization, and the ferromagnetic order behavior at room temperature can be induced by the density of boundary defects with remanence and coercivity influenced by crystal size as a main mechanism and determined via MFM, VSM, HR-TEM, and vibrational characterization. Re-entry magneto-transport at different temperatures in GO-BPA samples synthesized at $T_{CA} = 973 \text{ K}$ was observed and we found that the type of majority charge-carrier depends on the compromise between thermal energy and internal magnetic energy. At temperatures ranging from 360 to 400 K, samples exhibit negative magnetoresistance at values from -0.5% to -5.5% and showing n-type semiconductor behavior due to electrons gaining thermal energy to escape from magnetic domains and lead the current conduction. At temperatures between 200 and 360 K, samples presented positive magnetoresistance from +0.5% to +2.5% and exhibited p-type semiconductor behavior because electrons are trapped in magnetic domains and holes lead the current conduction. At temperatures values of $T < 190 \text{ K}$, samples show negative magnetoresistance around -0.25% and present n-type semiconductor behavior because at low temperatures internal magnetic energy increases by increments of coercive field, then, holes are trapped in magnetic domains and electrons lead the current conduction. Magnetoresistance measurements were carried out by using a PPMS system.

These results confirm that GO-BPA behaves structurally, thermally, electrically, and magnetically similar to reduced graphene oxide (RGO) sheets obtained through more sophisticated synthesis methods, and suggest a material that exhibits polycrystalline structure due to disordered crystalline structure with random periodicity for basic studies of new physics. Thermal, electrical, and magnetic transport mechanisms identified in this work suggest the potential uses of these samples in some possible future electronic applications, like FET and biosensor configurations, among others. These GO-BPA samples offer future opportunities to obtain 2D materials, like graphene oxide, by using an environmentally sustainable and commercially feasible synthesis method from renewable natural resources that would benefit from a fully scaled technology, and advanced electronics for sensors and devices.

Resumen

El grafito oxidado (GO) es un interesante candidato para el desarrollo de aplicaciones en el campo de la electrónica, por lo que los esfuerzos importantes se dedican a la producción de GO, tanto a gran escala como a bajo costo, siendo considerado como un producto intermedio en la producción de grafeno. Al mismo tiempo, los esfuerzos de investigación tienen como objetivo identificar el papel de los defectos, las impurezas y el desorden en las propiedades térmicas, eléctricas y magnéticas de las plaquetas de GO para futuras aplicaciones en electrónica. Dado el gran interés en la fabricación, en las propiedades básicas y la aplicación de materiales basados en carbón, por primera vez, en este trabajo presentamos un nuevo método de fácil y bajo costo de implementación, para la síntesis de plaquetas de grafito oxidado (GO), a partir de los ácidos piroleñosos extraídos del bambú-guadua (BPA) como material precursor, el estudio básico de sus mecanismos de transporte térmico, eléctrico y magnético y se discutieron las posibles futuras aplicaciones de estos mecanismos básicos en electrónica avanzada de sensores y dispositivos. Las muestras de GO-BPA se sintetizaron utilizando el método de doble descomposición térmica en un sistema de pirólisis bajo temperatura y atmósfera de nitrógeno controladas, para diferentes temperaturas de carbonización (T_{CA}), las cuales varían de 673 a 973 K. Estas muestras se obtuvieron del bambú-guadua debido a sus altas tasas de crecimiento y producción (aproximadamente de 3 a 5 años), su buen rendimiento de carbonización (de 28 % a 17 %), buena abundancia en la región tropical (1600 especies, 67 % Asia y Oceanía, 30 % América y 3 % África) y que los productos de desecho de la industria del bambú-guadua se consideran en torno al 30 % (aproximadamente 1500 usos). Encontramos que al aumentar la T_{CA} , disminuye el rendimiento de carbonización del 28 % al 18 %, según el método de diferencia de peso, también aumenta la conversión de grafito (presencia de carbono) en el rango de valores comprendido desde 83 % hasta 95 % y la cobertura de oxígeno de 17 % a 5 %; estos valores fueron medidos por XPS (espectroscopía de fotoelectrones de rayos X) y EDS (espectroscopía de rayos de energía dispersiva) y asociados al efecto de la desorción de óxidos multifuncionales por la descomposición térmica de los BPA.

Las propiedades morfológicas, estructurales, elementales, térmicas, eléctricas y magnéticas, se estudiaron empleando las técnicas de HR-TEM (microscopía de electrones de transmisión de alta resolución), TEM, ED (difracción de electrones), SEM (microscopía de barrido de electrones), XRD (difracción de rayos X), EELS (espectroscopía de pérdida de energía de los electrones), XPS (espectroscopía de fotoelectrones por rayos X), EDS (espectroscopía dispersiva de energía de rayos X), RS (espectroscopía Raman), FTIR (infrarrojo por transformada de Fourier), curvas IV (corriente voltaje), MFM (microscopía de fuerza magnética) y VSM (magnetómetro de muestra vibrante) en muestras de GO-BPA obtenidas mediante diferentes T_{CA} , respectivamente. La identificación de la estructura de GO en muestras de GO-BPA se llevó a cabo mediante el uso de diferentes caracterizaciones empleando las técnicas de HR-TEM, TEM, ED, XRD, EELS, XPS, EDS, Raman y FTIR. Encontramos que las muestras de GO-BPA presentan un desorden por apilamiento de las capas de grafeno oxidado que las componen, tal como se espera en materiales policristalinos, con dimensiones laterales desde 5 hasta 100 μm y espesores menores a 100 nm, como nanoplaquetas, confirmadas por HR-TEM, TEM, ED y SEM. A partir de los espectros de

pérdida de energía de los electrones, se obtuvo que la fracción sp^2 ($sp^2 / (sp^2 + sp^3)$) es igual a 87 % y 66 % para las muestras preparadas a 973 y 673 K, respectivamente, la cuales presentaron un orden cristalino de corto-mediano rango, determinado por EELS. El comportamiento estructural muestra que al aumentar la T_{CA} , disminuye el espaciamiento interplanar d y la longitud promedio de los enlaces C-C, identificado por XRD y atribuido a la desorción de algunos compuestos orgánicos y óxidos multifuncionales por efectos de la descomposición térmica de los BPA.

En el comportamiento térmico a temperatura ambiente se encontró que al aumentar la T_{CA} , se incrementan la conversión a grafito, la densidad de defectos de contorno que varía desde $5,0 \times 10^{-4}$ hasta $6,0 \times 10^{-4} \text{ cm}^{-2}$ y concuerda con los valores conocidos y reportados en el rango comprendido desde $4,9 \times 10^{-4}$ hasta $5,3 \times 10^{-4} \text{ cm}^{-2}$, para el material de grafeno oxidado reducido (RGO), también aumenta la desorción de algunos compuestos orgánicos, óxidos multifuncionales y la respuesta fonónica, establecidas empleando las técnicas de espectroscopías de Raman y FTIR. Investigamos las dependencias con la temperatura de los modos de frecuencia y los anchos de línea en los espectros de Raman en muestras de GO-BPA, las cuales se lograron describir muy bien utilizando un modelo lineal basado en la anarmonicidad de la red, y la expansión térmica del material y empleando el modelo no lineal, denominado modelo de Bose-Einstein, basado en el mecanismo de interacción fonón-fonón, respectivamente. Se encontró que al aumentar la temperatura, se aumenta la relación I_D/I_G , posiblemente asociada al incremento en la densidad de defectos por efecto de la anarmonicidad de la red, y se disminuye el tamaño del cristal en el plano Raman de 1.9 a 1.3 nm, posiblemente debido al comportamiento de la expansión térmica del material. Además, la dependencia de la temperatura con el tiempo de relajación se determinó a partir del ancho de línea Raman versus temperatura y encontramos que los principales mecanismos de transporte se pueden atribuir a las interacciones de los fonones con los defectos y las impurezas a temperaturas que varían desde 95 a 190 K, y a la interacción fonón-fonón para temperaturas comprendidas desde 190 hasta 325 K. Estos resultados se identificaron mediante el uso de la técnica de espectroscopía Raman. Además, los grupos funcionales en 3426, 2927-2850, 2350, 1680, 1590, 1435-1370, 1157 y 1066 cm^{-1} , se lograron atribuir a los enlaces O-H, C-H, CO_2 , C=O, C=C, C-H, C-O-C y C-O, respectivamente, y fueron identificados mediante la técnica de espectroscopía FTIR.

Para determinar las propiedades eléctricas mediante la caracterización por curvas I-V en nanoplaquetas individuales de GO-BPA, estas fueron contactadas por nanocables de Pt, los cuales fueron depositados empleando las técnicas de deposición inducida de electrones e iones enfocados (FEBID/FIBID). A temperatura ambiente, se observó conductividad eléctrica aumentada en dos órdenes de magnitud a medida que el contenido de oxígeno disminuye del 17 % al 5 %, alcanzando un valor de $2,3 \times 10^3 \text{ Sm}^{-1}$ con el contenido de oxígeno más bajo (de $6,3 \times 10^1 \text{ Sm}^{-1}$ con cobertura de oxígeno del 17 %); estimamos la dependencia de la cobertura de oxígeno con la energía de banda prohibida (E_g) en las nanoplaquetas individuales de GO-BPA, y se encontró que al aumentar la cobertura de oxígeno, se incrementa E_g , la cual varía de 0,11 a 0,30 eV, tal como un semiconductor de banda estrecha. Este comportamiento se logró describir mediante el mecanismo de dispersión de portadores de carga eléctrica con las impurezas, como principal mecanismo de transporte eléctrico. También, estos comportamientos se corroboraron utilizando la teoría funcional de densidad (DFT) por medio de simulación computacional y considerando el modelo molecular

aproximado de grafeno oxidado propuesto en este trabajo. La dependencia de la temperatura con la conductividad eléctrica revela un comportamiento de transporte de semiconductores, descrito por el mecanismo de Mott por salto de rango variable tridimensional (3D-VRH). La dependencia de la temperatura con la energía de banda prohibida se determinó a partir de la caracterización eléctrica en una sola nanoplaqueta de GO-BPA al 5 % de cobertura de oxígeno, y se encontró que $E_g(T)$ puede describirse por la expresión fenomenológica de Varshni, tal como se esperaba para un material semiconductor, lográndose obtener los coeficientes de Varshni de $E_g(0\text{ K}) = 0,292\text{ eV}$, $\alpha = 6,70 \times 10^{-4}\text{ eV / K}$ y $\beta = 34\text{ K}$, que concuerdan con el orden de magnitud de los coeficientes de Varshni reportados para otros semiconductores de banda estrecha, como el InAs ($E_g(0\text{ K}) = 0,417\text{ eV}$, $\alpha = 2,76 \times 10^{-4}\text{ eV / K}$ y $\beta = 93\text{ K}$) y el InSb ($E_g(0\text{ K}) = 0,235\text{ eV}$, $\alpha = 3,90 \times 10^{-4}\text{ eV / K}$ y $\beta = 140\text{ K}$).

Se observó orden ferromagnético (FM) a temperatura ambiente inducido por la densidad de defectos de contorno en muestras de GO-BPA sintetizadas para diferentes temperaturas de carbonización. Encontramos que al aumentar la T_{CA} , se incrementa en un orden de magnitud la magnetización de saturación desde $2,0 \times 10^{-3}$ hasta $3,9 \times 10^{-2}\text{ emu/g}$, atribuido a los incrementos en la densidad de los defectos de contorno, los cuales variaron desde $5,0 \times 10^{-4}$ hasta $6,0 \times 10^{-4}\text{ cm}^{-2}$ y se disminuyen en un orden de magnitud, la magnetización de remanencia de $1,8 \times 10^{-3}$ hasta $9,0 \times 10^{-4}\text{ emu/g}$ y el campo coercitivo de 83 a 5,2 Oe, ambos asociados al tamaño del cristal variando de 1,9 a 1,3 nm y medidos por VSM, MFM, espectroscopia Raman y observado por las técnicas de HR-TEM; todos estos resultados magnéticos concuerdan con los mismos valores reportados para el material RGO, como se esperaba para un material ferromagnético blando.

Las correlaciones entre los mecanismos de transporte en muestras de GO-BPA se demostraron mediante experimentos de magnetorresistencia (MR), tomados a diferentes temperaturas desde 100 hasta 400 K, y encontramos que el transporte de portadores de carga puede verse influenciado por el mecanismo 3D-VHR, como se corroboró mediante la caracterización eléctrica; las variaciones en temperatura pueden verse afectadas por el transporte térmico mediante los mecanismos de interacción de los fonones con los defectos y las impurezas a bajas temperaturas (95 - 190 K) y el mecanismo de interacción fonón-fonón a altas temperaturas (190 - 325 K). Estos mecanismos fueron obtenidos mediante la caracterización térmica, además, se encontró que el comportamiento de orden ferromagnético a temperatura ambiente puede ser inducido por la densidad de defectos de contorno, con remanencia y coercitividad influenciadas por el tamaño del cristal, como mecanismos principales y determinados por medio de MFM, VSM, HR-TEM y caracterización térmica. Además, se observó magneto-transporte re-entrante a diferentes temperaturas en la muestra de GO-BPA sintetizada a $T_{CA} = 973\text{ K}$ y encontramos que el tipo de portador de carga mayoritario depende del compromiso entre la energía térmica y la energía magnética interna. A temperaturas que oscilan entre 360 y 400 K, la muestra presenta magnetorresistencia negativa cuyos valores varían de -0,5 % a -5,5 % y la muestra exhibe el comportamiento de semiconductor tipo n, debido a que los electrones obtienen energía térmica para escapar de los dominios magnéticos del material y conducir la corriente eléctrica. A temperaturas que oscilaron entre 200 y 360 K, la muestra presentó magnetorresistencia positiva que varía de +0,5 % a +2,5 % y exhibe comportamiento de semiconductor tipo p debido a que los electrones quedan atrapados en los dominios magnéticos y los huecos son los responsables de conducir la corriente eléctrica. Además, a valores de temperatura de $T < 190\text{ K}$, la muestra

presenta magnetorresistencia negativa alrededor de $-0,25\%$ y exhibe comportamiento semiconductor tipo n debido a que a bajas temperaturas aumenta la energía magnética interna por incrementos del campo coercitivo que hace que los huecos queden atrapados por el campo magnético de los dominios y los electrones conducen la corriente eléctrica. Estas medidas de magnetorresistencia se llevaron a cabo mediante un sistema PPMS.

Estos resultados confirman que las muestras de GO-BPA se comportan de forma estructural, térmica, eléctrica y magnéticamente similar a las monocapas de grafeno oxidado reducido (RGO) obtenidas mediante métodos de síntesis más sofisticados, y sugieren un material que exhibe una estructura policristalina debido a que su estructura cristalina es desordenada y presenta periodicidad aleatoria por la presencia de defectos e impurezas, de gran interés científico en física básica. Además, los mecanismos de transporte térmico, eléctrico y magnético identificados en este trabajo, sugieren usos potenciales de estas muestras en algunas posibles futuras aplicaciones electrónicas, como las configuraciones de FET y biosensores, entre otras. Además, estas muestras de GO-BPA también ofrecen oportunidades futuras para obtener materiales en 2D, como grafeno oxidado, mediante un método de síntesis ambientalmente sostenible y comercialmente viable, considerando recursos naturales renovables que se beneficiarían de una tecnología completamente escalable y una electrónica avanzada de dispositivos y sensores.

Brief Overview

Graphene is a two-dimensional honeycomb arrangement of carbon atoms that exhibit physical and chemical properties of great interest in basic research and it is revolutionizing technology. In 2010, its discovery was so significant that it earned Russian scientists Andre Geim and Konstantin Novoselov the Nobel Prize in Physics.

All these scientific and technological efforts are because it is a two-dimensional material, with the best electrical conductivity of any material, which can be used to manufacture very small devices, opening research into relativistic quantum mechanics and offering potential uses, like ultrafast battery charging and bendable batteries. This material is also useful in the collection of radioactive waste for easier clean-up, faster flash memory, stronger and better-balanced tools and sporting equipment, such as tennis racquets; ultra-thin touchscreens that can be pasted onto non-breakable materials. Other applications include graphene-based e-paper that can be updated with new information; quick and efficient biosensor devices to measure blood glucose, cholesterol, and possibly DNA; headphones with phenomenal frequency response; supercapacitors that essentially make batteries obsolete; novel waterproof coatings; stronger and lighter aircraft and armor parts. Graphene may also aid in tissue regeneration, purification of salt water into drinking water, and creation of bionic devices that can connect directly to the body's neurons, among a host of other potential applications.

However, technological applications with band gap different from zero required oxidation of their structure or the use of intense electrical fields; therefore, an alternative way of tuning band gap energy and increasing the technological impact of graphene is through graphene oxide materials obtained via graphite oxide.

Graphite oxide is an interesting candidate for electronic applications, thereby, great efforts are being dedicated to large-scale and low-cost graphite oxide production as an intermediate in graphene production. At the same time, research is aimed at identifying the role of defects, impurities, and disorder in the thermal, electrical, and magnetic properties of platelets for future electronic applications.

One of the most common techniques to obtain graphene is the oxidization and subsequent exfoliation of graphite. For large-scale production, this technique has the disadvantage of being time consuming and environmentally toxic. Therefore, this thesis proposes and employs a new, simple, cost-effective pyrolytic double-thermal decomposition method (DTD-method) to synthesize graphite oxide (GO) platelets by using bamboo pyrolygneous acid (BPA) as source material.

Given high interest in the fabrication, basic properties, and application of carbon-based materials, for the first time, this work introduces a new and cost-effective method for the synthesis of GO platelets by using BPA as source material. We explored its thermal,

electrical, and magnetic transport mechanisms, as well as the possible future applications of these basic mechanisms in advanced electronic sensors and devices.

The GO-BPA samples were synthesized by using the DTD method in a pyrolysis system by controlling temperature and nitrogen atmosphere, for different T_{CA} , from 673 to 973 K. We used bamboo as precursor material because it has high growth and production rates (approx. 3-5 years), good carbonization yield (28% - 18%), good abundance in the tropical region (1600 species, 67% Asia and Oceania, 30% America, and 3% Africa) and reports approximately 1500 uses.

The results of this thesis confirm that GO-BPA samples behave structurally, thermally, electrically, and magnetically similar to the reduced graphene oxide (RGO) sheets obtained through more sophisticated synthesis methods. We discuss the outlook of this work in new basic open question as to how to describe the basic physical properties in terms of the random periodicity and disorder exhibited by GO-BPA samples. The work also suggests some opportunities for GO-BPA in future applications in electronics as FET and biosensor configurations, among others, showing possible potential applications of GO-BPA samples involving thermal, electrical, and magnetic responses that would benefit from a fully scaled technology and advanced electronics for sensors and devices.

Chapter 1

1. Introduction. Graphite oxide platelets obtained from bamboo.

Transport processes in nano/submicron-sized materials are the basis of current research to develop new basic and technological concepts for advanced electronic sensors and devices, which are framed within the, so-called, advanced electronics [1-6]. Downscaling of the characteristic dimensions in novel devices requires investigating about the thermal, electrical, and magnetic properties of nanoplatelets, enabling the study of the stability and reproducibility of their scattering processes. Besides their technological relevance, nanostructured two-dimensional materials, like graphene, offer a fascinating scenario to study the effect of the competition between phonons, charge-carriers, and dipolar and spin moments, among others.

It is known that several carbon nanostructures, like fullerenes, graphene sheets, graphite oxide (GO) platelets, carbon tubes, carbon amorphous spheres, and carbon chains have shown increased interest in the development of new-generation methods of environmentally sustainable energy production [2] and the development of the next generation of electronic devices and sensors [3]. The technological potential of these nanomaterials is based on the specific electronic properties of each of the structures. For example, for GO platelets, relocation of the bonds can produce van der Waals forces between induced electric dipoles, which influences the electrical transport properties [4, 5] and, therefore, this effect can be exploited in the construction of advanced devices and magnetic, electronic, thermo-electric, optical, photo-mechanical, and electro-optical sensors, among others [6].

Graphene sheets constitute an exciting and advanced material studied for over 50 years, experimentally discovered for the first time in 2004 by A. K. Geim and K. S. Novoselov (2010 Nobel prize in physics) [7, 8]. Graphene is an excellent electronic and thermal 2D material and has been considered a promising candidate for the post-silicon age. All this due to its large theoretical specific surface area ($2630 \text{ m}^2\text{g}^{-1}$), high intrinsic mobility ($250,000 \text{ cm}^2\text{v}^{-1}\text{s}^{-1}$), good electrical conductivity ($1.04 \times 10^2 \text{ Sm}^{-1}$), good thermal conductivity ($\sim 5000 \text{ Wm}^{-1}\text{K}^{-1}$), high Young's modulus ($\sim 1.0 \text{ TPa}$), and optical transmittance ($\sim 97.7\%$) [7-13].

This material has an enormous potential in advanced electronic sensors and devices as field-effect transistor and transparent conductive electrodes, among many other potential applications [12]. Despite great scientific and technological interest in graphene, this field requires reliably producing high-quality samples, especially in scalable fashion, and controllably tuning the graphene band gap. An alternative way of tuning the graphene band gap is by using multifunctional oxides present in this “graphene oxide” 2D structure [12-15]. Recently, graphene oxide has received special interest in physics, chemistry, and materials

science, given its unique and outstanding physical-chemical properties [15-19]. In addition, it can be described as an oxidized form of graphene, with the presence of hydroxyl, carboxyl, and epoxy functional groups distributed randomly along the hexagonal network of carbon atoms [15-19]. The multifunctionality given by the oxides, in combination with the exceptional properties of graphene, allows considering graphene oxide a versatile candidate material for next-generation electronics and optoelectronics, as well as for energy conversion and storage technologies [15-17, 20-22]. By tuning the oxide composition and crystal structure, its physical-chemical properties can be modified and functionalized [15].

Furthermore, graphene oxide multilayers are considered GO platelets, making them an interesting material because the oxide composition is variable; its structure may be of hexagonal or rhombohedral type and these advantages may change the physical properties of graphite. The multifunctional oxides present in graphite structures should be considered a new focus of basic concepts in physics, given that the oxide random distribution on the GO surface can produce random disorder and a polycrystalline structure with hyperuniform behavior [23]. In 1859, Brodie was the first to oxidize graphite by using the method of adding potassium chlorate [24]. Later, the concept of GO was gradually incorporated into the scientific world. Graphite oxide can be obtained by the traditional Brodie [25], Hummer [7, 25-28], Staudenmaier [7, 28], or Tang Lau [29] methods and modifications of these methods. However, these methods yield only micron-sized graphene flakes and requires using strong oxides (Brodie and Hummer methods) or glucose (Tang Lau method), herein considered as the traditional methods. Although the latter are excellent for basic research, the GO obtained with these methods decomposes at temperatures between 553 and 573 K, becoming amorphous carbon and losing many of the oxides present in the material. For these reasons, this work proposes a new low-cost, effective method known as the double-thermal decomposition method to obtain GO materials easily, which are thermodynamically stable at high temperatures (<1800 K) and quite different from the traditional methods with possibilities of large-scale production.

Other relevant scientific interests in GO are based on the possibility of obtaining graphene through exfoliation methods [27, 30, 31] in the presence of oxygen atoms [26, 27, 30, 31], nitrogen [30], hydrogen [26, 27], or the combination thereof, which can provide bandgap effects in the graphene band structure [32], an aspect of great scientific and technological interest.

Specifically, GO platelets are being used in the production of bipolar plates for batteries and fuel cells [33], advanced nanocomposites [34], development of flow sensors and energy conversion [35], development of cancer cell sensors with high electrical noise suppression [36], development of nano-antennae [37], nanomaterials for CO₂ absorption [38], catalysis [39], metal adsorption [40, 41], hydrogen storage [42], electric charge storage [43], electrodes for sodium ion electric batteries [44], electrodes for supercapacitors [45], base material to manufacture composites for anodes [46], and graphene oxide [30] with excellent surface properties and 2D structure [24-26, 30, 48], which can accommodate different types of oxygen-based functional groups [26, 31, 41, 48], biosorbents [25], and several organic metal compounds [26, 49]. It is also known that GO is rich in defects and is a carbonaceous material [24], which, according to particle thickness, can be obtained in the form of nanoplatelets [6]. The GO platelet materials are studied for the development of supercapacitors and solar cells,

among other electronic devices (printable electronics, printed electronics devices, and zener tunneling) [3, 43, 50].

This research sought to obtain and characterize the GO-BPA (Graphite Oxide from Bamboo Pyroligneous Acid) samples at temperatures above 573 K and these samples are more stable thermally than GO obtained via traditional methods. To achieve this, we considered the thermal decomposition method using an automated pyrolysis system, it is a low-cost method of producing GO-BPA at carbonization temperatures varying from 573 to 973 K, values at higher temperatures than traditional methods allow. It is expected that the transport properties of these materials obtained through pyrolysis are different from those known for GO obtained via traditional methods, which can be exploited in future electronic applications. Therefore, it is an open field of research and this is the first study of the synthesis, as well as the thermal, electrical, and magnetic transport mechanisms in GO-BPA samples obtained by the double-thermal decomposition (DTD)-method in a pyrolysis system [51-60].

In addition, in the case of GO-BPA, the composition and structure depend on the degree of graphitization and, therefore, depend on the carbonization temperature of the samples in the pyrolysis system (independent variable). It is noteworthy that this pyrolysis system was implemented and automated electronically at the Organic Materials Laboratory of the Interdisciplinary Institute of Sciences at Universidad del Quindío and was sponsored by COLCIENCIAS [51-60].

Given this scientific and technological potential, this research aimed to study transport mechanisms in GO-BPA samples, and to answer the question: What are the main transport mechanisms present in the GO-BPA samples obtained at different carbonization temperatures? To our knowledge, transport mechanisms in these samples still have not been systematically studied and no correlation thereof is known; recent reports indicate a growing interest in elucidating the mechanisms involved in the transport physics of these materials, which is an excellent opportunity to develop said advanced electronics in the near future.

Within this context, examples of current research include:

Regarding electrical transport properties, it accepted that, due to the anisotropy of graphite, GO displays metallic behavior in the direction parallel to the graphene layer, similar to that reported for graphene and graphene oxide [12], and semiconducting behavior in the perpendicular direction to the graphene layers; this provides electrical characteristics, which depend on the direction taken by electrons within the GO structure when accelerated by an externally applied electric field. Hence, it is known that electrical conduction mechanisms have been well-established in graphene and graphene oxide, explained by tunneling, hopping, or percolation mechanisms, according to the degree of oxidation [12]; this is also true for graphite [4, 61, 62]. However, to our knowledge, no systematic studies on GO identify the mechanisms of charge-carrier scattering that influence the electric transport in these materials and the role of oxides in electrical conduction, this despite the devices and sensors that have been developed [3, 30, 33-46, 50]. This research also aims to elucidate the mechanisms involved in the scattering processes of the electrical charge-carrier transport in GO-BPA for advanced electronics applications. For heat transport properties, it is known that, due to the

graphite anisotropy, GO presents good thermal behavior in the parallel direction to the graphene sheet, similar to that reported for graphene and graphene oxide [12] and thermal insulating behavior in the perpendicular direction of the graphene layers; this provides thermal characteristics that depend on the direction taken when the phonons propagate through the GO structure, when influenced by a thermal potential applied externally. In this regard, thermal conduction mechanisms have been well-established in the case of graphene, graphene oxide [12], and graphite [4, 63].

However, as far as we know, for GO-BPA materials, no systematic studies exist to identify the mechanisms that influence the thermal scattering processes involved in thermal transport and the role of disorder, defects, and oxides in thermal conduction, given that studies thus far have concentrated on the thermal properties of composite materials [34, 64] in which GO platelets are mixed with polymeric materials, finding that the thermal conductivity of the composites increases with increasing GO concentration and this behavior has been explained by percolation mechanisms of phonons through the polymer [65]. Thereby, this research also sought to explore the mechanisms involved in scattering processes of thermal transport in the GO-BPA material to develop thermo-electronic devices.

Furthermore, great interest exists in researching magnetic properties and spin dependent transport. The possibility of obtaining ferromagnetic (FM) order at room temperature, based on carbon (graphite-doped synthetic C60 fullerenes, graphene, and carbon compounds, among others), has enormous technological potential combining ferromagnetic properties, biocompatibility, and semiconductor materials. Thus, the "magnetic coal" is seen as a promising material for spintronics [66-69], biocompatible electronic devices [66, 68], and information storage systems, with flexible, adaptable and transparent characteristics [12].

From a theoretical point of view, the existence of FM order in these systems is a subject of great scientific discussion, as it nullifies the concept that only shallow electron transition metals (such as iron, nickel, cobalt or some of their alloys) are responsible of FM at room temperature; this finding has led to reconsider the theory of magnetism [66, 68, 69]. New theories suggest that the origin of the FM intrinsic nanostructures based on graphite are due to localized spin states caused by the presence of structural defects [70-74], vacancy defects [71, 74-76], absorption of hydrogen atoms [74-76], and dimensionality effects [74], among others. The biggest problem in this case is the fact that spin polarization is local and the possibility of reaching a magnetically ordered state depends on a delicate balance among the several interactions of the system. This scientific effort to understand and control the magnetic properties of these materials is quite evident; however, the whole mechanism to explain the magnetic properties of both pure graphene systems, like the GO, remains the subject of controversy and discussion and still requires further experimental evidence of reproducibility [74].

In Colombia and the rest of the world, no research groups have systematically studied the problem of magnetism in carbon precursors obtained from *Guadua angustifolia* Kunth bamboo (GO-BPA). Therefore, this is the first research aimed at providing a structured path with experimental evidence, knowledge on the subject, and identifying possible mechanisms responsible for the magnetism observed in GO-BPA samples. Additionally, this research was

an excellent opportunity to contribute with experimental evidence, theoretical approximation, and publications to the knowledge of this issue.

This is the scientific and technological landscape of transport properties in GO-BPA; currently, it is an interesting open field of research, of high interest in high-impact journals in the scientific and technological community and, therefore, for basic and innovative reasons, this research seeks to shed light on the mechanisms involved in the thermal, electrical, and magnetic transport mechanisms in GO-BPA samples for future electronic applications. Moreover, by performing this work, we will be continuing the research being conducted in recent years on the issue of carbon obtained by using bamboo-guadua as precursor [51-60].

Given the scientific and technological interest in GO, one of the most common techniques to obtain graphene oxide is the oxidization and subsequent exfoliation of graphite. However, for large-scale production, this technique has the disadvantages of being time consuming, environmentally toxic, with high corrugation effects; also, graphene oxide decomposes at temperatures between 553 and 573 K, becoming amorphous carbon and losing many of the oxides present in the material. Therefore, we proposed and employed a new, simple, cost-effective pyrolytic method to synthesize graphite oxide or graphene oxide multilayers as nanoplatelets, by using Colombian bamboo pyroligneous acid (BPA) as source material [54-55]. The GO-BPA can be considered a good candidate for large-scale production of GO materials because of its advantages, such as low time consumption (around 30 h), environmentally not toxic, very low corrugation effects, and more thermally stable than traditional GO material, given that it decomposes at temperatures >1800 K. For these reasons, this work presents the synthesis method, thermal, electrical, and magnetic main transport mechanisms, complementary characterizations, and a discussion of possible future electronic applications by using GO-BPA samples obtained from Colombian bamboo.

For this purpose, this thesis is organized as follows:

It begins with an overview of the fundamental theoretical concepts necessary to understand the experimental results obtained in this work, thereby: Chapter 1 shows the importance of GO and the basic open question as introduction. Chapter 2 discusses relevant basic concepts of transport theory background and presents main physical characteristics of GO. Chapter 3 describes the experimental methods for sample preparation and characterization. Chapter 4 illustrates the results about the identification of main transport mechanisms in GO-BPA samples at different carbonization temperatures and a discussion of the possible future advanced electronic for sensors and devices. The concluding Chapter 5 summarizes and provides an outlook of the results achieved. Additional information for scientific support of this work can be found in the Appendix section.

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Chapter 2

2. Theoretical Background

This chapter offers an overview of the transport phenomena, important in understanding the experimental results found in this thesis. The first part concentrates on an introduction to the relevant interactions contributing to the occurrence of scattering processes from a microscopic and a micro-transport point of view. Thereafter, the basic transport principles are presented. The last part of this chapter provides an overview of the structural, morphological, thermal, electrical, and magnetic properties of the Graphite Oxide (GO) compounds.

2.1 Basic Transport Principles

The study of transport phenomena in any material requires knowledge of the thermal (Q), electrical (E), and magnetic (H) effects in the flow, J , of the charge, heat or spin, respectively; considering non-local and memory effects in the space occupied by matter, $\mathbf{r}$, and time, t , as shown in [Table 2.1](#).

Table 2.1. Onsager magnitude, units, perturbation, response and Fourier images in electrical and thermal transport.

Onsager Magnitude ($\hat{x}$)	Units $\frac{d\hat{x}}{dt}$	Perturbation	Response	Fourier Image
Charge (q)	$J_q = \frac{\text{Charge}}{\text{time area}}$	$-\nabla\phi$ $= E$	Local $J_q = \sigma E$ Non-local J_q $= \iint f(\mathbf{r}, \mathbf{r}', t, t') E(\mathbf{r}, t) d\mathbf{r}' dt$	$J_q(\mathbf{r}, \omega) = \sigma(\omega) E(\mathbf{r}, \omega)$
Heat (Q)	$J_Q = \frac{\text{Heat}}{\text{time area}}$	∇T	Local $J_Q = -k \nabla T$ Non-Local J_Q $= \iint f(\mathbf{r}, \mathbf{r}', t, t') E(\mathbf{r}, t) d\mathbf{r}' dt$	$J_Q(\mathbf{r}, \omega)$ $= -k(\omega) \nabla T(\mathbf{r}, \omega)$

The generalized transport theory considering the Onsager formalism and magnitude as charge and heat is presented in [Table 2.1](#). Electrical field or thermal potential can perturb

these magnitudes and linear response can be studied by using the electrical charge or heat flow with local and non-local effects. These flows depend on time and, by obtaining the Fourier images, it is possible to determine information on the frequency domain. In the charge case, the response of the current flow due to electric field can be derived from the general relation, given by [1-3]:

$$\mathbf{J}(\mathbf{r}, t) = \iint f(\mathbf{r}, \mathbf{r}', t, t') \mathbf{E}(\mathbf{r}, t) d\mathbf{r}' dt' \quad (2.1)$$

If considering only memory effects, the time dispersion effect is:

$$\mathbf{J}(t) = \int_{-t}^t f(t, t') \mathbf{E}(t') dt' \quad (2.2)$$

Expression (2.1) is for the isotropy material. Now, by using the Fourier transformation in $f(t)$; so,

$$f(t) = \frac{1}{2\pi} \int f(\omega) e^{-i\omega t} d\omega \quad (2.3)$$

It is possible to obtain the Fourier images from expression (2.2) and present them as follows:

$$\mathbf{J}(\omega) = f(\omega) \mathbf{E}(\omega) \quad (2.4)$$

In expression (2.4), the linear response function $f(\omega) = \sigma$ is the generalized conductivity and expression (2.4) can be written as:

$$\mathbf{J} = \sigma \mathbf{E} \quad (2.5)$$

Expression (2.5) can be used in the thermal and electrical transport as the Fourier and Ohm laws, respectively.

For the anisotropy material, conductivity depends on the direction of the heat, current, or magnetic flow. Then, expression (2.5) can be written as:

$$J_i = \sigma_{ij} E_j \quad (2.6)$$

The σ_{ij} is the generalized conductivity tensor and given by:

$$\begin{pmatrix} J_x \\ J_y \\ J_z \end{pmatrix} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix} \quad (2.7)$$

Where the conductivity matrix is known as the Onsager matrix. It is known that due to the GO anisotropy, expression (2.7) can be written as expression (2.8):

$$\begin{pmatrix} J_x \\ J_y \\ J_z \end{pmatrix} = \begin{pmatrix} 0 & \sigma_{xy} & 0 \\ \sigma_{yx} & 0 & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix} \quad (2.8)$$

The Onsager matrix in GO only has values different from zero in the xy plane and z direction.

The generalized conductivity concept has been discussed; the following will present the mechanisms involved in thermal, electrical, and magnetic transport.

2.1.1 Thermal Transport Mechanisms

Considering expression (2.5) as the heat flow, $\mathbf{q}$, due to temperature gradient, ∇T , in the material under study, then $\mathbf{J} = \mathbf{q}$, $\sigma = k$, and $\mathbf{E} = \nabla T$; therefore, expression (2.5) can be written as [4]:

$$\mathbf{q} = -k\nabla T \quad (2.9)$$

Expression (2.5) is the so-called the Fourier law for heat conduction, where thermal conductivity is k and it is related with a material's heat conduction material. In SI units, thermal conductivity is measured in watts per meter kelvin (W/(m·K)).

It is known that heat transport in both amorphous and crystalline dielectric solids is due to elastic vibrations of the lattice (phonons). This transport mode is limited by the elastic scattering of acoustic phonons at lattice defects.

Two different ways exist to calculate the thermal conductivity of a system or material, the Green-Kubo relations and the relaxation time approach methods. This work used the second method in which the relaxation time, τ_{ph} , is due to the anharmonicity within the crystal potential; the phonons in the system or material can be scattered by different mechanisms. From the Kinetic theory [5] thermal conductivity, as a function of the relaxation time is:

$$k = \frac{1}{3} n C_v v^2 \tau_{ph} \quad (2.10)$$

Where n is the phonon density, C_v is the heat capacity, and v is the thermal velocity. In expression (2.10) there are four main scattering mechanisms, which are: 1) Phonon-Boundary defect scattering, a phonon interacts with the boundary defect of a system in a relaxation time, τ_{ph-B} ; 2) Phonon-Mass defect scattering, a phonon hitting an impurity within the system scatters in a characteristic time, τ_{ph-I} ; 3) Phonon-phonon scattering, a

phonon breaking into two lower energy phonons or a phonon collides with another phonon and merges into a higher-energy phonon, this is processed in a relaxation time, τ_{ph-ph} ; and 4) Phonon-electron interaction in which a phonon can be scattered with the electron in a characteristic time, τ_{ph-e} . All these mechanisms are related through the Matthiessen rule, given by [6, 7]:

$$\frac{1}{\tau_{ph}} = \frac{1}{\tau_{ph-B}} + \frac{1}{\tau_{ph-I}} + \frac{1}{\tau_{ph-ph}} + \frac{1}{\tau_{ph-e}} \quad (2.11)$$

In expression (2.11), the dominant mechanism is that with the lowest relaxation time value. Each phonon scattering mechanism is shown ahead:

Phonon-Boundary Scattering. It is particularly important for low-dimensional nanostructures and its relaxation time is given by [8]:

$$\frac{1}{\tau_{ph-B}} = \frac{v}{D} (1 - p) \quad (2.12)$$

Where v is the phonon velocity, D is the system dimension, and p represents the surface roughness parameter. In expression (2.12), when $p = 1$, the relaxation time goes to ∞ , meaning a smooth perfect surface and the scattering is purely specular; hence, boundary scattering does not affect thermal transport. The value of $p = 0$ represents a very rough surface and the scattering is then purely diffusive, which gives [9]:

$$\frac{1}{\tau_{ph-B}} = \frac{v}{D} \quad (2.13)$$

Expression (2.13) is known as the Casimir limit.

Phonon-Mass-difference Impurity Scattering. It is particularly a scatter process due to the impurity present and has a nonlinear dependence on the frequency, ω , and independent of the temperature. This relaxation time is given by [8]:

$$\frac{1}{\tau_{ph-I}} = \frac{V_o \aleph \omega^4}{4\pi v_g^3} \quad (2.14)$$

Where $\aleph$ is a measure of the impurity scattering strength, V_o is the volume per atom, and v_g is the group thermal velocity that depends on the dispersion curves.

Phonon-Phonon scattering. These are effects due to normal processes (processes which conserve the phonon wave vector - N processes), ignored in favor of Umklapp processes (U processes). Because normal processes vary linearly with the frequency, ω , and

Umklapp processes vary with ω^2 , Umklapp scattering dominates at high frequency and has an inverse linear dependence on temperature, T , [10]. Then, τ_{ph-ph} is given by:

$$\frac{1}{\tau_{ph-ph}} = 2\gamma^2 \frac{k_B T}{\mu V_0} \frac{\omega^2}{\omega_D} \quad (2.15)$$

Where γ is Gruneisen anharmonicity parameter, μ is shear modulus, V_0 is volume per atom, and ω_D is the Debye frequency.

Phonon-Electron scattering. This contribution is present when the material is slightly doped, has nonlinear dependence on temperature, T , and inverse dependence on frequency, ω . The corresponding relaxation time is given as [5]:

$$\frac{1}{\tau_{ph-e}} = \frac{n_e \epsilon^2 \omega}{\rho V^2 k_B T} \sqrt{\frac{\pi m^* V^2}{2 k_B T}} \exp\left(-\frac{m^* V^2}{2 k_B T}\right) \quad (2.16)$$

Where the parameter n_e is the concentration of conduction electrons, ϵ is deformation potential, ρ is mass density, and m^* is effective electron mass. It is usually assumed that contribution to thermal conductivity by phonon-electron scattering is negligible.

For the GO-BPA sample, it is likely that, at low temperatures, the main thermal transport mechanism is the phonon-disorder interaction due to boundary defects and impurities, like multifunctional oxides, among others, as described by expressions 2.12 and 2.14. At room temperature, it is very possible that the main scattering process is given by phonon-phonon interaction as given by expression 2.15.

Thus far, basic concepts about thermal transport mechanisms have been presented; hereinafter, some basics related to the electrical transport mechanisms will be discussed.

2.1.2 Electrical Transport Mechanisms

Considering expression (2.5) as the electric current flow, J , due to applied electric field, E , in the material studied, then σ is the electric conductivity; therefore, expression (2.5) is:

$$J = \sigma E$$

Expression (2.5) is the so-called Ohm law for electric conduction, where the electrical conductivity is associated with the material's electricity conduction property. In SI units, electrical conductivity is measured in Siemens per meter (S/m) [5]. It is known that electrical transport in doped semiconductor materials can be attributed to carrier-impurity scattering processes. This transport mode is limited by the elastic and inelastic scattering of charge carriers as electrons and holes.

As with thermal conductivity, there are two different ways of calculating the electrical conductivity of a system or material, the Green-Kubo relations and the relaxation time approach methods. In this investigation, we used the latter method in which the relaxation time, τ_c , is due to the electrostatic forces within matter interaction. Different carrier scattering processes exist. In the Kinetic theory [11, 12] and the quantum model, electrons are accelerated by the electric field and interact with the crystal lattice by transferring part of their power and causing the Joule effect. Upon dispersion in a collision within the lattice, the free electrons must recombine with the holes after the collision, which occurs with most electric charge carriers. Essentially, this model shares with the classical Drude model, the idea that carriers interacting with the crystal lattice cause electrons to move at a steady rate and do not accelerate beyond a certain limit, although the two models differ quantitatively, especially at low temperatures.

Now, considering that the quantum model conductivity agrees superficially with the classic model given by Drude equation [4, 5]:

$$\sigma = \frac{ne^2\tau_e}{m^*} \quad (2.17)$$

Here, n is the electron density per volume unit, e is the electron charge, and m^* is the effective mass. If quantum reasoning for this is to calculate the probability of spread, we have the electrical charge-carrier characteristic time (τ_c), which in our case is similar to τ_e , given by:

$$\tau_c = \frac{1}{P_{sct}} = \frac{1}{n_{sct} \sum v_f} \quad (2.18)$$

Where P_{sct} is the scattering probability, n_{sct} is number scattered ions per volume unit, and v_f is the electron velocity that has a determined Fermi energy. Expression (2.18) has three main scattering mechanisms, thus: 1) Carrier-impurity scattering, a charge carrier hitting an impurity within the system scatters in a characteristic time, τ_{c-I} ; 2) Carrier-lattice scattering, a charge-carrier interacts with the crystal lattice of a system in a relaxation time, τ_{c-L} ; 3) Carrier-defect scattering, in which a charge carrier can be scattered with the defects in a characteristic time, τ_{c-D} . All these mechanisms are related through the Matthiessen rule, given by [6, 11]:

$$\frac{1}{\tau_c} = \frac{1}{\tau_{c-I}} + \frac{1}{\tau_{c-L}} + \frac{1}{\tau_{c-D}} + \dots \quad (2.19)$$

In expression (2.19), the dominant mechanism is the one with the lowest relaxation time value. Each charge-carrier scattering mechanism is discussed by the following:

Carrier-Ionized Impurity Scattering. In quantum mechanics, it is the scattering of charge carriers by ionization in the lattice. The most basic models can be understood as a particle responding to unbalanced local charge-carriers that arise near an impurity; similar to

an electron encountering an electric field, but in this case due to local impurity electric field. Ionized impurity scattering is a process for highly doped semiconductors.

Conwell and Weisskopf [13] were the first to propose the mobility models. They used the Boltzmann transport equation and, considering scattering cross section of a charge carrier in the Coulomb field of an ionized impurity for an iterative solution, found mobility models. This yields a modified velocity distribution, which is then used to calculate the electric field dependence on the current density. Carrier-impurity scattering is the mechanism by which doping decreases electrical conductivity and its relaxation time is given by [14]:

$$\frac{1}{\tau_{c-I}} = \frac{e^4 K_0 N_i}{16\pi\epsilon^2 (2m^*)^{1/2}} \epsilon^{3/2} \quad (2.20)$$

Where N_i is the ionized impurity density and K_0 is a weak function of energy (may be assumed constant in the calculations), ϵ is the dielectric permittivity, and ϵ is the impurity energy.

Carrier-Lattice Scattering. In very pure crystals, the scattering of the charge carriers is due to the vibrations of the lattice and this form of scattering must impose an upper limit on mobility for any material. The simplest form of lattice scattering would occur if there were only one atom per unit cell. The vibrations would then be solely of the acoustic type. In fact, acoustic-mode lattice scattering is predominant in a number of semiconductors in which there is more than one atom per unit cell, even when these atoms are not all of the same species.

Acoustic-mode lattice scattering can be attributed to local changes in density, brought about by the thermal vibrations, which, in turn, lead to fluctuations in the strength of the periodic potential through which the charge carriers move. The deformation-potential method to calculate scattering due to acoustic vibrations has been developed by Bardeen and Shockley. It leads to an expression for the relaxation time [11, 15].

$$\frac{1}{\tau_{c-L}} = \frac{(8\pi^2)^{3/2} \Delta^2}{h^4 v^2 \rho} \frac{m^{*3/2}}{E^{-1/2}} \quad (2.21)$$

Where v is the velocity of the longitudinal sound waves, ρ is the density, E is the acoustic phonon energy, and Δ is the so-called deformation-potential constant. The deformation-potential constant represents the rate of change with the volume of potential energy at the band edge.

Scattering by lattice waves includes absorption or emission of either acoustical or optical phonons. These phonons represent the quantum of mechanical waves that travel through the semiconductor crystal. Given that the density of phonons in a solid increase with temperature, the scattering time due to this mechanism will decrease with temperature, as will the mobility. Theoretical calculations reveal that the mobility in non-polar semiconductors, such as silicon and germanium, is dominated by acoustic phonon interaction. The resulting mobility is

expected to be proportional to $T^{-3/2}$, while the mobility due to optical phonon scattering is only expected to be proportional to $T^{-1/2}$.

Carrier-Defects Scattering. The dangling bond energy levels are eigenvalues of wave functions that describe electrons near to defects. In the typical consideration of carrier scattering, this corresponds to the final state in Fermi's Golden Rule of scattering frequency and it is independent of T [10]. Then, τ_{c-D} is given by:

$$\frac{1}{\tau_{c-D}} = \frac{ne^4}{2\pi\sqrt{2m^*(E_c - E_{db})}\hbar^2\mathcal{E}\mathcal{E}_r} \left(\frac{1}{q_s^2} - \frac{1}{q_s^2 + \frac{8m^*(E_c - E_{db})}{\hbar^2}} \right) \quad (2.22)$$

Where n is the charge number, e the electron charge, m^* effective mass, E_c conduction energy level, E_{db} dangling bond energy level, $\mathcal{E}$ dielectric permittivity constant, $\mathcal{E}_r$ relative dielectric permittivity, and q_s is the Debye length wave vector correction due to charge screening. Expression (2.22) involved shallow defects; when considering the deep defects, it is necessary to modify this equation.

In the case of the electrical transport mechanism in GO-BPA, it is possible to hope that at room temperature or fixed temperature, the main scattering process can be the carrier-impurity interaction, as given by expression 2.20. To describe the temperature dependence on the electrical conductivity in disordered materials, like GO-BPA, the hopping model is well known.

Mott's Variable Range Hopping (VRH). This model describes low-temperature (T) conduction in disordered systems with localized charge carrier states [16-18]. In this model, the electrical conductivity is described by hopping of the free charge-carrier and has a generalized dependence on temperature given by:

$$\sigma = \sigma_0 \exp\left(-\frac{T_0}{T}\right)^{\frac{1}{d+1}} \quad (2.23)$$

Here, σ_0 is the conductance independent of temperature, T_0 is the characteristic temperature, and d is the dimensionality. For three-dimensional conductance, expression (2.23) can be written as:

$$\sigma = \sigma_0 \exp\left(-\frac{T_0}{T}\right)^{\frac{1}{4}} \quad (2.24)$$

With $d = 3$, expression 2.24 is the so-called three-dimensional-variable range hopping (3D-VRH) model. At low temperature, this model can possibly describe the electrical conductivity response in GO-BPA samples.

Hopping conduction at low temperatures is of great interest from basic and applied research because the semiconductor industry needs materials with good conduction characteristics [17, 18]. The following illustrates some basics of band gap energy.

Band Gap Energy. In solid-state physics, it is an energy range in a solid where there are no electron states. In the electronic structure graphics of solid bands, the band gap generally refers to the difference in energy (in electron-volts) between the top part of the valence band and the bottom part of the conduction band in insulators and semiconductors. It is the energy required to promote a valence electron bound to an atom to become electron conduction, move freely within the crystal lattice, and serve as a charge-carrier to conduct the electric current. In chemistry, it is closely related to the HOMO/LUMO gap. If the valence band is completely full and the conduction band is completely empty, then the electrons cannot move in the solid; however, if some electrons are transferred from the valence to the conduction band, then the electrical current can flow. Therefore, the band gap energy is a best factor to determine the electrical conductivity of a solid. Substances with large band gap energy values are generally insulators, those with smaller band gaps are semiconductors, while conductive materials have very small or no band gaps because the valence and conduction bands overlap.

Each solid material has a characteristic energy band structure. The differences between the band structures of the materials are responsible for the wide range of electrical characteristics observed in several materials. In semiconductor and insulating materials, electrons are confined in several energy bands and are forbidden in other regions or portions of energy. The term "*energy band gap*" refers to the difference in energy between the upper part of the valence band and the lower part of the conduction band. Electrons can jump from one energy band to another. However, for an electron to jump from a valence band to a conduction band, it requires a specific minimum amount of energy to make the transition. The value of the transition energy required depends on the atomic spacing of the material. Electrons can gain enough energy to jump energetically to the conduction band by absorbing a phonon (heat) or a photon (light).

A semiconductor is a material with a small value in the non-zero bandgap energy and can behave as an insulator at absolute zero temperature; however, it allows thermal excitation of the electrons in the conduction band at temperatures below their melting point. Conversely, a material with a high band gap energy value is an electrical insulator. In materials that are good electricity conductors, the valence and conduction energy bands can overlap, so the band gap energy is zero electron volts, as mentioned.

The conductivity of intrinsic semiconductors is strongly dependent on the energy band gap. The only charge-carriers available for conduction are the electrons that have enough thermal energy to be excited across the band gap and the holes that are left off by electrons when such excitation occurs. When the temperature of a pure, undoped semiconductor is increased, the electrons in the valence band are energetically excited through the band gap energy to the conduction band (this is the intrinsic ionization). The electrons in the conduction band and the unoccupied electron sites in the valence band (electron holes) can move in the presence of an electric field. The holes produced by electrons behave as though they were positively charged and move in the opposite direction of the electrons. The intrinsic

ionization, thus, produces pairs of electron (e) and hole (h) charge-carriers in the same proportion, then:

$$0 = e + h \quad (2.25)$$

Now, the equilibrium constant for the intrinsic ionization dependent on energy band gap and temperature, T , is [19]:

$$K_i = n \cdot p = N_c N_v \exp\left(-\frac{E_g}{kT}\right) \quad (2.26)$$

Where n and p are the electron and hole concentrations, respectively. N_c and N_v are the density of states in conduction and valence bands, respectively. The band gap energy $E_g = E_c - E_v$ is the difference between energies in conduction, E_c , and valence bands, E_v .

In an intrinsic semiconductor, the concentrations of electrons and holes are equal and, thus [19]:

$$n = p = K_i^{1/2} = \sqrt{N_c N_v} \exp\left(-\frac{E_g}{2kT}\right) \quad (2.27)$$

And the electronic conductivity, σ , then becomes

$$\sigma = \sigma_n + \sigma_p = en\mu_n + ep\mu_p = e\sqrt{N_c N_v} (u_n + u_p) \exp\left(-\frac{E_g}{2kT}\right) \quad (2.28)$$

Due to differences in mobility, one of the charge-carriers may dominate. It may be noted that N_c and N_v are temperature dependent and that u_n and u_p may also be dependent on temperature. If the latter are not exponential (as in diffusional hopping conduction processes) the exponential term of the band gap energy tends to dominate the temperature dependence and, as an approximation of expression (2.28), it is then often written as [19]:

$$\sigma(T) = \sigma_0 \exp\left(-\frac{E_g}{2kT}\right) \quad (2.29)$$

Here, σ_0 is the electronic conductivity independent of temperature. In some cases, in which the low doped regime in semiconductors is considered, the approximation of expression (2.29) can be used and it is necessary to know the σ_0 dependence on temperature and other parameters under study.

Also, the band gap energy can be dependent on the composition or impurity concentration $E_g(x)$ at a fixed temperature. Experimentally, it has been demonstrated that the lowest direct band gap in many semiconductor alloys of compounds has an approximately quadratic dependence on the mole fraction of one compound x , given by [20]:

$$E_g(x) = a + bx + cx^2 \quad (2.30)$$

Where the nonlinear or bowing parameter c is four times the deviation of E_g from linearity at the equimolar concentration $x = 0.5$. The other two parameters a (term-independent of x) and b are determined by the values of E_g observed in the pure semiconducting compounds.

The energy band gap can be dependent on temperature and this dependence is known to describe different phenomenological expressions for $E_g(T)$. Some expressions for $E_g(T)$ are the Varshni, Bose-Einstein, Magnoogian-Wooley, Viña and Pässler models. The Varshni empirical expression describes the temperature dependence on the band gap energy in semiconductors, given by [21, 22]:

$$E_g(T) = E_g(0) - \left(\frac{\alpha T^2}{T + \beta} \right) \quad (2.31)$$

Where $E_g(0)$ is the extrapolated band gap energy value at zero temperature; α and β are fitting parameters characteristic of a given material [21, 22]. This model considers the temperature effect in the band gap energy, but the Varshni coefficients offer a few physics descriptions about the carriers or exciton interactions involved in some semiconductors; for this reason, the Bose-Einstein model considers these effects in $E_g(T)$.

The Bose-Einstein expression, obtained from considering the 3N oscillator theory of the specific heat problem, is a model that considers the free charge-carriers or exciton interactions with the phonon average participant, and has the following functional form [23]:

$$E_g(T) = E_g(0) - \left(\frac{2a_B}{\exp\left(\frac{\theta_B}{T}\right) - 1} \right) \quad (2.32)$$

Here, $E_g(0)$ is the extrapolated band gap energy value at zero temperature, a_B and θ_B are the fitting parameters, characteristic of a given material and related with the coupling strength between charge-carrier and excitons, and average characteristic temperature of the phonon participant (optical or acoustic phonon), respectively. This model does not consider the lattice dilation contribution in $E_g(T)$; for this reason, the Magnoogian-Wooley model appears.

The Magnoogian-Wooley expression considers the effect of thermal expansion and electron-phonon interaction in the band gap energy, and it is given by [24]:

$$E_g(T) = E_g(0) + UT^s + V\theta \left[\coth\left(\frac{\theta}{2T}\right) - 1 \right] \quad (2.33)$$

Where the first term, $E_g(0)$, is the band gap at $T = 0$ K, the second term represents the lattice dilation with U as the lattice dilation coefficient, S describes the average exciton-phonon coupling strength, and the third term is related with the electron-phonon interaction; V is the temperature-dependent shift in the band gap and θ is the temperature-related parameter. The fitting parameters are U , S , and θ and they are independent of the temperature [24]. Expression (2.33) has five fitting parameters and due to this a similar model with lower fitting parameters was proposed by the Viña expression.

Viña *et al.*, [25] fitted data on the critical-point energies of germanium to the Varshni relation, but pointed out that they can also fit these data to an expression where the energy thresholds decrease proportional to Bose-Einstein statistical factors for phonon emission plus absorption, and proposed that:

$$E_g(T) = E_g(0) - b \left[1 + \frac{2}{\exp\left(\frac{\theta}{T}\right) - 1} \right] \quad (2.34)$$

Here, b is an energy factor related with the phonon emission plus absorption and θ is the temperature-related parameter. The term within the brackets in expression (2.34) readily reduces to $\coth(\theta/2T)$ so that equation (2.34) can be written in a form comparable with expression (2.33). Equation (2.34) describes $E_g(T)$ in terms of Bose-Einstein statistical factors for phonon emission plus absorption via exponential factor. Another interpretation of $E_g(T)$ in terms of power law was proposed by the Pässler model [26].

The Pässler expression has another focus and it is related with the band gap energy dependent on temperature, $E_g(T)$, via power law behavior for phononic contribution and it is given by [26]:

$$E_g(T) = E_g(0) - \alpha_p \theta \left[\sqrt[p]{1 + \left(\frac{2T}{\theta}\right)^p} - 1 \right] \quad (2.35)$$

Where $E_g(0)$ is the band gap energy at 0 K, α_p is a factor that represents the strength of the phononic contribution, θ is the effective phonon temperature and the exponent p is related with the symmetry of the phononic contribution to the band gap energy. In the results of chapter 4, a comparison was presented between these $E_g(T)$ different models given by expressions (2.31-2.35) to describe the experimental data of the temperature dependence on the band gap energy in GO-BPA samples studied in this work.

Additionally, band gaps also depend on pressure. Band gaps can be either direct or indirect, depending on the electronic band structure; more details can be found in P.Y. Yu,

M. Cardona, Fundamentals of Semiconductors, Graduate Texts in Physics, 4th ed., Springer-Verlag, Berlin Heidelberg (2010) (DOI: 10.1007/978-3-642-00710-1_2).

The electrical transport mechanisms were presented to this point; the following will explain some basics related with magnetism and its transport mechanisms.

2.1.3 Magnetism

The study of the magnetic properties requires knowledge on electric ($\mathbf{E}$) and magnetic fields ($\mathbf{B}$) in the space occupied by matter. These fields are derived from the Maxwell equations:

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\epsilon_0} \quad (2.36)$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \quad (2.37)$$

$$\nabla \cdot \mathbf{B} = 0 \quad (2.38)$$

$$\nabla \times \mathbf{B} = \mu_0 \left(\mathbf{J} + \epsilon_0 \frac{\partial \mathbf{E}}{\partial t} \right) \quad (2.39)$$

Where $\mathbf{J}$ is the flow current density, ρ is the electrical charge density, while ϵ_0 and μ_0 are the electrical and magnetic permittivity of free space, respectively. The magnetic induction is given by:

$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M}) \quad (2.40)$$

With $\mathbf{M}$ being the magnetization related with the total dipole moment per volume unit, and very similar to expression (2.5), this magnetization is related with the external field, $\mathbf{H}$, via magnetic susceptibility, χ , so:

$$\mathbf{M} = \chi \mathbf{H} \quad (2.41)$$

Replacing expression (2.41) in equation (2.40), we obtained that:

$$\mathbf{B} = \mu_0(\mathbf{H} + \chi \mathbf{H}) = \mu_0(1 + \chi)\mathbf{H} \quad (2.42)$$

Depending on the sign and magnitude of χ , different types of magnetism are distinguished [27, 28]. In the case of $\chi < 0$, the material is defined as diamagnetic; whereas for $\chi > 0$, we speak of paramagnetism. A third type of magnetism is ferromagnetism; however, it cannot be described by simply using expression (2.42), given that these materials

exhibit a residual magnetic moment below a critical temperature even in the absence of an applied external field.

Ferromagnetism (FM). Before taking up the problem of the magnetic behavior of the carbon-based structures, we must briefly introduce some relevant concepts of magnetism physics. Ferromagnetism is the basic mechanism by which some materials (such as iron, cobalt, and nickel) form permanent magnets, or are attracted to magnets.

Many examples of physical systems with stable magnetic moment in the ground state have been reported [29-31]. These systems have similar characteristics, atoms, molecules, and ions exhibiting an odd number of electrons, and some molecules with an even number of electrons (like O₂ and some organic compounds) and atoms (ions) with unfilled (3d-, 4f-, 5f-) shells. Within each shell, the electrons can be specified according to their orbital angular momenta. Then, s-electron have no angular momentum, p-electrons have one quantum of angular momentum, d-electrons have two, and f-electrons have three. The s- and p-states tend to fill before d-states as the atomic number Z increased. Each electron has a half-quantum intrinsic angular momentum or spin [32, 33]. It only has two orientations relative to any given direction, parallel or antiparallel. “Magnetic materials, [31, 34-36] as a rule, can be metals, semiconductors or insulators, which contain the ions of the transition metals or rare-earth metals with unfilled shells [29-31]. Strong magnetic materials, as a rule, include 3d- ions with unfilled shells [37]” as reported by Kuzemsky [29].

The traditional ferromagnetic properties present in materials, like iron, nickel, and cobalt, the group of rare earths, as well as their alloys are explained through an intrinsic mechanism of quantum origin called exchange interaction originated in 3d and 4f electrons; the traditional theoretical models do not admit the existence of an FM type ordering in materials with the presence of sp electrons; however, recently several independent experimental works have reported such an arrangement in coal-derived materials [29, 38-46].

The origin of magnetism is in the orbital and spin motions of electrons and the way the electrons interact with one another [29, 34-37]. The basic magnetism concept in condensed matter is the magnetic moment, $\mathbf{m}$. It can be imagined as a magnetic dipole. Magnetic moment, $\mathbf{m} = g\mu_B\mathbf{J}$, is proportional to the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$, where $\mathbf{L}$ is orbital moment and $\mathbf{S}$ is the spin moment. In terms of the Brillouin function, $B_J(\beta)$, the quantum statistical mechanics of an atom with a spin degree of freedom in an applied field yields μ , is:

$$\mu = m B_J(\beta) \quad (2.43)$$

Where $B_J(\beta)$ is [47],

$$B_J(\beta) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J} \beta\right) - \frac{1}{2J} \coth\left(\frac{1}{2J} \beta\right) \quad (2.44)$$

Expression (2.44) has two special cases, $J = 1/2$ and $J = \infty$, given by:

$$\mathbf{B}_{1/2}(\beta) = \tanh(\beta) \quad (2.45)$$

and

$$\mathbf{B}_{\infty}(\beta) = L(\beta) = \coth(\beta) - \frac{1}{\beta} \quad (2.46)$$

In expression (2.46) the coth function is not friendly and its leading term is the $\frac{1}{\beta}$, which is implicitly subtracted in the Langevin function, $L(\beta)$. This Langevin expression is used to describe hysteretic behavior as FM order and equation 2.45 is used to explain paramagnetic behavior. Another important alternative way of obtaining expression 2.46 is the main field theory proposed in 1907, for the first time by Pierre Weiss (1865-1940).

The Main Field Theory. The MFT or Weiss theory (also known as self-consistent field theory) is a classical model, which studies the behavior of large and complex stochastic models by using a simpler model. Such models consider a large number of small single components that interact with each other. The effect of all the other single components on any given single component is approximated by a single averaged effect, thus, reducing a many-body problem to a one-body problem [27, 28, 31, 34].

Weiss supposed an internal field $H_w = wJ$ (w is the Weiss factor and J is the magnetic polarization) in superposition with the external field, H , as presented in the FM behavior, therefore, in the orientation polarization, the potential energy, W , of a magnetic moment (or dipole), m , in all magnetic fields, $H + H_w$, is given by:

$$W(x) = -m\mu_0(H + H_w) \cos(\phi) = -m\mu_0(H + wJ) \cos(\phi) \quad (2.47)$$

Now, the Boltzmann distribution of energies is:

$$N(W) = c \exp\left(\frac{W}{kT}\right) = c \exp\left(\frac{-m\mu_0(H + wJ) \cos(\phi)}{kT}\right) \quad (2.48)$$

With a constant c that has yet to be determined. This Boltzmann distribution equation provides the number of dipoles with a certain angle relative to the field direction. However, we are only interested in the component of the dipole moment parallel to the field. Therefore, the sum of the components of the dipole moments is the induced magnetization, m_{ind} , and represented by:

$$m_{ind} = (N \cdot d(\Omega))\mu_0 \cos(\phi) \quad (2.49)$$

The average dipole moment induced of expression 2.49, which is what we want to calculate, will now be obtained by summing up the contributions from all the $d\Omega$, so.

$$\langle m_{ind} \rangle = \frac{\int_0^\pi N[W(\phi)] \mu_0 \cos(\phi) d\Omega}{\int_0^\pi N[W(\phi)] d\Omega} \quad (2.50)$$

And the integrals have to be taken from the “top” of the sphere to the “bottom”, i.e., from 0 to π . As $d\Omega = 2\pi \sin\phi d\phi$, and introducing everything together, we obtained an integral for m_{ind} that runs from 0 to π , so:

$$\langle m_{ind} \rangle = \frac{\int_0^\pi \exp\left(\frac{\mu_0 m(H + wJ) \cos(\phi)}{kT}\right) \mu_0 \cos(\phi) \sin\phi d\phi}{\int_0^\pi \exp\left(\frac{\mu_0 m(H + wJ) \cos(\phi)}{kT}\right) \sin\phi d\phi} \quad (2.51)$$

By using the following substitutions, $\beta = \frac{\mu_0 m(H + wJ)}{kT}$ and $x = \cos(\phi)$ in expression (2.51), we obtained that:

$$\langle m_{ind} \rangle = \frac{\int_{-1}^1 x \exp(\beta x) \mu_0 dx}{\int_{-1}^1 \exp(\beta x) dx} \quad (2.52)$$

The final solution of expression (2.52) is:

$$\langle m_{ind} \rangle = \mu_0 L(\beta) \quad (2.53)$$

In expression (2.40) the m_{ind} is proportional to the Langevin function, as presented in equation (2.33):

$$L(\beta) = \coth(\beta) - \frac{1}{\beta}$$

Then, the result for the m_{ind} and the total magnetization, M , is:

$$M = NmL(\beta) \quad (2.54)$$

Replacing expression (2.46) in equation (2.54) and β , we obtained that:

$$M(H) = N m \left[\coth\left(\frac{\mu_0 m(H + wJ)}{kT}\right) - \frac{kT}{\mu_0 m(H + wJ)} \right] \quad (2.55)$$

Expression (2.55) is the classical expression to describe magnetic hysteresis in different systems [27, 28]. However, H and J do not admit simultaneity events because in the Weiss

approximation these fields consider only the sum, then J can take the zero value and the m_{ind} is possible. But, in the case of magnetism in carbon material induced by any physical mechanism, the internal field requires considering the simultaneity of events with the external field, H , for that material exhibiting FM order. For this reason, no theoretical model exists to explain the FM order found experimentally in carbon-based materials [29, 38-46], like GO-BPA. This work described the experimental results of the FM order in GO-BPA samples by considering the influence of Raman boundary density defects and crystal size to explain experimental results of FM order at room temperature presented in the results of chapter 4 as discussed here.

Furthermore, it is known that the correlation of the thermal, electrical, and magnetic transport mechanisms in any material can be studied by using magnetoresistance (MR) measurements for different temperatures.

Magnetoresistance (MR). This is the tendency of any material to vary its electrical resistance or conductance when an external magnetic field is applied. A variety of effects or behaviors can be called magnetoresistance; some of them occur in bulk non-magnetic metals [48] and semiconductors [49], such as geometric magnetoresistance [50], Shubnikov de Haas oscillations [51], or the common positive magnetoresistance in metals [52], among others [53]. Other effects occur in magnetic metals, such as negative magnetoresistance in ferromagnets [54] or anisotropic magnetoresistance (AMR) [55]. Finally, in multicomponent or multilayered systems (*e.g.* magnetic tunnel junctions), giant magnetoresistance (GMR) [56], tunnel magnetoresistance (TMR) [57], colossal magnetoresistance (CMR) [58], and extraordinary magnetoresistance (EMR) can be observed [59].

In 1851, the first magneto-resistive effect was discovered by William Thomson (better known as Lord Kelvin), but he was unable to reduce the electrical resistance of anything by more than 5%. Nowadays, systems are known (*e.g.* semimetals or concentric ring EMR structures) where a magnetic field can change resistance by orders of magnitude [57-59]. Given that resistance may depend on magnetic field through several mechanisms, it is useful to separately consider situations where it depends on magnetic field directly (*e.g.* geometric magnetoresistance, multiband magnetoresistance) and those where it does so indirectly through magnetization (*e.g.* AMR, TMR).

Normally, a conductor in an applied magnetic field responds with a quadratic magnetoresistance (MR) that saturates at low fields and displays a relatively small magnitude [60]. Positive, negative, and re-entry (alternating from positive to negative or vice versa) MR has been experimentally observed and described theoretically under these considerations.

The total MR is, in fact, the sum of the negative $\left(\frac{\Delta R}{R}\right)^{-}$ and positive $\left(\frac{\Delta R}{R}\right)^{+}$ contributions [61]:

$$MR = \left(\frac{\Delta R}{R}\right)_t = \left(\frac{\Delta R}{R}\right)^{+} + \left(\frac{\Delta R}{R}\right)^{-} \quad (2.56)$$

Several models representing the effects of magnetoresistance in isotropic semiconductors have been reported and applied to the weak localization regime [62, 63] or are empirical [64]. Only two theories, to our knowledge, have been developed that consider Mott's variable range hopping regime. (a) Shklovskii and Efros [65] considered the positive contribution on the basis of the Miller-Abrahams [66] resistor network model.

When conductivity follows Mott's law [16], the carriers find an exponential resistivity increase with H due to the shrinking of the wave functions of the localized electrons. In equation (2.56), the positive MR contribution for the classically moderate field is given by the Shklovskii and Efros expression [65]. The first term or contribution describes the usual positive exponential magnetoresistance. The low- H magnetoresistance has the form [67]:

$$\left(\frac{\Delta R}{R}\right)^+ = \exp(\gamma H^2) - 1 \quad (2.57)$$

The γ parameter can depend on the temperature in the high-field region and depends on the variable range hopping mechanism. In expression (2.57), the positive MR does not saturate, always grows with the square of the external field, H , and when the $H=0$ Oe, MR is equal to zero. For this reason, equation (2.57) is only used in some materials. Experimentally, many materials present positive MR behavior with saturation effects and this model does not apply, like our case of positive MR in GO-BPA material and discussed in chapter 4.

The second contribution in expression (2.56) is the negative MR that can consider the model of localized magnetic moments in which, according to Toyozawa [62, 63], the conduction electrons can be scattered by the localized magnetic moments of impurities. The application of an external magnetic field produces ordering of these magnetic moments, so conductivity increases and the negative MR stemming from the spin diffusion in paramagnetic materials takes the following form [61]:

$$\left(\frac{\Delta R}{R}\right)^- = \lambda L^2 \left(\frac{\mu^* H}{k_B (T + \theta)} \right) \quad (2.58)$$

Where λ is a proportional constant, $L^2(x) = \coth(x) - (1/x)$ is the Langevin function, μ^* is the effective magnetic moment of scattering centers, k_B is the Boltzmann constant, and θ is the Curie temperature.

Expression (2.58) suggests that the negative component of the magnetoresistance can be explained by the magnetization of localized magnetic moments by impurities present. To analyze the negative MR response in the GO-BPA samples studied in this work, a similar model is proposed considering the presence of localized magnetic moments by the density of boundary defects, as presented in the results of the negative MR analysis in chapter 4.

Herein, some basics of magnetism were presented; the following section introduces some transport properties in hexagonal graphite structures.

2.2. Transport Properties in Hexagonal Graphite

Due to their valency, carbon atoms can form eight main allotropes, as presented in **Figure 2.1**.

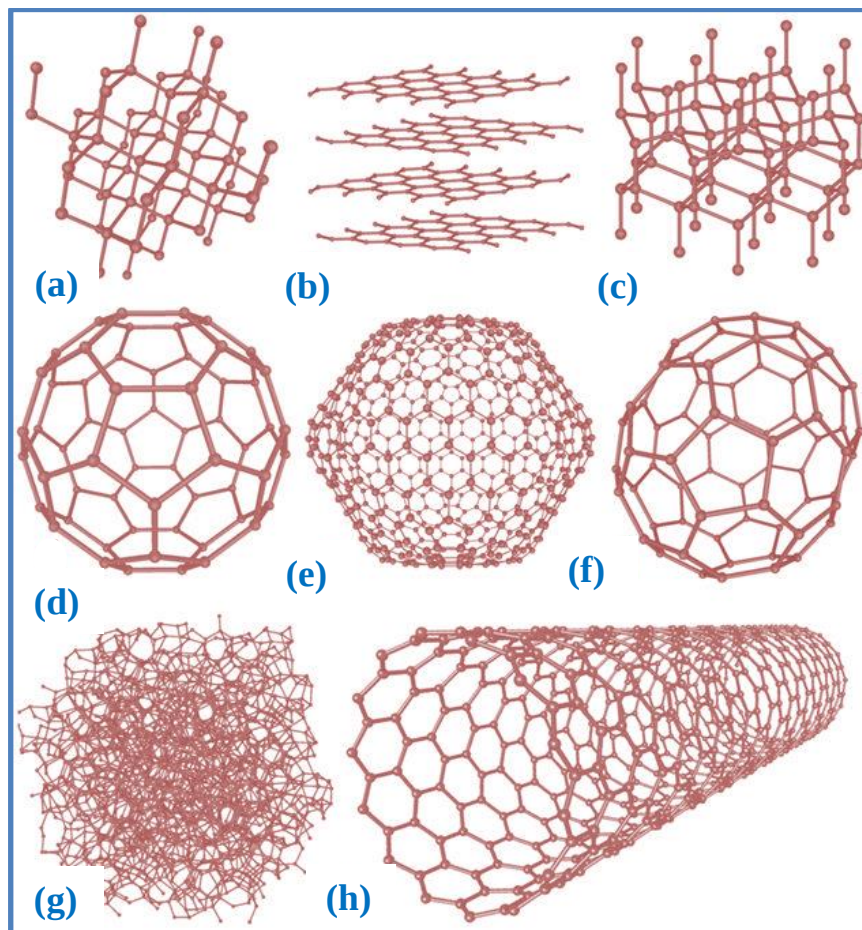


Figure 2.1. Carbon allotropes: **(a)** Diamond. **(b)** Graphite. **(c)** Lonsdaleite. **(d)** C60 (Buckminsterfullerene or Bucky ball). **(e)** C540. **(f)** C70. **(g)** Amorphous carbon. **(h)** Single-walled carbon nanotube or Bucky tube. Taken and adapted from reference [68].

Well-known carbon forms include diamond and graphite. In recent decades, many more allotropes and carbon forms have been discovered and researched, such as ball shapes (*i.e.* Buckminsterfullerene) and graphene sheets. Some carbon larger scale structures include nanotubes, nano-buds, and nanoribbons. Other unusual carbon forms exist at very high temperature or extreme pressures.

In the graphite structure case, it is known that this structure is possibly due to the graphene sheet superposition by van der Waals bonds and covalent bonds with a characteristic distance of $c = 0.34$ nm and $a = 0.14$ nm [69], respectively, as presented in **Figure 2.2**.

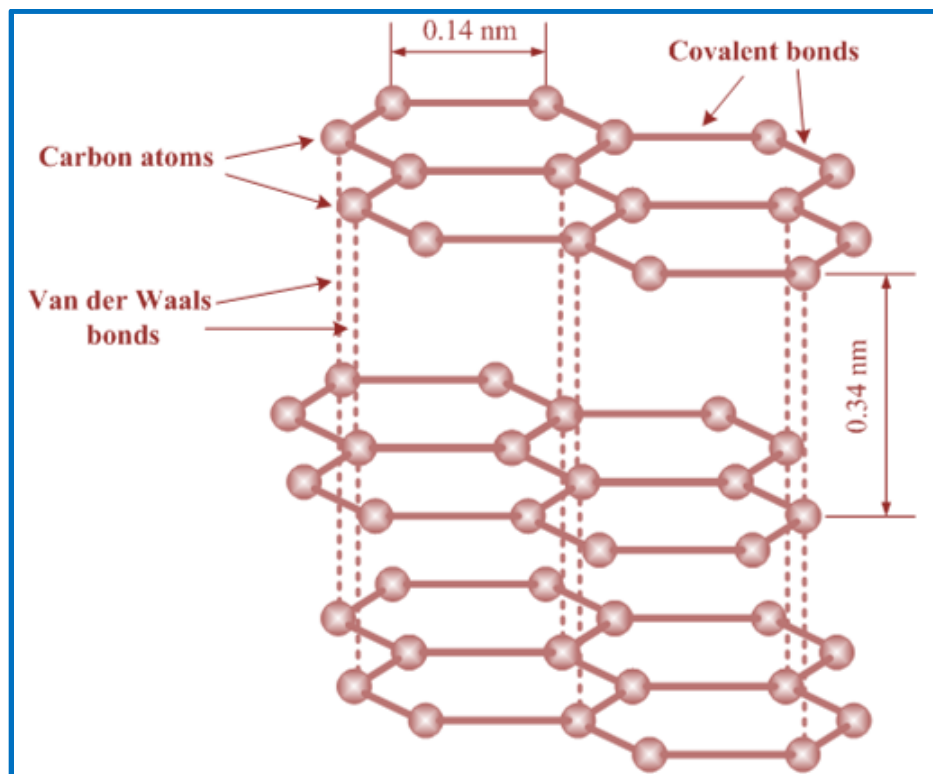


Figure 2.2. Graphite structure composed by hexagonal carbon bonds forming graphene sheets and the superposition of these graphene sheets. Taken and adapted from reference [69].

Graphite has a layered planar structure; in each layer, the carbon atoms are arranged in a honeycomb lattice. Atoms in the plane are bonded covalently, with only three of the four potential bonding sites satisfied. The fourth electron is free to migrate in the plane, making graphite electrically conductive (the same as the graphene sheet). However, it does not conduct in a direction at right angles to the plane. Bonding between layers is via weak van der Waals bonds, which allows graphite layers to be easily separated or to slide past each other.

The graphene superposition in the graphite structure is only possible by two known forms of graphite, alpha (hexagonal) and beta (rhombohedral). Both structures have very similar physical properties, except the graphene layers stack somewhat differently [70]. Hexagonal graphite may be either flat or buckled [71]. The alpha form can be converted into the beta form through mechanical treatment and the beta form reverts to the alpha form when it is heated above 1300 °C [72].

In 1789, Abraham Gottlob Werner named graphite from the Greek *γράφειν* (graphein, “to draw/write”, for its use in pencils) and it is one of the most common carbon allotropes. Graphite conducts electricity, due to delocalization of the π bond electrons above and below the planes of the carbon atoms. These electrons are free to move, so they are able to conduct electricity. However, electricity is only conducted along the plane of the layers. In graphite,

each carbon atom uses only 3 of its 4 outer energy level electrons in covalently bonding to three other carbon atoms in a plane.

Each carbon atom contributes with one electron to a delocalized system of electrons that is also a part of the chemical bonding. The delocalized electrons are free to move throughout the plane. For this reason, graphite conducts electricity along the planes of carbon atoms, but does not conduct in a direction at right angles to the plane.

Graphene: A single layer of graphite in [Figure 2.2](#) is the so-called graphene and has extraordinary electrical, thermal, and physical properties [\[73\]](#). It can be produced by epitaxy on an insulating or conducting substrate or by mechanical exfoliation (repeated peeling), among others, from graphite. Its applications may include replacing silicon in high-performance electronic devices [\[73\]](#).

In 1947, P. R. Wallace, using the “*tight binding*” approach, proposed for the first time the band theory of graphite [\[1\]](#). The main result of this work was known as the structure of the electronic energy bands and Brillouin zones for graphite and graphene; later in 1984, G. W. Semenoff found the massless Dirac equation of graphene. Also, in 2004, A. K. Geim and K. S. Novoselov achieved an isolated atomic layer of graphene from graphite; in 2005, both found that graphene can provide massless Dirac Fermions. In 2010, the Nobel Prize in Physics was awarded to Andre Geim and Konstantin Novoselov “*for ground-breaking experiments regarding the two-dimensional material graphene*”.

The rich physics introduced by graphene due to its band structure can be described by a simple two-band tight binding model, considering only the P_z orbital (π electron) out of four valence electrons and the nearest-neighbor hopping energy and unit cell shown in [Figure 2.3](#). Then the tight binding Hamiltonian, H , of graphene can be written as:

$$H = \begin{bmatrix} 0 & tf(k) \\ tf(k) & 0 \end{bmatrix} \quad (2.59)$$

Where $t \sim 2.7 \text{ eV}$ is the nearest-neighbor hopping energy and considering that

$$f(k) = \exp(ik\mathbf{R}_1) + \exp(ik\mathbf{R}_2) + \exp(ik\mathbf{R}_3) \quad (2.60)$$

With $\mathbf{R}_i$ ($i= 1,2,3$) as the location vector of the nearest-neighbor atoms [\[74\]](#). The band structure calculated from expressions (2.59) and (2.60) is given by:

$$E(k_x, k_y) = \pm t \sqrt{1 + 4 \cos\left(\frac{\sqrt{3}k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) + 4 \cos^2\left(\frac{k_y a}{2}\right)} \quad (2.61)$$

Here, a is the carbon-carbon nearest neighbor distance, as shown in [Figure 2.2](#). The dispersion relation given by expression (2.61) is presented in [Figure 2.4](#). It is clear from the zoom diagram that there is no band gap in graphene. Instead, the conduction band and the

valence band meet at the K points of the first Brillouin zone, which is also referred to as the Dirac point in graphene related literature. Near this point, the dispersion relation can be simply represented by:

$$E(k) = \pm \hbar v_F |k| \quad (2.62)$$

Where v_F is the Fermi velocity ($\sim 10^6$ m/s), $\hbar$ is the Plank constant and k is the electron momentum relative to the Dirac point. This linear energy dispersion relation can be associated to the one of massless relativistic particles, then the effective mass is zero, the vanishing density of states near the Dirac point and the suppression of the backscattering (Klein tunneling) [75, 76].

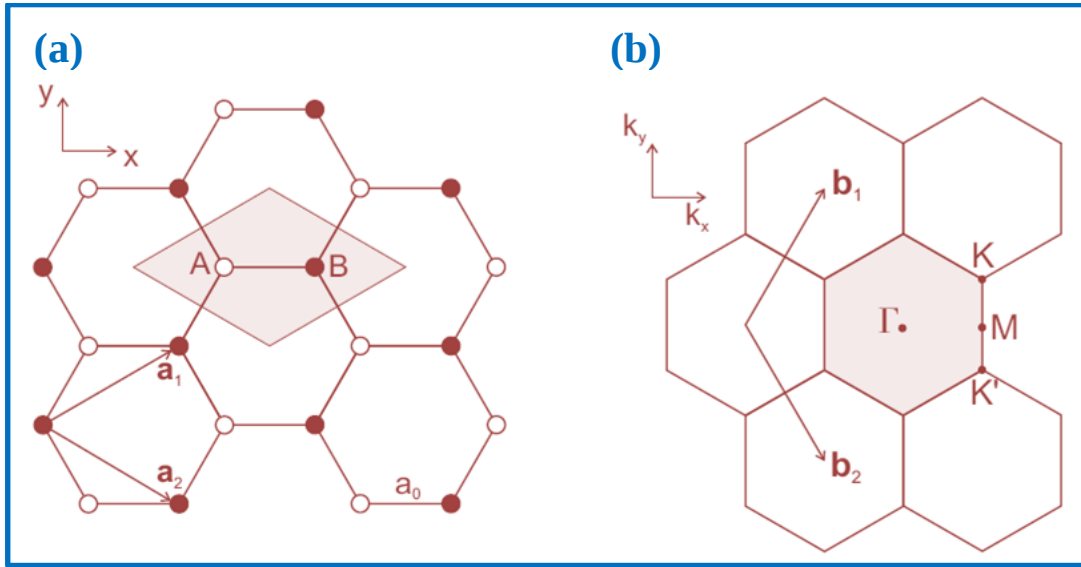


Figure 2.3. Graphene: (a) characteristic honeycomb lattice with unit cell in red. The lattice can be seen as two interpenetrating triangular lattices established by red and white atoms. The unit cell contains one atom from each sublattice, shown by lattice vector $\mathbf{a}_1$ and $\mathbf{a}_2$. (b) The Brillouin zone colored red into reciprocal lattice; where, $\mathbf{b}_1$ and $\mathbf{b}_2$ are the reciprocal lattice vectors and Γ , $\mathbf{M}$, $\mathbf{k}$ and $\mathbf{k}'$ are different symmetry points of the reciprocal lattice, taken and adapted from reference [77].

The charge-carriers in graphene can be described by the 2D Dirac equation and actually behave as if they were massless relativistic particles where the role of the speed of light is played by the Fermi velocity. This result is an important difference from a conventional 2D electron gas system, which has a parabolic dispersion relation (semiconductor) and, therefore, is described by the 2D Schrodinger equation, as shown in Figure 2.5.

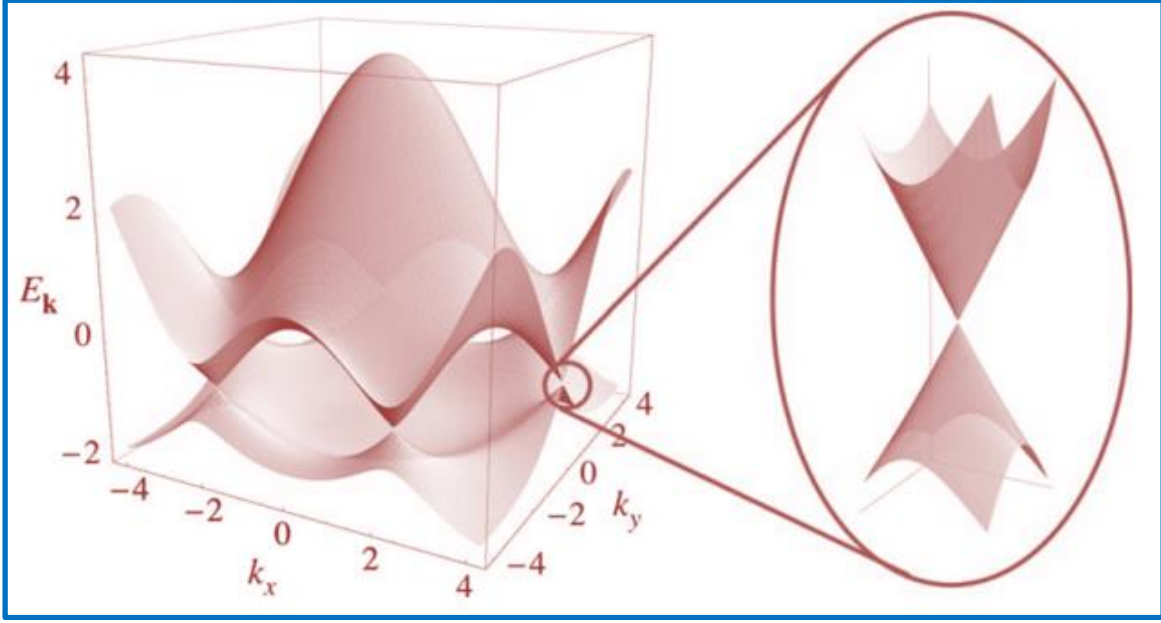


Figure 2.4. Band structure of graphene. Energy vanishes at points k , k' , and those equivalent to them. The conductance band touches the valence band at the same points. Taken and adapted from reference [78].

Graphene Bilayer. It is composed only through superposition of two graphene layers (Figure 2.2.). Using a similar procedure, as the calculated dispersion relation in graphene sheet, it is possible to obtain expression (2.63), which represents the band diagram considering a potential Δ difference between the graphene layers. Under this situation, these behaviors for the low energy subbands become [79, 80]:

$$E_{k,\pm} \approx \pm \left(\Delta - \frac{2\Delta v_F^2 k^2}{\gamma_1} + \frac{v_F^4 k^4}{2\Delta \gamma_1^2} \right) \quad (2.63)$$

Where γ_1 is the splitting energy (~ 300 meV), which is relatively large given the separations from both the conduction band and the valence band for the low-energy case. Expression (2.34) represents a band gap effect formed around the Dirac point. For the first order, the size of this band gap is approximately 2Δ , which is exactly the potential difference between layers [79, 80].

Also, this gap is referred to the field-induced gap (Δ_{EFD}) in bilayer graphene related literature and shown in Figure 2.6., given that the potential difference between two planes with fixed distance is equivalent to a perpendicular electric field. The potential difference can be created by putting different charge-carriers in the two layers and increasing the band gap.

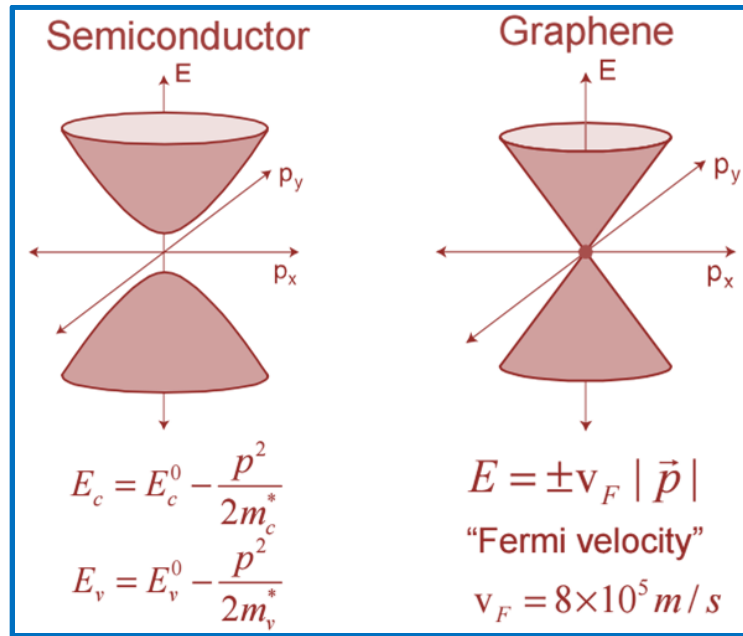


Figure 2.5. Band structures comparison between semiconductor (parabolic bands) and graphene (conic bands). Mass particles and massless particles, respectively. Taken and adapted from (www.physics.upenn.edu/~kane/pedagogical/295lec3.pdf).

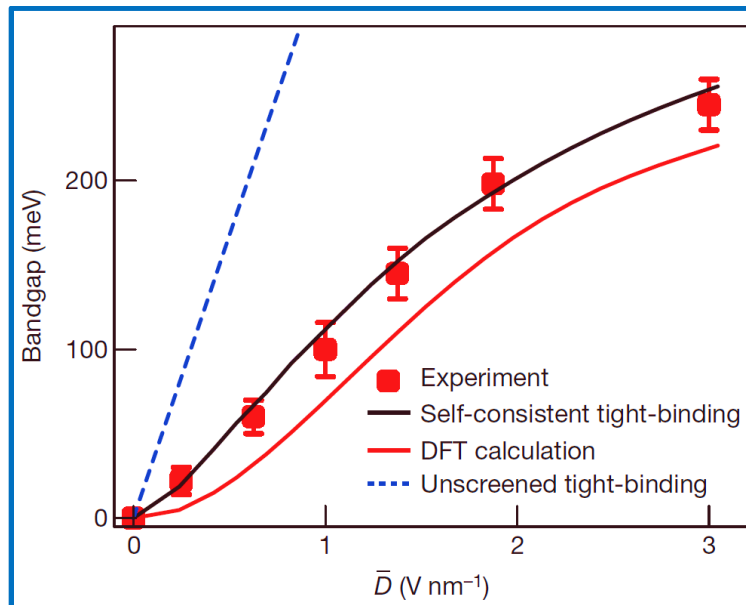


Figure 2.6. Band gap energy as a function of external electric field in graphene bilayer. The experimental data are the red dots and the black curve is the theoretical fitted by using the self-consistent tight-binding theory. Taken and adapted from reference [81].

Experimentally, the graphene sheet has been observed by using HR-TEM and AFM, as shown in **Figure 2.7**.

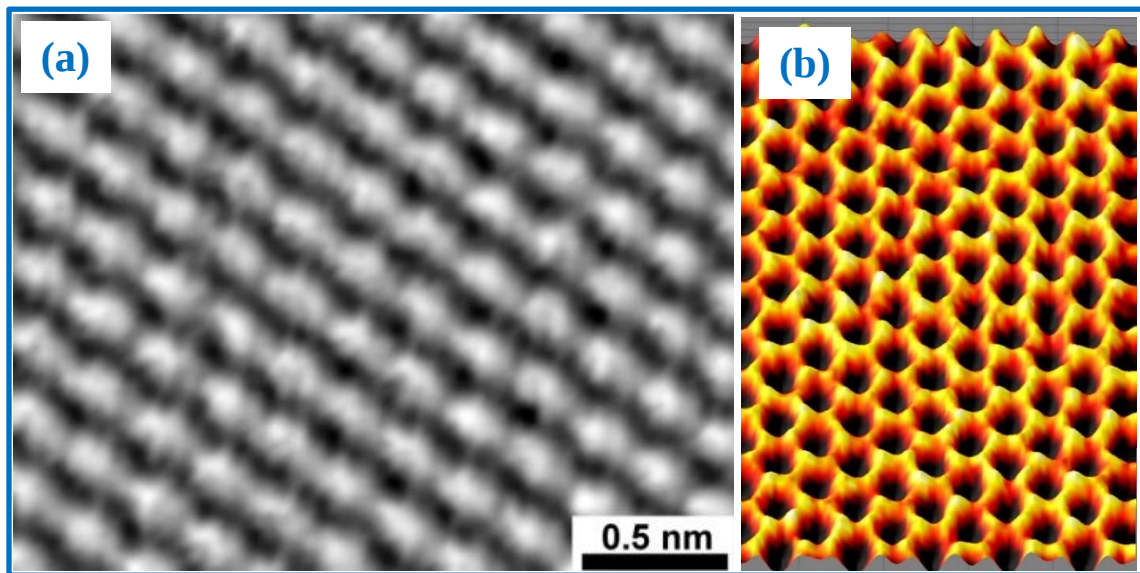


Figure 2.7. Graphene images measured by using: **(a)** Scanning Tunneling Microscopy (STM), taken from reference [82]. And **(b)** Scanning Probe Microscopy (SPM), taken from reference [83]. It is possible to observe the honeycomb or hexagonal structure in graphene.

Some basic concepts related with the electronic properties in graphene were presented; the following will discuss some relevant transport properties in graphene.

Thermal Properties in Graphene. These are very important in future applications related with electronic devices because thermal management is one of the key factors for better performance and reliability of the electronic components with high heat dissipation. Carbon allotropes, such as graphite, diamond, carbon nanotubes, and graphene have shown higher thermal conductivity due to strong C-C covalent bonds and phonon scattering.

Table 2.2 displays the thermal conductivities of graphene and graphene oxide. Thermal conductivity can be affected by different mechanisms, like boundary defects or boundary scattering [84] and isotopic doping [85]. In general, all these mechanisms are detrimental to conductivity due to phonon scattering at the defect and localization of phonon modes by doping [73].

Graphene oxide has very low thermal conductivity compared with the graphene sheet due to the presence of oxides, its conductivity can be modified and this behavior increases technological opportunities of applying graphene oxide as coating in electronic devices, where thermal management is one of the key factors for better performance and reliability of the coatings in electronic components to dissipate the heat generated in electronic devices.

Table 2.2. Thermal conductivities of graphene and graphene oxide. Taken and adapted from reference [73].

Method	Material	Thermal conductivity	Reference
Confocal micro-Raman spectroscopy	Single layer graphene	4840 – 5300 W/mK at Room Temperature (RT)	[86]
Confocal micro-Raman spectroscopy	Suspended graphene flake	4100 – 4800 W/mK at RT	[87]
Thermal measurement method	Single layer (suspended)	3000 – 5000 W/mK at RT	[88]
Thermal measurement method	Single layer (on SiO ₂ support)	600 W/mK at RT	[88]
Electrical four-point measurement	Reduce graphene oxide flake	0.14 – 0.87 W/mK	[89]

Electrical Properties in Graphene. These are characterized by zero band gap energy and unusual nature of charge-carriers due to massless relativistic particles (Dirac fermions). The behavior of Dirac fermions is guide abnormal compared to electrons when subjected to magnetic fields; for example, the anomalous integer quantum Hall effect (QHE) at low temperature [90, 91] and at room temperature [92] is different compared with other integer QHE in other metals and semiconductor materials.

The high electronic conductivity exhibited by single-layered graphene can be attributed to the high quality characterized by the low density of defects present in its crystal lattice. Defects can act as scattering sites and inhibit charge-carrier transport by limiting the electron mean free path or τ ; relaxation time is described by expressions 2.18 and 2.19. Evidence shows that pristine graphene is free of defects, thus, its conductivity must be affected by some extrinsic source.

Several factors have been proposed that affect conductivity, such as interaction with the underlying substrate during measurement, surface charge traps [93, 94], interfacial phonons [95], and substrate ripples [96]. Some comparative values of electrical conductivity measurements at room temperature have been reported by Yan Geng *et al.*, and are presented in Table 2.3. [97].

Table 2.3 shows that oxides present in graphene structures can modify electrical conductivity by several orders of magnitude and the can also affect charge carrier mobility. Electric current induced annealing improves mobility by up to 230,000 cm²/Vs [73].

Graphene is a potential material for future-generation electronic devices; it has zero energy band gap even at the charge neutrality point, which is one of the hurdles for using graphene as an electronic material, for example, in graphene-based FET. For this reason, the multifunctional oxides present in graphene (graphene oxide) offer possibilities of opening the band gap and this is technologically convenient in the development of advanced electronic sensors and devices.

Table 2.3. Electrical conductivity of graphite nanoplatelets (GNP), graphite oxide nanoplatelets (GONP), and graphene. Taken and adapted from reference [97].

Material	Electrical conductivity (S/m)
GNP	$(5.98 \pm 0.11) \times 10^4$
GONP	$(2.65 \pm 1.06) \times 10^{-3}$
Graphene	$(1.28 \pm 0.04) \times 10^2$

Magnetic Properties of Graphene. Strong experimental evidence exists along with an important scientific discussion related to the fact that boundary states in the disordered network of graphene and nano graphite govern their magnetic properties or ferromagnetism (FM).

These results cancel out the concept that only the transition metals of surface electrons (such as iron, nickel, cobalt or some of their alloys) are responsible of FM at room temperature; this finding has led to reconsidering the theory of magnetism [27-31, 41-45].

New theories suggest that the origin of the FM intrinsic nanostructures based on graphite as graphene are due to localized spin states caused by the presence of structural defects [27-31, 41-45], vacancy defects [29], absorption of hydrogen atoms (chemisorption) [30, 44], and dimensionality effects [45], as shown in Figure 2.8.

“Carbon adatoms (Figure 2.8.a) have a magnetic moment of about $0.5 \mu_B$, whereas carbon vacancies in the graphitic network generate a magnetic moment of about $1 \mu_B$ [99]. Vacancies in graphite, both ordinary (Figure 2.8.b), and hydrogenated (Figure 2.8.c), create new states below the Fermi level. The extra π -electrons are induced to the system when vacancies are introduced. For non-interacting vacancies, these extra electrons give rise to an unpaired spin associated with the vacancy [100]”. This entire paragraph was taken and adapted from reference [98].

Stone–Wales defects (Figure 2.8.d, e and f) are associated to a positive or negative Gaussian curvature in carbon structures (possibly due to graphene corrugation). This type of defect provides a mechanism for steric protection of the unpaired spin [101] and is caused by the rotation of carbon atoms, which leads to the formation of five or sevenfold rings [98].

Boundary defects produce electronic states strongly influenced by the existence and shape of the graphite edge, and zigzag edges favor spin polarization with ferromagnetic

alignment. Nano-graphite, a stack of nano-sized graphene layers, is a nano-sized π -electron system with open or closed (porous) edges (**Figure 2.8.g and h**) [98].

Some basic characteristics of hexagonal graphite and graphene structures have been discussed; the following section will explore some transport properties in graphite oxide structures.

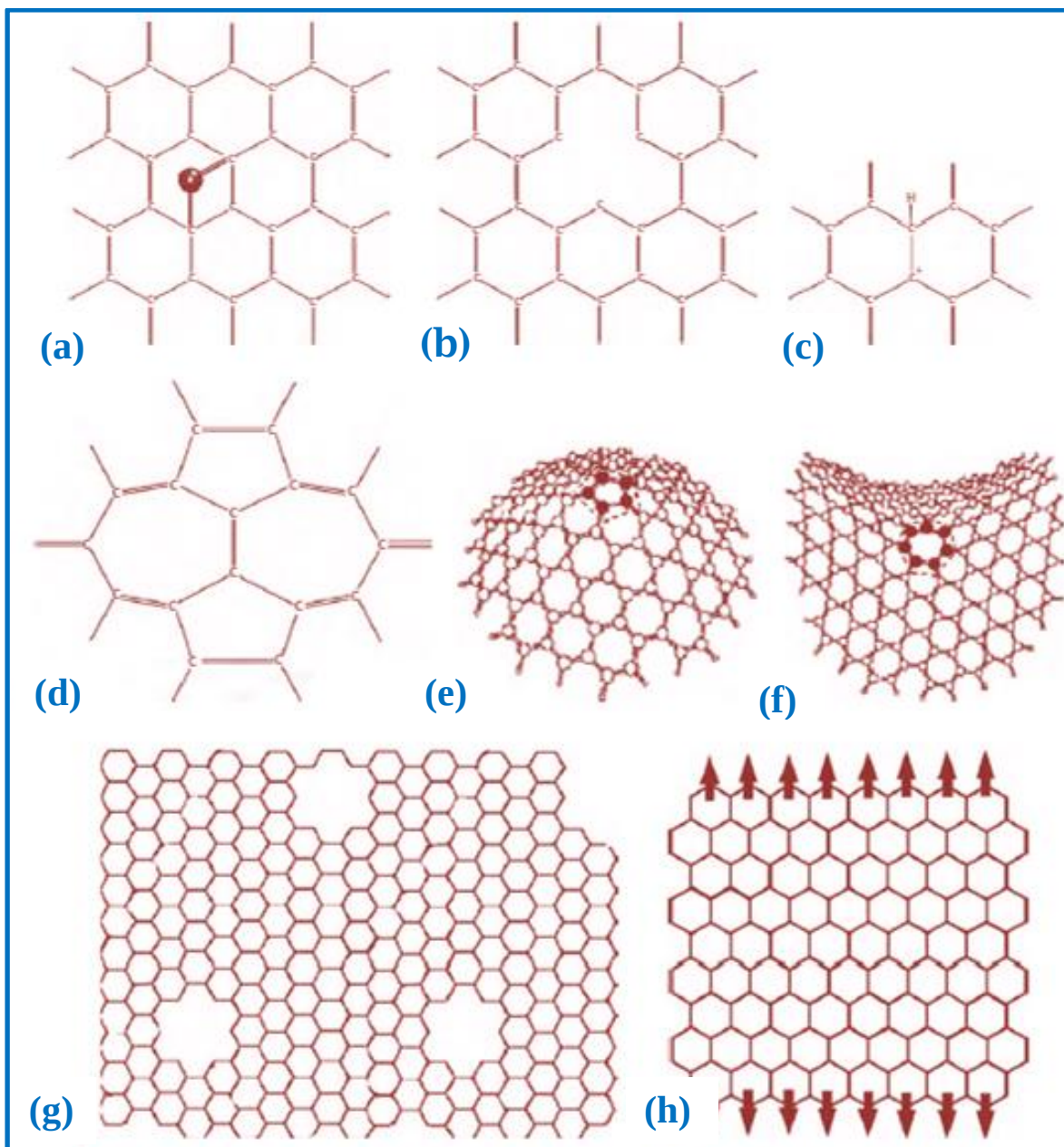


Figure 2.8. Intrinsic graphene defects, which are thought to lead to magnetic ordering in carbon structures. **(a)** Adatom. **(b)** Vacancy. **(c)** Hydrogen chemisorption. **(d)** Stone-Wales defect. **(e)** Positive curvature. **(f)** Negative curvature. **(g)** Porosity. And **(h)** Zigzag edge. Taken and adapted from reference [98].

2.3 Graphite Oxide (GO) Compounds

In recent years, graphite oxide (GO) has been of special interest due to its use as important precursor for exfoliated graphene oxide synthesis. Moreover, GO is also of interest due to its special surface properties and layered structure, making it a versatile material for applications [102]. By tuning the oxide composition and crystal structure, its physicochemical properties can be modified and functionalized. Graphite oxide can be obtained as platelets, microplatelets, and nanoplatelets [97].

In these platelets, the π -bond delocalization can produce the van der Waals forces between induced electric dipoles that influence the transport properties [103]. The presence of defects can, likewise, influence transport properties [104] and these effects can be exploited in the fabrication of advanced devices and sensors: magnetic, electronic, thermoelectric, optical, photomechanical and electro-optical, etc. [105].

For these reasons, GO platelets can be used in batteries [106–109], electrical energy storage [110, 111], advanced electronic sensors and devices [112–119], catalysis [120], metal sorption [121], hydrogen storage [122], and to obtain oxidized graphene [123]. Graphite oxide can be obtained through traditional Brodie [124], Hummer [125], or Tang Lau [126] methods and their modifications.

However, these methods produce only micron-sized graphene flakes and require using strong oxides (Brodie and Hummer methods) or glucose (Tang Lau method), as already mentioned. Although the latter is excellent for basic research, the GO obtained with these methods decomposes at temperatures between 553 and 573 K, becoming amorphous carbon and losing many of the oxides present in the material. For this reasons, this work proposed a new method for obtaining GO-BPA samples, which are more thermodynamically stable at high temperatures than the GO obtained through typical methods, as presented in chapter 3; hence, the double-thermal decomposition method (DTD) by using a pyrolysis system under controlled temperatures and nitrogen atmosphere.

This DTD method is a low-cost alternative to obtaining GO from bamboo pyrolygneous acid (GO-BPA) at higher temperatures from 573 to 973 K, as presented in this work, which differs from the traditional methods [127].

As presented ahead, composition, stage structure, defects, and graphitization degree depend strongly on the T_{CA} . Higher temperatures promote the elimination of organic compounds and oxygen functional groups, leading to an improved crystal structure and having a positive impact on the electrical transport. Increasing the temperature from 573 to 973 K leads to reduced oxygen content from 17% to 5% and an increase by around two orders of magnitude of the electrical conductivity, as evidenced by electrical measurements performed on single platelets [128] (chapter 4).

It is also expected that the thermal conductivity of GO-BPA platelets diminishes when oxygen content decreases, as found recently in GO [129], which could be important for electronic applications.

In addition, it is known that the graphite and graphene oxide molecular structures can be modeled by using several older structural models, as shown in **Figure 2.9**. It is possible to observe that the Hofmann structure consists of functional groups, including an oxygen atom joined by single bonds to two adjacent carbon atoms. These oxygen functional groups are spread over the basal planes of graphite so that graphene oxide in this model has a chemical formula of C_2O . The Ruess model is a modified version of the Hofmann structure that takes into account the hydrogen content of graphene oxide. Besides, the Ruess model takes another chemical functional group in the basal planes.

These other functional groups contain an oxygen atom connected to a hydrogen atom by a covalent bond (hydroxyl groups). In this alternative model, the basal plane structure does not have the sp^2 hybridized system of the *Hofmann* model and changes it into the sp^3 hybridized system.

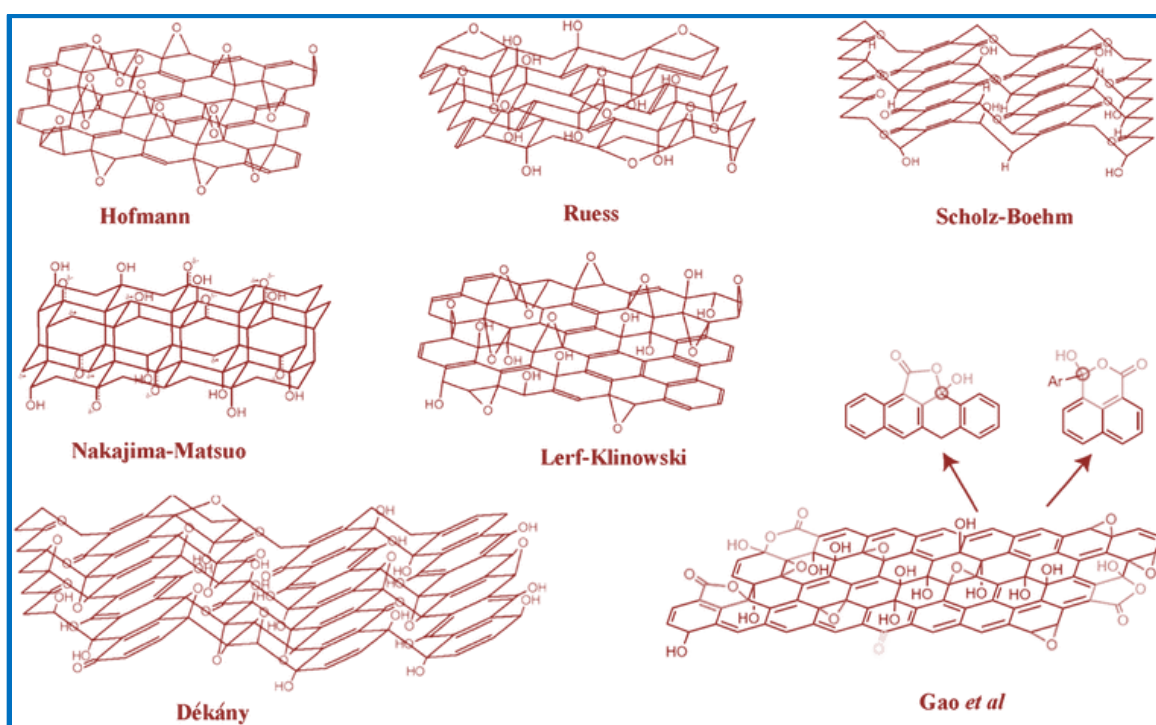


Figure 2.9. Structural molecular models of GO. Taken and adapted from reference [130].

The Scholz-Boehm molecular structure is another model proposed to describe oxides in graphene in which the epoxide and ether groups are removed. It has regular quinoidal species in a corrugated backbone. The Nakajima-Matsuo molecular model is another proposed structure of GO that, like the other three models introduced so far, is formed by repeated units. The Lerf-Klinowski molecular structure is the most recent model proposed. It assumes that graphene oxide is disordered and non-stoichiometric and, therefore, is the only graphene oxide structure introduced here that is not based on a lattice (that is, formed by repeated units). This structure is the first to be proposed by using observations based on solid-state nuclear (NMR) spectroscopy [131], while the first four models were based on other

techniques, like X-ray diffraction, reactivity, and elemental composition. The Dékány molecular structure is a GO model formed by the corrugated basal plane and forming hydroxyl and carboxyl functional groups intercalated throughout the structure. The Gao *et al.*, molecular model is a structure composed by complex functional groups in the graphene sheet edge.

Reduced Graphene Oxide (RGO). When the GO is reduced and exfoliated by physical or chemical methods it is called reduced graphene oxide (RGO). In RGO, oxygen coverage is low and may be known as a low multifunctional oxide concentration regime. Reduced graphene oxide is considered an intermediate way to obtain graphene. Some basic physical characteristics has been studied; recently, Alpana Thakur *et al.*, [132] reported that in the structural characterization by using XRD, the highest peak at position 26.11° was attributed to the (002) lattice plane of RGO with interlayer spacing (d-spacing) of 3.4 Å, indicating the formation of sp^2 network of carbon bonded structure with the graphitic character of carbon.

The peak at 22.80° was attributed to the (100) plane of RGO with interlayer spacing of 3.8 Å. The in-plane crystallite size of 4 nm with approximately 8 layers in the RGO crystal was determined by using the Scherrer relation over the (100) and (002) peaks. Also, in FTIR results, they found that the broad peak around 3400 cm^{-1} was associated to O-H stretching vibrations. The peaks around $2600\text{--}2800\text{ cm}^{-1}$ were related to several C-H stretching vibrations and the peaks near 1600 cm^{-1} were associated to various skeletal vibrations of C=C aromatic unoxidized graphitic domains. Peaks around $1100\text{--}1200\text{ cm}^{-1}$ were associated to C-C and C-OH stretching vibrations and the peak at 1043 cm^{-1} was attributed to the presence of the C-O alkoxy group [132].

Alpana Thakur *et al.*, [132] reported that the Raman spectrum of graphite shows characteristic peaks designated as G band at 1580 cm^{-1} and D band at 1350 cm^{-1} . The D mode is activated by the presence of defects and its intensity is computed for short-range disorder, whereas the G mode is caused by the first-order scattering of the E_{2g} mode. In the Raman spectrum of the RGO reported [132], the D peak for RGO was observed at 1350 cm^{-1} and the G peak was observed at 1579.39 cm^{-1} . The D band is more intense compared to the G band, which agrees with previous results observed for graphene samples [133]. The substantial increase in the intensity of the D band can be associated with the presence of disorder in graphene sheets (partially ordered graphite crystal structure) and possibly associated to oxidation and ultrasonic exfoliation, which results in the decrease of the in-plane sp^2 domain size of the graphene nano-sheets.

The in-plane crystal size, L_a , can be determined by the intensity ratio of the G band and the D band by using the relation $L_a = 4.4 (I_G/I_D)$ [132]. The (I_G/I_D) ratio was found and reported at 0.83 and the in-plane crystallite size was about 3.6 nm [132]. The D/G ratio was large and can be attributed to the contribution of disordered edge states in graphene samples. The 2D peak for our sample was found at around 2696 cm^{-1} [132], which agrees with the results reported for the single-layered graphene within experimental accuracy [134]. Also, this 2D band is associated with stacking order along the c-axis, the number of layers, and for the single-layered graphene the 2D band shows reasonably strong Raman intensity. Basic transport characteristics of RGO are presented in Table 2.4.

Table 2.4. Some transport properties of RGO.

Characteristic	Range	References
Thermal conductivity	0.14 – 2.87 W/mK	[73, 89]
Electrical conductivity	50 – 300 S/m	[73, 135]
Field-effect mobility	2 – 200 cm ² /Vs	[73, 135]
Saturation magnetization, FM induced by the presence of defects	2 x10 ⁻³ – 0.24 emu/g at RT	[136, 137]
Coercive field, FM attributed to presence of N impurities	50 – 200 Oe at RT	[138]
Negative Magnetoresistance	-2.5% at 5 K	[136]

Aspects related with the fabrication and structural representation of graphite or graphene oxide were presented in this section, aspects related with thermal, electrical, and magnetic transport in graphite oxide will be discussed hereinafter.

Electrical Conduction Mechanisms of GO. In graphene and graphene oxide, electrical conduction mechanisms have been well established and explained by tunneling, hopping, or percolation mechanisms, according to the degree of oxidation [73], as presented in Figure 2.10. In graphite, electron transport is also well understood [103]. However, to our knowledge, for GO, no systematic studies have been carried out to identify the charge-carrier scattering mechanisms that influence the electron or hole transport in these materials and the role of oxides in electrical conduction, although devices and sensors have been developed [112-119]. This research also seeks to contribute to the issue by understanding from the basic standpoint of dispersion mechanisms involved in the transport of electric charge in the GO-BPA, in hopes of developing flexible electronic applications.

Graphite is a material formed by stacking or superposition of multiple layers of graphene bonded by van der Waals-type forces; each graphene layer is a monolayer of carbon atoms arranged in a regular hexagonal pattern with covalent bonds, which are generated from the superposition of the sp² hybrids. Graphene has attracted much interest in materials science because of its novel electronic structure and transport properties, which earned the 2010 Nobel Prize. Theoretical predictions suggest that charge carriers in graphene behave like massless Dirac fermions, which is a direct consequence of the linear dispersion relation of energy present in this material. These results demonstrate peculiar electronic properties, such as quantum anomalous Hall Effect attributed to the absence of localization of electrons in this material.

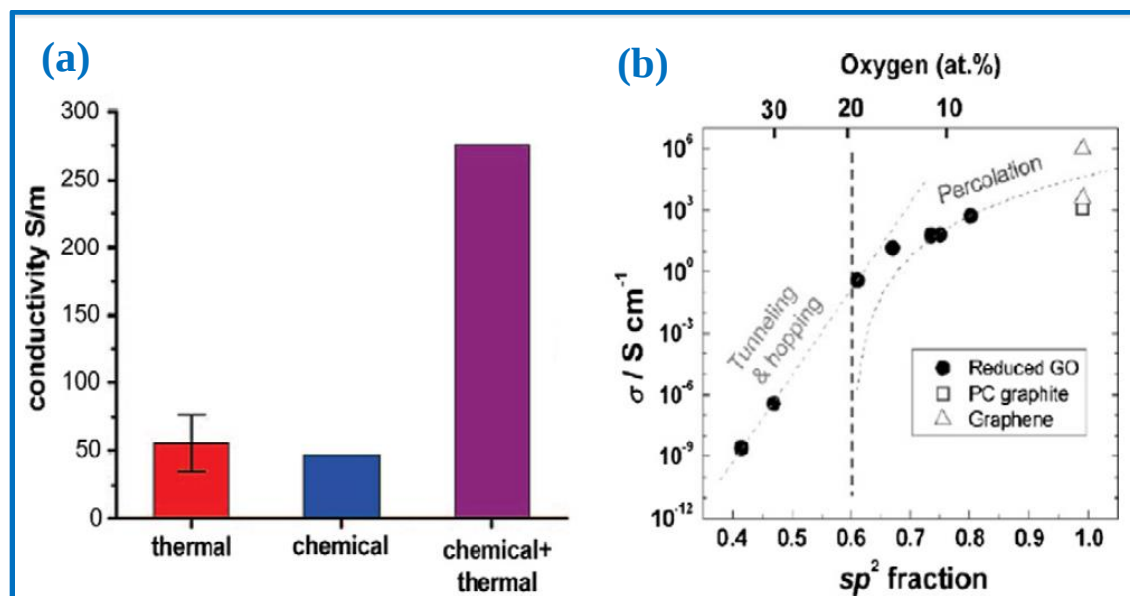


Figure 2.10. (a) Electrical conductivity of oxidized graphene (few layers) and RGO obtained through three different reduction methods: thermal, chemical, and chemical plus thermal. **(b)** Thermally reduced GO conductivity as a function of the fraction of sp^2 carbon. The vertical dashed line indicates the percolation threshold fraction at approximately 0.6 sp^2 . The fit to the experimental data revealed two different regimes for electrical transport with the sp^2 fraction. Tunneling and/or hopping (dotted line) are the dominant mechanisms for the sp^2 fraction values, below 0.6, while the percolation mechanism is dominant for values greater than 0.6 of the sp^2 fraction. The material with 100% sp^2 fraction is polycrystalline graphite (PC, polycrystalline) and graphene. The two conductivity values are for doped graphene (triangle above the dotted line) and intrinsic (triangle below the dotted line). Taken and adapted from reference [73].

Charge carriers also provide a bridge between condensed matter physics and quantum electrodynamics; thus, the electrons in graphene are, in a sense, “relativistic particles” in condensed matter. Semi-metallic behavior in graphene and graphite in the perpendicular direction indicates narrow-gap semiconductor behavior. Moreover, it requires the oxidation of carbon atoms in graphene and graphite to increase the value of band gap energy, which opens new opportunities to exploit technological characteristics of semiconductor prospects in the development of advanced devices, sensors and other mechanical, magnetic, thermal, electrical, and optical applications.

Heat Transfer Properties in GO. It is known that thermal conductivity is governed by lattice vibrations (phonon). The graphene 2-D structure forming the graphite has high thermal conductivity (3000 W/mK), making it an excellent candidate in various polymeric matrices in which the presence of graphene, graphite or GO increases heat transport because graphite anisotropy plays a key role, so the GO presents thermally conductive behavior in the direction parallel to the graphene layers, similar to that reported for graphene and oxidized graphene [73] and thermal insulation behavior in the direction perpendicular to the layers of

graphene direction. This provides thermal characteristics that depend on the direction taken when the phonons propagate through the GO structure when influenced by a difference of potential externally applied heat, as in electric transport. The mechanisms that explain thermal conduction have been established for graphene, oxidized graphene [73], and graphite [103, 139].

To our knowledge, for the case of GO-BPA, no systematic studies exist to identify the mechanisms that influence the thermal dispersion transport in these materials and the role of oxides in thermal conduction or scattering processes. Studies conducted to date in GO have focused primarily on the study of thermal properties of composite materials [140, 141] in which GO platelets are mixed with polymeric materials, finding that the thermal conductivity of composites increases with increased GO concentration and these behaviors have been explained by percolation mechanisms in which the phonons are conducted through the polymer matrix [142]. This research also aims to contribute to the understanding of scattering mechanisms involved in thermal transport in GO-BPA samples to develop thermo-electronic devices.

Magnetic Response of GO. Interest in carbon-based materials, such as GO, focuses, among others, on the presence of FM order with Curie temperatures above room temperature, considering the fact that in contrast to traditional magnetic materials, in these materials only sp electrons are present. Traditional FM properties present in materials, like iron, nickel, and cobalt, the group of rare earths, as well as their alloys are explained through an intrinsic mechanism of quantum origin called exchange interaction originated in 3d and 4f electrons.

The traditional theoretical models do not admit the existence of an FM-type ordering in materials with the presence of sp electrons; however, recently several independent experimental works have reported such an arrangement in carbon-derived materials [37-46].

The FM order in graphitic materials has been shown to be closely linked to the presence of structural defects, as has been demonstrated in experiments where the FM order has been induced in graphite through bombardment with protons, which has aimed to artificially induce imperfections and increase the concentration of defects, resulting in increased magnetic signal [37-44]. Investigations in the theoretical field [44-46, 143, 144] suggests the origin of FM to the mixture of carbon atoms with sp² and sp³ bonds, in the presence of structural defects [144], vacancy defects [44], absorption of hydrogen atoms or other species, like N [44], O [145], and Si [146], as well as for dimensionality and border effects [147].

The biggest problem in this case is that the spin polarization originated by such effects is local in nature and the possibility of a magnetically ordered long-range state depends on a delicate balance among various system interactions; thus, compromising the degree of reproducibility of the experiments [37].

From the viewpoint of magnetic properties, the graphite block is known as a diamagnetic material, as are most carbon allotropes; the FM phenomenon in organic materials is rare because their atomic structure differs significantly from that of transition metals; however, experimental evidence has been presented of the induction of an FM system above 300 K in

highly ordered pyrolytic graphite (HOPG) [40]; said system has been induced in the sample after being subjected to proton bombardment.

This effect was also confirmed by using bombardment of high-energy ions [42, 43]. Ferromagnetism explains the origin of the phenomenon in these materials after the effect of ion bombardment, it remains a subject for debate; however, inclusion of structural defects (vacancies or defects by atom adsorption) caused by bombardment with high-energy particles are linked to the presence of FM. These “magnetism-induced defects” have been theoretically studied based on the density functional theory (DFT) calculations, where such defects, vacancies interpreted as pz orbital of the C atom, have profound effects on the ideal graphene electronic structure [148].

In the simplest approach, the defect vacancy, removing a C atom in a graphene subnet introduces a quasi-localized state near the Fermi level, which provides a magnetic moment of about $1 \mu_B$. A representation of the density distribution of spins in the vicinity of defects is shown in **Figure 2.11**. The magnetic moments associated with these localized defects are clearly observed for the chemical adsorption of the H atom, as presented in **Figure 2.11 a)** and for defect by vacancy, as shown in **Figure 2.11 b)**.

It is worth mentioning that other possible scenarios have been proposed that support the presence of the FM order in carbon-based materials, which, among others, are related to network deformations and edge effects [98, 147]. Also, other theoretical works have raised the effect on the magnetic properties by the adsorption of Si [146], N [44], Na, or O [145] atoms in graphitic material, which have reached similar conclusions for the adsorption of H atoms [148] or OH-functional group [149].

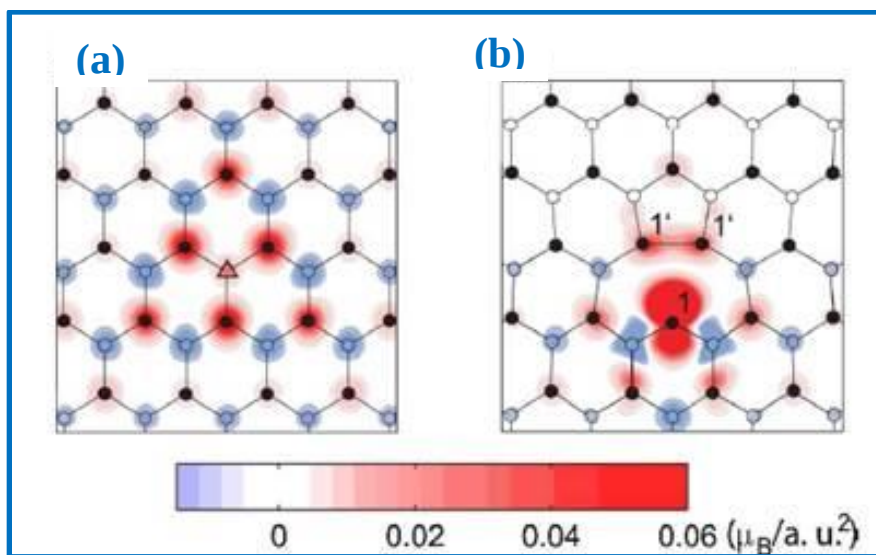


Figure 2.11. Spin density projection (in $\mu_B/a.u.^2$) in the graphene plane around (a) the defect through hydrogen adsorption (Δ) and (b) the vacancy defect in subnet A. Carbon atoms corresponding to subnet A ($\circ$) and subnet B ($\bullet$) are specified. Taken and adapted from reference [148].

First principles calculations are practical for simple systems, which considers lattice of very regular and periodic defects; however, such defects have been randomly distributed so that theoretical calculations fall short, if – in addition – more complex systems, such as oxidized graphite, are considered.

The role of defects due to vacancies, adsorption of atoms, and structural defects continues being the object of study; within this thematic, most studies have focused on graphene and graphite systems, as well as on other allotropic forms of carbon-based materials.

Nevertheless, not many works have been published on oxidized graphite systems, which is the object of study within the present investigation. According to different mechanisms that induce FM order in GO material, as presented in [Figure 2.8](#). [Table 2.5](#) presents theoretical magnetic moments in different mechanisms that aim to explain the FM order in GO samples. It is possible to observe that the main theoretical mechanism is the boundary defects with a magnetic moment of 2.76 [\[150\]](#).

Table 2.5. Magnetic moments of each theoretical mechanism that seeks to explain FM order in graphene.

FM Mechanism	Magnetic Moment ($\mu_B/\text{\AA}$)	References
Vacancy (Dangling bonds)	0.60 - 1.00	[148, 151]
Hydrogen chemisorption	1.00 – 1.25	[151, 152]
OH groups chemisorption	1.00	[149]
Zig-zag edge	0.01 – 0.35	[148]
Disordered graphene (Hubbard model)	0.01 – 0.15	[148]
Topological line defect	0.030 – 0.140	[153]
Grain boundary defects	1.732 – 2.707	[150]

Important aspects related to magnetism in GO were presented in this part of the chapter, some correlations aspects of magnetoresistance in GO will now be discussed.

Magnetoresistance (MR) in GO. Magnetoresistance, as expected in GO and RGO materials, can exhibit reentry MR; changes from positive and negative MR have been studied recently [154]. The origin of reentry MR is still unknown and it is an open field of basic research. In recent years, great scientific effort has taken place to understand and control magnetic properties in these GO materials; moreover, the complete mechanism that explains the magnetic properties in both pure graphene systems and in GO is still a matter of controversy and discussion and the execution of systematic and reproducible experimental studies is still required.

As far as we know, in Colombia and in the world, no research groups are systematically studying the problem of magnetism in GO obtained from bamboo-Guadua as source (GO-BPA samples), which provides an excellent opportunity to publish in the subject and Universidad del Valle and Universidad del Quindío. For these reasons, this work is an original venture and the first time in this frontier of knowledge in physics.

It should be noted again that finding the path to obtaining GO with magnetic, electrical, and thermal properties in a controlled manner could be the first step to venture into the development of advanced electronic devices and sensors for electrical and thermal storage, use of bio-compatible magnets for applications in medicine and biology as bio-sensors, among other potential uses. This research is an excellent opportunity to contribute with publications to the knowledge on the subject, provide experimental evidence to enrich the scientific discussion around the subject, and position the material studied within it, to point to the generation of science and its technology.

The basics of transport mechanisms in GO materials have been presented, chapter 3 will elaborate important aspects of the experimental methods used in this work.

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Chapter 3

3. Experimental Methods

This chapter summarizes the key experimental techniques used to fabricate and characterize graphite oxide obtained from bamboo (GO-BPA) as platelet samples synthesized at different carbonization temperatures (T_{CA}). The samples were fabricated via double-thermal decomposition method (DTD method); section 3.1 details this technique [1-40]. The morphological [41-50], structural [51-62], elemental [63-66], thermal or vibrational [67-76], electrical [77-84], and magnetic [85-88] properties were studied by using high-resolution transmission electron microscopy (HR-TEM) [41-47], TEM, electron diffraction (ED), scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD), energy electron loss spectroscopy (EELS), X-ray photoelectron spectroscopy (XPS), energy-dispersive X-ray spectroscopy (EDS), Raman spectroscopy (RS), Fourier Transform Infrared (FTIR) spectroscopy, Current-Voltage (I-V) curves, magnetic force microscopy (MFM), and vibrating sample magnetometer (VSM) techniques in GO-BPA samples obtained at different T_{CA} . One of the most relevant purposes of this thesis is the investigation of the basic transport mechanisms in GO-BPA materials; for this, the Raman, FTIR, I-V curves, MFM, and VSM were employed to determine the main transport mechanisms in the GO-BPA samples; whereas, magnetization reversal processes and the domain structure in the as-prepared-state, as well as under external applied fields is visualized by means of MFM. In order to establish a first approximation of the GO-BPA molecular model, DFT computational simulations were carried out, as presented in section 3.2.

3.1 Sample Preparation

Graphene oxide (GO) can be obtained via traditional Brodie [1], Hummer [1, 2], or Tang Lau [3] methods and their modifications. In 1859, for the first time Brodie obtained GO by means of treated graphitic powder with potassium chlorate in concentrated fuming nitric acid and synthesized GO, as top-down method. In 1899, Staudenmaier treated graphitic powder with potassium chlorate in concentrated fuming sulfuric acid and obtained GO, as top-down method. In 1958, Hummer, by using potassium permanganate and sodium nitrate in concentrated sulfuric acid, shortened oxidation time to several hours and obtained GO, as top-down method. In 2012, Tan Lau, by using glucose as the sole source, obtained GO, as bottom-up method. Today, the route of methodologies for obtaining GO and graphene nanoplatelets from graphite is accepted, as presented in Figure 3.1.

However, these methods yield only micron-sized graphene flakes and require using strong oxides (Brodie and Hummer methods) or glucose (Tang Lau method), among other disadvantages. Although the latter are excellent for basic research, the GO obtained with these methods decomposes at temperatures between 553 and 573 K, becoming amorphous

carbon and losing many of the oxides present in the material. In recent years, an alternative way has been proposed and employed to synthesize graphene oxide multilayers, powdered GO-BPA samples, or single GO-BPA nanoplatelets, which is the so-called DTD method [4, 5].

The GO-BPA samples were synthesized through the DTD method in a pyrolysis system under controlled temperature and nitrogen atmosphere, for different T_{CA} from 673 to 973 K.

By using the preparation process employing the DTD method presented in **Figure 3.2.**, more details have been published by our group in references [4-13], and the samples were obtained from bamboo due to its high growth and production rates (approx. 3-5 years), good carbonization yield (28% - 18%), good abundance in the tropical region (1600 species, 65% Asia and Oceania, 28% America, and 7% Africa, food source and agriculture (2005)) [14] and the waste products from the bamboo industry are considered around 30% (approx. 1500 uses) [14-17].

Bamboo has water retention and purification, contributes to soil conservation, produces 35% more oxygen than trees, absorbs from 3 to 5 tons of carbon (CO_2) per hectare, with a world market of US\$4.5 billion (1999) and US\$ 60 billion per year (2015) [14-17].

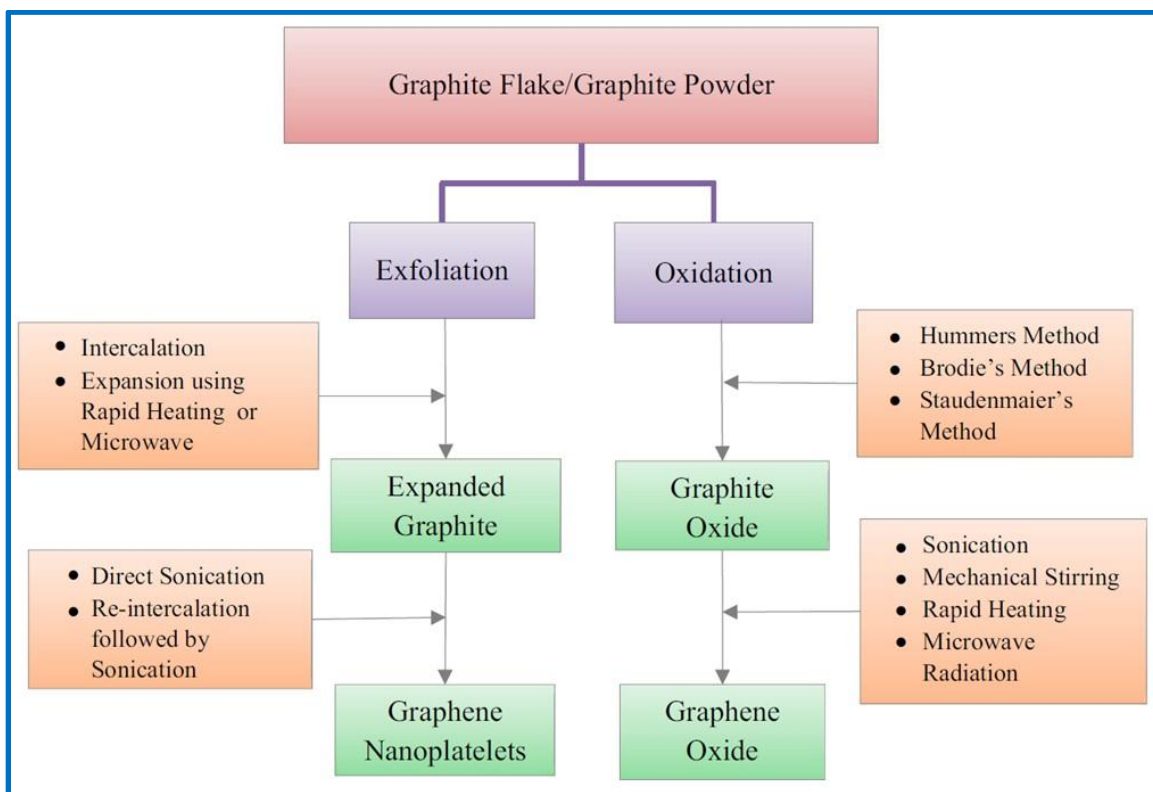


Figure 3.1. Diagram of the methodology route to obtain graphene oxide and graphene nanoplatelets from graphite. Taken and adapted from reference [18].

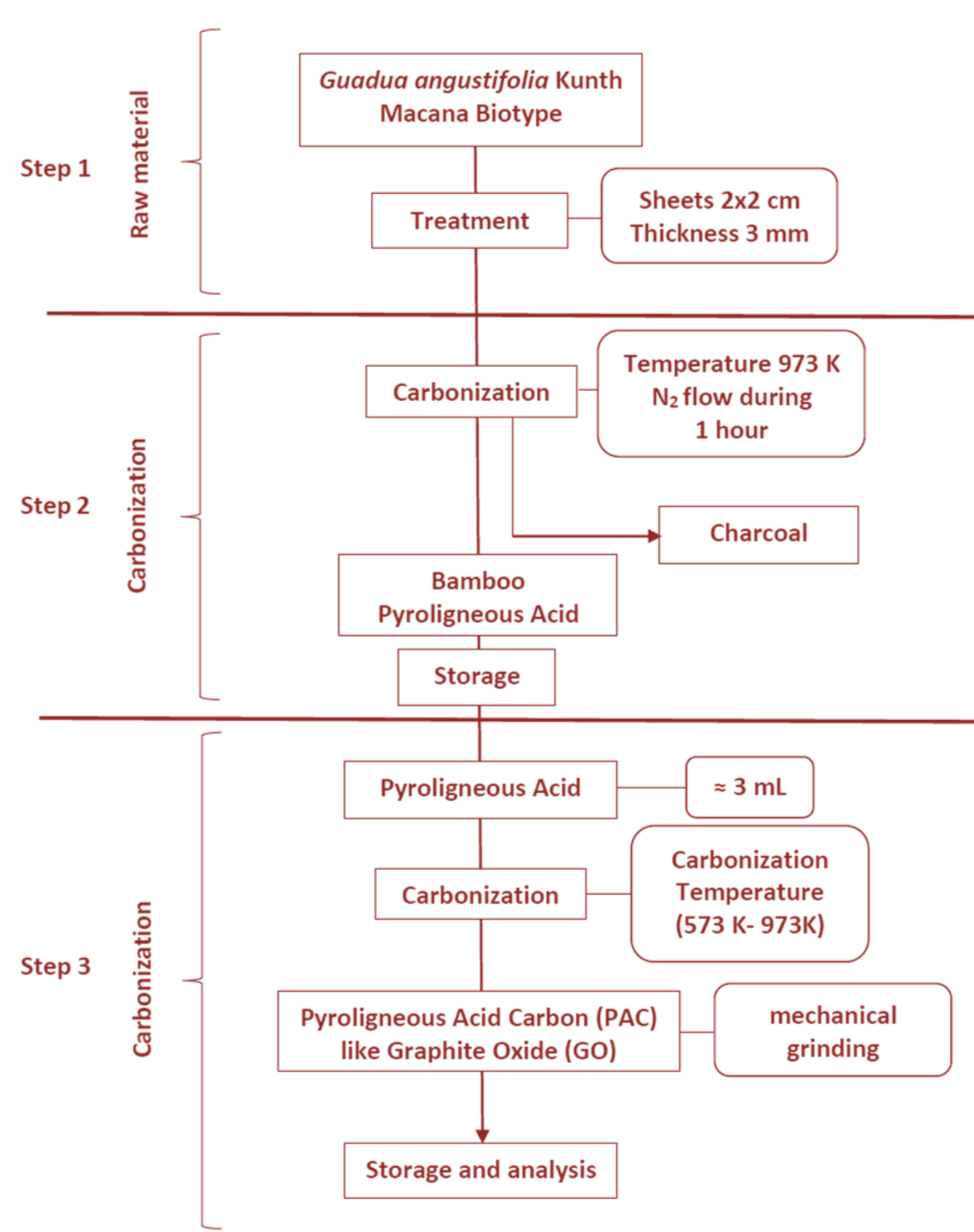


Figure 3.2. Scheme of the GO-BPA sample preparation processes by using the DTD method. Taken and adapted from our group's reference [4].

Bamboo as source to synthesize GO. *Guadua angustifolia* Kunth, popularly called guadua or tacuara, is a botanical species of the grass subfamily *Bambusoideae*, which has its habitat in the humid tropical forest on the banks of rivers. It is native to the Venezuelan

jungle, and extends through the forests of the Guyana's, Brazil, Ecuador, Colombia, Guyana, Peru, and Suriname and from San Ángel in México, passing through Costa Rica, El Salvador, Guatemala, Honduras, Nicaragua, and Panama.

The chemical constituents of bamboo fiber are 73.83% cellulose, 12.49% hemicellulose, 10.15% lignin, 3.16% aqueous extract, and 0.37% pectin [19]. Additionally, bamboo tar is very rich in phenol groups with high oxygen content, as reported by W. M. Qiao *et al.*, [20].

Colombia ranks second in bamboo diversity in Latin America. Currently, 9 genera and 70 species are reported, with 24 species being endemic and at least 12 to be described [21]. The Andean region has the largest quantity and the greatest diversity in population of tree species (89%) and the eastern cordillera the richest, with 55% of bamboo forests reported so far. The departments of Colombia with the greatest diversity of bamboo forests are Norte de Santander, Cundinamarca, Cauca, Valle del Cauca, Antioquia, Huila, Nariño, and Quindío. The majority of species belong to the *Chusquea* genus (30%) and the rest belong to the *Neurolepis*, *Arthrostylidium*, *Aulonemia*, *Elytrostachys*, *Merostachys*, *Rhipidocladum*, *Guadua*, and *Otatea* genera [22]. The *Guadua* genus is distributed along the central cordillera and the central zone of the country in the departments of Antioquia, Cauca, Caldas, Cundinamarca, Huila, Quindío, Risaralda, Tolima, and Valle del Cauca. According to some studies, it is estimated that there are between 50,000 and 60,000 ha of *Guadua* of which 95% are natural *guadua* and 5% cultivated; only 40% of the total is used, that is, approximately 24,000 ha [22]. Some authors argue that "natural and planted areas reach 36,181 ha, of which 31,286 ha are in the coffee region, Tolima, and Valle del Cauca" [22]. For the other departments, the information is fragmented, although according to some estimations in Antioquia, Huila, Putumayo, Caquetá, Cundinamarca, Cauca, and Nariño there are important forest coverings of *Guadua*, which do not have information records [22]. For Cundinamarca, the Regional Unit of Agricultural Planning (URPA, for the term in Spanish) indicates the presence of 1965 ha and in Huila, a current area of 3500 ha is estimated. In the department of Cauca, it is estimated that sugar mills have about 700 ha of *Guadua* and a potential of 1000 ha for planting (Minagricultura 2005) [14].

The coffee region has 31,286 ha of *Guadua* of which 26,985 ha are natural and 4301 ha are planted; this guarantees a constant supply of raw material, unlike other sources or precursors used to produce activated carbon that do not have such a vast supply of raw material for its production; like bone or coal coming from other woods and even coconut shell, which is obviously scarce in the region [22].

The bamboo's short harvest cycles, which fluctuate between 2 and 6 years, are at least 15 times lower than the rotation cycles of forest trees. Intensive silvic-cultural systems with constant production of *Guadua*, the almost integral use of the raw material, and minimal maintenance have made *Guadua* patches highly attractive economically and environmentally in relation to round-wood and other types of raw materials for the production of activated carbon [9]. *Guadua* is a useful and inexpensive raw material that can be used to obtain activated carbon [9], which is an adsorbent that can be manufactured in both granular and pulverized form. Adsorption is a process by which atoms on the surface of a solid attract and retain molecules from other compounds. The scale of needs of activated carbon ranges from

the use of a few grams of adsorbent in the laboratory to industrial plants, whose inventory of adsorbent exceeds 135,000 Kg, which implies having large amounts of this material [9].

It is also known that *Guadua angustifolia* K. is the most popular species of bamboo in Colombia due to its versatility, which allows having multiple uses, both in construction and industry [22, 23]. Currently, national research on this type of material focuses mostly on the areas of architecture and civil engineering [22, 23], with few studies related to the production of carbon to obtain samples of oxidized graphite for applications in electronics, only some studies have been reported by our group [4-13].

Therefore, this research is an excellent opportunity to contribute with publications for knowledge on the subject, providing experimental evidence to enrich the scientific discussion around the subject and positioning the material studied within it in order to point to the next generation of science and its technology.

Synthesis of GO-BPA samples. Figure 3.2. shows that the GO-BPA samples were prepared through three steps. In the first step, the raw material as *Guadua angustifolia* K. Macana biotype was cleaned and treated mechanically. In the second step, the bamboo pyrolygneous acid (BPA) was obtained from carbonization of bamboo raw material via a first pyrolysis process at 973 K and collected in a decanting funnel glass, where the bamboo tar was easily decanted and separated. In the third step, the bamboo tar of the BPA was then used as precursor for GO at T_{CA} from 673 to 973 K. At this temperature range, thermal decomposition of the aromatic structure of the phenol compounds in the bamboo tar gives rise to the formation of carbon structures, as reported by W. M. Qiao *et al.*, [20]. When the carbonization process of the BPA tar is completed, a carbon foam is obtained, which subsequently turns into platelet powders by mechanical grinding in a ceramic hand mortar. An overview of the fabrication process is schematized in Figure 3.2.

Figure 3.3. presents the T_{CA} dependence on the carbonization yield percentage. The yield is measured as the quotient between the GO-BPA sample weight after the carbonization process and pyrolygneous acid weight before the carbonization process. When T_{CA} increases, organic compounds present in the BPA are desorbed by thermal decomposition and, thus, the yield percentage decreases from 28% to 18%, as presented in Figure 3.3., the remaining part is converted into coal.

The methodology presented in Figure 3.2. offers the possibility of obtaining different sample types, as shown in Figures 3.4. and 3.5. However, the GO-BPA samples studied in this work are GO-BPA nanoplatelets, as shown in Figure 3.6. Thickness was measured and corroborated by using TEM, SEM, and AFM, as presented in Figure 3.7. Table 3.1. presents a comparative study of the elemental composition between measurements taken via XPS and EDS techniques (section 3.2) in GO-BPA samples for different T_{CA} . We found that increased T_{CA} (from 673 to 973 K) increased graphite conversion (carbon presence) in the range from 85.71% to 94.00% and decreased oxygen coverage from 12.99% to 5.25%, measured via XPS and EDS techniques (section 3.2); this behavior can be associated to multifunctional oxides desorption by thermal decomposition effects, as presented in Figure 3.3.

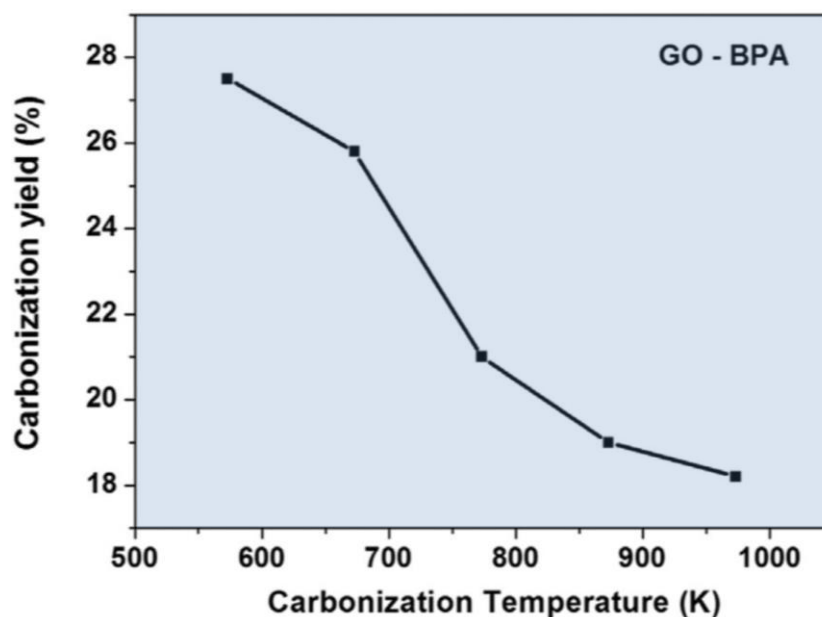


Figure 3.3. Carbonization yield percentage as a function of T_{CA} . Taken and adapted from reference [4].

Table 3.1. shows that the GO-BPA samples contain a few impurities of N from 0.61% to 0.75% and Na from 0.60% to 2.77%, both measured via XPS and EDS techniques (more details in section 3.2). The N impurity appears in the pyrolysis process due to nitrogen flow during synthesis process of samples. Na impurities appear as native contamination because bamboo tar contains this native sodium or contamination by activated process of carbon in the pyrolysis system.

Both N and Na impurities have been considered, despite this work, due to very low concentration and their influence on transport properties can be attributed mainly to carbon and multifunctional oxides present, as discussed in chapter 4. Differences in elemental composition measurements by using XPS and EDS techniques (section 3.2) are lower than 17.33%, as shown in **Table 3.1.** as $\Delta O/O$. The analysis introduced in chapter 4 was carried out by considering only XPS measurements of elemental composition and EDS results as confirming this elemental composition.

In addition, the presence of H impurities was not quantified in this work, given its abundance decrease with increased T_{CA} by desorption effect, as presented in **Figure 3.8.** and H is not easily detected. For these reasons, we performed indirect measurements of H present in the GO-BPA sample by using the FTIR spectra analysis (section 3.2). **Figure 3.8.** presents relative transmittance as a function of T_{CA} obtained from the FTIR spectra analysis in GO-BPA, as shown in the inset of **Figure 3.8.**, and it is related with the hydrogen present in GO-BPA. Hence, increased T_{CA} decreases hydrogen presence.

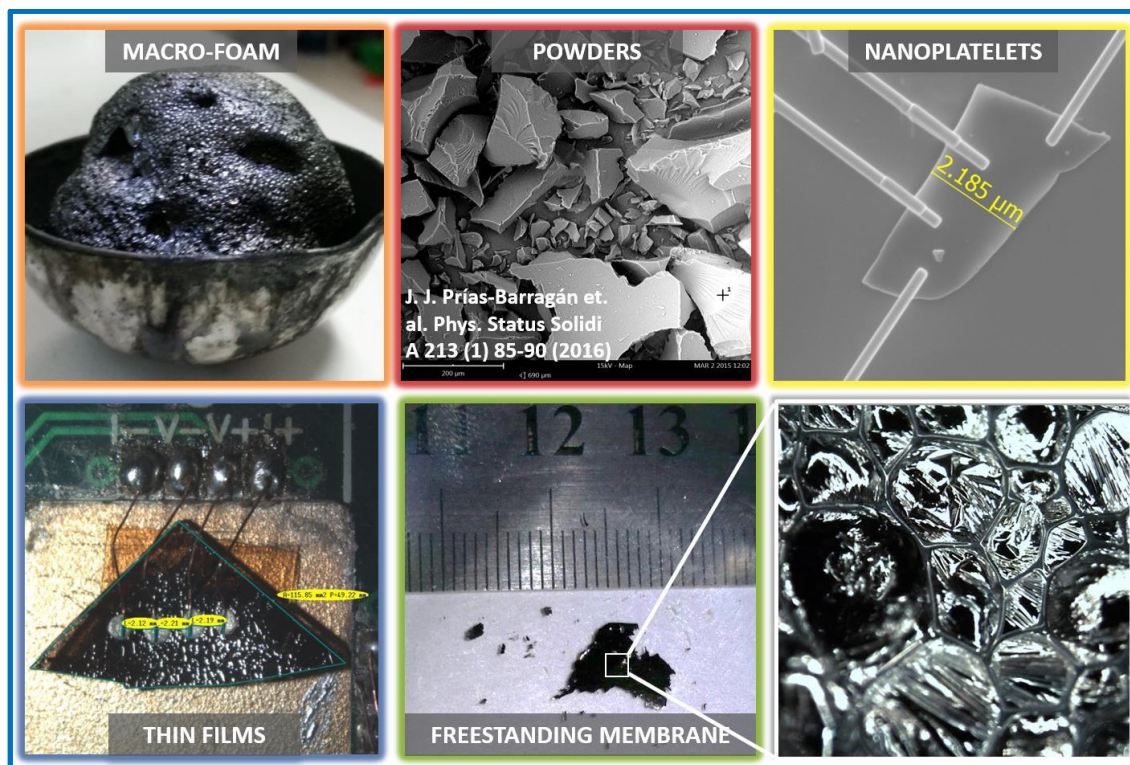


Figure 3.4. Types of GO samples synthesized from BPA by using the DTD method and obtained in this work as macro-foam, powders, nanoplatelets, thin films, and free-standing membranes for basic studies in physics and technological applications.

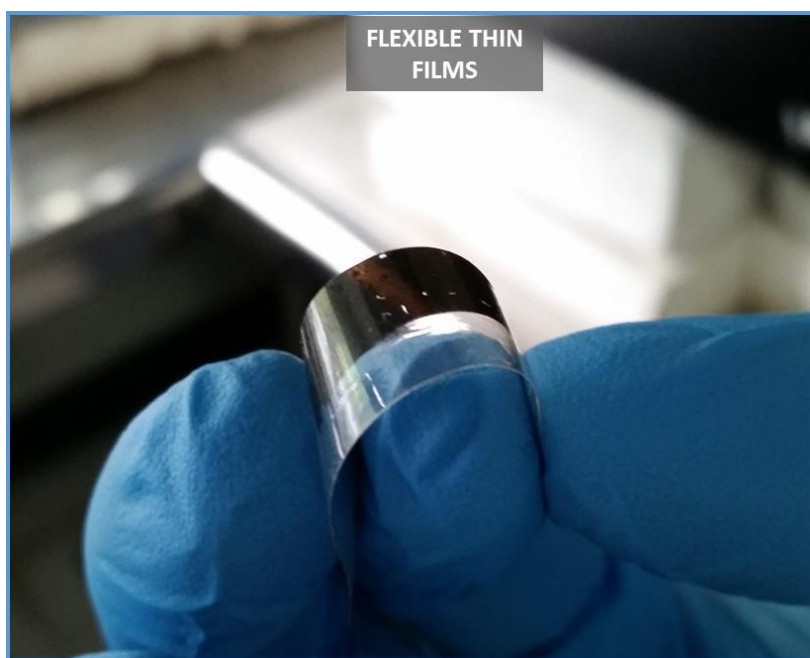


Figure 3.5. Flexible thin film of GO-BPA obtained by DTD method and proposed in this work.

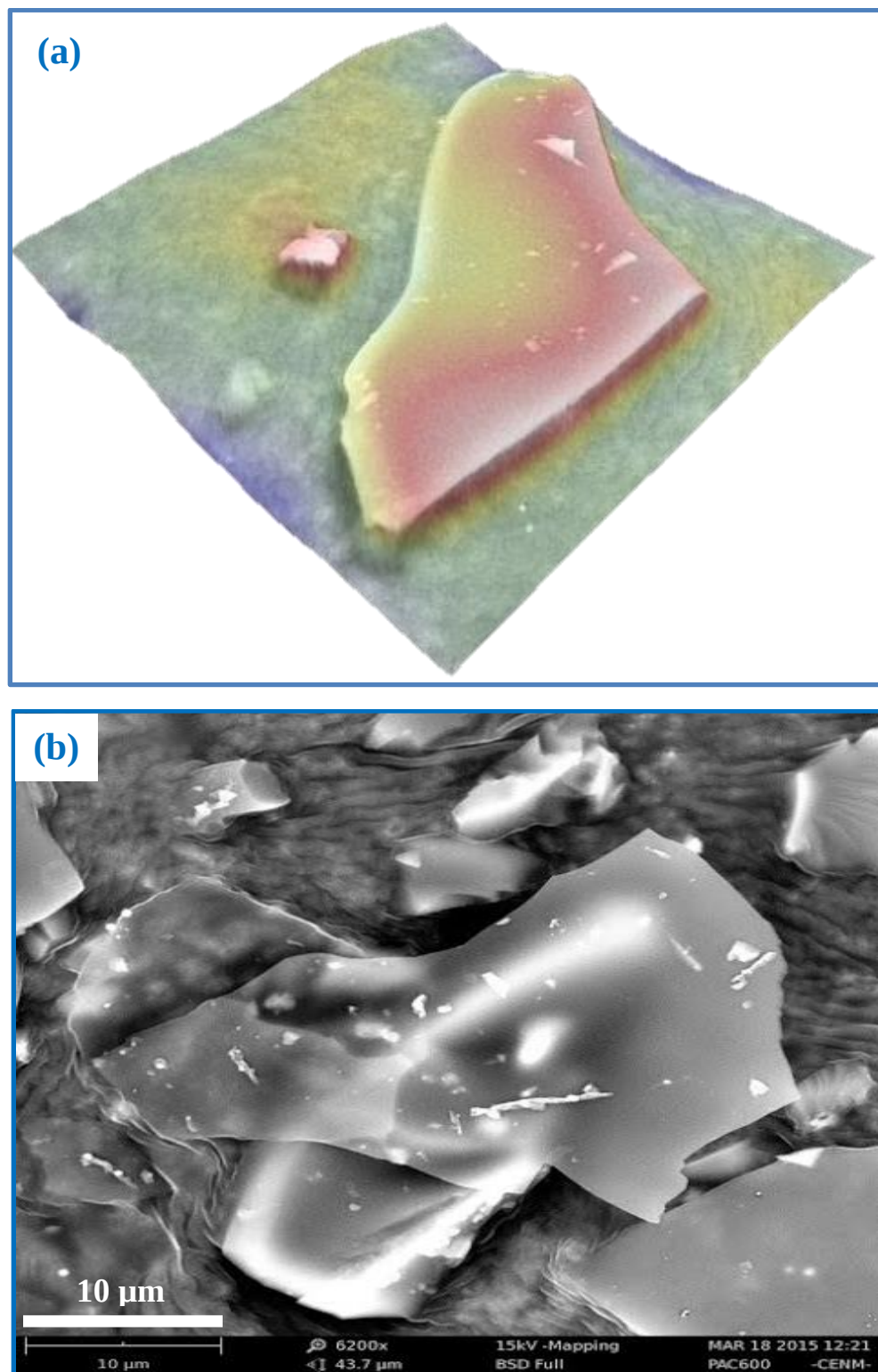


Figure 3.6. GO-BPA nanoplatelet prepared by DTD method and proposed in this work. **(a)** 3D SEM image. **(b)** SEM image, lateral dimensions of 20 μm with irregular form and thickness of 80 nm; this behavior agrees with recent ISO standard classification as nanoplatelet [24]. The high electron transparency can be associated to very low thickness.

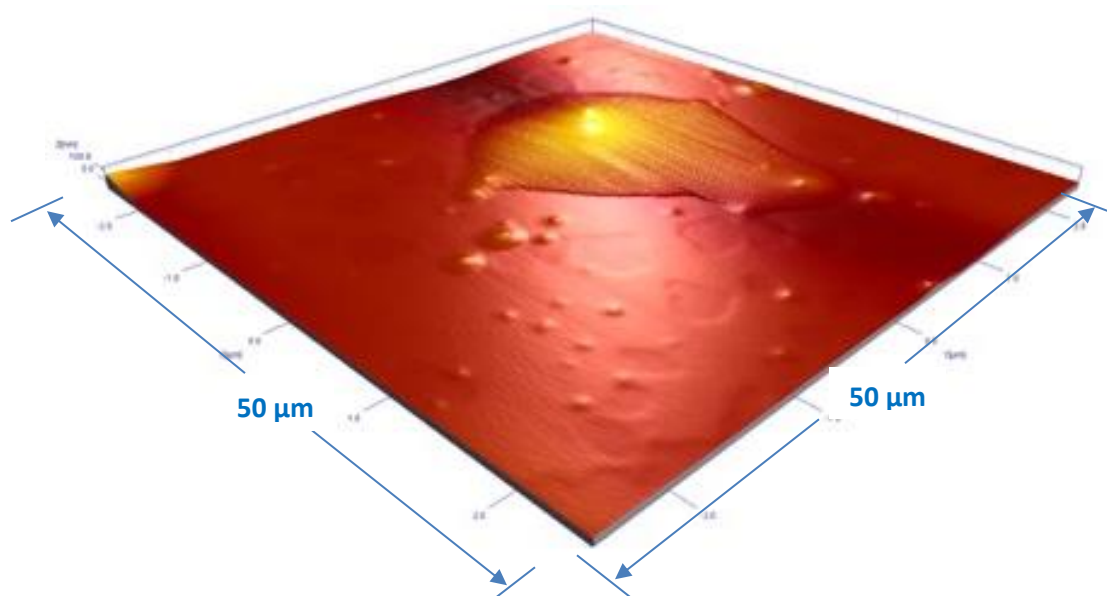


Figure 3.7. 3D AFM image in single GO-BPA nanoplatelet with thickness around 80 nm and maximum lateral dimensions of 30 μm .

The differences observed between the XPS and EDS measurements of elemental composition presented in **Table 3.1.** can be because the XPS was sensitive to low nitrogen presence and EDS was not sensitive to low nitrogen presence through basic physics processes involved in these techniques and discussed in section 3.2.

Table 3.1. Comparison between elemental composition measurements by XPS and EDS techniques in GO-BPA samples obtained at different T_{CA} .

GO-BPA	XPS measurements				EDS measurements				Difference
T_{CA} (K)	C-1s (%)	O-1s (%)	N-1s (%)	Na-1s (%)	C-K (%)	O-K (%)	N-K (%)	Na-K (%)	$\Delta O/O$ (%)
673	85.71	12.99	0.70	0.60	85.30	13.18	----	1.52	1.46
773	92.15	7.16	0.69	----	90.74	7.84	----	1.42	9.50
873	87.49	9.69	0.61	2.21	89.95	10.05	----	----	3.71
973	94.00	5.25	0.75	----	91.07	6.16	----	2.77	17.33

The compositional analysis presented in **Table 3.1.** shows that our GO-BPA samples agree with the low oxide coverage regime, similar and comparable to reduced graphene oxide (RGO) materials reported by Sabina Drewniak *et al.*, [25]. The GO-BPA samples can be described as an oxidized form of graphene, accompanied mostly by hydroxyl, carboxyl, and epoxy functional groups distributed randomly along the hexagonal network of carbon atoms

[26-30], as proposed in this work through the molecular model presented in **Figure 3.9** (chapter 4). The multifunctionality given by the oxides, in combination with the exceptional properties of graphene, allows considering the GO-BPA sample as a versatile candidate material for applications in electronics similar to RGO in next-generation electronics and optoelectronics, as well as in energy conversion and storage technologies [26-28, 31-33]. By tuning the oxide composition and crystal structure, its physicochemical properties can be modified and functionalized [26].

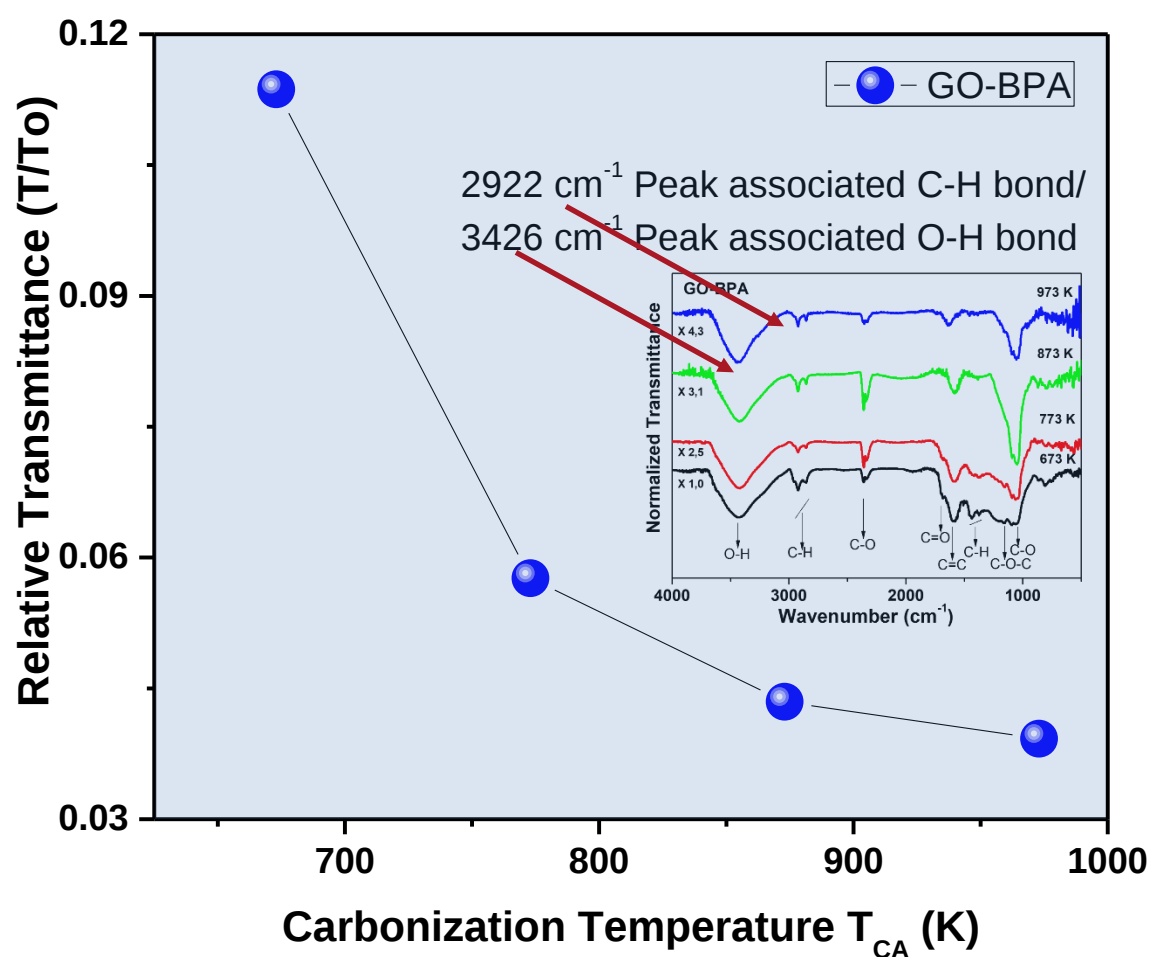


Figure 3.8. T_{CA} dependence on relative transmittance (T/T_o) between C-H and O-H peaks in GO-BPA samples, determined by using FTIR spectra analysis (inset). Inset, FTIR spectra in GO-BPA samples for different T_{CA} .

Given this scientific and technological interest in GO, one of the most common techniques to obtain GO is the oxidation and subsequent exfoliation of graphite, as presented in **Figure 3.1**. However, for large-scale production, this technique has the disadvantages of being time consuming, environmentally toxic, with high corrugation effects, and decomposes between 553 and 573 K, becoming amorphous carbon and losing many of the oxides present in the material. Therefore, we proposed and employed a new, simple, cost-effective pyrolytic method to synthesize GO or graphene oxide multilayers as nanoplatelets, microplatelets, platelets, and thin films synthesized over rigid or flexible

substrates, as presented in [Figure 3.5.](#), by using Colombian bamboo as source [\[4-13\]](#). The GO-BPA samples can be considered a good candidate for large-scale production of GO materials due to its advantages of low time consumption (around 30 h), environmentally not toxic, with low corrugations effects, and it is more thermally stable than GO traditional material because it decomposes at temperatures above 1800 K. For these reasons, this work studied the transport mechanisms in GO-BPA platelets synthesized via DTD method.

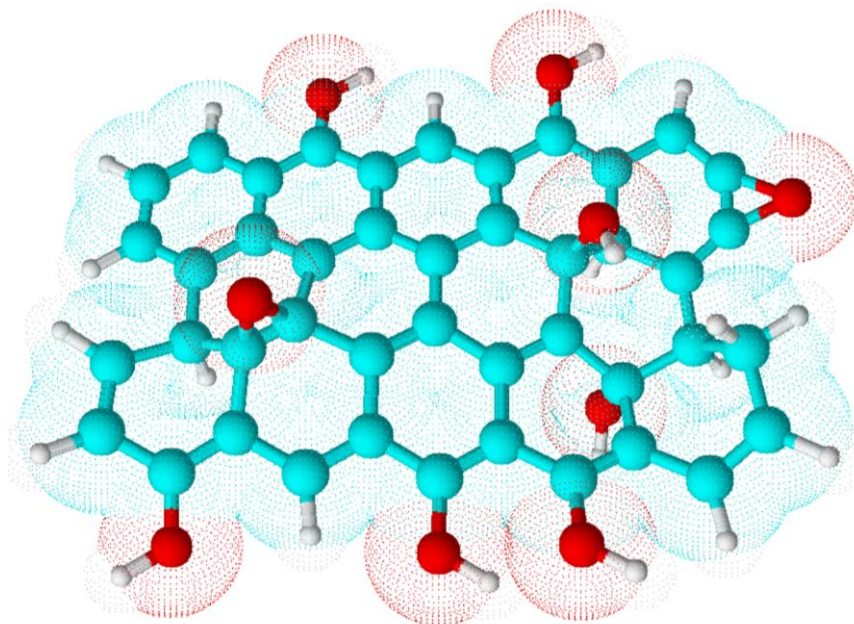


Figure 3.9. Example of the molecular model approach proposed in this work to describe possible graphene oxide layer sheet configurations in single GONP-BPA samples (C-atoms, blue; O-atoms, red; H-Atoms, white) [\[34\]](#).

Synthesis of GO-BPA samples and their basic characteristics were presented here; the following section will discuss basics of the DTD method for sample preparation.

3.1.1 Double-Thermal Decomposition (DTD) Method

The thermal decomposition method is based on desorption of some organic and inorganic substances from biomass by heating at high temperatures (so-called, carbonization temperatures) in controlled atmosphere (this work only used nitrogen atmosphere) until obtaining mainly carbon formations with multifunctional oxides in a pyrolysis system. Pyrolysis is one of the most promising technologies in the conversion of biomass to carbon-based materials, with attractive physicochemical properties for the development of advantageous products [\[20, 35\]](#). Biomass pyrolysis produces gas, bio-oil, coal, and graphite oxide. Thermal decomposition at high temperatures of BPA in controlled nitrogen atmosphere is used to produce coal and by using the double-thermal decomposition technique of bamboo tar, it is possible to obtain GO-BPA samples, as described in section 3.1. The DTD method can be experimentally implemented by employing a pyrolysis system, as shown in [Figure 3.10](#).

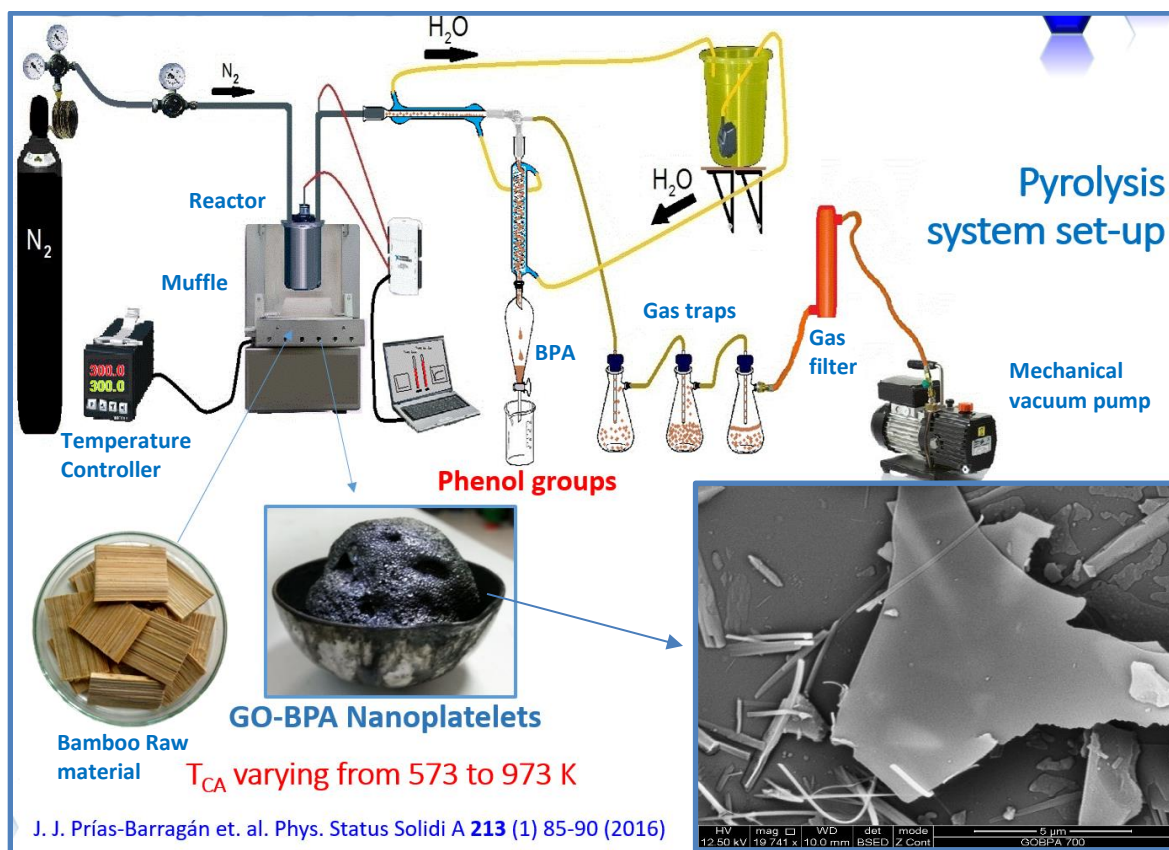


Figure 3.10. Experimental set-up of the DTD method used in this work to synthesize the GO-BPA samples.

The vacuum in the pyrolysis system was established by using a mechanical vacuum pump around 10^{-3} Torr. In a first thermal decomposition process, experimental set-up in **Figure 3.10.**, the pyrolysis process starts when the raw material or biomass is placed into a reactor and by controlling temperature and nitrogen atmosphere, it is possible to obtain the conversion of biomass into carbon, and the bamboo tar is condensed in a decanting funnel glass and non-condensable gases trapped in our own output filter. Thereafter, in a second thermal decomposition process, the bamboo tar returns to the reactor and by controlling T_{CA} and nitrogen atmosphere, finally, the GO-BPA samples are obtained as foam with platelets obtained by using a manual mechanical mortar.

In the DTD method, T_{CA} is an important parameter to control because it modifies the multifunctional oxide present in the GO-BPA samples. For this reason, accuracy in T_{CA} plays a special role. To establish appropriate T_{CA} control, it was necessary to have a furnace muffle design by considering the thermodynamics of the problem and the first principles [36, 37].

Thereby, considering the first thermodynamic law in which the heat generated by the furnace muffle is a thermal energy form, E_{Th} , produced by electrical energy, E_E , then from the energy conservation law, we can obtain:

$$E_{Th} - E_E = 0 \quad (3.1)$$

And in terms of power law, expression (3.1) can be written as:

$$P_{Th} - P_E = 0 \quad (3.2)$$

By choosing parallel plaques technology in the muffle, it is possible to establish that the thermal power in expression (3.2) is given by [38, 39]:

$$P_{Th} = \frac{\Delta T}{R_{Th}} = \frac{T_f - T_{RT}}{R_{Th}} \quad (3.3)$$

Where T_f is the final maximum temperature considered in the pyrolysis system; the criterion used in this parameter was 1073 K. T_{RT} is the room temperature at 300 K. R_{Th} is the total thermal resistance in the muffle and considering each heater wall in the muffle as double layered system composed of CONCRAX refractory material with 1.04 W/mK as thermal conductivity k_1 , and ceramic fiber blanket with thermal conductivity k_2 of 0.28 W/mK and 1" thickness of each layer, then, the thermal resistance is determined by [38]:

$$R_T = R_1 + R_2 = \frac{l_1}{k_1 A} + \frac{l_2}{k_2 A} \quad (3.4)$$

And $A = bh$ is the area of the parallel plaque with b as base and h as height. The electrical power is [38]:

$$P_E = VI = I^2 R_E = \frac{V^2}{R_E} \quad (3.5)$$

Here, V is the electrical applied voltage in wire heater, I is the electrical current, and R_E is the electrical resistance of the muffle. Similar to expression 3.4, at 293 K (20 °C) the electrical resistance is [38]:

$$R_{E(293\text{ K})} = \frac{\rho_{293\text{ K}} L}{A} \quad (3.6)$$

Where $\rho_{293\text{ K}} = 2.89 \times 10^{-6} \Omega/\text{m}$ is the electrical resistivity at room temperature. L is the length of the wire, and $A = \frac{\pi d^2}{4}$ is the area of the wire with d as diameter. The electrical resistance at working temperature of 1473 K (200 °C) is:

$$R_{E(1473\text{ K})} = C_{1473\text{ K}} R_{E(293\text{ K})} \quad (3.7)$$

With $C_{1473\text{ K}} = 1.04$ as the resistivity coefficient [37, 40]. Then, the length, L , of the quantitative material used as nickel-chrome heater (each heater) is determined by:

$$L = \frac{R_E}{R_{E(1473\text{ K})}} \quad (3.8)$$

Knowing that the thermal resistance is given by expression (3.4), it is possible to calculate thermal power by considering expression (3.3) and determine the electrical power required by using expression (3.2). Now, by using expression (3.5), it is possible to calculate electrical resistance for each heater and by considering expression (3.8), it was possible to determine the length of each heater.

Table 3.2. presents the technical electrical characteristics of the DTD method used in this work to synthesize the GO-BPA samples.

Table 3.2. Characteristics of the DTD method.

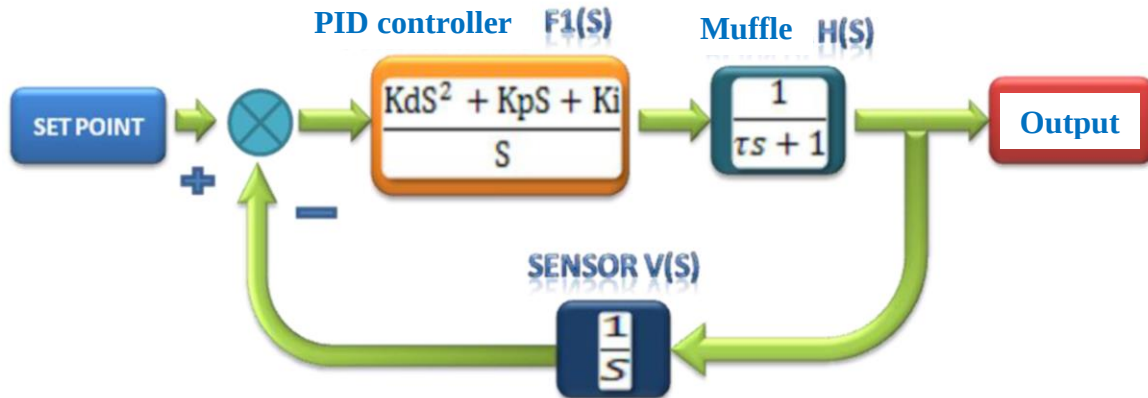
Technical characteristic	Value
Voltage supply (V)	220 V
Electrical resistance of heater (R_E)	16 Ω
Electrical current (I)	13.75 A
Operation power (P_E)	3 KW
Muffle dimensions	35 cm x 35 cm x 50 cm
Maximum operation temperature	1073 K

The dynamics analysis of the pyrolysis system presented in **Figure 3.10.** can be modeled by using the closed-loop system, shown in **Figure 3.11.** The transfer functions of the controller, muffle, and temperature sensor of a nickel-chrome k-type thermocouple used in this work.

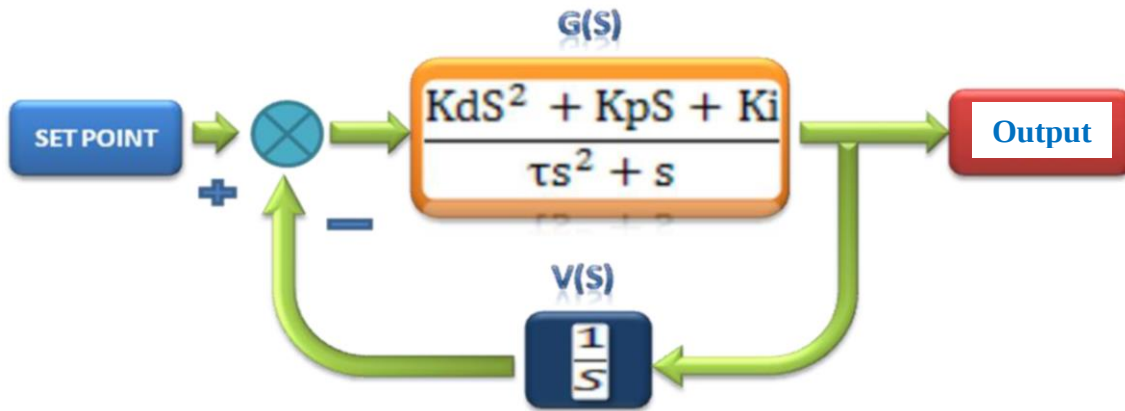
The experimental temperature evolution in the muffle is presented in **Figure 3.12.** It is possible to observe that increased time increases the muffle internal temperature from room temperature to stationary state or set point at 673 K of T_{CA} , as the first-order system observed in **Figure 3.11.**

Therefore, the parameters of the temperature controller were determined by considering the muffle furnace as a first-order thermal system in the transfer function of the muffle, as presented in **Figure 3.10.**

(a)



(b)



(c)

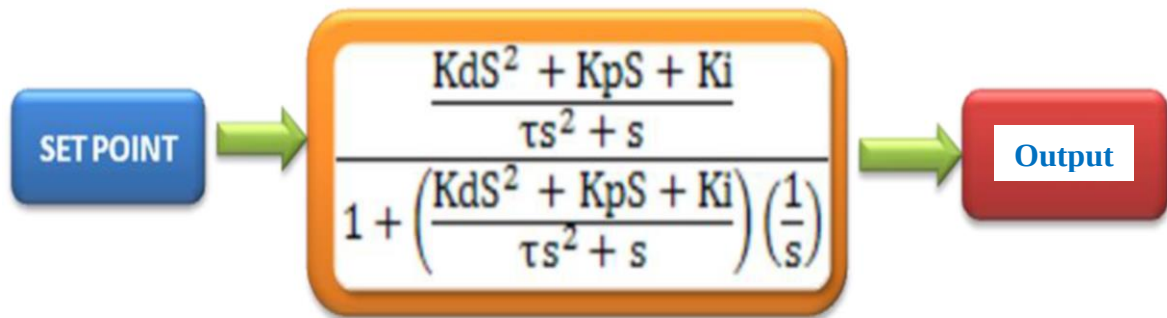


Figure 3.11. Closed-loop dynamic pyrolysis system used to obtain theoretical temperature evolution in the DTD method. (a) Laplace transfer functions of PID controller, muffle, and thermocouple. (b) Transfer function solved of PID controller and muffle. (c) Total transfer function. Taken and adapted from reference [40].

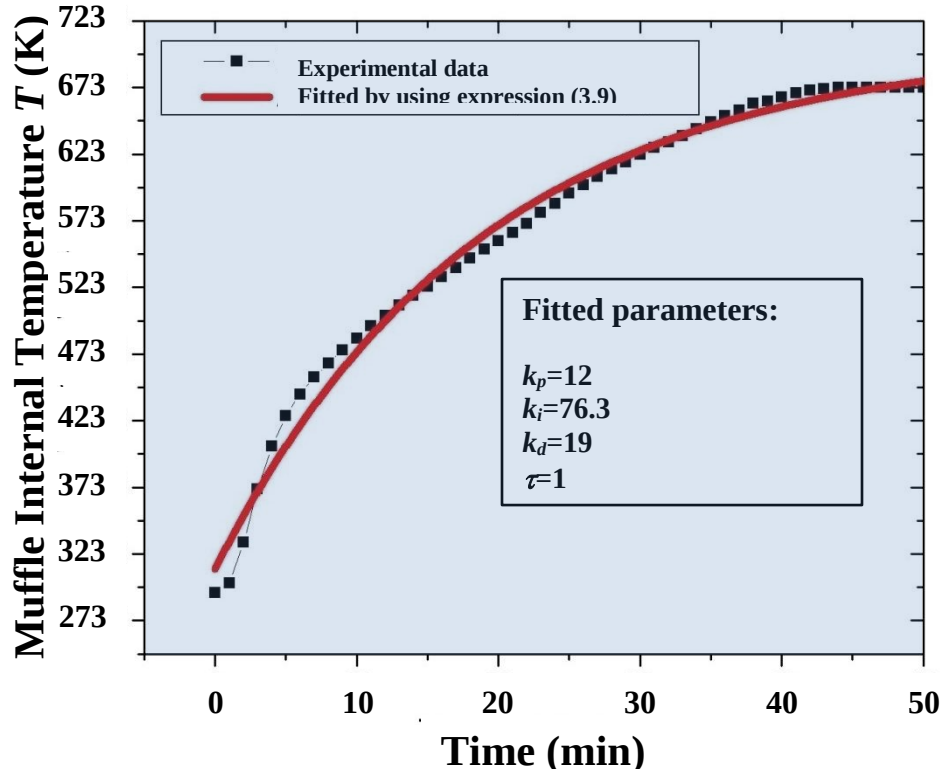


Figure 3.12. Evolution of the muffle internal temperature in the DTD method developed in this work. Black squares are the experimental data and the red curve is the theoretical fit by using expression (3.9). Taken and adapted from reference [40].

By determining the total transfer function, as presented in [Figure 3.11.](#), and obtaining the Laplace inverse in time domain, it was possible to describe theoretically the temperature evolution in the muffle as:

$$T(t) = \left[\left(\left(\frac{k_d}{\tau} - k_p + k_i \tau \right) (12 \times 10^{-3} T_{SP}) - T_{RT} \right) \left(1 - \exp \left(-\frac{t}{\tau} \right) \right) + \left((k_p - k_i \tau) + k_i \right) (83.3 \times 10^{-3} T_{RT}) \right] \mu(t) \quad (3.9)$$

Here, k_p , k_i , k_d are the proportional, integral, and derivative constants of the PID controller, respectively, and τ is the characteristic time of the system related with the thermal resistance and capacity of the thermal pyrolysis system. T_{SP} and T_{RT} are the set point temperature or T_{CA} and room temperature, respectively. $\mu(t) = 1$ is associated to the temperature measurement system.

In expression (3.9), when the time is very big $T(t)$ tends to T_{SP} , called steady-state and agrees with T_{CA} , then, expression (3.9) can be written as:

$$T(t) = T_{SP}\mu(t) = T_{CA} \quad (3.10)$$

Expression (3.10) demonstrates that in steady-state it was possible to control T_{CA} as set point temperature with a precision under 10% and a characteristic time of 1 s. **Figure 3.13.** shows the DTD -method developed in this work to synthesize GO-BPA samples and implemented in the Organic Lab at the Interdisciplinary Institute of Sciences in Universidad del Quindío, Colombia.

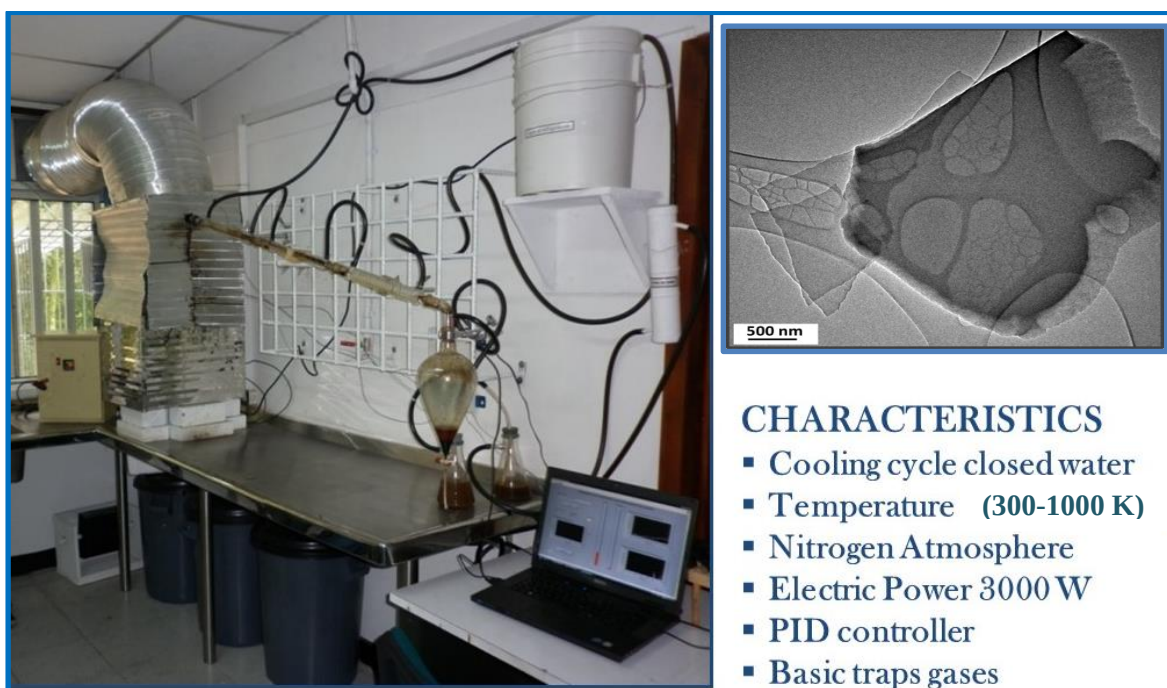
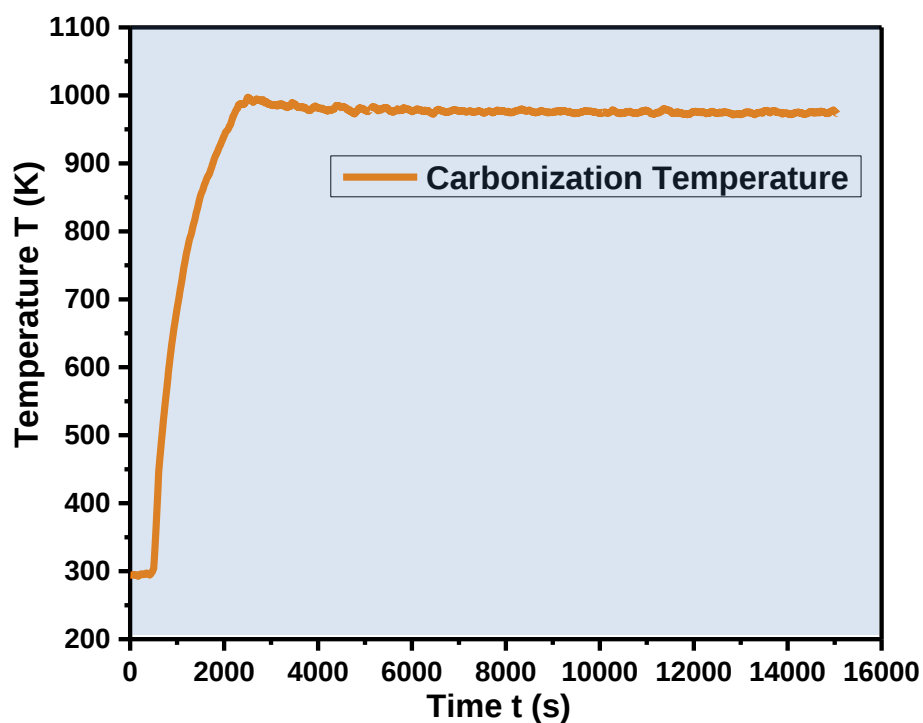


Figure 3.13. DTD method proposed and implemented in this work. Characteristics and SEM image of the GO-BPA nanoplatelets. Located at the Interdisciplinary Institute of Sciences in Universidad del Quindío, Colombia.

By using the precise PID temperature control of the T_{CA} in the DTD method, it was possible to measure the output temperature evolution in the pyrolysis system during carbonization process, as shown in **Figure 3.14.** Note that increased time increases temperature in the reactor from room temperature to T_{CA} in steady state, as presented in **Figure 3.14. (a).**

Figure 3.14. (b) shows the desorption process of water (H_2O) at 370 K in 1000 s, bamboo pyroligneous acid (BPA) at 403 K in 1300 s, and non-condensable gases at 333 K from 3000 to 6000 s, during the bamboo to carbon conversion time. This behavior can be explained by thermal decomposition effects. The water and BPA are condensed and stored in a decanting funnel glass. The non-condensable gases are trapped in basic gas traps and gas filter, as presented in **Figure 3.10.**

(a)



(b)

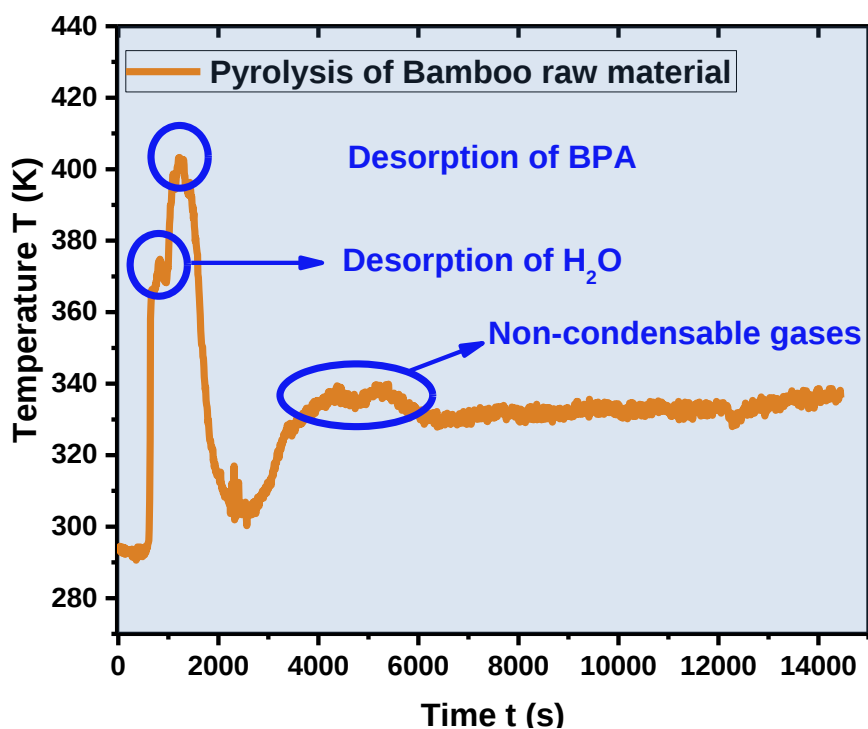


Figure 3.14. Temperature evolution in bamboo raw material (first step) by using the DTD method at $T_{CA} = 973$ K, during 3.5 h: (a) Inside reactor, and (b) output of the reactor in the first step of the thermal decomposition of bamboo as raw material.

The GO-BPA samples studied in this work were synthesized by using the DTD method, considering all these basics presented until here. The characterization techniques used to identify the main transport mechanism of GO-BPA samples will be discussed ahead.

3.2 DFT Computational simulations

Density functional theory (DFT) is a computational method of quantum mechanical modeling used in physics, chemistry, and materials science to investigate the electronic structure (mainly the ground state) of many body systems, particularly atoms, molecules, and condensed phases. By using this theory, the properties of a system of many electrons can be determined by a functional, which in this case is the electron density dependent on space. Hence, the functional theory of the density of names comes from using functional electron density. The DFT is one of the most popular and versatile methods available in condensed matter physics, computational physics, and computational chemistry.

This investigation used DFT computational simulations to: (1) obtain an approximation of the molecular configuration model of our GO-BPA samples; (2) determine the dependence of the energy band gap values on oxygen coverage; and (3) visualize the surface charge density by varying the oxygen coverage. The molecular model was obtained by using ACDLabs freeware 2015 software with 3D Viewer, ChemBasic and ChemSketch tools, in a Pentium V processor. All the surface charge screening density and the sigma-profile were predicted by using the implicit solvation COSMO method, a thermodynamic model based on quantum chemistry calculations.

The 3D structures of the GO structures considered in this study were built by using HyperChemProfessional 7, which calculates the most stable conformational structures under the force field method. The raw 3D structure was exported as .xyz file format to Tmolex and its molecular optimization by TURBOMOLE 6.3 quantum chemical program package by using high quality quantum chemical ab-initio electronic structure optimization on the BP-TSVP-COSMO quantum basis to create the COSMO file. Subsequently, its COSMO file was used as input in COSMOtherm13 statistical thermodynamic code to calculate the specific density and volume of the chemical species studied at 298 K.

According to our chosen quantum method, the functional and the basis set, we used the corresponding parameterization BP-TZVP-C21-1010 required to calculate physicochemical data and which contains intrinsic parameters of COSMOtherm13, as well as element-specific parameters.

This ends the description of the experimental methods used in this research; chapter 4 will show the results of the transport mechanisms in the GO-BPA samples identified after the experimental methods presented in this chapter.

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Chapter 4

4. Experimental Results

This section summarizes the key experimental results on the synthesis, basic properties, identification of main transport mechanisms, physical correlations, and discussion of future applications in electronics of GO-BPA samples. Section 4.1 presents the basic results of the synthesis, morphological, structural, and elemental properties exhibited by the GO-BPA samples. The identification of the main transport mechanisms in GO-BPA samples is presented in section 4.2. Some possible physical correlations among the results are presented in section 4.3. Additionally, the discussion of the future application in electronics of the main transport mechanisms shown by the GO-BPA samples will be presented in section 4.4.

This work benefits from experience gained in sample preparation to focus on the investigation of the transport mechanisms present in the GO-BPA samples as nanoplatelets, which is still an open field. This study was conducted as a function of T_{CA} as a main independent variable established through the DTD method, oxide coverage measured via XPS, carbon atoms out-plane calculated from XRD results analysis, and density defects and crystal size determined from Raman results analysis. The studies presented in this chapter are important to understand the influence of the disorder, defects, and impurities on the transport mechanisms of GO-BPA samples as nanoplatelets.

One of the most common techniques to obtain graphene is the oxidization and subsequent exfoliation of graphite (chapters 2 and 3). However, for large-scale production, this technique has the disadvantages of being time consuming and environmentally toxic. In this investigation, we proposed and employed a new, simple, cost-effective pyrolytic method to synthesize graphite oxide (GO) nanoplatelets by using bamboo pyrolygneous acid (BPA) as source material (chapter 3 section 3.1). The morphological, structural, elemental, vibrational, electrical, and magnetic properties in GO-BPA samples were studied, finding an alternative way to obtain graphene oxide multilayers with high stability and reproducibility in their transport properties. High-resolution transmission electron microscopy (HRTM) and EELS have provided a complete structural and chemical description at the local scale in GO-BPA samples. In particular, we found that at the highest T_{CA} (973 K), the single GO-BPA nanoplatelet is mainly in sp^2 bonding configuration (87% sp^2 fraction), as presented in section 4.1.

From vibrational characterization analysis in GO-BPA samples by using Raman and FTIR spectroscopies (chapter 3), we identified that the possible main thermal transport mechanisms in GO-BPA samples are: first, at room temperature, it is possibly attributed to the phonon-phonon interaction, and second, at low temperature, it can be associated to the phonon-disorder interaction induced by defects and impurities, as multifunctional oxides present (chapter 2). To determine the electrical properties of single nanoplatelets, these were

contacted by using Pt nanowires deposited through focused-ion-beam-induced deposition techniques (chapter 3). Increased conductivity by two orders of magnitude was observed as oxygen content decreased from 17% to 5%, reaching a value of 2.3×10^3 S/m at the lowest oxygen content.

Temperature dependence on electrical conductivity showed typical semiconductor behavior. Band-gap energy estimations showed variation from 0.30 to 0.11 eV by decreasing oxygen content. At room temperature, the main electrical transport mechanism can be due to charge carrier-impurity interaction and at low temperatures it is possibly described by 3D-VRH (chapter 2), as presented in section 4.2 of this chapter.

Furthermore, this chapter presents the experimental results concerning magnetic characterization, finding that the FM order induced by defects was observed at room temperature, as presented in section 4.2, and re-entrant magnetoresistance was exhibited by the GO-BPA samples for temperatures from 100 to 400 K, which can be attributed to changes in the type of electric charge carrier majority, possibly induced by a compromise between thermal and internal magnetic energies, as presented in section 4.3.

These results confirm that GO-BPA samples behave structurally, thermally, electrically, and magnetically similar to the reduced graphene oxide (RGO) sheets obtained through more sophisticated synthesis methods and suggests potential uses of these samples in some possible electronic applications, as discussed in section 4.4 of this chapter.

Moreover, these GO-BPA samples offer future opportunities to obtain 2D materials, like graphene oxide by using an environmentally sustainable and commercially feasible synthesis method from renewable natural resources, as proposed by our group in the references from annex 2.

4.1 GO-BPA Samples as Nanoplatelets: Synthesis, Morphological, Structural, and Elemental Properties

The GO-BPA samples were synthesized by DTD method at different T_{CA} and their morphological, structural, and elemental properties were studied by using the HR-TEM, TEM, ED, SEM, AFM, XRD, EELS, XPS, EDS, RS, FTIR spectroscopy, I-V curves, MFM, and VSM techniques, respectively, considering experimental aspects presented in chapter 3.

Synthesis of GO-BPA samples. Figure 4.1. presents the GO-BPA samples as foam, which is a preliminary step to obtain nanoplatelets. It was observed that increased T_{CA} and the digital images of the samples show blue shift color; this observation is an important macroscopic experimental evidence of the thermal decomposition effect in the physical properties of the samples. When T_{CA} increases, it can produce desorption of some organic compounds and oxides that increase internal defects in the material. Additionally, these macroscopic observations revealed possible effects of the T_{CA} in morphological, structural, and elemental properties of GO-BPA.

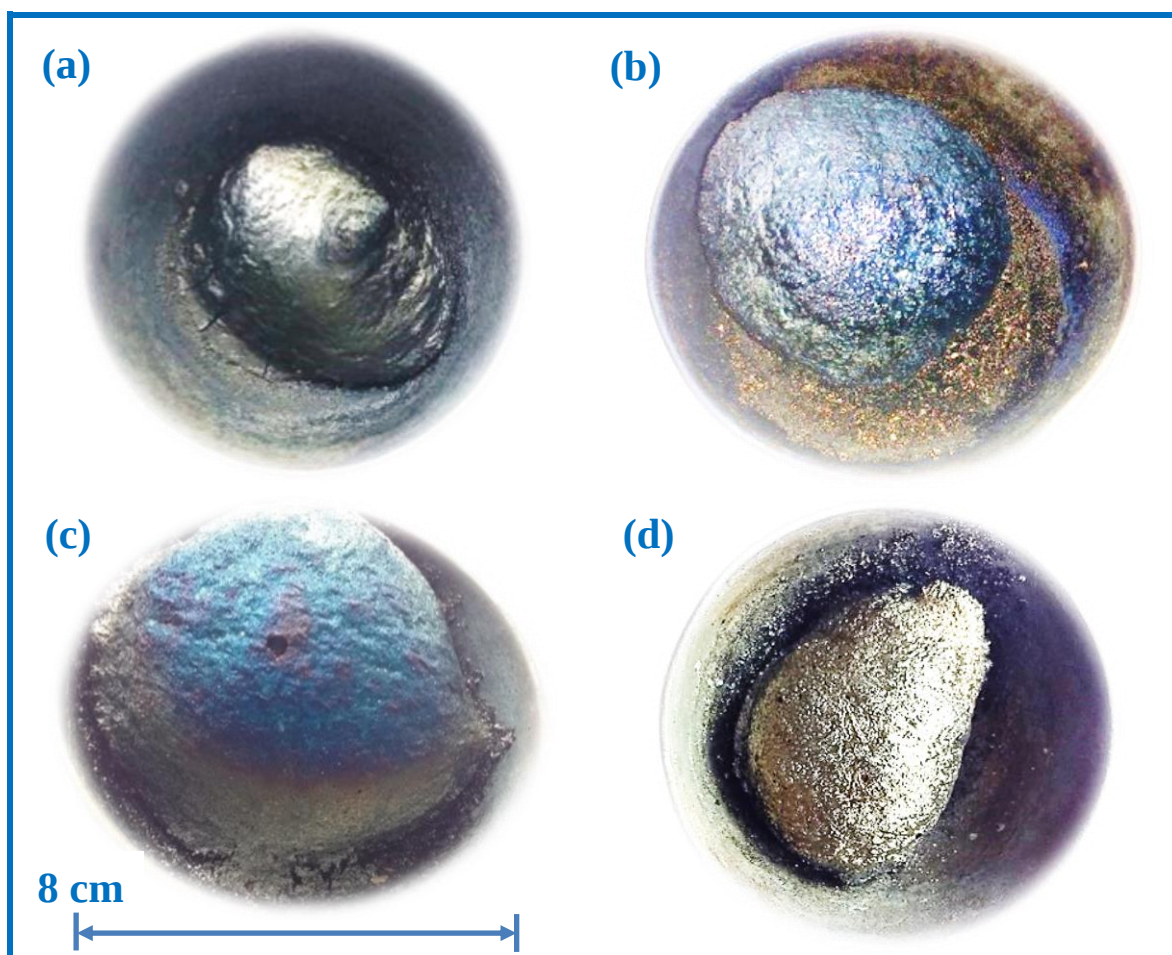


Figure 4.1. Digital images of GO-BPA samples as foam synthesized by DTD method, for different T_{CA} : (a) 673 K, (b) 773 K, (c) 873 K, and (d) 973 K. Showing blue-shift color by the effect of the thermal decomposition of BPA.

Morphological Properties of GO-BPA Samples. Figures 4.2. (a) and (b) show TEM micrographs of the samples prepared with the highest (973 K) and lowest T_{CA} (673 K), respectively, both taken at 2 μm scale in GO-BPA samples and revealed that the samples have graphitic plaque-type formations and irregular geometry, as expected [1, 2]. Thin nanoplatelets are clearly visible on the TEM carbon membrane. Nanoplatelet size is typically in the order of a dozen micrometers, then, the lateral size is typically in the order of 5-100 μm and presents a thickness <100 nm, as estimated from low-loss EELS spectra, typically ranging between 25 and 60 nm and agreeing with SEM measurements. Figures 4.2. (c) and (d) illustrate two HR-TEM micrographs of the samples prepared with T_{CA} of 973 and 673 K, respectively. The presence of disordered graphitic clusters is clearly highlighted (orange arrows in Figure 4.2 (c)) for the sample prepared at T_{CA} of 973 K, while the micrograph of the sample prepared at T_{CA} of 673 K is more characteristic of disordered materials. Interlayer d-spacing measured through analysis of HR-TEM images, by using Fiji-64 bit software, yields the average value of 0.34 nm that agrees with our values ranging from 0.3355 to 0.3496 nm, measured via XRD technique in this work (Table 4.1).

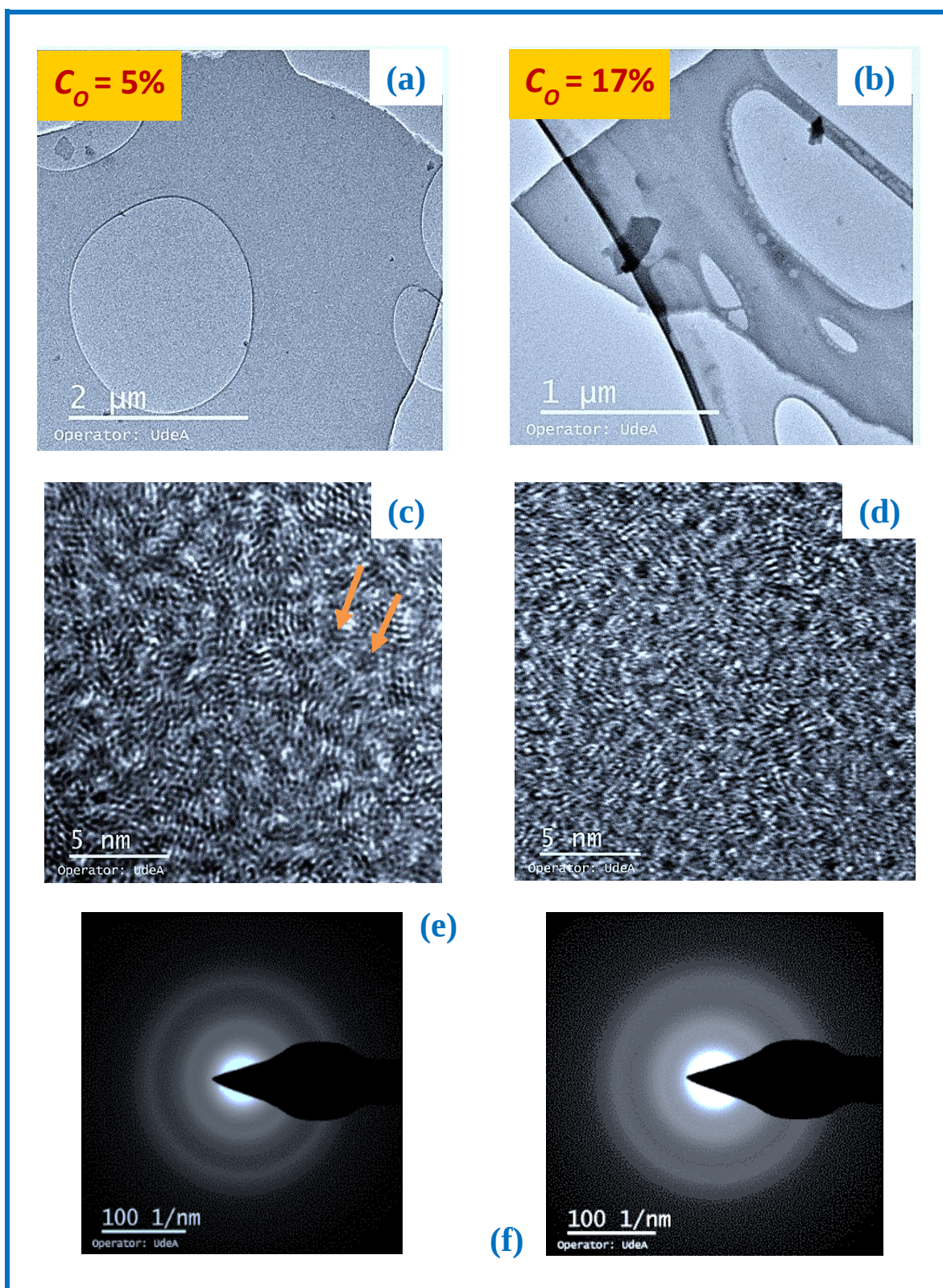


Figure 4.2. TEM, HR-TEM, and ED images in GO-BPA samples as nanoplatelets synthesized through DTD method, for different oxygen coverage C_o : (a), (c) and (e) at $C_o = 5\%$, respectively. (b), (d) and (f) at $C_o = 17\%$, respectively.

Figure 4.2. (e) and (f) present ED results in GO-BPA nanoplatelets at 5% and 17%, respectively, and shown diffused rings characteristic of disordered polycrystalline material described in **Figure 3.21. (c)**.

The random attachments of the oxygen functional groups on the top and bottom surfaces of GO-BPA monolayers play a crucial role in determining the stacking order because these: (1) break the symmetry of the subjacent honeycomb carbon lattice; (2) introduce a slight roughness (or corrugation effect), which is originated from carbon atoms out-of-plane lattice distortions of the C–O bonds and defects; and, (3) increase the XRD-interlayer d-spacing, as presented in **Table 4.1.** (with exceptional behavior of the GO-BPA sample at 973 K that exhibits more XRD-crystalline peaks than the other samples) and confirms increased interlayer spacing with increasing oxygen content.

Due to the higher interlayer spacing, individual layers show rotational and tilt disorder relative to their neighbors and, thus, no preferred stacking orientation and produce stacking disorder. Nevertheless, it is worth mentioning that diffracted rings are better defined for the sample prepared at T_{CA} of 973 K and, thus, confirm the higher local order of this sample.

The thickness values of the GO-BPA nanoplatelets were corroborated via SEM, therefore, **Figure 4.3.** displays the SEM image of GO-BPA nanoplatelets synthesized at 773 K T_{CA} at working distance of 9.9 mm. The superposition of different nanoplatelets is observed with thickness measurements varying from 65.51 to 92.65 nm; these values agree with the thickness values <100 nm and measured by using the EELS and TEM techniques, as expected through nano-object criteria of nanoplatelets reported by the ISO technical specification [3].

Considering these GO-BPA nanoplatelets as multilayered material, with thicknesses <100 nm, as mentioned, and the XRD-interlayer d-spacing from 0.3367 to 0.3496 nm, as presented in **Table 4.1.**, the maximum and minimum number of layers are 298 and 287 layers for each nanoplatelet obtained at T_{CA} of 773 and 973 K, respectively. Therefore, GO-BPA samples exhibit morphological behavior with nanoplatelet geometric dimensions.

Structural Properties of GO-BPA Samples. **Figure 4.4.** shows the XRD pattern of analytical grade graphite as reference. This pattern exhibits four characteristic peaks in (002), (100), (101), (004) directions at 26.58°, 43.34°, 44.48°, and 54.43° diffraction angles, respectively, revealing crystal broadening, as expected, and agreeing with the same directions at values of 26.472°, 42.342°, 44.474°, and 54.602° reported by Li Hui *et al.*, [4]. The small differences among these values, can be attributed experimentally to stacking disorder and imperfections of graphite, as also demonstrated by Li Hui *et al.*, [4].

The (002) direction via 2θ diffraction angle is related with interlayer d-spacing $d_{(002)}$, the nano-crystallite thickness D_{002} , and the layer number N by considering expressions (3.11), (3.12), and (3.13), respectively, observed in the inset of **Figure 4.4.** The other peaks offer information about the carbon-carbon atom lengths in the sample, but, this investigation only presents results of the XRD analysis at 002 direction because all samples exhibit crystalline broadening in this direction.

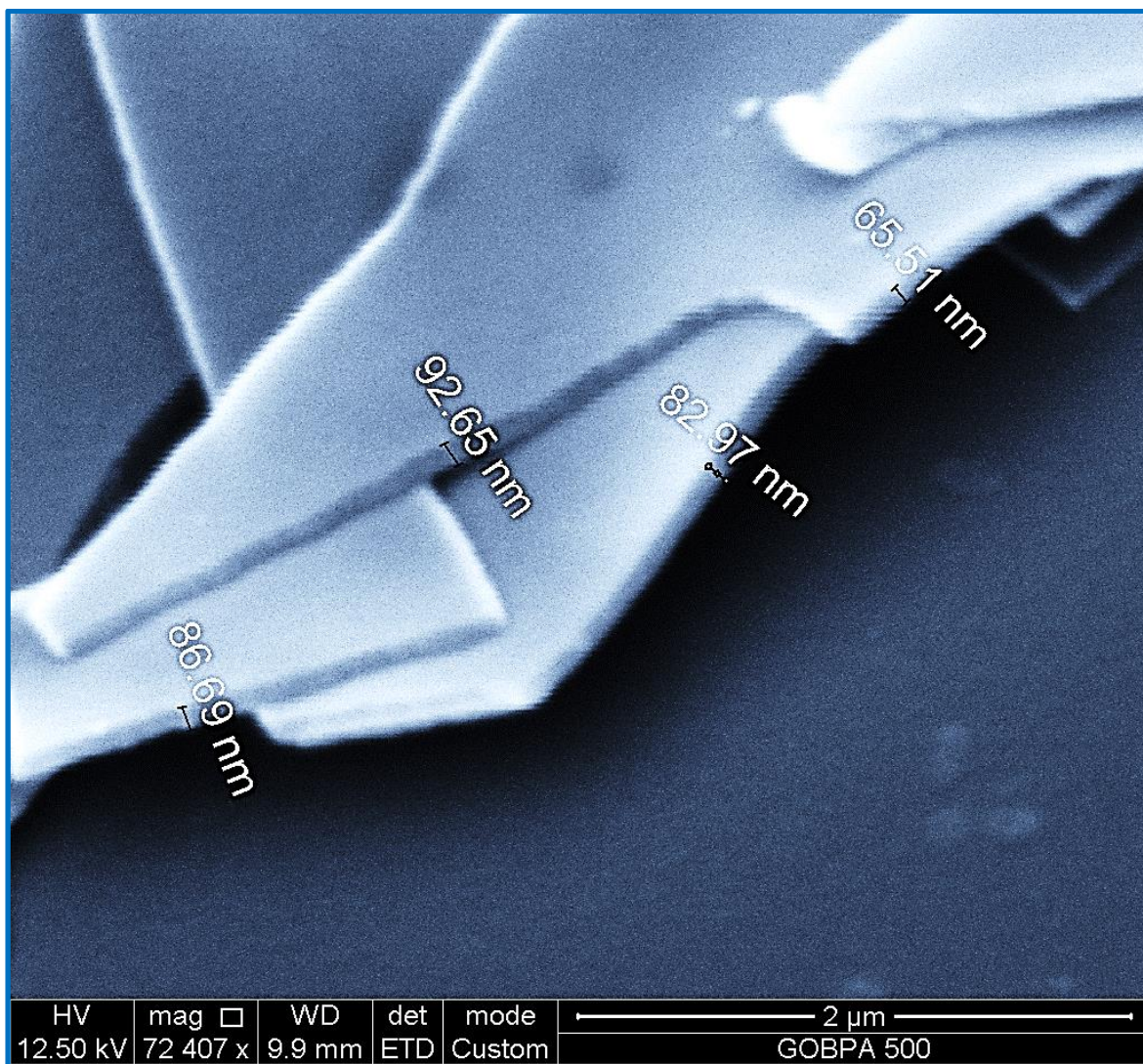


Figure 4.3. SEM image in GO-BPA nanoplatelets synthesized at $T_{CA} = 773$ K by DTD method and their thickness measurements.

Figure 4.5. presents the consolidated XRD patterns of Graphite and GO-BPA samples synthesized at different T_{CA} , observing in the GO-BPA samples the characteristic peaks of hexagonal Graphite in the (002), (100), (101), and (004) directions. Increased XRD intensity at low diffraction angles can be associated to fluorescence contribution by the presence of multifunctional oxides, organic compounds, and defects. Then, increased T_{CA} decreased XPS-oxide coverage, and increased Raman-defect density, as presented in [Table 4.1](#). X-ray diffraction patterns are shown in [Figure 4.5](#).

It was found that the GO-BPA samples exhibit polycrystalline structural behavior through the presence of multifunctional oxides, organic compounds, and defects, as well as hexagonal graphite as two phases. These results agree with the XRD patterns expected for different GO materials [5-9]. As reported by Ch. N. Barnakov *et al.*, [10], from the analysis of the crystalline 002 peak in all samples studied in this work, it was possible to obtain

information about the layer packing density and the degree of graphitization of the samples by considering the following: layer packing density or XRD density, ρ , can be determined by using the relation given by [10]:

$$\rho = \frac{0.762(\text{g}/\text{cm}^3)}{d_{002}} \quad (4.1)$$

Also, the degree of graphitization can be determined by [4, 10]:

$$Y = \frac{3.440 \text{ \AA} - d_{002} (\text{\AA})}{3.440 \text{ \AA} - 3.354 \text{ \AA}} \times 100 \% \quad (4.2)$$

Where 3.440 Å is a value related with the interplanar d-spacing associated to the carbon structure with a higher stacking disorder, and 3.354 Å is related with the interplanar d-spacing of the hexagonal graphite structure.

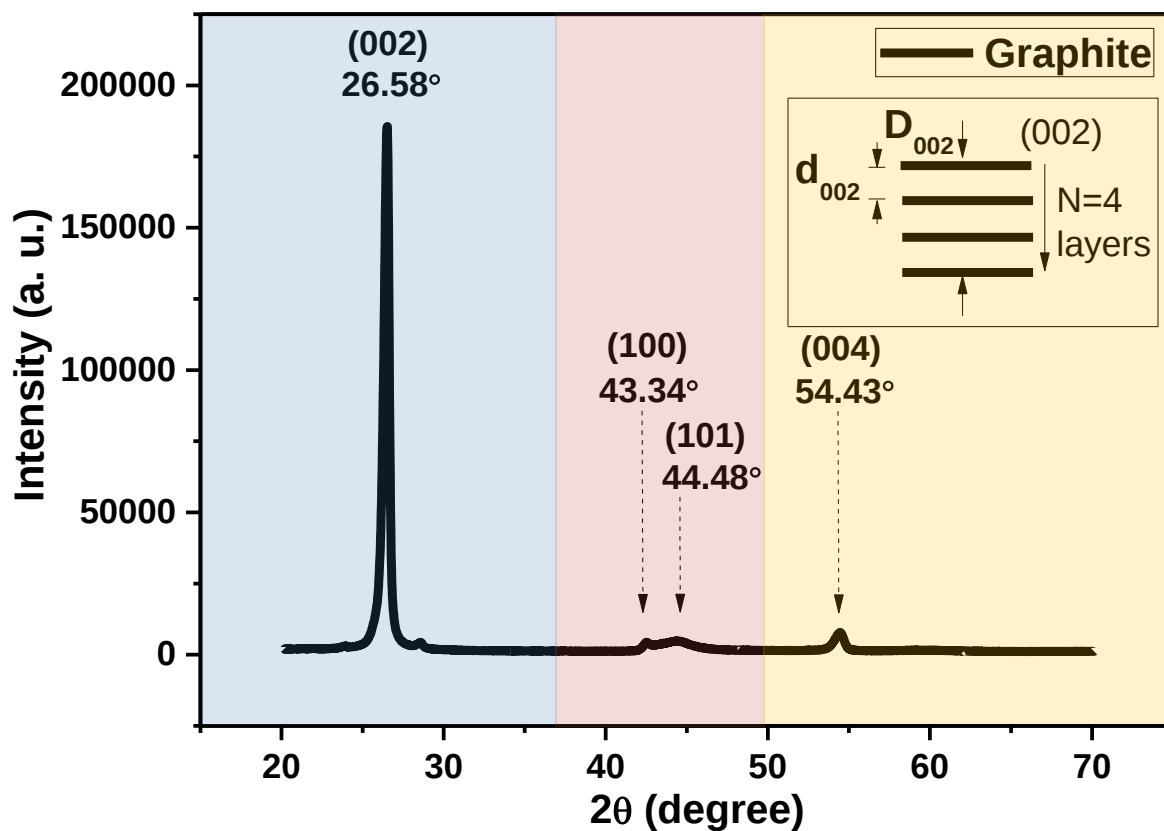


Figure 4.4. XRD patterns of the analytical-grade graphite sample taken as reference in this investigation. Elemental analysis by using SEM-EDS revealed as at %: Carbon and Oxygen atoms of 98.54% and 1.46%, respectively. Inset: schematic representation of the graphite structure in 002 direction, showing d_{002} as the d-spacing, D_{002} as the nano-crystallite thickness, and N as the number of layers.

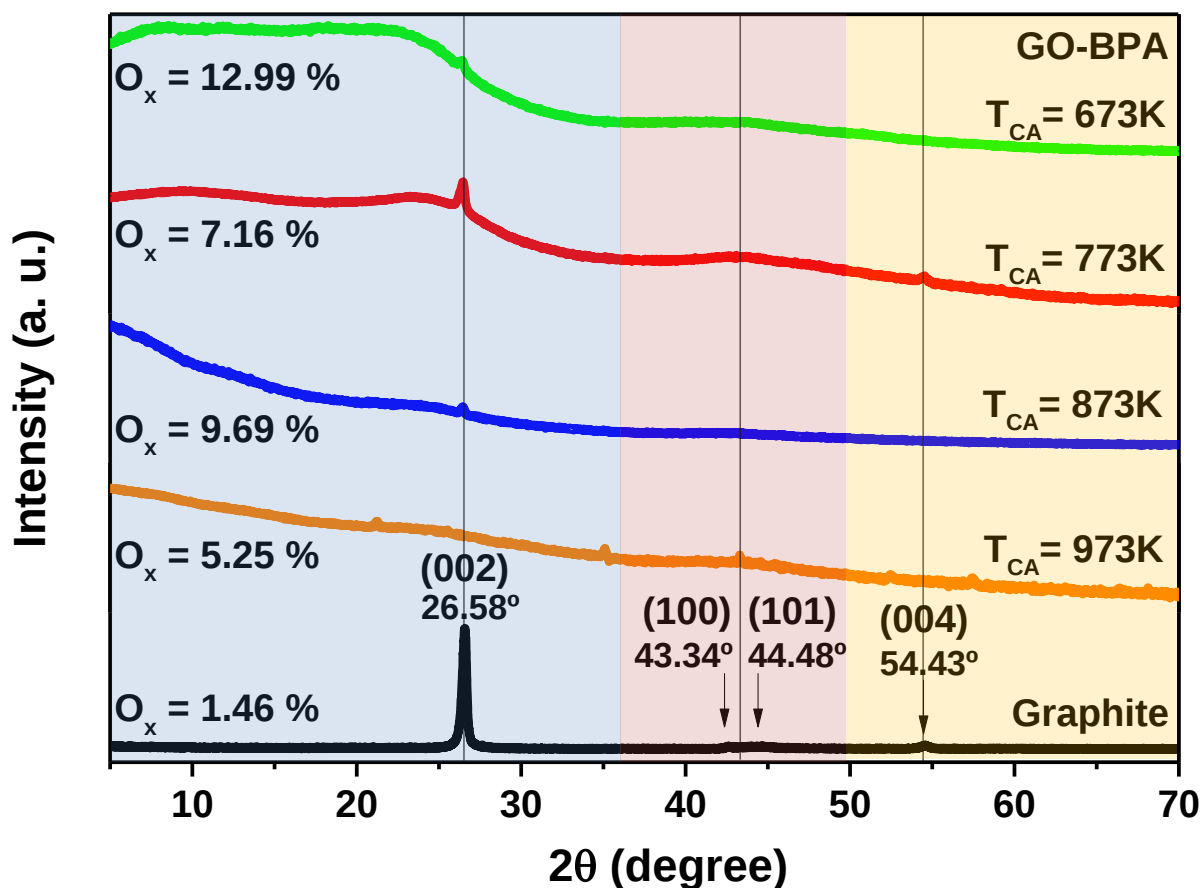


Figure 4.5. XRD patterns in GO-BPA samples synthesized via DTD method for different T_{CA} . Graphite XRD pattern taken as reference.

Expressions (3.11), (3.12), (3.13), (4.1), and (4.2) were required to describe structural properties in the crystalline 002 peak of the samples studied. Therefore, this work proposed that the theoretical analysis of the XRD pattern in the 002 direction can be described by using the convolution of two Gaussian functions as crystalline broadening contributions, associated to the random distribution to the multifunctional oxide present (at low diffraction angle values) and defects (at high diffraction angle values), which produce different interlayer d-spacing by both mechanisms, according to the schematic XRD model interpretation discussed in chapter 3, and reported by Seung Hun Huh [6]; also assuming that d_{002} in defects, d_{Df} , and multifunctional oxides, d_{Ox} , correspond to $d_{Df} < d_{Ox} < d_{Graphite}$ criteria.

The Gaussian line-shape distributions were considered in this investigation, assuming that XRD diffraction at the 002 direction in the samples is dominated by oxides and defects presence distributed randomly as independent processes (Figures 4.2. (c) and (d)) and present the best theoretical description of the experimental data with regression constants of 0.97023, 0.99713, 0.97453, 0.96499, and 0.99713 in the GO-BPA samples synthesized at 673, 773, 873, 973 K and graphite sample, respectively.

Figure 4.6. shows the XRD pattern analysis in the 002 direction in graphite and GO-BPA samples (black solid line) with the respective theoretical fit by using the convolution of two Gaussian contributions (red solid line) and by using the linear subtraction of the fluorescent XRD background produced by organic compounds present in the samples. This criteria is valid because the narrow broadenings of the 002 peaks take a value one order of magnitude less than the order of magnitude-range of the diffraction angles of each XRD pattern in the 002 direction and, therefore, this contribution can be considered negligible. It was observed that the theoretical fit proposed in this work agrees well with the experimental data as expected.

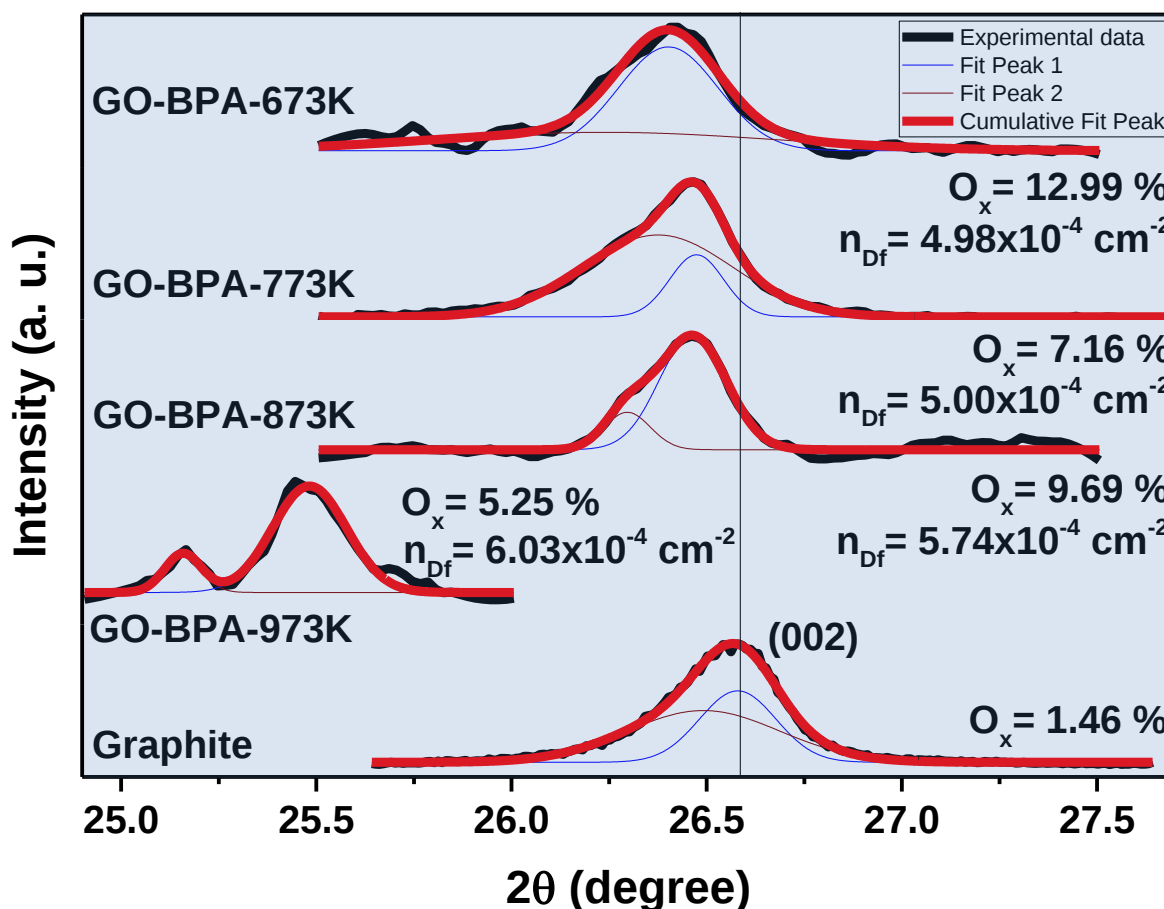


Figure 4.6. Analysis of XRD patterns in the (002) peak in GO-BPA samples at different T_{CA} and analytical-grade graphite as reference. The experimental data were fitted by using two Gaussian distributions due to the presence of many independent processes, possibly associated to random defect (peak 1) and multifunctional oxide (peak 2) distributions in the samples, according to the model introduced in chapter 3 section 3.2.2. **Figure 3.20.**, and assuming that d_{002} in defects, d_{Df} , and multifunctional oxides, d_{Ox} , correspond to $d_{Df} < d_{Ox} < d_{Graphite}$ criteria.

It was found that the XRD patterns of GO-BPA samples in the 002 direction exhibit systematic shifts towards low diffraction angle values, as oxide concentration increases and

defect density decreases. In addition, it was observed that the XRD pattern of the GO-BPA-973 sample undergoes the maximum shift in the diffraction angle values compared with the graphite XRD pattern; this behavior can be attributed to stacking disorder by increasing density of defects, as reported by Li Hui *et al.*, [4].

The consolidated values calculated from the analysis of the XRD pattern shown in **Figure 4.6.** are listed in **Tables 4.1.** and **4.2.** from each contribution and peak 1 and peak 2 associated to contributions of the XRD peaks due to presence of defects and multifunctional oxides, respectively. Without considering the results of the GO-BPA sample synthesized at 973 K, given that it exhibits more crystalline peaks behavior, it was observed that increased T_{CA} increases diffraction angle (2θ), graphitization phase (Y), and density of Raman-defects (η_{Df}). Increased oxide coverage (O_x) and increased interlayer d-spacing (d_{002}), and the nano-crystallite thickness (D_{002}) as expected [5]. It was found that XRD density (ρ) is independent of the T_{CA} and these values agree with our values obtained through EELS technique.

Table 4.1. Consolidated of results obtained from XRD patterns analysis by fitting the (002) peak 1 using Gaussian distribution in GO-BPA samples obtained at different T_{CA} and graphite as reference*.

GO-BPA T_{CA} (K)	(002) peak 1								
	2θ (°)	FWHM (°)	$d_{(002)1}$ (Å)	D_{002} (Å)	N	P (g/cm ³)	Y (%)	O_x (%)	η_{Df} $\times 10^{-4}$ (cm ⁻²)
673	26.402	0.300	3.376	4.692	2	2.26	74.41	12.99	4.98
773	26.474	0.162	3.367	8.680	4	2.26	84.88	7.16	5.00
873	26.464	0.204	3.368	6.924	3	2.26	83.72	9.69	5.74
973	25.482	0.223	3.496	6.304	3	2.18	65.12	5.25	6.03
Graphite	26.579	0.230	3.354	6.125	3	2.27	100	1.46	---

* 2θ is the diffraction angle in the 002 position; **FWHM** is the Full Width at Half Maximum; d_{002} is the d-spacing interlayer distance; D_{002} is the nano-crystallite thickness; **N** is the number of layers; ρ is the XRD density; **Y** is the graphitization degree; O_x is the oxygen coverage measured by using XPS technique; η_{Df} is the defects density determined by using Raman results analysis. For more details, see **Figure 4.16.**

Figure 4.7. shows a comparison between the XRD patterns in the graphite sample as reference and the GO-BPA sample synthesized at 973 K as T_{CA} . The hexagonal graphite shifting peaks at low diffraction angles in the 002, 100, 004, and 103 directions were observed and calculated from the first principle by using the structure factor (red arrows) [11] and attributed to variations in the average length of carbon-carbon atoms with a value of 2.461 Å, greater than the value of 2.456 Å for graphite. This behavior can be attributed to the

presence of high Raman-density defects and the presence of high stacking disorder, according to the low value of $Y = 65.12\%$ (**Table 4.1.**), as reported by Li Hui *et al.*, [4].

The other peaks at 21.22° and 31.17° were attributed to multifunctional oxides present, as identified via FTIR spectra analysis (more details are given in **Figure 4.23.**).

It was observed that the GO-BPA sample at $T_{CA} = 973$ K has more crystalline optimization (very different from the turbostratic carbon structure) than other GO-BPA samples and has the maximum values of interlayer d-spacing and minimum oxide coverage, possibly due to the high density of Raman-defects and stacking disorder present.

Table 4.2. Consolidated of XRD patterns analysis by fitting of (002) peak 2 using Gaussian distribution in GO-BPA samples obtained at different T_{CA} and graphite as reference*.

GO-BPA		(002) peak 2							
T_{CA} (K)	2θ ($^\circ$)	FWHM ($^\circ$)	$d_{(002)2}$ (Å)	D_{002} (Å)	N	ρ (g/cm ³)	Y (%)	Δd_{002} (pm)	ndf $\times 10^{-4}$ (cm ⁻²)
673	26.240	1.023	3.397	1.379	1	2.24	50.00	2.1	4.98
773	26.375	0.452	3.379	3.122	2	2.25	70.93	1.2	5.00
873	26.297	0.138	3.389	10.188	4	2.25	59.30	2.1	5.74
973	25.158	0.111	3.540	0.109	1	2.15	16.28	4.4	6.03
Graphite	26.491	0.459	3.365	3.073	2	2.26	87.21	1.1	----

* $\Delta d_{002} = d_{(002)2} - d_{(002)1}$ was proposed as displacement of the carbon atoms out-plane in this investigation.

Stacking disorder can be influenced by carbon atoms out-plane; therefore, this work proposed that the displacement of average carbon atoms out-plane (Δd_{002}) can be determined by:

$$\Delta d_{002} = d_{(002)2} - d_{(002)1} \quad (4.3)$$

Where $d_{(002)1}$ and $d_{(002)2}$ are the interplanar d-spacing in the samples at the (002) peaks 1 and 2, associated in this work to defects ($d_{(002)1} = d_{Df}$) and multifunctional oxides present ($d_{(002)2} = d_{Ox}$), respectively, as considered in the XRD-GO-model of interpretation reported by Seung Hun Huh [6].

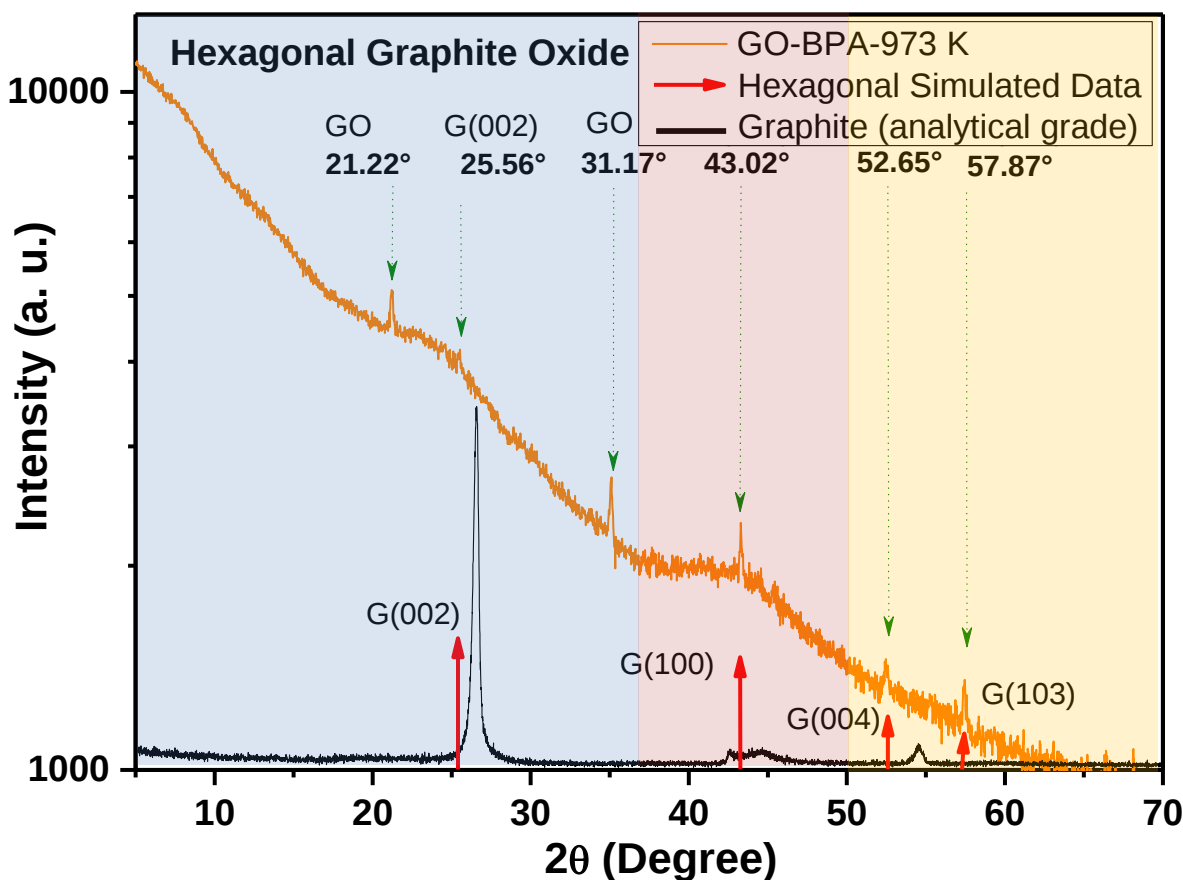


Figure 4.7. XRD pattern comparison between the GO-BPA sample obtained at $T_{CA} = 973$ K and the graphite sample. Red arrow represents the peak shift in GO-BPA-973 K calculated from the XRD theory by considering the electronic factor.

By using expression (4.3), the carbon out-plane influence in the graphitization phase of graphite and GO-BPA samples synthesized at different T_{CA} was determined and presented in **Figure 4.8**. It was found that decreased carbon out-plane increased graphitization phase; this behavior may be explained by the increase of the density of Raman defects and stacking disorder, as discussed in the physical correlations presented in section 4.3.

The inset in **Figure 4.8** shows the schematic model used in this investigation to interpret XRD results presented in this chapter. It is possible to observe that this model is based on the difference of interlayer d-spacing produced by oxides and defects present in the sample, according to criteria that oxides produce more d-spacing than defects due to multifunctional oxides presenting molecular dimensions greater than defects, nano-holes, and empty space between graphene phase layers.

As discussed in section 4.3, the physical correlations between multifunctional oxides present, defects and carbon out-plane mechanisms shown that the effect of the carbon out-plane is more affected by the density of Raman defects than the presence of multifunctional oxides. This is a very important result because it indicates that GO-BPA samples synthesized via DTD method are structurally described as polycrystalline samples with defective

graphene oxide multilayers and suggest that this behavior can be tuned experimentally by the fine control of T_{CA} in the DTD method.

Figure 4.9. represents the main structural modifications affecting GO-BPA samples through multifunctional oxide and defect edges present. This figure indicated that our GO-BPA sample at $T_{CA} = 973$ K can modify its structure by the presence of oxides and defects from 3.354 Å (in graphite) to 3.496 Å (in our sample), as interlayer d-spacing. Variations are also present in carbon-carbon bond length values from 2.456 Å (in graphite) to 2.461 Å (in our sample).

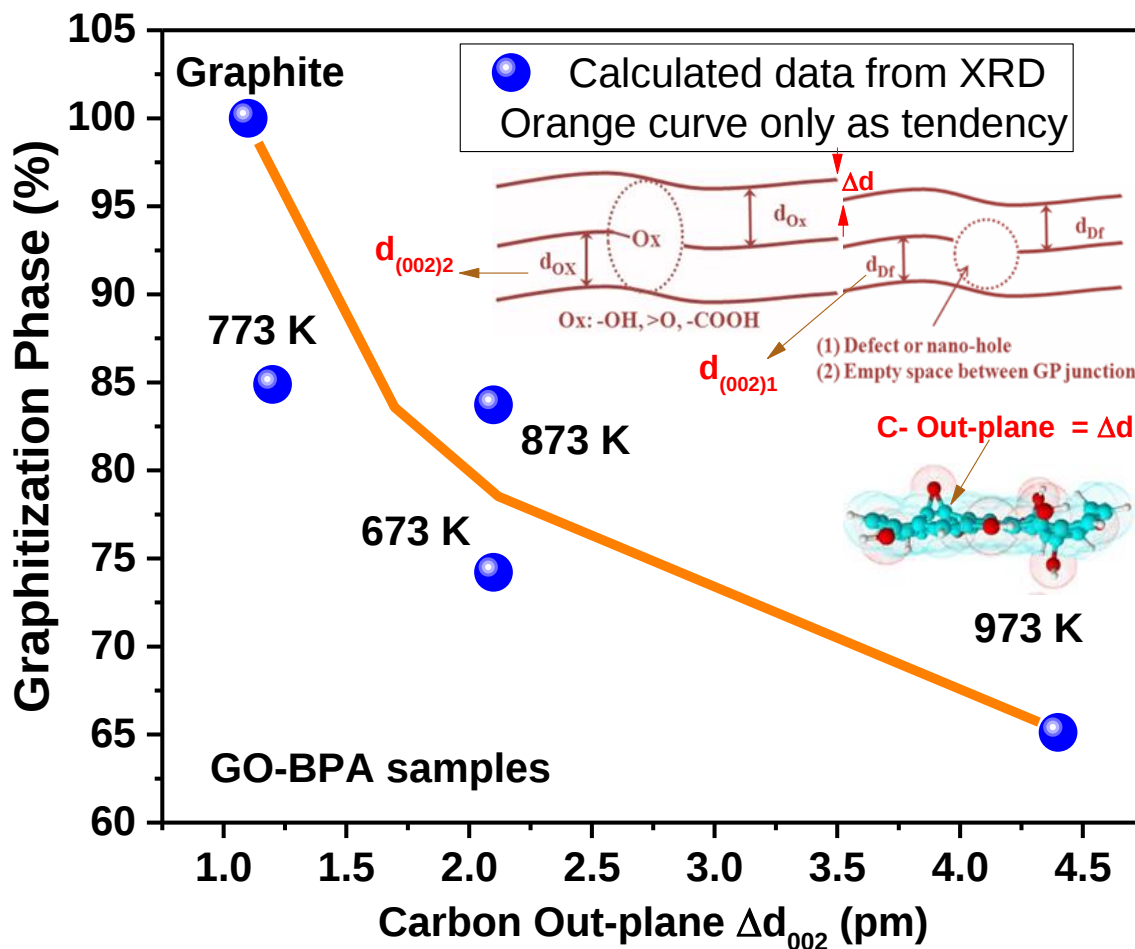


Figure 4.8. Carbon out-plane influence in graphitization phase of Graphite and GO-BPA samples obtained at different T_{CA} . Inset: Graphite oxide XRD model proposed in this investigation.

This work found that increased T_{CA} decreased interlayer d-spacing and increased graphite conversion by organic compound desorption and this behavior can be interpreted as a volumetric or 3-D expansion, as expected in GO materials. The molecular configuration of the GO-BPA sample proposed in this work and found by using DFT computational simulation is presented in **Figure 4.9.**

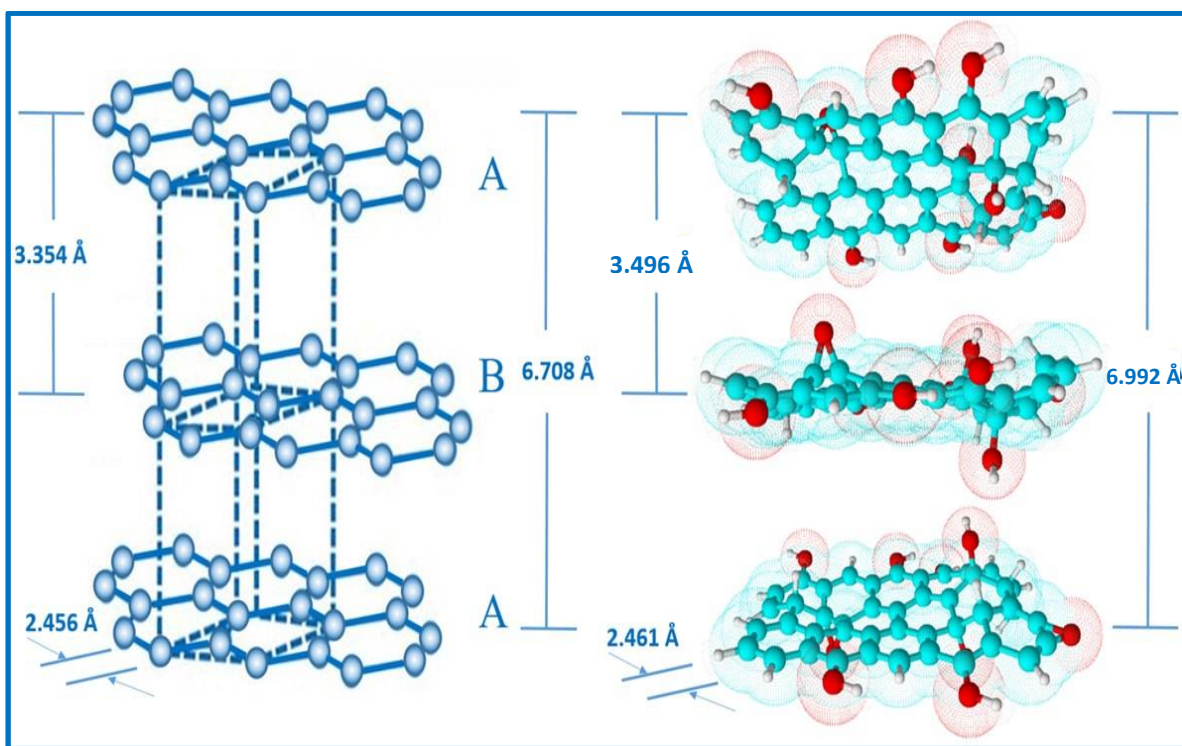


Figure 4.9. Schematic representation of oxide presence in GO-BPA samples at $T_{CA} = 973$ K, as graphite structural configuration, determined by using XRD pattern analysis.

The GO molecular configuration was obtained by DFT computational simulation of the basic electrical transport studies, as presented in section 4.2.2 (**Figure 4.28.**). **Figure 4.10.** shows a representative EELS spectrum acquired on one of the single GO-BPA nanoplatelets synthesized at $T_{CA} = 973$ K. The C–K edges (roughly situated between 280 and 325 eV) and the O–K edge (situated around 530 eV) are clearly visible. All the platelets are found to be chemically homogeneous and of similar composition. The O/(C+O) ratio is, in this case, around 3%; thereby, showing slight oxidation of the platelets and agreeing with the value of 5.25% measured via XPS in the elemental characterization of the samples.

The C–K edge presents characteristic fine structure, similar to graphite (green arrows in the inset of **Figure 4.10**), thus, indicating the influence of band-structure effect. This is of importance because it shows that locally the carbon is mainly in threefold sp^2 bonding configuration. The inset presents a zoom-in of the C–K edge of the GO-BPA-973 K sample (black curve) and two reference spectra of amorphous carbon (red curve), and highly ordered pyrolytic graphite (HOPG, blue curve) [12]. The green arrows highlight characteristic graphite fine structures. This EELS comparison result demonstrated that the structure of our GO-BPA samples agree well with the hexagonal graphite structure and does not agree with the amorphous carbon structure. Despite the short-range crystal order and the incoherence along the d direction due to high interlayer d-spacing values, accurate EELS measurements evidenced the high level of sp^2 -bonds in our nanoplatelets. **Figure 4.11. (a)** shows the EELS spectra of the samples prepared at 973 and 673 K. The C–K edge (roughly situated between 280 and 325 eV) and the O–K edge (situated around 530 eV) are clearly visible. In addition,

a change of the slope around 400 eV (highlighted by a red arrow in **Figure 4.11. (a)**) indicates the presence of nitrogen, at a ratio determined by EELS, is around 0.3% and 1.2% for the samples prepared at 973 and 673 K, respectively, although it is important to bear in mind that precise and accurate EELS quantification requires comparison with reference materials [13–18] and agrees with XPS results, as presented in **Table 3.1**. **Figure 4.11. (b)** shows the C–K edge of the two samples with a higher resolution. Between 290 and 305 eV, the spectrum of the sample prepared at 973 K presents characteristic graphite-like fine structures (blue arrows in **Figure 4.11. (b)**), indicating the influence of the band-structure effect.

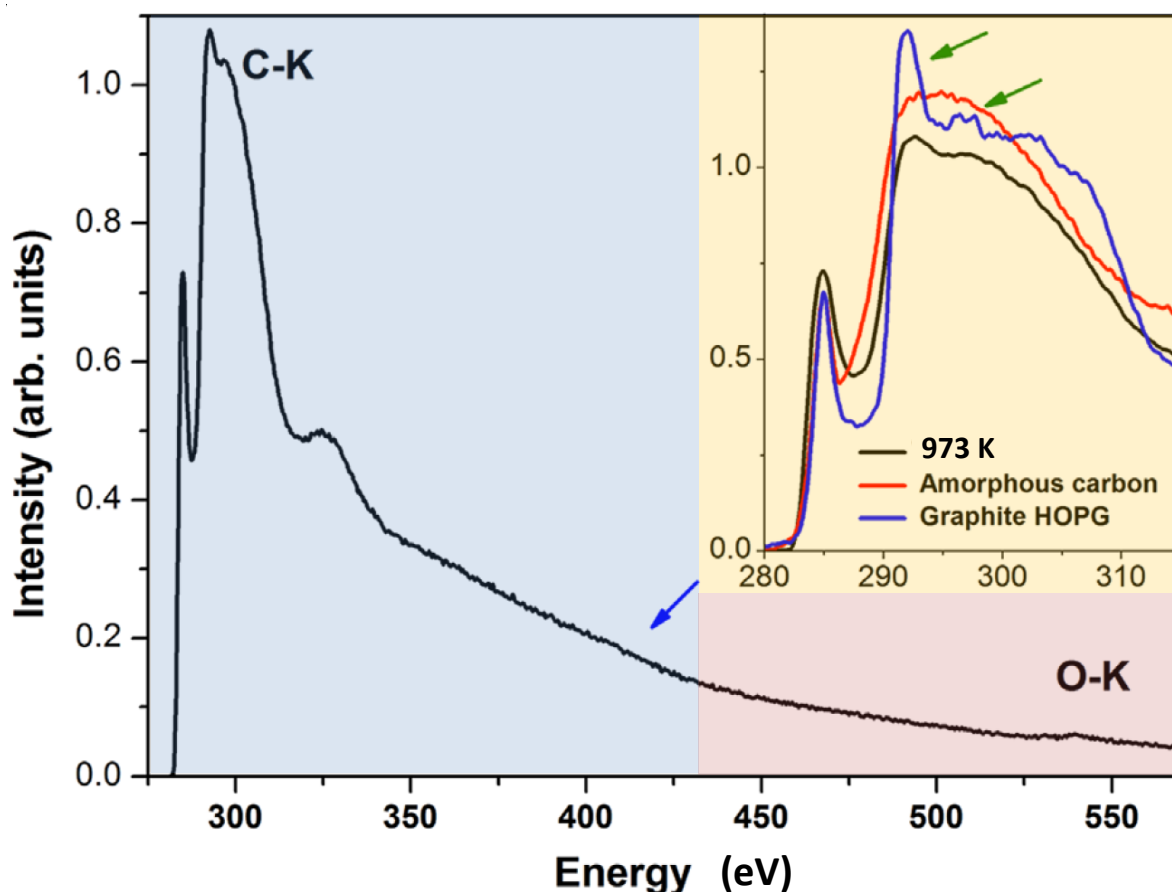


Figure 4.10. EELS spectrum of the GO-BPA-973 K sample showing the C–K and O–K edges at RT. The inset shows a zoom-in of the C–K edge of the sample (black curve) and two reference spectra of amorphous carbon (red curve) and highly ordered pyrolytic graphite (HOPG, blue curve) and green arrow to indicate graphite peaks, as reported by our group [18].

This is of importance because it confirms the presence of a short-range crystalline order and shows that locally the carbon is mainly in threefold (sp^2) bonding configuration. In the same energy range, the C–K edge of the sample prepared at 673 K is featureless and similar to the spectra of disordered carbons [13, 14]. At 286.7 eV, the spectrum of the sample prepared at 673 K shows a supplementary peak (green arrow in **Figure 4.11. (b)**), which could be linked to the presence of oxygen.

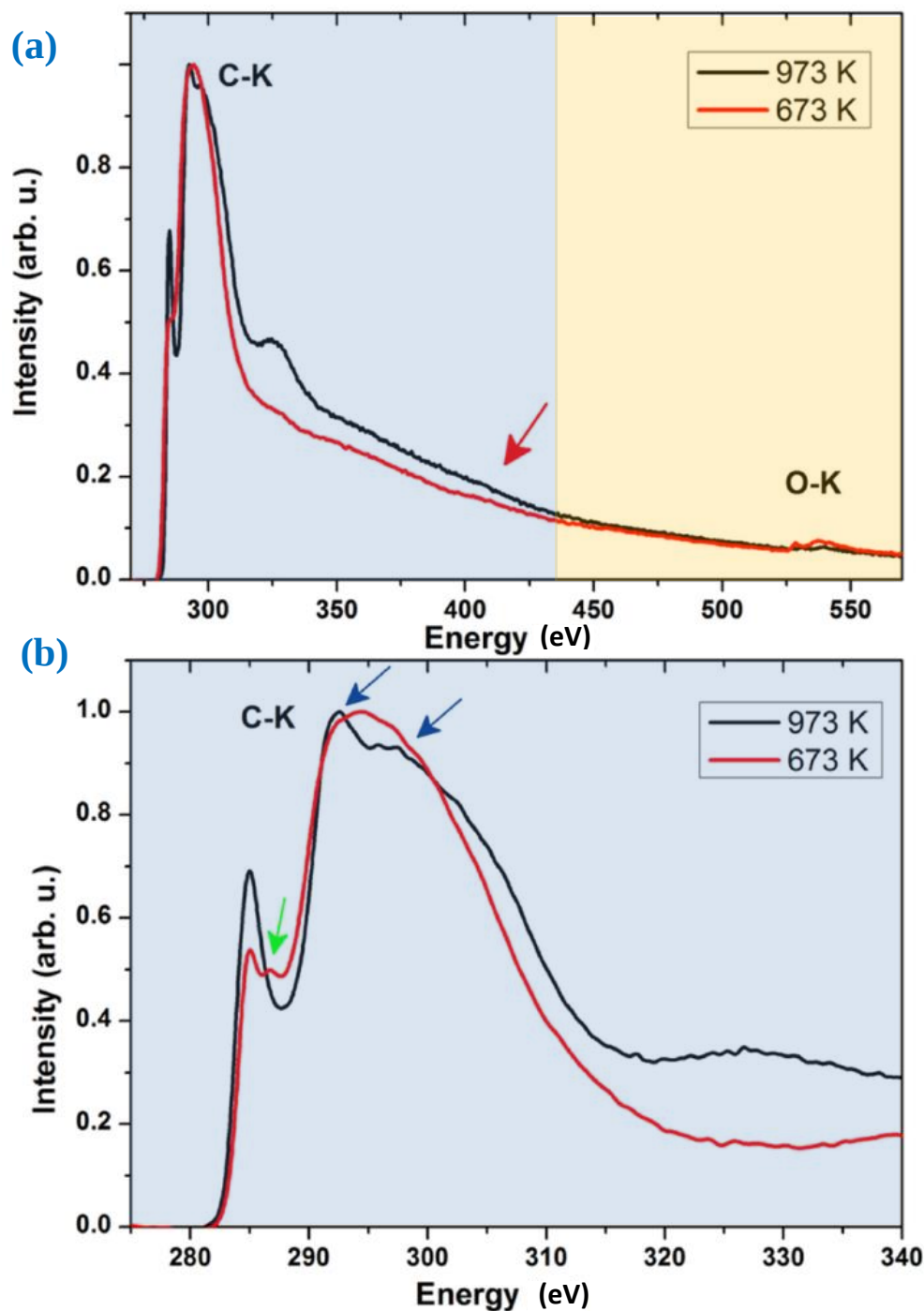


Figure 4.11. (a) EELS spectra of the samples prepared with T_{CA} at 973 (black curve) and 673 K (red curve) and recorded with a dispersion of 0.2 eV/pixel at RT. The red arrow highlights the position of the N–K edge. (b) EELS spectra of the C–K edge recorded with a dispersion of 0.05 eV/pixel. The blue arrows highlight the graphitic fine structures of the sample prepared at 973 K and the green arrow highlights the supplementary peak observed at 286.7 eV for the sample prepared at 673 K (see text for more details) [18]. For more details, all these spectra have been published as references to the EELS database and available in: <https://eelsdb.eu/spectra/oxidized-graphenic-nanoplatelets-obtained-from-bamboo/>.

For instance, C=O bonds give rise to transitions at π^* states in the energy range between 287.7 and 288.3 eV and C–H bonds give rise to transitions at σ^* states in the energy range between 287.6 and 288.2 eV [15-18]. However, determination of the origin of this supplementary transition based solely on the energy position is particularly difficult.

From the core-loss spectra, the sp^2 fraction (sp^2 character/(sp^2+sp^3 characters)) has been derived and is equal to 87% and 66% for the samples prepared at 973 and 673 K, respectively.

The decreased sp^2 character is also confirmed by the low-loss spectra, which show a strong decrease of the π Plasmon for the same sample. In addition, the mass density of the nanoplatelets was calculated from the low-loss spectra and is around 1.80 and 1.92 g/cm³ for the samples prepared with a T_{CA} of 973 and 673 K and agree with the same values of 2.18 and 2.26 g/cm³ calculated from XRD pattern analyses, respectively, as listed in Table 4.1.

These values constitute an intermediate between the values corresponding to glassy carbon and pure graphite (1.44 and 2.27 g/cm³, respectively) [17, 18]. The results obtained via ED, HR-TEM, and EELS analyses are consistent and provide a complete structural and chemical description at the local scale of these samples.

During synthesis, the lowest T_{CA} yields nanoplatelets that are mostly disordered and with an O/(C+O) ratio of 12% and agree with the value of 12.99% measured via XPS technique and listed in Tables 3.1 and 4.1. In addition, as mentioned, the highest T_{CA} yields nanoplatelets that show mostly sp^2 bonding configuration with a short-range crystalline order and an O/(C+O) ratio of 3% and agree with the value of 5.25% measured via XPS technique and listed in Table 4.1. These important chemical and structural modifications should have a strong impact on the transport properties of the GO-BPA samples [18].

Elemental Properties. Figure 4.12. presents the solid phase diagram related with the influence of T_{CA} in oxygen and carbon at % of GO-BPA samples, both measurements were carried out by using XPS technique, as described in chapter 3.

It was observed that increased T_{CA} from 673 to 973 K decreased oxygen coverage from 12.99% to 5.25% and increased carbon at % from 85.71% to 94.00%, as listed in Tables 3.1. and 4.1.

These oxygen and carbon content agree with the values ranging from 13.18% to 6.16% and from 85.30% to 91.07%, respectively. Both measurements were performed through EDS-SEM technique, as listed in Table 3.1. The consolidated result of the chemical elemental measurements by using XPS and EDS techniques can be observed in annex 1 (see more details).

Main results of the morphological, structural, and elemental analyses have been presented; the following discusses the analysis on the identification of the transport mechanisms in GO-BPA samples.

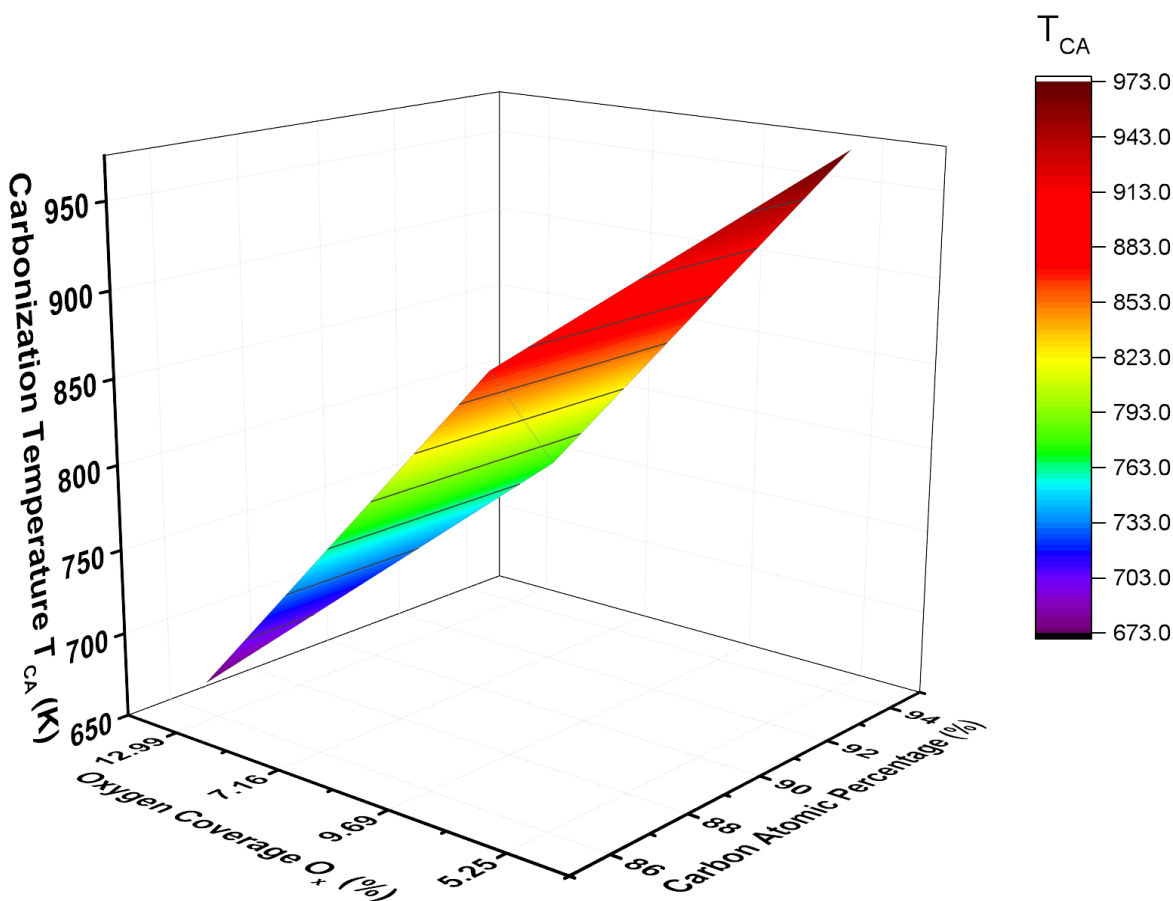


Figure 4.12. Phase diagram of oxygen coverage and carbon atomic percentage dependence on T_{CA} in GO-BPA samples.

4.2 Transport Mechanisms in GO-BPA Samples

The thermal, electrical, and magnetic properties were studied by using the RS, FTIR, I-V curves, MFM, and VSM techniques in GO-BPA samples obtained at different T_{CA} , respectively, by considering the experimental procedure described in chapter 3. Identification of the main thermal, electrical and magnetic transport mechanisms in GO-BPA took place by considering different fine experiments at low temperatures, as described in chapter 3 (more details in sections 3.2.4, 3.2.5, and 3.2.6).

Identification of the main thermal scattering processes in GO-BPA samples was carried out via estimations of relaxation time by analyzing the width of Raman spectra (taken at different temperatures) and considering the quantum limit given by the time-energy Werner Heisenberg uncertainty principle [19].

The main electrical scattering process was identified via relaxation time estimations by using the graphitic materials time-conductivity Wallace model [20]. The magnetism mechanism in GO-BPA samples was identified by using physical correlations with the calculus of defect density and crystal size, both from Raman spectra analysis. Interpretation

of magnetoresistance in GO-BPA samples was performed by considering the physical correlations with the results of the main thermal and electrical transport mechanisms.

4.2.1 Thermal or Vibrational Transport Mechanisms

Vibrational properties in GO-BPA samples were studied by using Raman and FTIR spectroscopies. From the analysis of the Raman spectra, it was possible to identify the main thermal transport mechanisms and by employing FTIR spectroscopy we identified the functional groups present in the samples; the respective results are shown ahead.

Raman Technique in GO-BPA Samples. [Figure 4.13.](#) shows the Raman spectra of GO-BPA sample synthesized at T_{CA} 973 K (black square dots). The Raman spectra analysis was carried out by using a fit with six Lorentzian function contributions associated to:

G band peak at 1550 cm^{-1} (from 1550 to 1580 cm^{-1} peak), indicating the formation of a graphitized structure by the vibration of sp^2 bonded carbon atoms [[21-25](#)].

D band peak around 1330 cm^{-1} (from 1330 to 1360 cm^{-1} peak), corresponding to the disorder-induced phonon mode by defects present, related with the elastic scattering due to structural defects, like grain boundaries, oxides, and sp^3 defects (C-O-C, C-OH and C-H, as observed via FTIR results in this work, respectively, see [Figure 4.23.](#)) [[21-25](#)].

D' band peak at 1593 cm^{-1} (from 1593 to 1620 cm^{-1} peak) due to the Raman inelastic scattering caused by the absorption or emission of phonons confined in defects, which can produce expansion and contraction of graphene oxide layers [[21-25](#)].

2D, D+G, and 2D' band peaks around 2697 , 2900 , and 3110 cm^{-1} values; respectively, suggests the stacking presence of many graphene layers with edges, defects, and sp^2 regions, which are prevalent features of GO materials [[21-25](#)].

[Figure 4.14.](#) illustrates normalized Raman spectra of GO-BPA samples synthesized at different T_{CA} and taken at room temperature. Note that according to the T_{CA} , the spectra show different fluorescence background; this can be attributed to the presence of organic compounds. By increasing T_{CA} , the organic compounds are lost and the fluorescence background decreases. The graphitic characteristic of GO-BPA is confirmed by this technique.

As shown in [Figure 4.15.](#) and after the subtraction of the linear background and normalization to the height of the G peak, all spectra could be deconvoluted into the characteristic peaks: G-band peak around 1560 cm^{-1} and D-band peak around 1350 cm^{-1} ; the presence of these bands indicates the formation of a graphitized structure, while the latter corresponds to the disorder-induced phonon mode.

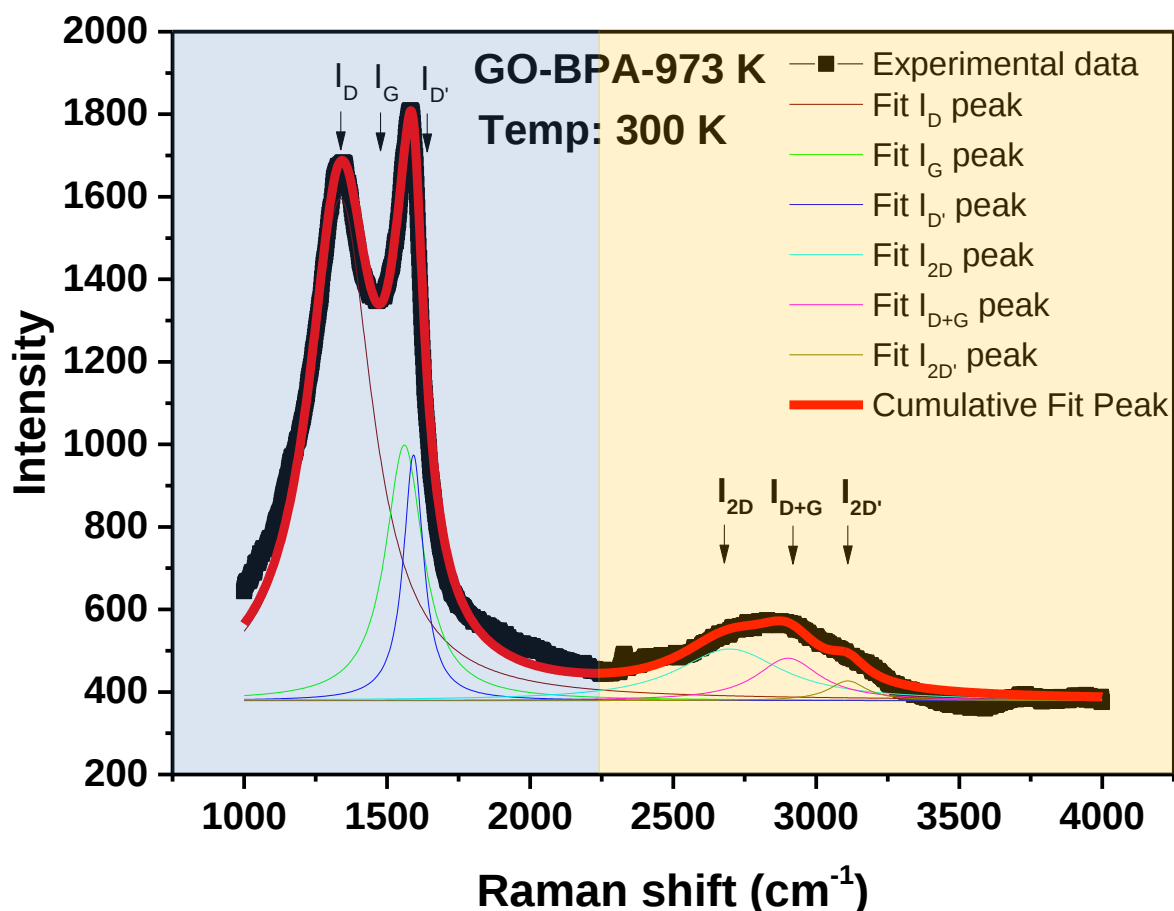


Figure 4.13. Raman spectra in the GO-BPA-973 K sample excited with visible laser light at 532 nm wavelength, taken at room temperature and fitted by using six Lorentzian functions, which involve processes of resonant forced behavior, showing responses of the tones (blue region) and overtones (yellow region) in the sample.

A third peak was identified as D' band around 1590 cm^{-1} , associated with the presence of boundary defects. The wide 2D, D+G, and 2D' bands around the 2800 cm^{-1} value suggests the presence of many graphene layers with edges, defects, and sp^2 regions, which are prevalent features of GO [21-25]. It was observed that the theoretical fit proposed in this investigation agrees well with the experimental Raman spectra.

From the respective results analysis of the theoretical fits presented in Figure 4.15. for each Raman spectra of GO-BPA samples, it was possible to determine the following Raman parameters: peak-shifts or vibrational modes, peak-width- ratios, peak intensity ratios (fitted data), and density of defects (calculated values), as listed in Tables 4.3., 4.4., 4.5., respectively.

These found that Raman: peak shifts present average values of 1339 , 1563 , 1594 cm^{-1} in each D, G and D' bands, as expected in RGO materials [26-28]. Peak-width ratios exhibit average values of 1.9, 3.7, and 2.0 for each ratio given by Γ_D/Γ_G , $\Gamma_D/\Gamma_{D'}$, $\Gamma_G/\Gamma_{D'}$, respectively, and agree with the range of values reported [28].

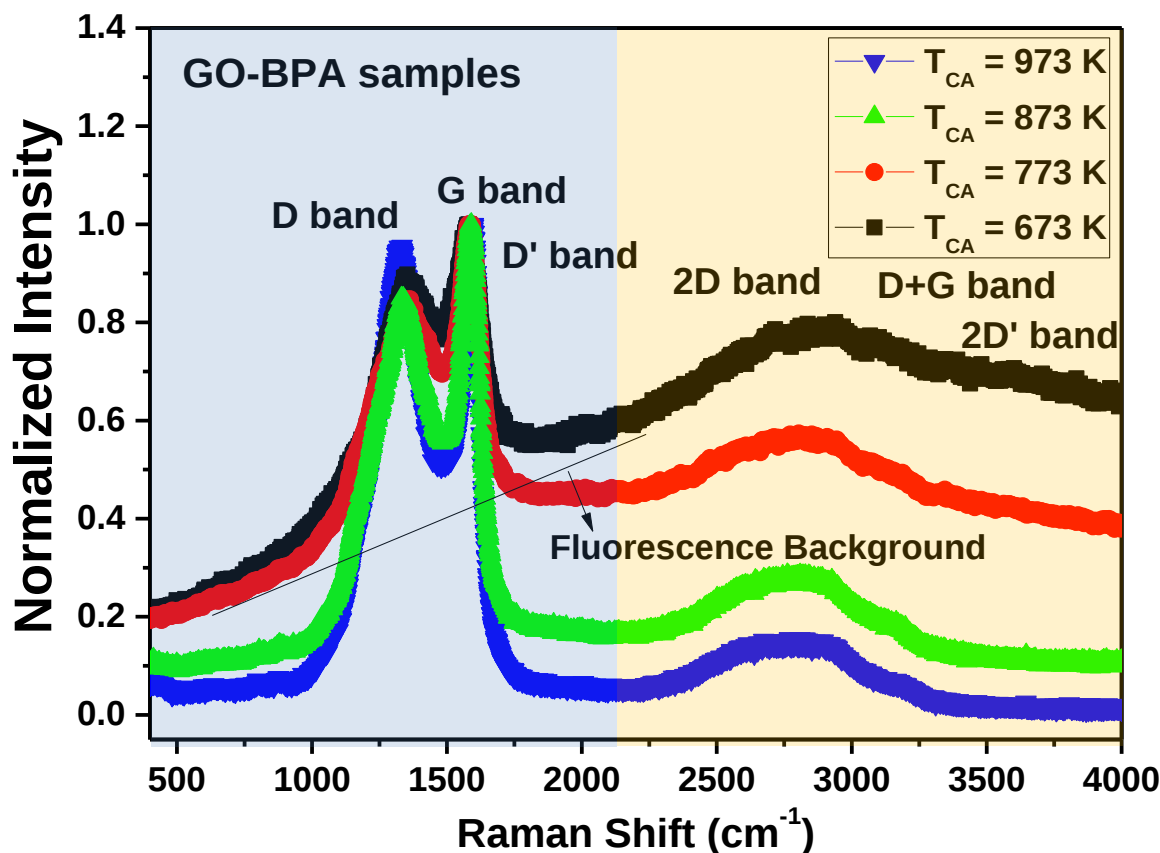


Figure 4.14. Normalized Raman spectra in GO-BPA samples obtained at different T_{CA} . Taken at room temperature and excited with visible laser light at 632.8 nm wavelength. Fluorescence background was observed in these Raman spectra, possibly attributed to organic compounds present in the samples.

Peak intensity ratios show values of 2.8, 1.9, and 1.5 for each I_D/I_G , $I_D/I_{D'}$, and $I_{D'}/I_G$ ratio, respectively. As suggested by Tuinstra and Koenig, increased I_D/I_G increases the disorder in the structure [29].

In 1970, for first time, Tuinstra and Koenig [29] using physical correlation between I_D/I_G and XRD patterns of graphite, demonstrated the origin of the D band in graphite and suggested possible relation between I_D/I_G and Raman-Crystal size and I_D/I_G and density of Raman defects [29].

However, further reduction reaction by desorption of organic compounds and oxides, creates more disorder and distortion on the sp^2 structure. Therefore, higher Γ_D/Γ_G and I_D/I_G ratios signifies that higher synthesis T_{CA} used in the DTD method and reaction environment aid in reduction of the GO-BPA samples and these values agree with values suggested by A. Bhaumik *et al.*, [28].

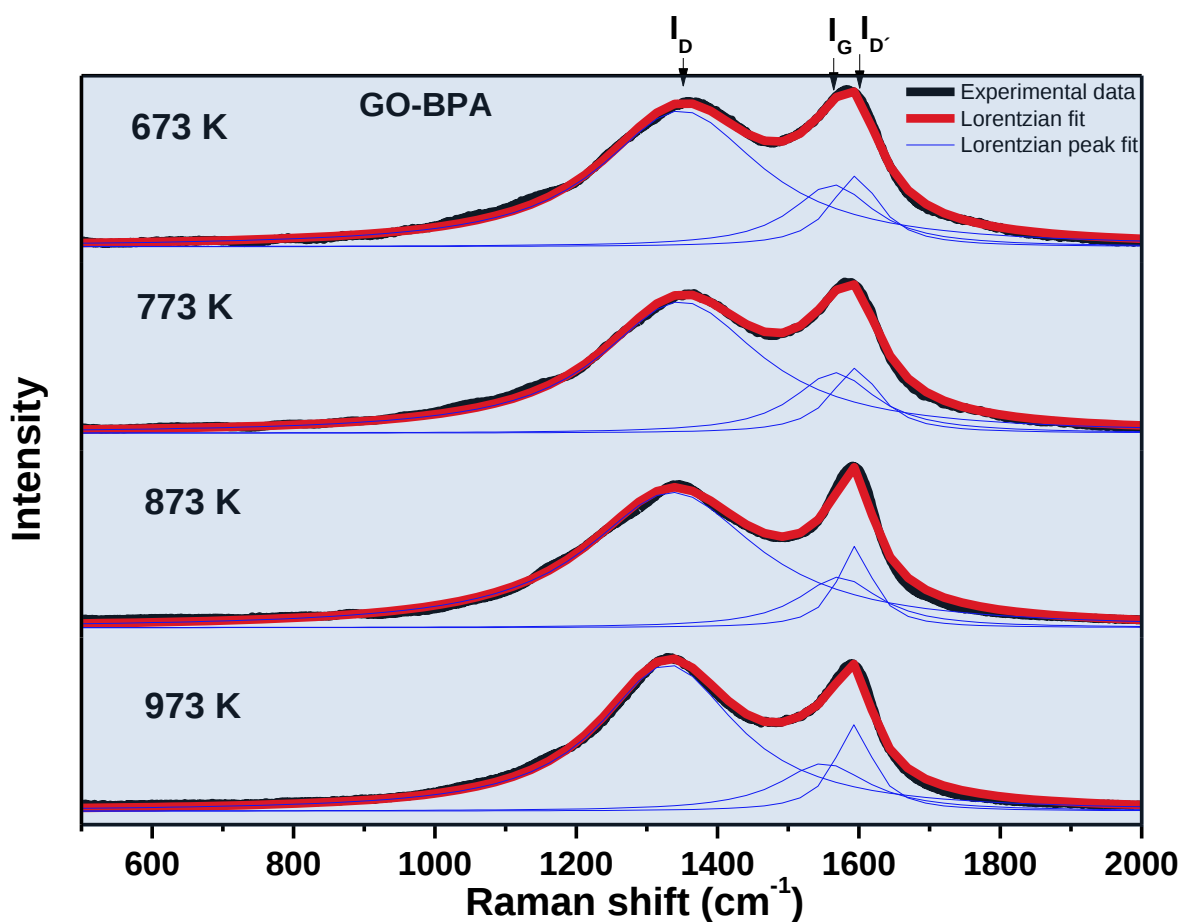


Figure 4.15. Raman spectra in GO-BPA samples obtained at different T_{CA} excited with visible laser light at 632.8 nm wavelength and Lorentzian deconvolution fit, assuming processes of resonant forced behavior in D, G, and D' bands, after subtraction of the fluorescence background, corresponding to the tone response.

Table 4.3. Raman peak shift or vibrational modes (obtained from fitted data) in GO-BPA samples for different T_{CA} .

Raman Shift/ T_{CA}	Peak	973 K	873 K	773 K	673 K
D (cm^{-1})		1330	1336	1348	1348
G (cm^{-1})		1550	1572	1566	1563
D' (cm^{-1})		1593	1595	1595	1595

Table 4.4. Raman peak-width ratios (fitted data) in GO-BPA samples for different T_{CA} .

Raman Peak Intensity Ratios/ T_{CA}	973 K	873 K	773 K	673 K
Γ_D/Γ_G	1.53	2.14	1.96	1.96
$\Gamma_D/\Gamma_{D'}$	3.61	4.85	3.26	3.26
$\Gamma_G/\Gamma_{D'}$	2.35	2.27	1.67	1.67

Table 4.5. T_{CA} , Raman intensity ratios (fitted data) and Raman defect density in GO-BPA samples determined by using expression (3.23) at different T_{CA} .

T_{CA} (K)	I_D/I_G	$I_D/I_{D'}$	$I_{D'}/I_G$	$n_{Df} \times 10^{-4}$ cm^{-2}
973	3.38	1.73	1.96	6.03
873	3.06	1.76	1.74	5.74
773	2.33	2.12	1.10	5.00
673	2.31	1.99	1.16	4.98

Raman spectra in GO-BPA samples synthesized at different T_{CA} were presented and analyzed; the following will explore the effect of T_{CA} in Raman-defect density and Raman-crystal size.

Influence of the T_{CA} on Raman Defect Density and Crystal Size of GO-BPA Samples. Considering expression (3.23), it was possible to determine the density of Raman defects for each T_{CA} , as listed in **Table 4.5**. **Figure 4.16**, presents the T_{CA} dependence on the density of Raman defects, along with its respective linear fit as a plausible theoretical description. It was found that increased T_{CA} increased density defects possibly explained by desorption of multifunctional oxides and some organic compounds due to thermal decomposition of BPA in the DTD method used to synthesize the samples in this work. Defect density increases from $4.98 \times 10^{-4} cm^{-2}$ to $6.03 \times 10^{-4} cm^{-2}$ with increased T_{CA} from 673 to 973 K, respectively. These values agree with the values varying from $5.3 \times 10^{-4} cm^{-2}$ to $4.9 \times 10^{-4} cm^{-2}$, as reported by Anagh Bhaumik and Jagdish Narayan [26]. We identified that the density of Raman defects mentioned is related with the boundary defects present in the samples, as shown in the inset of **Figure 4.16**. Because the I_D/I_G ratio is around 2.8, this value is approximately 3.0 and can be related with the boundary defects present, as expected.

In the inset of **Figure 4.16.**, it is possible to observe an HR-TEM image of the single GO-BPA nanoplatelet at 5% oxide coverage in 5-nm scale, with the boundary defects present highlighted with yellow ovals. The respective linear theoretical fit presented in **Figure 4.16.**, gives as slope a value of $3.87 \times 10^{-7} \text{ cm}^{-2}/\text{K}$, it is associated with the shift-ratio of defect density with the T_{CA} and intercept value of $2.26 \times 10^{-4} \text{ cm}^{-2}$, physically associated with the hypothetical minimum value of defect density that can be obtained by using the DTD method at lower experimentally possible T_{CA} .

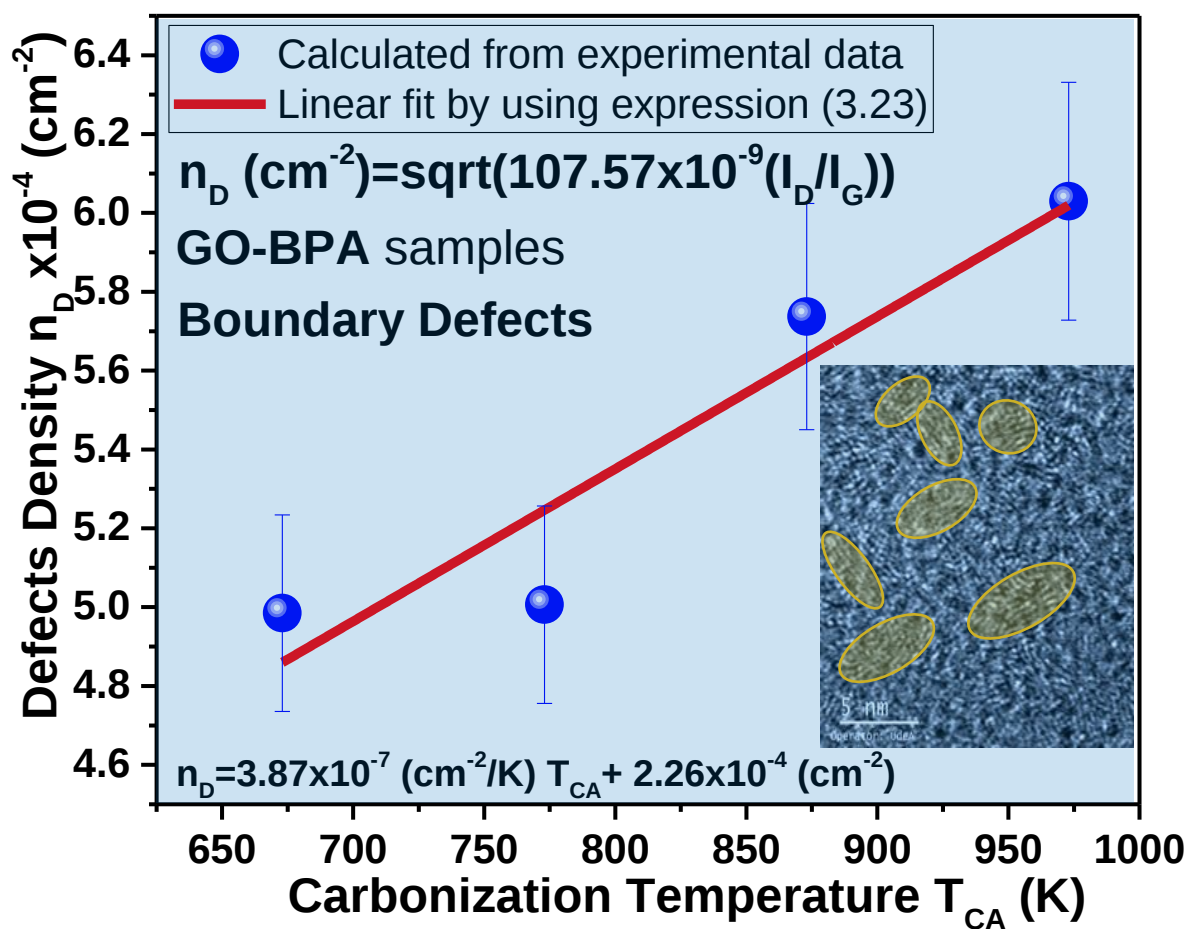


Figure 4.16. Influence of the T_{CA} in the density of Raman defects (blue circles) with 5% error in the experimental data and theoretical fit by using linear approximation (red solid line). Inset: HR-TEM image of single GO-BPA nanoplatelet (right bottom side) showing boundary defects (yellow ovals).

By using expression (3.22), it was possible to determine the Raman in-plane crystal size as a function of T_{CA} , as presented in **Figure 4.17.**, and its respective linear fit as a plausible theoretical description. It was found that decreased T_{CA} from 973 to 673 K increased crystal size from 1.302 to 1.905 nm, respectively, and these values agree with the value of 3.6 nm reported for RGO by Alpana Thakur *et al.*, [30]. This behavior is a consequence of boundary defects increasing with increased T_{CA} by thermal desorption of multifunctional oxides and some organic compounds in the samples, as shown in **Figure 4.16.**

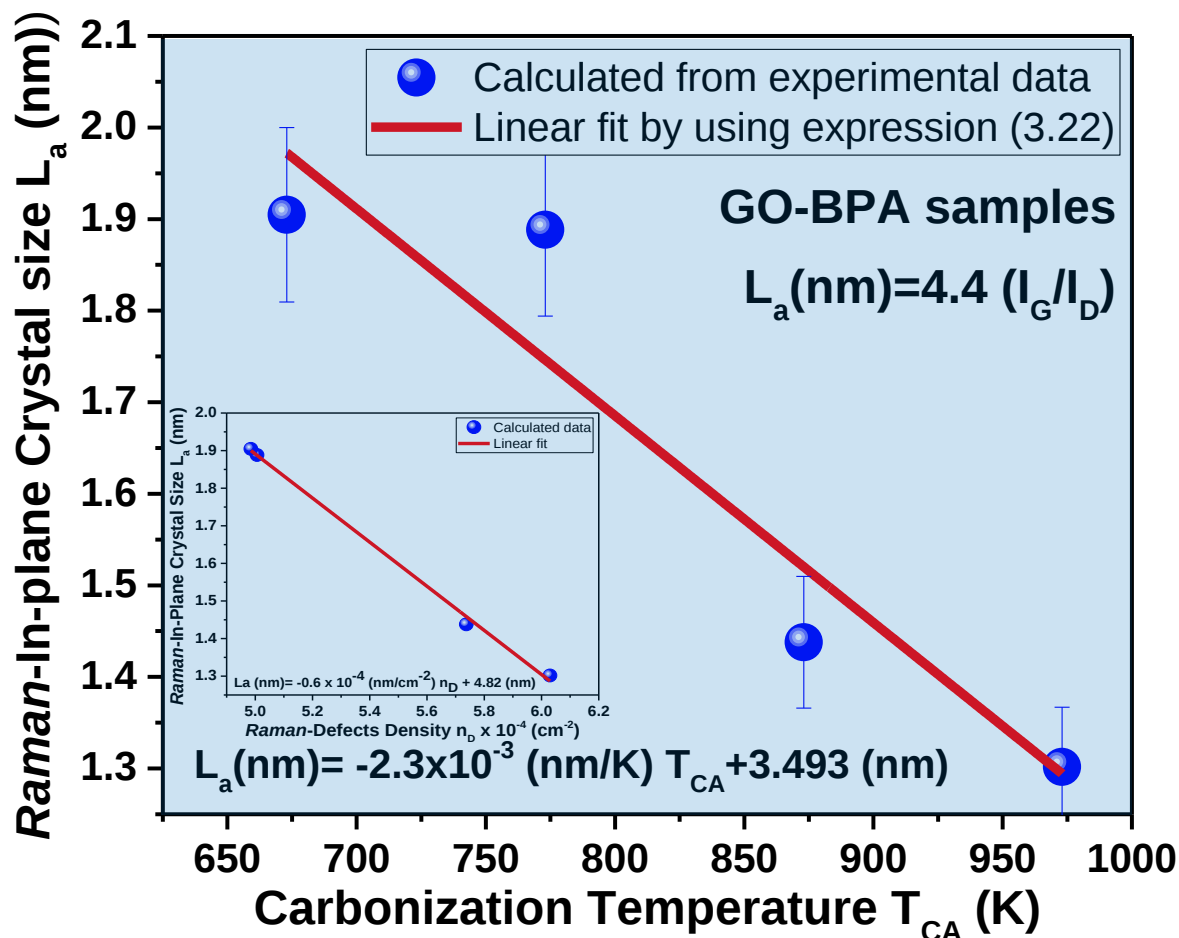


Figure 4.17. T_{CA} dependence on the Raman in-plane crystal size (blue circles) with 10% error in the experimental data and its theoretical fit by using linear relation (red solid line).

The linear fit in **Figure 4.17** shows a negative slope of $2.3 \times 10^{-3} \text{ nm/K}$ related with the shift-ratio of crystal size per Kelvin of change in T_{CA} and the intercept value of 3.493 nm, physically associated with the hypothetical maximum value of defect density that can be obtained by using the DTD method at lower experimentally possible T_{CA} . It was observed that decreased T_{CA} from 973 to 673 K increased crystal size from 1.30 to 1.90 nm; this behavior can be attributed to desorption of some organic compounds and oxides by thermal decomposition of samples, which modify the density of defects and produce variations in crystal size; hence, decreasing density of defects increased crystal size, as shown in the inset of **Figure 4.17**. Therefore, in this work, the analysis of the Raman spectra at room temperature in GO-BPA samples synthesized at different T_{CA} yields as a main result that increased T_{CA} increased the density of Raman defects and decreased crystal size in GO-BPA samples; both behaviors are possibly due to desorption of multifunctional oxides and organic compounds involved in the DTD method by conversion to graphite of BPA, which increases defects as a consequent decrease of in-plane crystal size. The effects of T_{CA} on the density of Raman defects and crystal size in GO-BPA samples synthesized at different T_{CA} have been discussed; hereinafter, we will look at the influence of temperature on the Raman spectra of GO-BPA samples.

Temperature Effect on the Raman Spectra of GO-BPA Samples. Figure 4.18. shows the Raman spectra in GO-BPA samples synthesized at $T_{CA} = 973$ K and taken at different temperatures from 95 to 325 K.

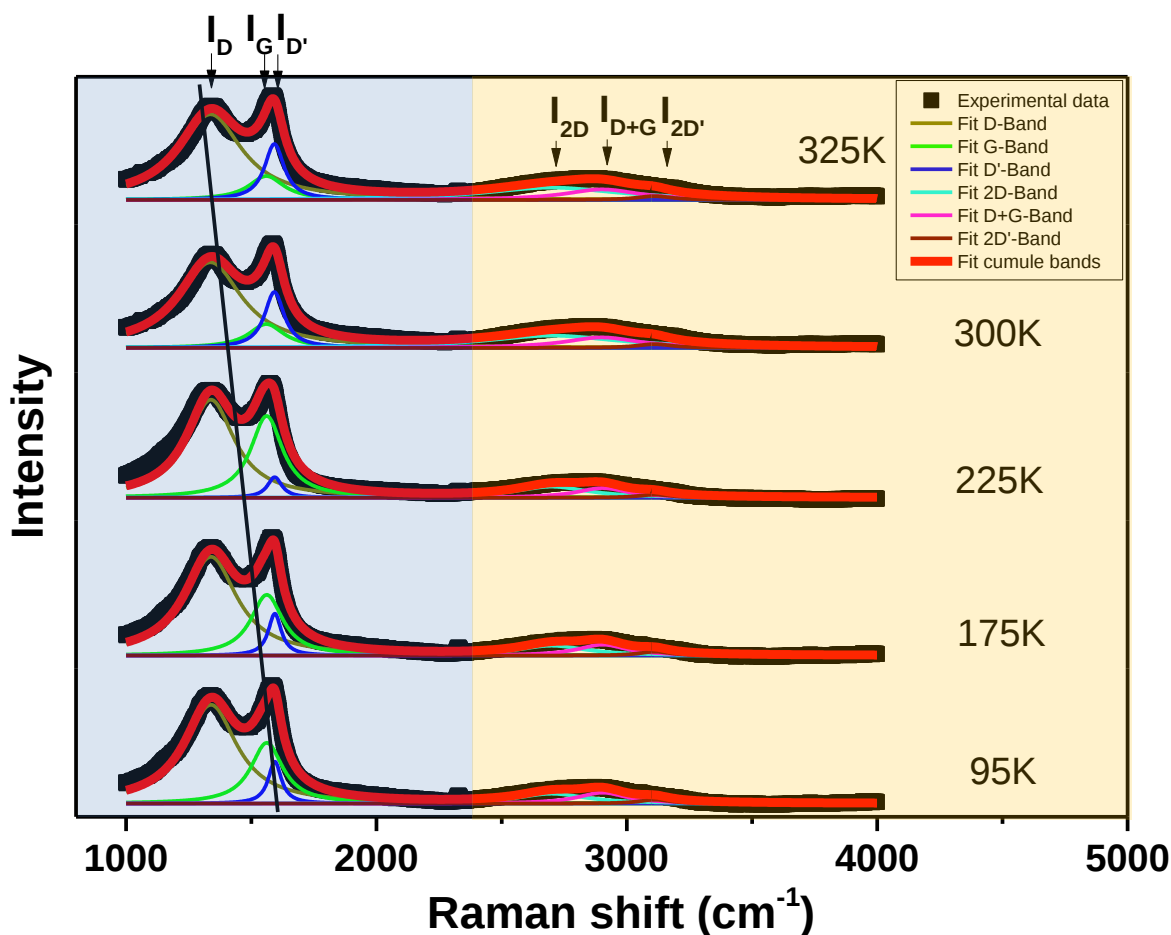


Figure 4.18. Raman spectra of the GO-BPA-973 K sample taken at different temperatures (325 – 95 K) excited with visible laser light at 532 nm wavelength and the respective fit in the tones (1000 - 2000 cm^{-1}) and overtones (2000 - 4000 cm^{-1}) regions by using six Lorentzian functions assuming processes of forced resonant behavior.

It was observed that increased temperature and the Raman spectra's red-shifted to low values of Raman frequencies. The Raman spectra analyses were carried out by fitting with six Lorentzian function contributions associated to: (1) G band peak at 1550 cm^{-1} indicating the formation of a graphitized structure by the vibration of sp^2 bonded carbon atoms; (2) D band peak around 1330 cm^{-1} , corresponding to the disorder-induced phonon mode by the presence of defects related with elastic scattering due to structural defects, like grain boundaries, oxides, and sp^3 defects; and (3) D' band peak at 1593 cm^{-1} is due to the Raman inelastic scattering caused by the absorption or emission of phonons confined in defects that can produce expansion and contraction of graphene oxide layers. D, G and D' bands are the so-called tone bands. (4 – 6) 2D, D+G, and 2D' bands around 2697, 2900, and 3110 cm^{-1} peak values; respectively, suggest the stacking presence of many graphene layers with edges,

defects, and sp^2 regions which are prevalent features of graphite oxide. The 2D, D+G, and 2D' bands are the overtone bands [21-25].

From the Raman spectra analysis shown in **Figure 4.18**, we found temperature dependence on the Raman shift center, I_D/I_G intensity ratios, and line-width ratios in the GO-BPA sample at $T_{CA} = 973$ K, as presented in **Figures 4.19**., **4.20**., and **4.21**., respectively.

Figure 4.19, presents the influence of temperature on Raman shift centers, obtaining that decreased temperature increased Raman shift centers, associated to variations of net anharmonicity and thermal expansion, as expected for the Graphite material [31]. These few red shifts suggest high thermal stability and quality of our samples.

As proposed by I. Calizo *et al.*, [31], the temperature dependence on the Raman shift centers in our sample for each Raman band can be represented by the following relation:

$$\omega(T) = \omega_0 - \chi T \quad (4.4)$$

Where ω_0 is the frequency of D, G, D', 2D, D+G, and 2D' modes when temperature, T, is extrapolated to 0 K and χ is the first-order temperature coefficient, which defines the negative slope of the dependence; involving two contributions, one associated to net anharmonicity by oxides and defects present and the other due to the thermal expansion of the sample and represents the red-shift of the Raman spectra shown in **Figure 4.18**.

The other second-order term or non-linear contribution to expression (4.4) is expected to appear only at high temperature (greater than 325 K), which is in line with the observations made for other carbon materials; for this reason, it was not considered in expression (4.4). The temperature coefficient, χ , of the G mode determines the Raman frequency shift of the G mode when the temperature of the sample increases by 1 °C (or K).

The negative value extracted at $\chi = 1.62 \pm 0.20 \times 10^{-2} \text{ cm}^{-1}/\text{K}$ was reported for single-layered graphene [31]. Similar measurements were carried out for the graphene bilayer with a value of $\chi = 1.54 \pm 0.06 \times 10^{-2} \text{ cm}^{-1}/\text{K}$ [31]; these values agree with our data of $\chi = 1.29 \pm 0.01 \times 10^{-2} \text{ cm}^{-1}/\text{K}$ obtained in this work by fitting with expression (4.4) in experimental results, as shown in **Figure 4.19**. The extrapolated ω_0 and χ values are shown in **Table 4.6**, and agree with previous value ranges reported [31].

Figure 4.20, Presents the Raman intensity ratio of I_D/I_G versus temperature and the inset shows the temperature influence on the Raman in-plane crystal size. It was observed that increased temperature increases the intensity ratio, which is possibly attributed to net anharmonicity by the increase of density defects and thermal expansion behaviors by decreased Raman in-plane crystalline size in the GO-BPA material, as presented in the inset of **Figure 4.20**.

These results agree with the boundary defects present in GO-BPA samples, as expected [12, 26, 33-37].

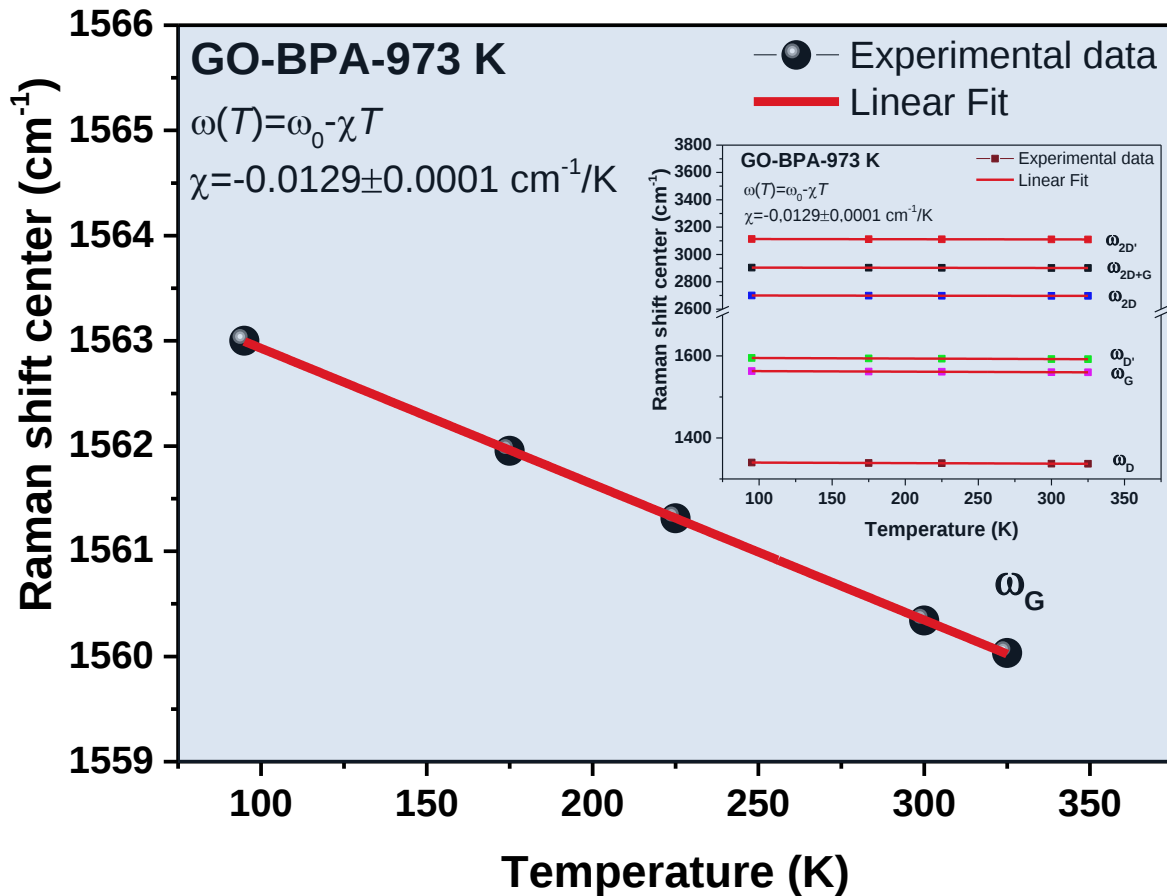


Figure 4.19. Temperature dependence on the Raman shift centers in the GO-BPA-973 K sample for the G-band. Linear dependence can be attributed to net anharmonicity and thermal expansion behavior. Inset: Raman shift centers versus temperature for D, G, D', 2D, D+G, and 2D' bands of the GO-BPA-973 K sample. We assumed similar linear behavior in all Raman vibrational modes, as a first problem approximation, given that net anharmonicity and thermal expansion behavior can be influenced by the presence of multifunctional oxides, defects, and stacking of graphene oxide layers in GO-BPA samples. Taken and adapted from our group reference [32].

Increased temperature increases the I_D/I_G relation and density of boundary defects and decreases Raman in-plane crystalline size (inset of [Figure 4.20.](#)), as expected [12]. It is known [33–37] that defect density is proportional to I_D/I_G and Raman in-plane crystalline size is proportional to (I_G/I_D) . Temperature variations of the intensity I_D/I_G ratio can be attributed to net anharmonicity by increased density of the defects and the thermal expansion behavior by decreased Raman in-plane crystalline size in GO-BPA material, as expected.

This thermal expansion behavior involves the boundary defects in our samples presenting thermal dilation greater than the graphene structure. These differences in thermal dilation agree with the experimental observations of thermal dilation in graphene oxide (6 layers), GO, and graphite samples obtained through methods different from those proposed in this work and reported elsewhere [38, 39].

Table 4.6. Fitted data consolidated by using expression (4.4) in the theoretical description of the experimental data, as presented in **Figure 4.18**.

Raman shift center $\omega(T)$	ω_0 (cm^{-1})	χ (Fitted value) ($\times 10^{-2} \text{ cm}^{-1}/\text{K}$)
ω_D	1341.22 ± 0.01	1.29 ± 0.01
ω_G	1564.22 ± 0.01	1.29 ± 0.01
$\omega_{D'}$	1596.22 ± 0.01	1.29 ± 0.01
ω_{2D}	2701.22 ± 0.01	1.29 ± 0.01
ω_{D+G}	2905.22 ± 0.01	1.29 ± 0.01
$\omega_{2D'}$	3114.22 ± 0.01	1.29 ± 0.01

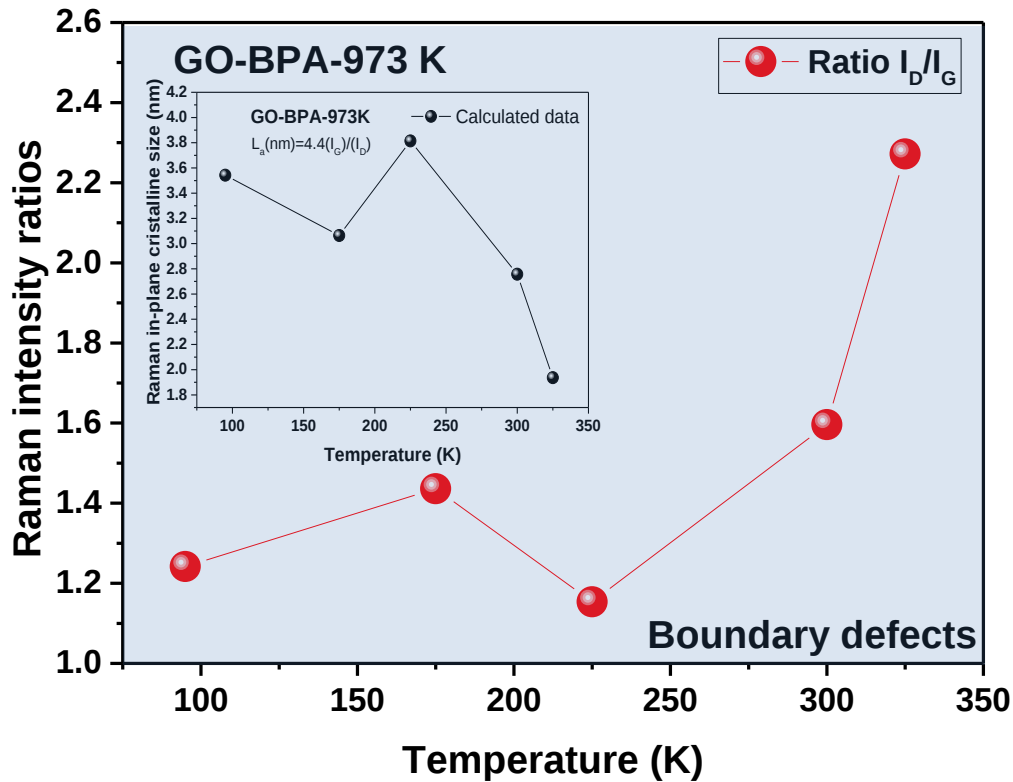


Figure 4.20. Temperature dependence on the Raman intensities ratio I_D/I_G in the GO-BPA-973 K sample. Inset shows temperature variations of the Raman in-plane crystalline size in the same sample.

Temperature effect on the Raman spectra of GO-BPA samples was illustrated, the procedure proposed in this investigation will now be discussed to identify the phonon scattering process in our samples.

Identification of the Phonon Scattering Processes in the GO-BPA Sample. **Figure 4.21.** shows the temperature dependence on the G-band Raman line-shape width and the inset shows the Raman line-shape width for each band, both present the respective theoretical fit by using the Bose-Einstein (BE) model and it was found that increased temperature increased Raman widths due to phonon scattering processes.

The line-shape width increases from 331 to 651 meV for temperatures from 95 to 325 K; these high Raman width values indicate the high localization effect of impurities and defects in the GO-BPA samples.

By considering expression (2.10) in which thermal conductivity is proportional to the relaxation time and according to the Matthiessen rule given by expression (2.11), the relaxation time that dominates the scattering processes in thermal properties of the samples studied is the relaxation time with the minimum value, as discussed in section 2.2.

Then, assuming these basics discussed in section 2.1.1, the main scattering processes that dominate thermal conductivity and other thermal properties can be identified by analysis of the $\Gamma_{2D}(T)$ because this relation has the maximum Raman width values as a function of temperature, as shown in **Figure 4.21.**, and to produce the minimum relaxation time according to expression (4.6).

Therefore, identification of these scattering processes with temperature was carried out by using two ways, first, by considering the BE model and second by using the analysis of the temperature influence on the relaxation time.

First case: temperature dependence on the Raman width behavior can be described similar to semiconductor material by the BE model, given by [40]:

$$\Gamma(T) = \sqrt{\Gamma_0^2 + \Gamma_{p-p}^2 \left[\exp\left(\frac{\hbar\omega}{kT}\right) - 1 \right]^{-2}} \quad (4.5)$$

Where Γ_0 (cm^{-1}) is the broadening parameter independent of temperature, extrapolated value at $T = 0$ K, and related with the phonon-impurities and defects interactions, Γ_{p-p} is the phonon-phonon interaction intensity in cm^{-1} units, and $\hbar\omega$ is the average energy of the phonon participant in eV units, k is the Boltzmann constant and T the temperature in Kelvin.

Table 4.7. presents the values of the BE model parameters obtained from fitting the curves by using expression (4.5) and shown in **Figure 4.21.**

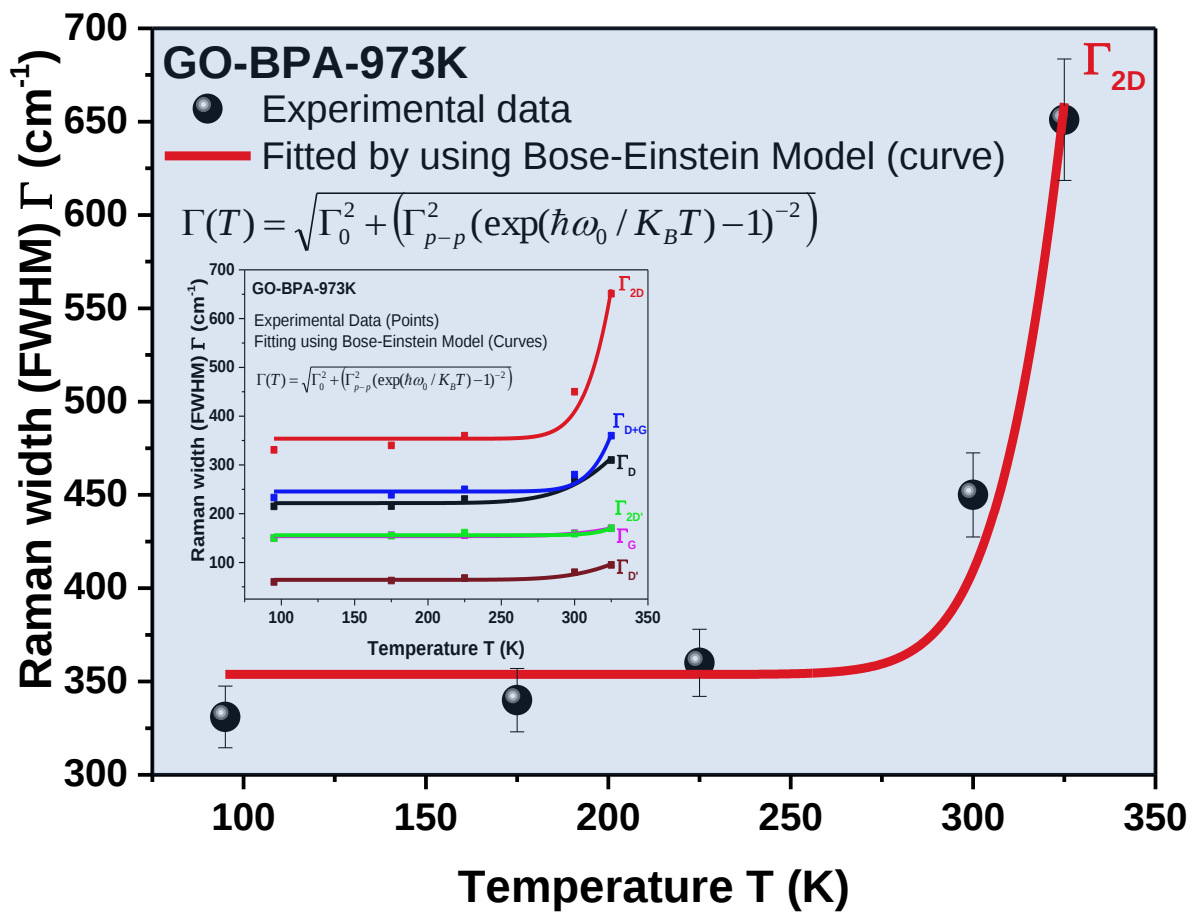


Figure 4.21. Temperature dependence on the Raman width in GO-BPA-973 K at 2D band (black circles), considering 5% error in experimental data and theoretical data described by fitting with the BE model, considering the following scattering process (red solid curve): Phonon-defect and phonon-impurity interactions at low temperatures (<190 K) and phonon-phonon interactions at temperatures ranging from 190 to 325 K. The inset shows the temperature influence on the Raman width for the other D, G, D', 2D, D+G, and 2D' bands (squares) and the respective fits by using expression (4.5) (solid curves).

The high average phonon energy can be attributed to localization of phonons in multifunctional oxides and defects present in the sample. It was found that this behavior can be attributed to phonon-phonon interaction (from 190 to 325 K), phonon-impurity interaction, and phonon-defect interaction (below 190 K).

These phonon dispersive processes were activated by temperature, as expected. The higher broadening values of the Raman spectra were obtained for the 2D band, as observed in the inset of **Figure 4.21.**, and possibly the thermal properties of GO-BPA are strongly influenced by the Γ_{2D} (T) behavior and independent of the phonon-electron interaction.

Table 4.7. BE model parameters obtained from fitting the curves shown in **Figure 4.21.** by using expression (4.5).

FWHM $\Gamma(T)$	$\Gamma_0(T = 0 \text{ K})$ (cm^{-1})	Γ_{p-p} (cm^{-1})	Phonon energy average $\hbar\omega$ (meV)
Γ_D	221 ± 1	$8.3 \times 10^4 \pm 0.6 \times 10^4$	166 ± 1
Γ_G	154 ± 1	$7.3 \times 10^4 \pm 0.7 \times 10^4$	194 ± 1
$\Gamma_{D'}$	64 ± 2	$8.3 \times 10^4 \pm 0.7 \times 10^4$	198 ± 1
Γ_{2D}	353 ± 15	$8.6 \times 10^7 \pm 0.5 \times 10^7$	335 ± 2
Γ_{D+G}	245 ± 7	$1.0 \times 10^8 \pm 0.1 \times 10^8$	360 ± 2
$\Gamma_{2D'}$	156 ± 2	$6.5 \times 10^7 \pm 0.1 \times 10^7$	386 ± 2

Second case: identification of the phonon scattering processes in the GO-BPA sample, conducted by determining the temperature dependence on the relaxation time via Raman line-shape width, as presented ahead.

By considering the time-energy Werner Heisenberg uncertainty principle in a forced resonant distribution (as Lorentzian functions used in the fitted Raman spectra), the minimum of the relaxation time, $\tau(T)$, as a function of temperature (according to basics discussed in section 2.1.1.) is given by [19]:

$$\tau(T) = \frac{\hbar}{2\Gamma_{2D}(T)} \quad (4.6)$$

Where $\Gamma_{2D}(T)$ is the temperature dependence on the 2D band-Raman width in eV units and $\hbar = 6.582119514 \times 10^{-16}$ eV s as reduced Planck constant. By using expression (4.6) and the $\Gamma_{2D}(T)$, as presented in **Figure 4.21.**, it was possible to estimate the temperature effect on the relaxation time (blue circles) and the fit by using linear fit (red solid line), as presented in **Figure 4.22.**

It was observed that relaxation time increases from 4×10^{-15} s to 8×10^{-15} s when temperature decreases from 325 to 95 K, these orders of magnitude in relaxation time are very low compared with the 10^{-13} s expected by vibration of molecules in the infrared spectral range [19]; however, these low values of relaxation time in the GO-BPA sample may be associated to high localization of impurities and defects, as discussed in results of **Figure 4.21.**

Analysis of temperature dependence on relaxation time (in log-log scale) by using linear fit, as presented in **Figure 4.22.**, shows that the GO-BPA sample exhibits $\tau(T)$ as proportional to T^{-n} for two cases:

(1) When $n = 0.04$ ($n \sim 0$) in low-temperature regime from 95 to 190 K, approximately, the temperature-independent regime can be associated to phonon-impurities and phonon-defect interactions, as expected by considering basics to describe in this thesis by expressions (2.13) and (2.14) in section 2.1.1. (2) When $n = 0.92$ ($n \sim 1$) in high-temperature regime from 190 until 325 K, approximately, the inverse temperature-dependence regime can be associated to phonon-phonon interactions, as expected by considering basics to describe in this thesis by expression (2.15) in section 2.1.1.

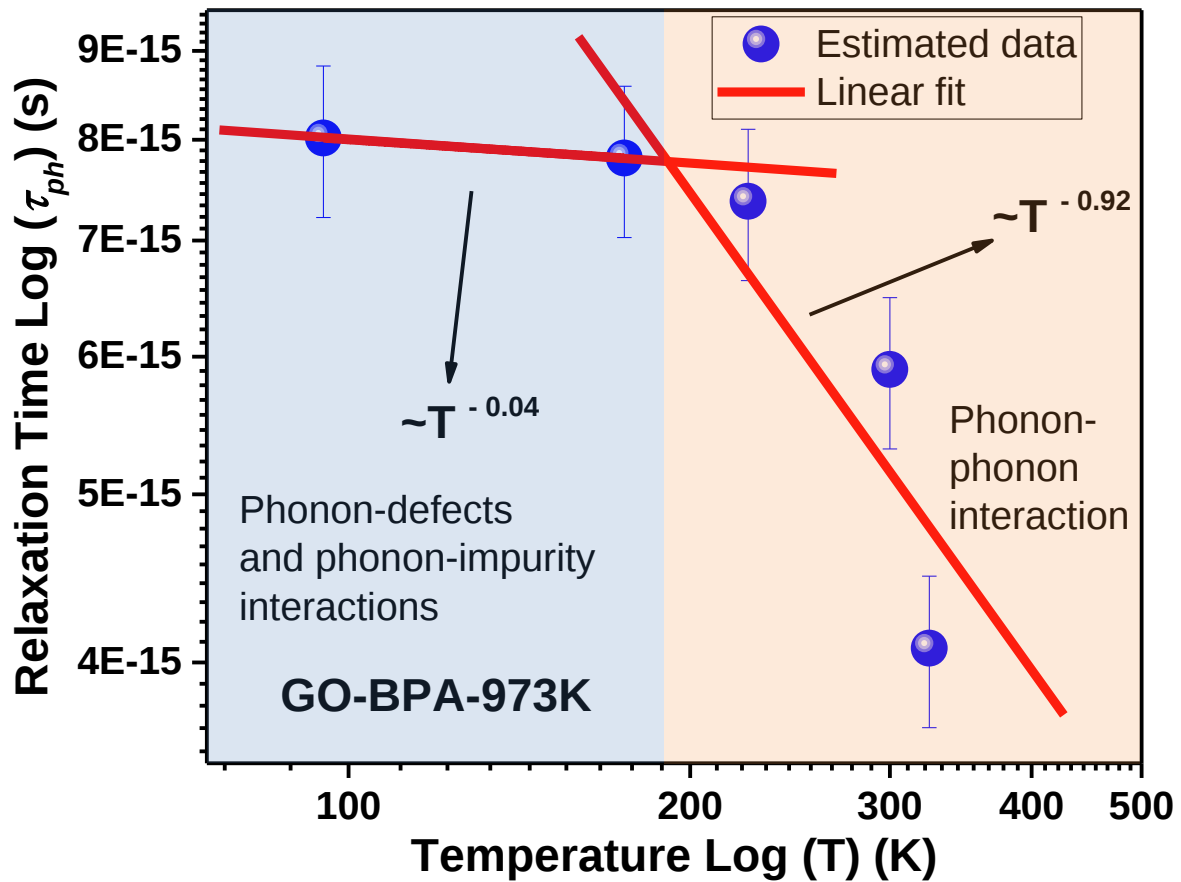


Figure 4.22. Temperature dependence on the phonon relaxation time in the GO-BPA sample synthesized at 973 K as T_{CA} , considering 10% error value in data estimated. Linear fits describe the following phonon scattering process: phonon-defect and phonon-impurity interactions at low temperatures from 95 to 190 K (blue region); this behavior is approximated independent of the temperature, as described by expressions (2.13) and (2.14), respectively, and phonon-phonon interactions at temperatures ranging from 190 to 325 K (orange region) with behavior inversely proportional to the temperature, as expected and described by expression (2.15).

These results suggests that in the GO-BPA samples the thermal properties cannot be influenced by phonon-electron interaction possibly due to high localization of impurities and defects, as observed by HR-TEM results and as shown in **Figures 4.2. (c) and (d)**; at room temperature, it can be explained by the electron-impurity interaction around $\tau \sim 10^{-16}$ s (**Figure 4.29.**), which is lower relaxation time by one order of magnitude than phonon-phonon interaction at $\tau \sim 10^{-15}$ s, as presented in **Figure 4.22.**

As mentioned, at room temperature the competition of the scattering processes in the GO-BPA sample suggests that thermal properties compete with the electrical properties by one order of magnitude and for this reason thermal properties are independent of phonon-electron or phonon-carrier interaction.

The vibrational properties studied in the GO-BPA samples involve identifying the functional groups, which was performed in this work by using FTIR spectra analysis, as seen ahead.

FTIR Technique in GO-BPA Samples. Fourier transform infrared spectroscopy is a versatile characterization tool used to study functional groups and organic compounds in carbon samples. **Figure 4.23.** presents the FTIR spectra in GO-BPA samples synthesized at different T_{CA} and graphite as reference.

As explicitly shown in **Figure 4.23.**, for the lowest T_{CA} , several peaks are detected at the following positions: 3426, 2927–2850, 2350, 1680, 1590, 1435–1370, 1157, and 1066 cm^{-1} , attributed to O–H, C–H, CO_2 due to experimental lab contribution, C=O, C=C, C–H, C–O–C, and C–O bonds, respectively. These results agree with peak positions previously reported [41] and presented in chapter 3.

However, when the T_{CA} increases from 673 to 973 K, desorption of some organic compounds and oxides also increases, varying oxide coverage from 12.99% to 5.25% in GO-BPA samples, respectively.

It is possible to observe that at 973 K the sample exhibits the presence of the C–H, C=C, and C–O bonds, as expected in pyrolysis processes by thermal decomposition. Additionally, it was observed that increased T_{CA} and FTIR spectra of GO-BPA samples exhibit conversion to carbon as graphite material.

Identification of the main thermal transport mechanisms in GO-BPA samples has been presented; the following section reviews some basic results about the identification of main electrical transport mechanisms in GO-BPA samples.

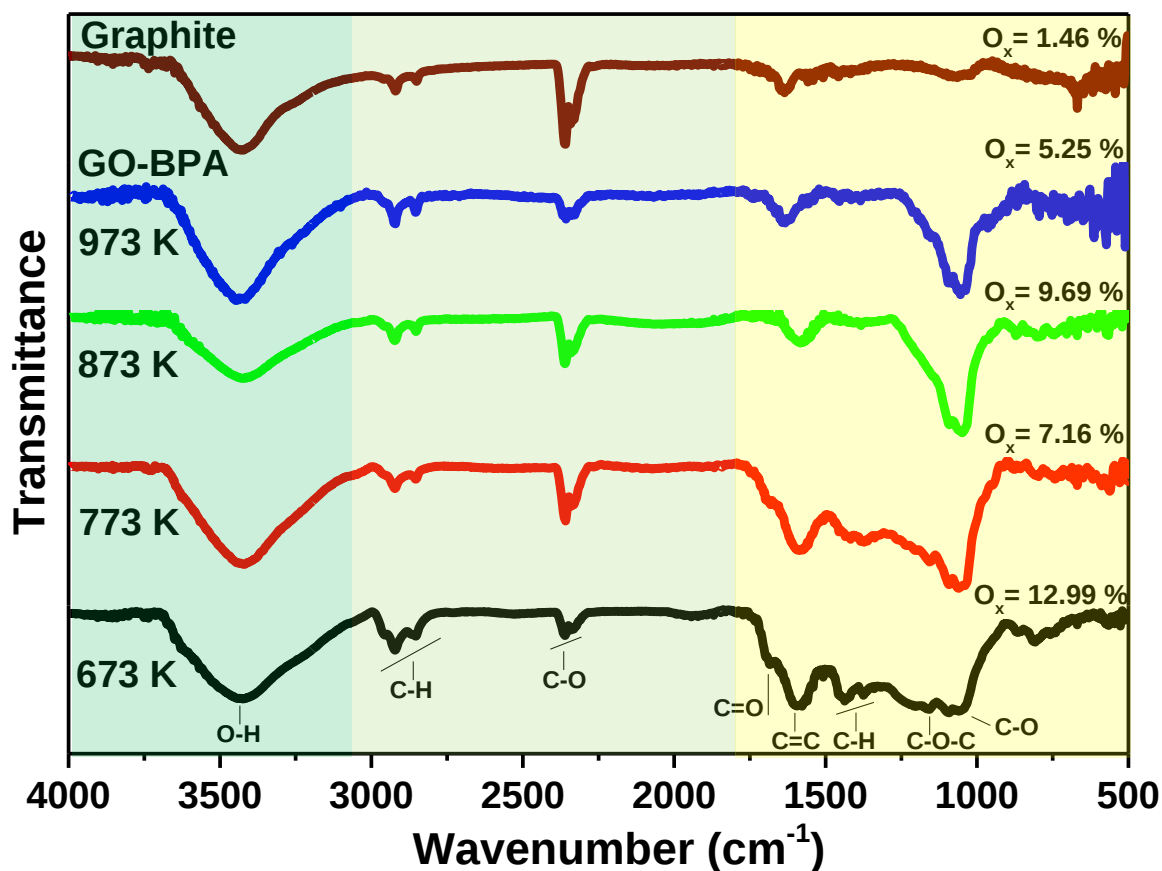


Figure 4.23. FTIR spectra in GO-BPA samples synthesized at different T_{CA} ; experiments were conducted at RT.

4.2.2 Electrical Transport Mechanisms

The main electrical scattering processes exhibited by GO-BPA samples were studied by considering electrical behavior in individual nanoplatelets via estimations of the relaxation time variations with the oxide at % at room temperature.

At low temperature, the scattering process was identified by using the hopping theory. To obtain the electrical response in single nanoplatelets, it was necessary to have nanowires at 300 nm as electrical contacts. A single GO-BPA sample electrically contacted is shown ahead.

Electrical contacts in single GO-BPA nanoplatelets. Figure 4.24. presents the SEM images in individual GO-BPA nanoplatelets electrically contacted by using FEBID-FIBID technique. We also used EDS in an SEM to complete the compositional study and check oxygen content (at %, C_O).

To perform electrical measurements of individual nanoplatelets, the samples were prepared by suspending GO-BPA nanoplatelets in isopropanol and deposit them in proximity

to the metallic contact pads (fabricated first via optical lithography) on an SiO_2/Si substrate. Individual nanoplatelets were then located at low voltages (<5 kV) using an SEM equipped with a focused ion beam (FIB) (Helios 650 model by FEI). The focused ion beam induced deposition (FIBID) technique was used to deposit four Pt lead wires to connect the nanoplatelets to the metallic contact pads, where micro-probes were positioned.

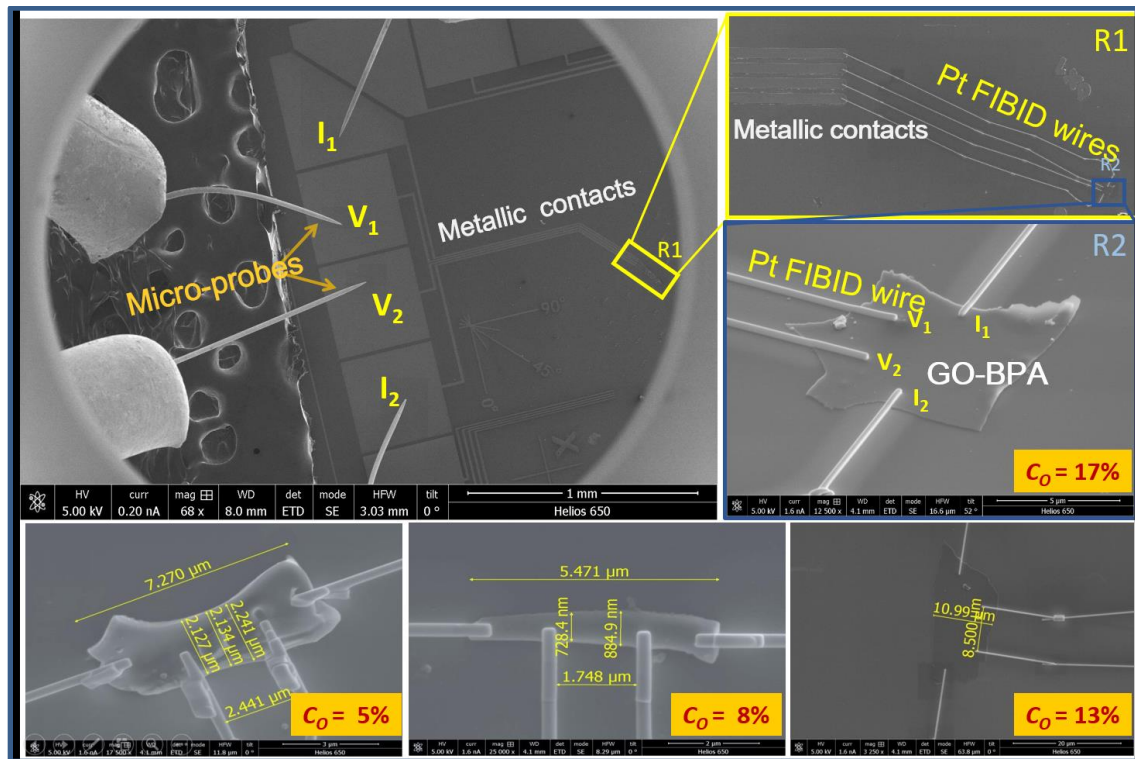


Figure 4.24. SEM image of the experimental setup displaying the micro-probes and the metallic contact pads (left), zoomed area of region R1 showing the Pt-wires grown via FIBID technique on an SiO_2/Si substrate (top right), and zoomed area of region R2 showing a typical single GO-BPA nanoplatelet with lateral dimensions around $7\ \mu\text{m}$ and thickness $t < 100\ \text{nm}$, and Pt contacts to perform the electrical measurements (bottom right). Taken and adapted from our group reference [18].

The Pt based contacts deposited optimally by FIBID allow low contact resistivity to perform noise-free electrical characterization of micro- or nanostructures [42, 43]; for more details of this technique refer to section 3.2.5 of this thesis and reference [44].

The SEM images of the experimental setup displaying the micro-probes, metallic contact pads, and Pt wires on single GO-BPA nanoplatelets are shown in Figure 4.24. The electrical measurements were performed by injecting current in a range of $\pm 6\ \mu\text{A}$ on the two external contacts using a Keithley 6220 DC current source; while voltage was measured at the two internal contacts with a Keithley 2182 A nano-voltmeter (see the bottom right panel in Figure 4.24). Temperature-dependent measurements of the resistance were performed within a vacuum chamber using a closed-cycle Helium cryostat system.

Room temperature conductivity: effect of the oxygen content. Variation of the synthesis conditions, specifically T_{CA} , leads to modification of the oxygen-containing functional groups, as well as of the crystal structure in GO-BPA as single nanoplatelets, as already presented and also confirmed via XRD and by other techniques, as reported by our group [12]. Figure 4.25. shows V-I measurements in single GO-BPA nanoplatelets obtained at different oxide coverage. Expected ohmic behavior was observed. To know the geometry of the samples by using SEM technique, it was possible to determine electrical conductivity in each single GO-BPA nanoplatelet.

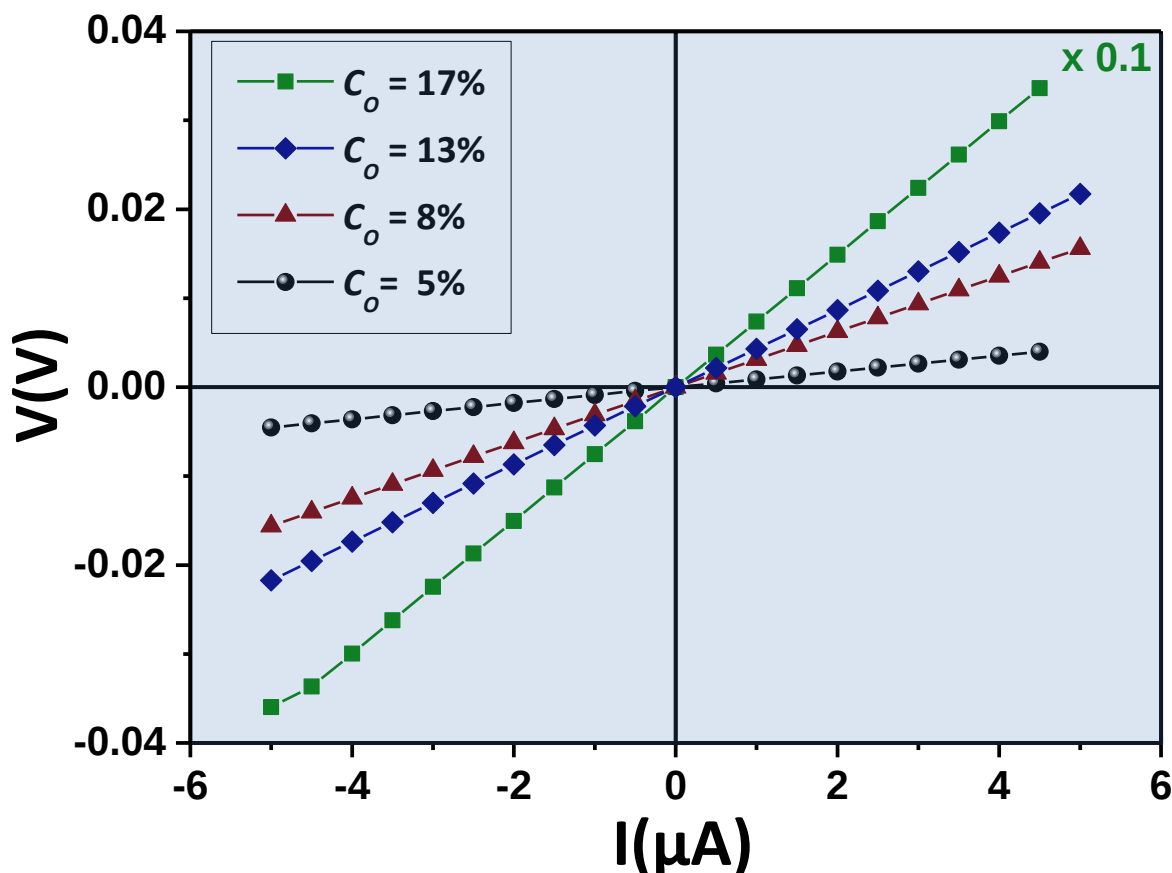


Figure 4.25. V-I measurements in single GO-BPA nanoplatelets obtained at different oxide coverage. Measurements at room temperature.

For electrical characterization, we focused on single GO-BPA nanoplatelets obtained at higher T_{CA} (873 and 973 K), which ensures an improved crystal structure, as confirmed by HR-TEM results, as presented in Figure 4.2. (c) and (d). Under these temperature conditions, the oxygen content is below 20%, which is of our interest, given that it is known that within this oxygen regime the electrical behavior in GO is still unclear. Room-temperature electrical conductivity was obtained via current-voltage (I-V) measurements for the oxygen atomic concentrations $C_o = 5\%$, 8% , 13% , and 17% . All I-V curves exhibit ohmic behavior along the entire current range ($\pm 6 \mu A$), allowing calculation of conductivity values from the slope and geometric parameters of the nanoplatelets obtained via SEM. Room-temperature conductivity as a function of C_o is shown in Figure 4.26. Decreased oxygen content from

17% to 5% resulted in conductivity rise by two orders of magnitude, starting from $6.4 \times 10^1 \text{ Sm}^{-1}$ and reaching a value of $2.3 \times 10^3 \text{ Sm}^{-1}$ at the lowest oxidation degree.

These values are comparable with literature reports on RGO obtained through chemical/thermal reduction methods, where it has been shown that conductivity can vary from 5 to $5 \times 10^4 \text{ Sm}^{-1}$, depending on the degree of reduction [45, 46] and agreeing with values presented in Table 2.3. When Oxygen atoms from the functional groups are released, the GO lattice, rich in sp^3 hybridization, transforms into a graphene-like structure due to the restoration of sp^2 hybridization and, thereby, its conductivity increases. Also, RGO sheets, obtained through chemical reduction, exhibit only moderate room-temperature conductivities, predominantly as a consequence of crystal defects (like extended holes) that cannot be healed during the reduction process. Formation of holes in our single GO-BPA nanoplatelets can be considered minimal, as evidenced by HR-TEM examinations.

To gain more insight on the dependence of conductivity on oxygen concentration, as shown in Figure 4.26, we consider the relation given by expression (2.27), which relates the carrier concentration to the temperature and bandgap energy E_g , for an intrinsic semiconductor with k being the Boltzmann constant. Thus, if a linear dependence of the bandgap on oxygen concentration is assumed, as proposed in [47], and because σ is proportional to n , $\ln(\sigma)$ will behave linearly with C_O , also presented in section 2.1.2.

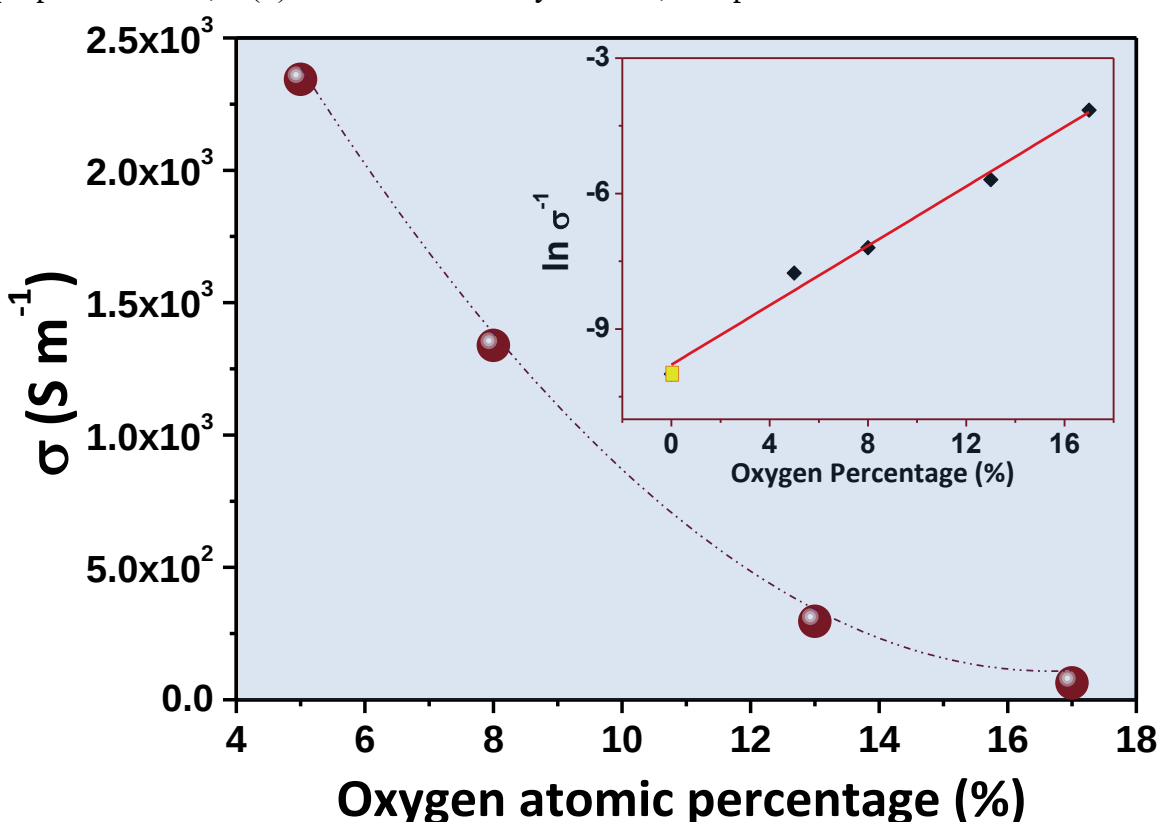


Figure 4.26. Electrical conductivity as a function of oxygen content ($C_O = 5\%$, 8% , 13% , and 17%). The line is a guide to the eye. Inset: fit (solid line) to the experimental data (full diamonds) by using the expression for carrier concentration for an intrinsic semiconductor. Determined at room temperature. Taken and adapted from our group reference [18].

Our experimental data, inset in [Figure 4.26.](#), agrees with these theoretical assumptions. For contextualization, we compared our data in this plot with that reported for graphite (yellow square). As can be seen, the conductivity for the lowest value of oxygen content found in single GO-BPA nanoplatelets is still around one order of magnitude lower than the value for graphite ($2 \times 10^4 \text{ Sm}^{-1}$), thereby, elucidating the direct effect of the oxygen functionalized groups on electrical conductivity.

By using the explicit relationship given by expression (2.29) $\sigma = \sigma_0 \exp(-E_g/(2kT))$ with $\sigma_0 = 2 \times 10^4 \text{ Sm}^{-1}$, as reported for graphite at $T = 300 \text{ K}$, and considering conductivity values for $C_O = 5\%$, 8% , 13% , and 17% , reported in [Figure 4.26.](#), we estimated the energy bandgap values as a function of C_O , as shown in [Figure 4.27.](#), along with a fitted line using the general quadratic dependence of the bandgap with the scatter center X applied for semiconductors [48, 49]. Bandgap energy shows a variation from 0.30 to 0.11 eV by decreasing the oxygen content. Agreement between our experimental results and theoretical prediction is quite remarkable, providing evidence of oxygen-mediated charge-transport scattering in our single GO-BPA nanoplatelets and suggesting that our samples exhibit narrow-gap semiconductor behavior, as expected and reported by our group [18].

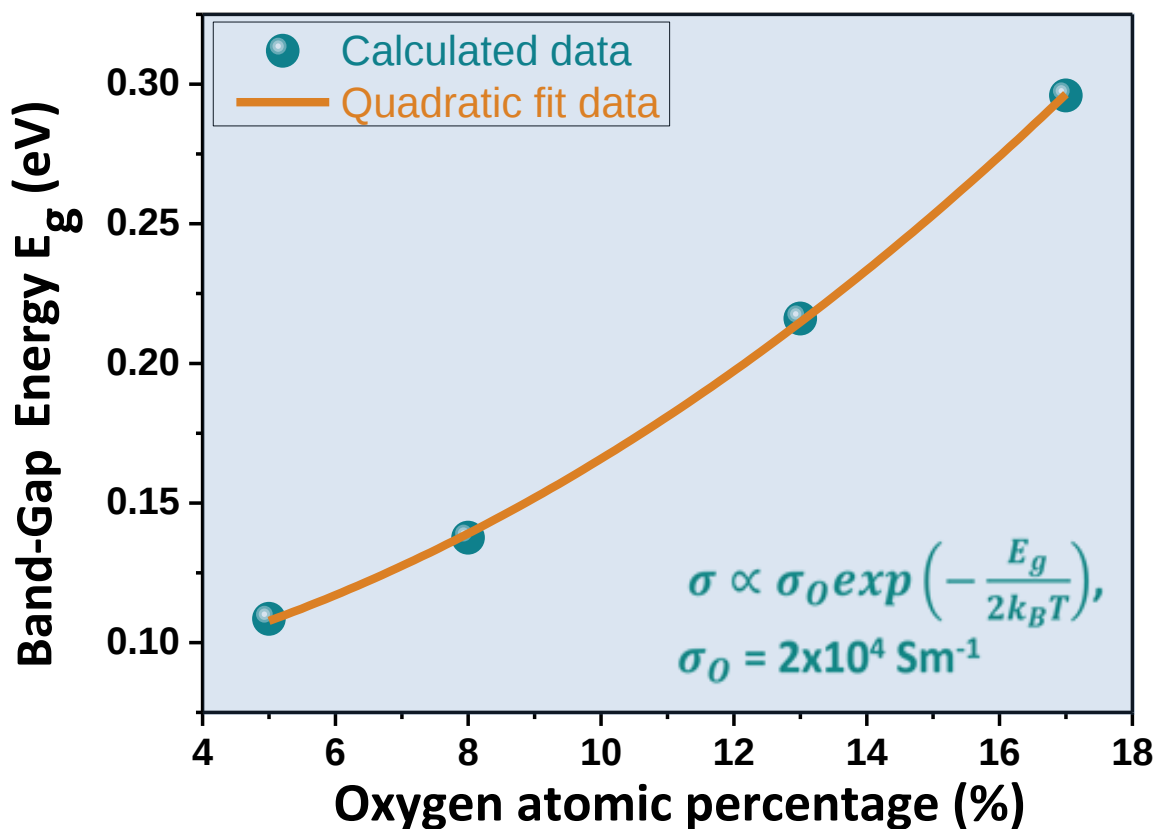


Figure 4.27. Band-gap (E_g) of single GO-BPA nanoplatelets plotted versus their corresponding oxygen at %; orange solid line is the fit by using the general quadratic dependence of the band gap on the scatter center, X, applied for semiconductors [48, 49]. Values estimated at room temperature. Taken and adapted from our reference [18].

The comparison behavior between theoretical and experimental results of oxygen coverage dependence on the band-gap energy is presented in **Figure 4.28. (a)**. Band-gap energy was determined for each oxygen coverage measured via EDX in our samples of graphene oxide multilayers (single GO-BPA nanoplatelets), as shown in **Figure 4.28. (a)**. Band-gap energy values (black points) shown a variation from 0.30 to 0.11 eV by decreasing the oxygen content, as expected for a narrow-gap semiconductor behavior. The red fitted curve is the general quadratic dependence of the band-gap on the scatter center, X , applied for semiconductors. [18, 48, 49].

The theoretical predictions of the band-gap energy variations with oxide coverage obtained via DFT computational simulations in graphene oxide molecular model, as presented in section 3.3, agrees with the experimental results, providing evidence of oxygen-mediated charge-carrier transport scattering.

The implicit solvation COSMO model is shown to visualize the surface charge screening density throughout the molecule. **Figure 4.28. (b)** shows surface charge screening density through the molecule for a representation of 12% oxygen content in single GO-BPA nanoplatelets. The surface charge density, as calculated by the COSMO model, is represented by green, blue, and red color zones, which represent the neutral, negative, and positive charge density values, respectively, or, in other words, the specific polarity on the molecular surface. As such, the negative surface charge density of the molecule is located on the right side of the σ -profile graph and has positive σ -values, while the positively charged parts are located on the left side and feature negative σ -values, as presented in **Figure 4.28. (c)**.

Figure 4.28. (c) Presents the quantity of the electrical surface charge screening density of graphene oxide structures for different oxygen coverage from 0% to 20% through the molecule (better known as the σ -profile). In general, the central region of the σ -profile is associated with nonpolar or weakly polar parts of the molecule, while strongly polar and potentially hydrogen bonding acceptor regions appear at the right-hand side and donor regions at the left-hand side of the σ -profiles. The carbon zones consist predominantly of nonpolar regions (green color in the surface charge screening density visualizations in **Figure 4.28. (b)**), which can be linked to exposed surfaces of carbon atoms. The peaks located in the hydrogen bonding acceptor zones correspond to oxygen atoms (red colored areas in the surface charge density), for the GO, this red region is due to epoxy groups in **Figure 4.28. (d)**. and agree with the Lerf-Klinowski molecular model of GO, as presented in section 2.3 and **Figure 2.9**.

Conversely, the peaks located in the hydrogen bonding donator region of the σ -profile correspond to hydrogen atoms of the alkyl side chain and hydroxyl groups (light blue regions). It was found that increasing oxygen coverage increases electron-hole pairs and electron acceptor donor abilities. Therefore, DFT simulations shown that in GO-BPA the electron donor abilities are more abundant than electron acceptor abilities, like n-type narrow gap semiconductor behavior. Identification of the main scattering processes in single GO-BPA nanoplatelets was done through the estimation of the influence of the oxygen coverage on relaxation time, as presented in **Figure 4.29**. via the linear Wallace model. See below some basics of this model.

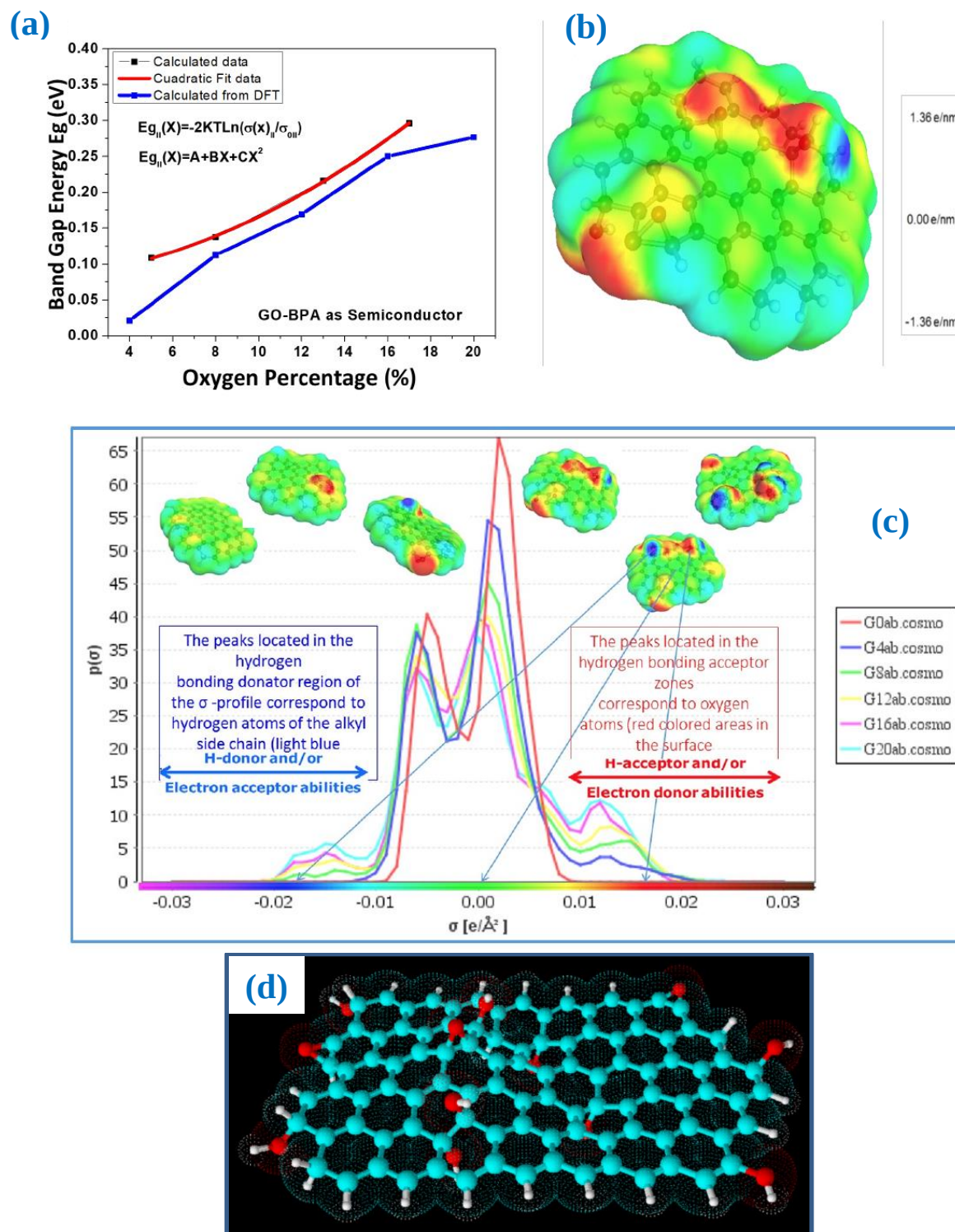


Figure 4.28. (a) Comparison between experimental data and theoretical calculation of the oxygen coverage dependence on the band-gap energy in a graphene oxide molecular configuration proposed in this work to represent the molecular model of single GO-BPA nanoplatelets. Theoretical results were performed under DFT-6-31G/B3LYP quantum level

theory **(b)** Visualization of surface charge screening density, as predicted by the conductor-like screening model for real solvents (COSMO-RS) for the GO under study. **(c)** The sigma-profile for the GO. **(d)** Graphene Oxide molecular model proposed and simulated in this investigation. Taken and adapted from our group reference [50].

In 1947, as proposed by P. R. Wallace [20], the relaxation time dependence on the parallel electrical conductivity in graphite, is given by:

$$\sigma = \frac{16 \pi e^2 (k_B T) \log(2)}{h^2 c} \tau \quad (4.7)$$

Here, σ is the electrical conductivity and $e = 1.6021766208(98) \times 10^{-19}$ Coulomb is the electron-charge constant, kT is the thermal energy at room temperature and equal to 26 meV, $h = 4.135667662(25) \times 10^{-15}$ eVs is the Planck constant, and $c = d_{002}$ is the interlayer d-spacing equal to the average value of 3.392 Å calculated from XRD measurement data presented in Table 4.1. Then, expression (4.7) can be written as:

$$\sigma = a \tau \quad (4.8)$$

Where a is the proportionality constant equal to $1.086 \times 10^{19} \text{ S m}^{-1} \text{ s}^{-1}$.

In 1946, as proposed by Conwell-Weisskopf [51, 52], the generalized carrier-impurity interaction can be described as $\tau \propto C_O^{-n}$ and when parameter $n = 1$ is a behavior associated to ionized impurities in a perfect crystal; however, in our results, additional contribution at $n = 0.87$ was observed, as shown in Figure 4.29. This behavior can be explained by: (1) our samples exhibit polycrystalline structural behavior with the high localization of impurities with random distribution, very different from the case of the impurities in a perfect crystal. (2) It is possible that in our samples not all impurities have ionized states. (3) In our samples, the dielectric permittivity can depend on ionized impurities. (4) Influence of the ionized impurities in the impurity energy. (5) In our samples, the effective mass can be affected by impurities present with random distribution. Also, (6) and/or local screening effects. Therefore, these aspects required more theoretical approximations.

Assuming that our samples exhibit chemical and electrical behaviors at low oxygen concentrations, similar to graphite, it was possible to consider that single GO-BPA nanoplatelets can be described by the linear relation of expression (4.7). Therefore, the effect of the oxygen coverage on relaxation time of single GO-BPA nanoplatelets (blue circles) and the theoretical fit (red solid line) by using the generalized Conwell-Weisskopf model described by expression (2.20), as presented in Figure 4.29., show that decreased oxygen coverage from 17% to 5% increased the carrier relaxation time from $2 \times 10^{-18} \text{ s}$ to $6 \times 10^{-16} \text{ s}$. These low values of the carrier relaxation times are only an estimation by considering the linear relation suggested by Wallace [20] and it possibly indicates that in our samples the localization of impurities can produce a strong interaction with the charge carriers. Therefore, the respective fit by using expression (2.20) describes well the values calculated from experimental data.

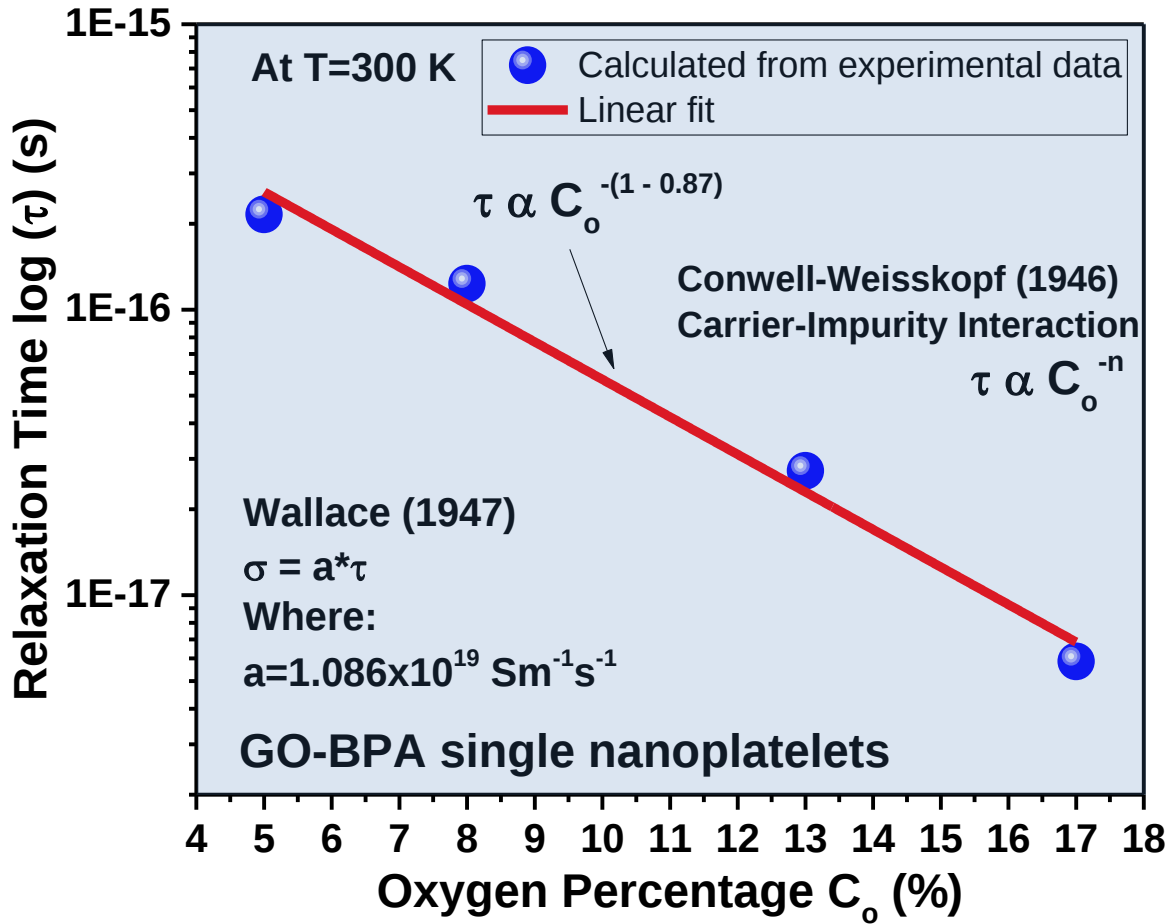


Figure 4.29. Influence of the oxygen coverage on relaxation time of single GO-BPA nanoplatelets (blue circles) and fitted by using the generalized Conwell-Weisskopf model given by expression (2.20) at room temperature. These results show that single GO-BPA nanoplatelets exhibit charge-carrier impurity interaction as a main scattering process at room temperature.

Therefore, at room temperature carrier-impurity interaction is the main scattering process in single GO-BPA nanoplatelets.

Temperature dependence on electrical conductivity. Figure 4.30. shows the temperature dependence on electrical resistivity in a single GO-BPA nanoplatelet at $C_o = 5\%$ (violet circles) and the inset presents the theoretical fit by using the 3D-VRH model described by expression (2.24). It is observed that the theory described very well the experimental data; these results indicate that our sample presents at low temperature electrical conduction by hopping.

It has been reported that temperature-dependent conductivity for the semiconductor-like behavior of RGO can be explained by VRH through the localized states [53-59]. For electrical conductive systems, percolation models are able to fit experimental data [60]. To gain insight into the energies associated with the charge transport in our single GO-BPA

nanoplatelets, the temperature dependence on conductivity was investigated. **Figure 4.30.** shows that resistivity increases with decreasing temperature, exhibiting a semiconductor-like behavior. The total variation of the resistivity in this range is less than one order of magnitude, showing weak temperature dependence on resistivity, as reported for highly reduced GO [46].

We have plotted $\ln(\sigma T^{1/2})$ as a function of $T^{-1/4}$ within 25 - 300 K, which is shown in **Figure 4.30.**, along with a best-fit line from the VRH model. These results suggest that the charge transport in GO-BPA is dominated by the Mott 3-D VRH transport behavior. For this case, the temperature dependence on conductivity can be expressed as expression (2.24).

$$\sigma = \frac{\sigma_0}{T^{1/2}} \exp \left[- \left(\frac{T_0}{T} \right)^{1/4} \right] \quad (4.9)$$

Here, σ_0 and T_0 are given by:

$$\sigma_0 = \frac{3e^2 v_{ph}}{(8\pi)^{1/2}} \times \left[- \left(\frac{N(E_F)}{\alpha k} \right) \right]^{1/2} \quad (4.10)$$

And,

$$T_0 = \frac{16\alpha^3}{kN(E_F)} \quad (4.11)$$

Where v_{ph} it is the phonon frequency ($\approx 10^{13}$ Hz) at Debye temperature. $N(E_F)$ is the density of the localized electron states at Fermi level and α is the inverse localization length of wave function associated with the localized state. As noted from the graph $\ln(\sigma T^{1/2})$ versus $T^{-1/4}$ in the inset of **Figure 4.30.**, the plot exhibits a very linear behavior along the entire T range, having a linearity factor of 0.997. From the slope and intercept values, parameters $T_0 = 7.1 \times 10^4$ K and $\sigma_0 = 8.8 \times 10^3$ Sm⁻¹ are obtained considering expression (4.9). Using the extracted values for T_0 and σ_0 , we calculated the density of the localized states at Fermi Level $N(E_F) = 1.2 \times 10^{21}$ eV⁻¹cm⁻³ and a value for α of 7.78×10^6 cm⁻¹ according to expressions (4.10) and (4.11).

Likewise, localization length, $\xi = 1/\alpha$, is determined at 1.3 nm; this value agrees with the average value of 1.6 nm determined by Raman in-plane crystal size, as shown in **Figure 4.17.** Thus, if assuming a wave function confined inside the graphitic domains of size $D \sim \xi$, and considering the linear dispersion relation for graphene as $E(\mathbf{k}) = \hbar v_F \mathbf{k}$, being v_F the graphene Fermi velocity, and with $\mathbf{k} \sim 1/2\xi$, the bandgap energy can be estimated to be 0.22 ± 0.02 eV, in good agreement with the value of 0.25 eV of oxidized graphene reported in reference [61]. Temperature dependence on the band-gap energy in a single GO-BPA nanoplatelet at 5% oxide coverage is presented in **Figure 4.31.**

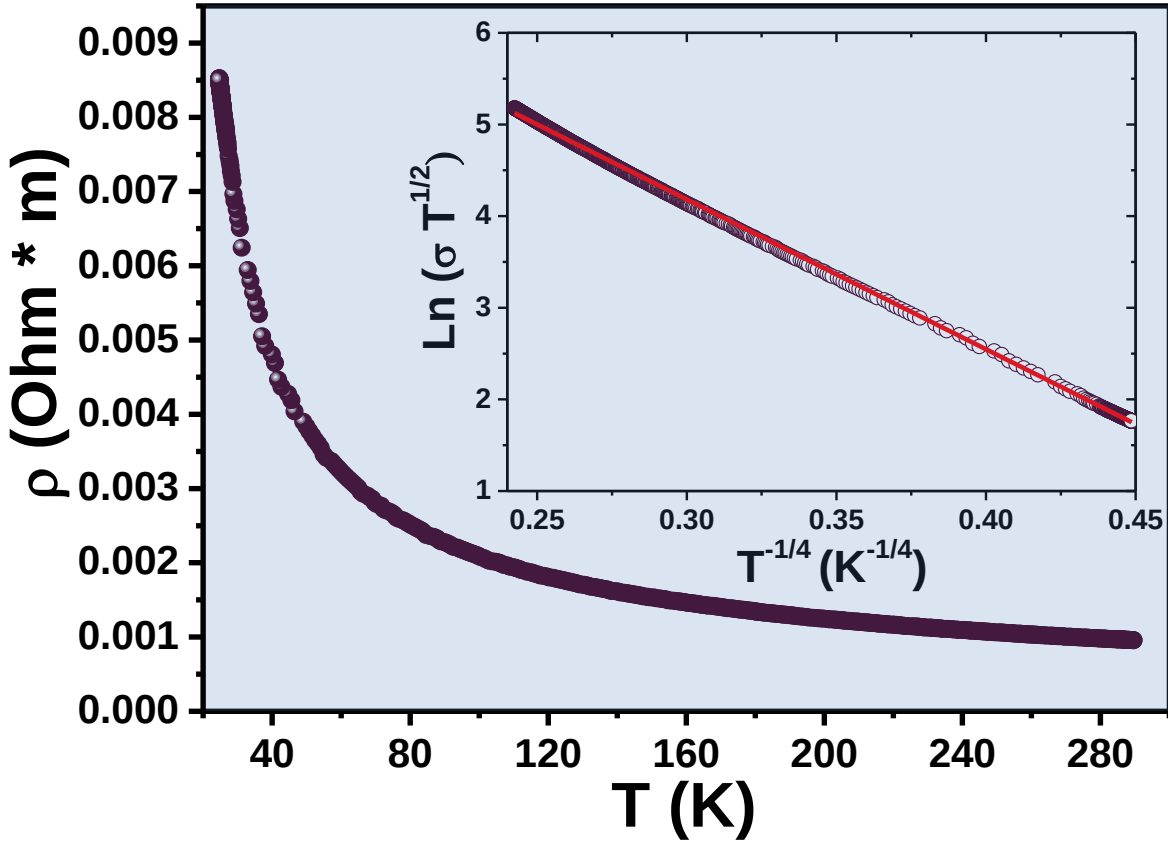


Figure 4.30. Temperature variation of electrical resistivity in a single GO-BPA nanoplatelet with 5% oxygen coverage content. Inset: Fitted (red solid line) to the experimental data (open circles) by using the Mott 3D-VRH transport model from expression (2.24). Taken and adapted from our group reference [18].

Due to the low 5% value of oxygen coverage exhibited by a single GO-BPA nanoplatelet, this work proposed that $E_g(T)$ behavior in this sample can be estimated by considering $\sigma(T)$ as inverse of experimental data presented in Figure 4.30., and replacing expression (4.7) in expression (2.29), then, we have that:

$$\sigma(T) = \sigma_G kT \exp\left(-\frac{E_g}{2kT}\right) \quad (4.12)$$

Here, σ_G is equal to 0.8×10^6 S/meV, a value that represents the shift-ratio of the electrical conductivity in graphite by thermal energy unit in meV, associated with the conductivity of graphite and independent of temperature, E_g is the band-gap energy and k is the Boltzmann constant. The exponential term is related with the temperature effect on the electrical response of the intrinsic semiconductor material and the additional terms represent the temperature dependence on the electrical conductivity of graphite, as proposed by the Wallace model. Then, obtaining $E_g(T)$ from expression (4.12), it can be written as:

$$E_g(T) = -2kT \ln\left(\frac{\sigma(T)}{\sigma_G kT}\right) + 2E_{g(300K)} \quad (4.13)$$

Where, two terms appear in expression (4.13). The first term is associated to temperature effect on band-gap energy of the GO material as semiconductor in the low-oxygen coverage regime (5% in single GO-BPA nanoplatelet, already mentioned). The second term is twice the band-gap energy value at room temperature (value previously known) required in expression (4.13) as a reference value to calibrate the curve and obtained from experimental data. Therefore, by replacing values of $\sigma(T)$, calculated from inverse of experimental data presented in [Figure 4.30.](#), and replacing $\sigma(T)$ in expression (4.13), it was possible to estimate the temperature influence on the band-gap energy of a single GO-BPA nanoplatelet, as shown in [Figure 4.31.](#)

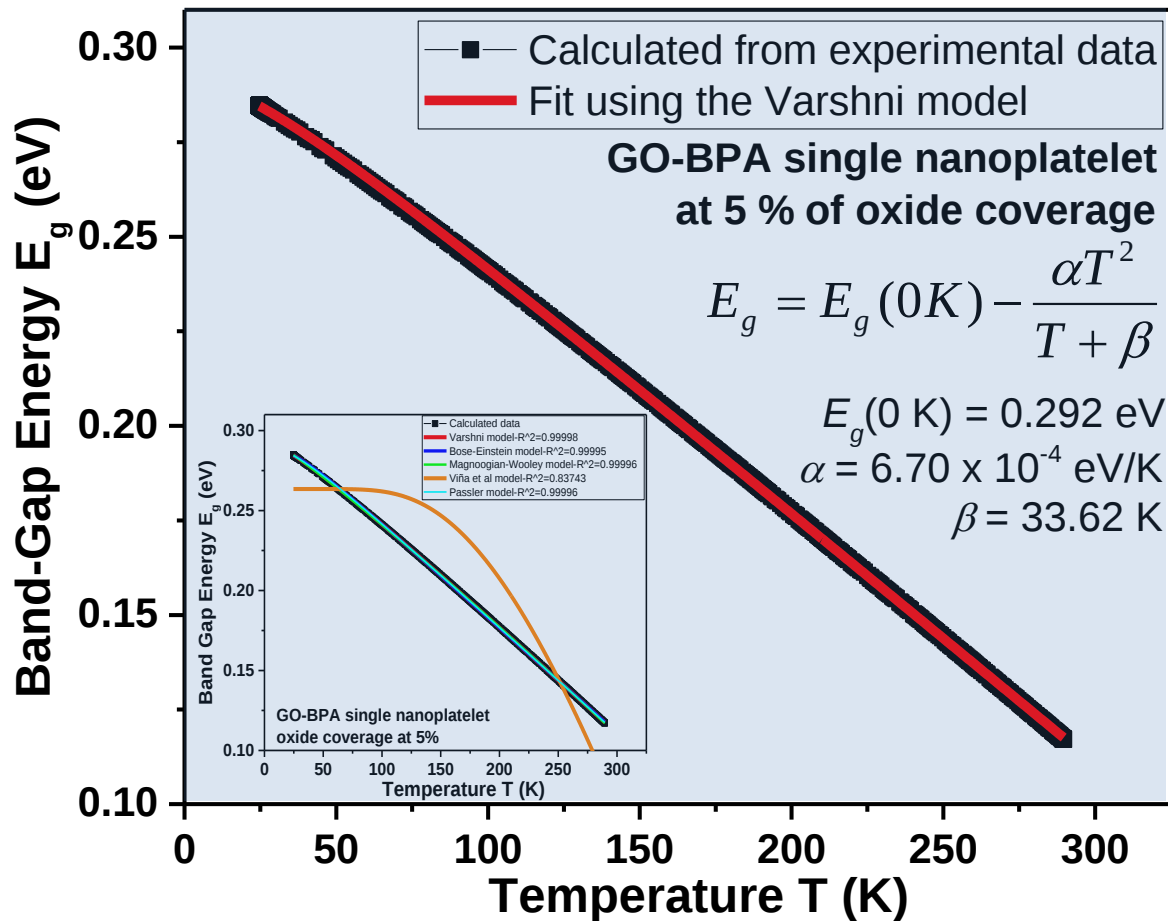


Figure 4.31. Temperature dependence on the band-gap energy in a single GO-BPA nanoplatelet at 5% oxygen coverage (black square), fitted by using the Varshni model and its respective parameters (red solid line). Inset: temperature versus band-gap energy and its respective fits by using different models reported, as presented in chapter 2 section 2.1.2.

It was observed that decreased temperature from 290 to 25 K increased band-gap energy from 0.117 to 0.285 eV, as expected for a narrow band-gap semiconductor material. The red solid line shows the fit of the data calculated by using the Varshni model described through expression (2.31), with square regression value at 0.99998 and $E_0(0K) = 0.292$ eV, as the best fit. Inset shows the same fit by using different phenomenological models, as presented in section 2.1.2. All fit parameters are listed in **Table 4.8**.

Figure 4.31. shows that the Viña model does not describe the experimental data as expected and presents the square regression value of 0.83743. The other models can be related by means of these fit parameters: $\beta \cong \Theta_B/2 \cong \Theta_P$ and $\alpha \cong \alpha_p/2$, as presented in **Table 4.8**. It was found that $E_g(T)$ can be described by the Varshni phenomenological expression, as expected for a semiconductor material, obtaining the Varshni coefficients at $E_g(0 K) = 0.292$ eV, $\alpha = 6.70 \times 10^{-4}$ eV/K, and $\beta \cong 34$ K; these values agree with the known order of magnitude of the Varshni coefficients reported for other narrow band-gap semiconductors, like InAs ($E_g(0K) = 0.417$ eV, $\alpha = 2.76 \times 10^{-4}$ eV/K, and $\beta = 93$ K) and InSb ($E_g(0 K) = 0.235$ eV, $\alpha = 3.90 \times 10^{-4}$ eV/K, and $\beta = 140$ K).

Table 4.8. List of fit parameters of the models used to describe the theoretical behavior of temperature dependence on the band-gap energy in a single GO-BPA nanoplatelet at 5% oxide percentage, as presented in **Figure 4.30**.

Models to describe $E_g(T)$				
Varshni	Bose-Einstein	Magnoonian -Wooley	Viña <i>et al.</i> ,	Päsler
$E_0(0 K) = 0.292$ eV	$E_0(0 K) = 0.288$ eV	$E_0(0 K) =$ 0.296 eV	$E_0(0 K) =$ 0.263 eV	$E_0(0 K) =$ 0.290 eV
$\alpha = 6.70 \times 10^{-4}$ eV/K	$\alpha_B = 0.022$ eV	$V = 0.999$ eV/K	$b = 1.2$ eV	$\alpha_p = 3.34 \times 10^{-4}$ eV/K
$\beta = 33.62$ K	$\Theta_B = 67.49$ K	$\Theta = 1.1 \times 10^{-5}$ K	$\Theta = 721$ K	$\Theta_P = 67$ K
----	----	$U = 1$	----	$P = 1.95$
----	----	$S = 1$	----	----
$R^2 = 0.99998$	$R^2 = 0.99995$	$R^2 =$ 0.99996	$R^2 =$ 0.83743	$R^2 =$ 0.99996

Identification of the main electrical transport mechanisms in GO-BPA samples has been presented; we will now see some basic results related with the possible mechanisms involved in magnetic characterization of GO-BPA samples.

4.2.3 Magnetism in GO-BPA samples

In this work, we report on the room temperature (RT) FM in GO-BPA samples synthesized at different T_{CA} , induced by topographic defects. Topographic defects, created during the fabrication process, arise from a natural formation of clusters, which drastically distort the graphitic basal plane giving rise to step edges and abrupt surface curvatures. The topographic defects are found to be source of magnetic signal, as evidenced by MFM and bulk magnetization measurements. Increased defect density, which is tuned by T_{CA} , results in enhanced magnetization. Thus, the results observed here provide new experimental evidence of defect-induced magnetism in graphene-related materials without requiring the high cost of ion bombardment experiments [62, 63]. Moreover, the semiconducting nature of our GO-BPA samples combined with RT-FM may raise the hopes of low-cost carbon-based novel information technologies.

Magnetism induced by topographic defects in single nanoplatelets. For an in-depth look into the effect of defects on the topography, the surface of single GO-BPA nanoplatelets were further observed by AFM/MFM techniques. **Figure 4.32. (a)** presents the morphology of a representative platelet obtained at $T_{CA} = 873$ K, after the corresponding sonication, filtering, and selection processes. In this image, a nanoplatelet with lateral dimensions around $5\ \mu\text{m}$ and a thickness around $60\ \text{nm}$ was observed; at the center of the platelet a cluster can be observed; moreover, around the cluster some terrace-like topography can also be distinguished.

For a better visualization of the terraces, **Figure 4.32. (b)** shows the zoomed AFM image taken on an area next to the cluster. This AFM image reveals a topography with the presence of step edges (yellow lines) forming terraces, along with some surface deformations of positive curvature (yellow circles) due to the presence of smaller clusters.

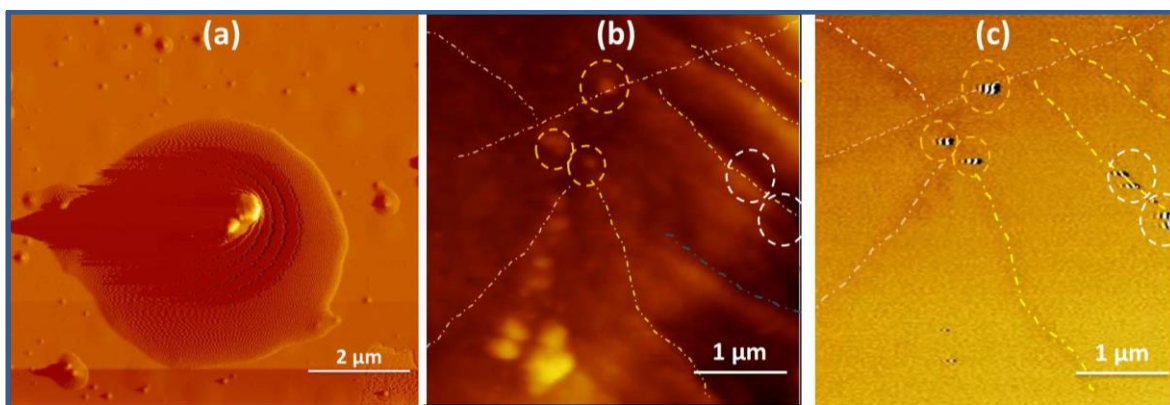


Figure 4.32. (a) AFM image of single GO-BPA nanoplatelet synthesized at $T_{CA} = 873$ K after cavitation, sonication, filtering, and selection processes. **(b)** AFM image and **(c)** corresponding MFM image of the topographic defects. Labels mark the different situations where surface deformations and magnetic contrast are correlated (see text). Taken and adapted from our group reference [68].

The corresponding MFM image taken at the same area with a 50-nm lift height is shown in **Figure 4.32. (c)**; from this image, dark magnetic contrast for four different situations can be identified: (1) at the position of most of the step edges, marked with yellow lines; (2) at the positions of some small clusters, marked with yellow circles; (3) at the positions marked with white-circles where no clusters are visible in the AFM image; (4) at the positions marked with white lines where no step edges are topographically visible in the AFM image.

Note that the intensity of the magnetic contrast is more pronounced for the positions marked with circles, that is, than that caused by the small clusters topographically visible or not. Magnetic contrast detected at the step edges can be attributed to the presence of the electronic edge states, which generally contribute to non-bonding pi-electronic states; these states produce a large density of states at the Fermi level, giving rise to the development of long-range magnetic order.

Additionally, magnetic contrast localized at the white-lines where no detectable topographic steps are visible can be attributed to originate from localized electron states at grain boundaries. Grain boundaries are edge states, like defects that although not detectable topographically under AFM, must be considered as a source of magnetic signal [64]. Moreover, considering the interrelation between grain boundaries and step edges and according to the findings reported by Cervenka *et al.*, [65] there is a statistical behavior for the occurrence of the magnetic signal originated by step edges, which not only depend on the step height but also on possible artifacts during the MFM measurement. Taking into account these observations, it is understandable that some steps do not generate magnetic contrast. Moreover, to discard a possible ambiguity of the magnetic contrast observed, we have performed repetitive MFM imaging by inverting the magnetization direction of the MFM tip.

These measurements have verified that reversed magnetization of the MFM tip resulted in a change from dark contrast to bright contrast, as presented in **Figure 4.32. (c)** and represented by white points; the latter discard that electrostatic interactions between defects and MFM tip causes the MFM contrast observed. Additional to the step edges and grain boundaries mentioned, we also observed even more pronounced magnetic signal arising from the small islands (case (2)). As mentioned, the fact that the 3-D deformation of graphene might lead to the appearance of magnetic signal being considered theoretically [66, 67]. These works have shown that strains, curvature, and structural deformations are possible routes to drastically modify the magnetization profile in carbon structures. Small clusters deforming the graphitic basal plane in our single GO-BPA nanoplatelet give rise to strong curvatures, thus, leading to significant magnetic signal.

At this point, we could identify, at a local level, the presence of defects inside the nanoplatelets and the magnetic signal arising from them. To investigate, on a general level, the effect of the defect density on the bulk magnetization of GO-BPA samples, we performed further analysis via Raman spectroscopy and $M(H)$ measurements on samples as powders, at room temperature. As shown in individual platelets, T_{CA} has a direct effect on the graphitization level and presence of defects; therefore, measurements in the bulk were also performed by varying T_{CA} .

Effect of the Raman defect density on room temperature ferromagnetism. Our focus on the effect of T_{CA} on the density of defects to understand the magnetic response at RT was presented in section 4.2.1., and it is considered here. **Figure 4.33.** presents the magnetization loops measured at 300 K in the external applied field range of -6000 to +6000 Oe for $T_{CA} = 673, 773, 873,$ and 973 K (here, the magnetization of the sample holder was introduced as reference). Ferromagnetic-like hysteresis loops, characterized by low remanence and coercivity values, are observed at RT in all samples.

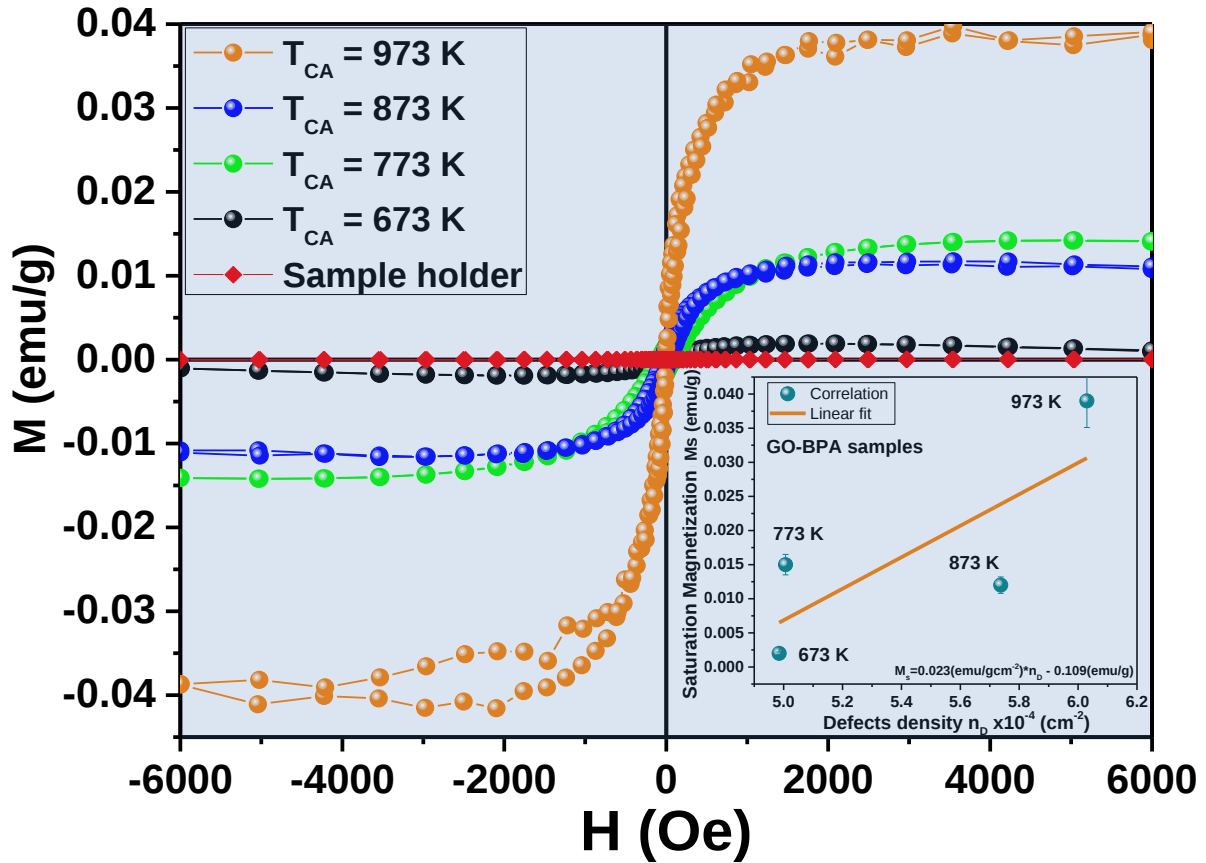


Figure 4.33. Magnetic hysteresis loops of GO-BPA samples synthesized at $T_{CA} = 673, 773, 873,$ and 973 K and measured at $T = 300$ K. The sample holder background (red diamonds) is also shown. No background subtraction has been performed. The inset is the defects density (calculated from Raman results) influence on the saturation magnetization (calculated from magnetic hysteresis) as correlation result (more details in section 4.3). Taken and adapted from our group reference [68].

The effect of T_{CA} on magnetization is clearly visible: as T_{CA} increases, the saturation magnetization (M_s) monotonically increases from $2 \cdot 10^{-3}$ emu/g at $T_{CA} = 673$ K to $40 \cdot 10^{-3}$ emu/g at $T_{CA} = 973$ K.

In correlation with the defects and as shown by SEM images, it can be stated that defects were more pronounced in the sample prepared at higher T_{CA} . The correlation between M_s and defect density obtained from Raman is plotted as inset.

To explain the magnetic metal impurity contribution, we employed XPS measurements with an analysis area of $700 \times 300 \mu\text{m}$ and a depth profile of $10 \mu\text{m}$ for all samples; within this measurement capacity, no magnetic impurities were detected.

By using a graphic method, it was possible to obtain the T_{CA} influence on M_s , coercive field, H_c , and magnetic remanence, M_R , as shown in [Figures 4.34.](#), [4.35.](#), and [4.36.](#), respectively. Also, the inset in [Figure 4.34.](#) presents the effect of the XRD-carbon atoms out-plane distance with the Raman defect density, finding that increased carbon out-plane distance increased defect density, and suggests that M_s increased. In other works, M_s can be affected by Raman defect density and XRD disorder produced by increased carbon out-plane distance (more details in section 4.3). The FM order in GO-BPA samples can be induced by boundary defect density and disorder, as reported by Sudipta Dutta *et al.*, [[64](#)].

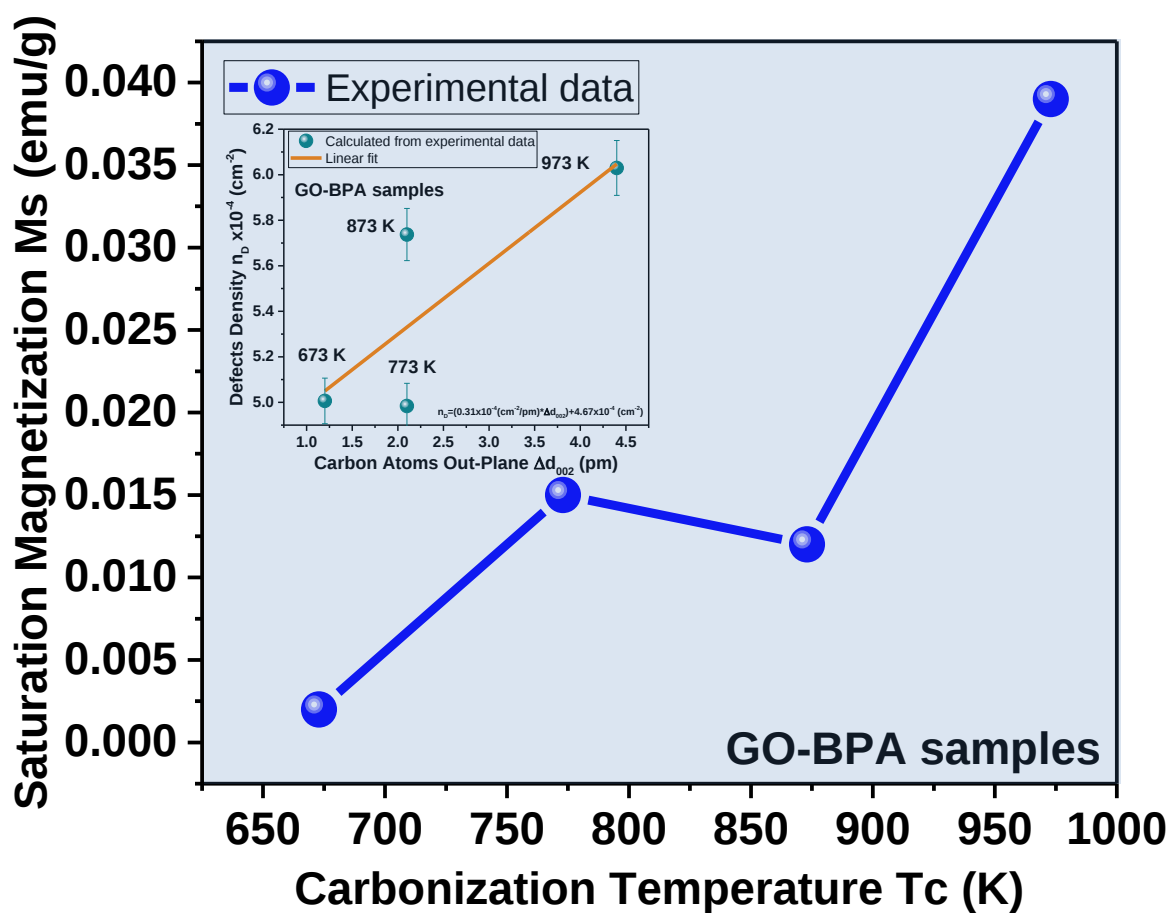


Figure 4.34. M_s as a function of T_{CA} in GO-BPA samples. Inset: XRD carbon atoms out-plane effect on Raman defect density as a physical correlation result.

Figure 4.35. presents the effect of T_{CA} on the H_c of GO-BPA samples and it was found that decreased T_{CA} increased H_c ; this behavior can be attributed to the effect of Raman in-plane crystal size on coercive magnetic energy involved in FM order exhibited by the samples, as presented in the inset: the effect of Raman-in-plane crystal size in H_c (blue

circles) and linear fit (red solid line) obtained as correlation behavior (more details in section 4.3). It was observed that increased crystal size increased H_c due to the coercive magnetic energy required to produce FM order, which increases by expansion of crystal size and this behavior occurs in GO-BPA samples when the T_{CA} decreases, as presented in Figure 4.17.

The linear fit to experimental data of crystal size dependence on the H_c (blue circles) by considering 5% error is shown in the inset of Figure 4.35. (red solid line). It was found that the linear behavior approach proposed in this investigation described the experimental data and offers physical information about the slope value of 128 Oe/nm as shift-ratio of the H_c affected by nanometer increments in crystal size and intercept value of -154 Oe as minimum possible H_c when the GO-BPA samples exhibit very low crystal sizes.

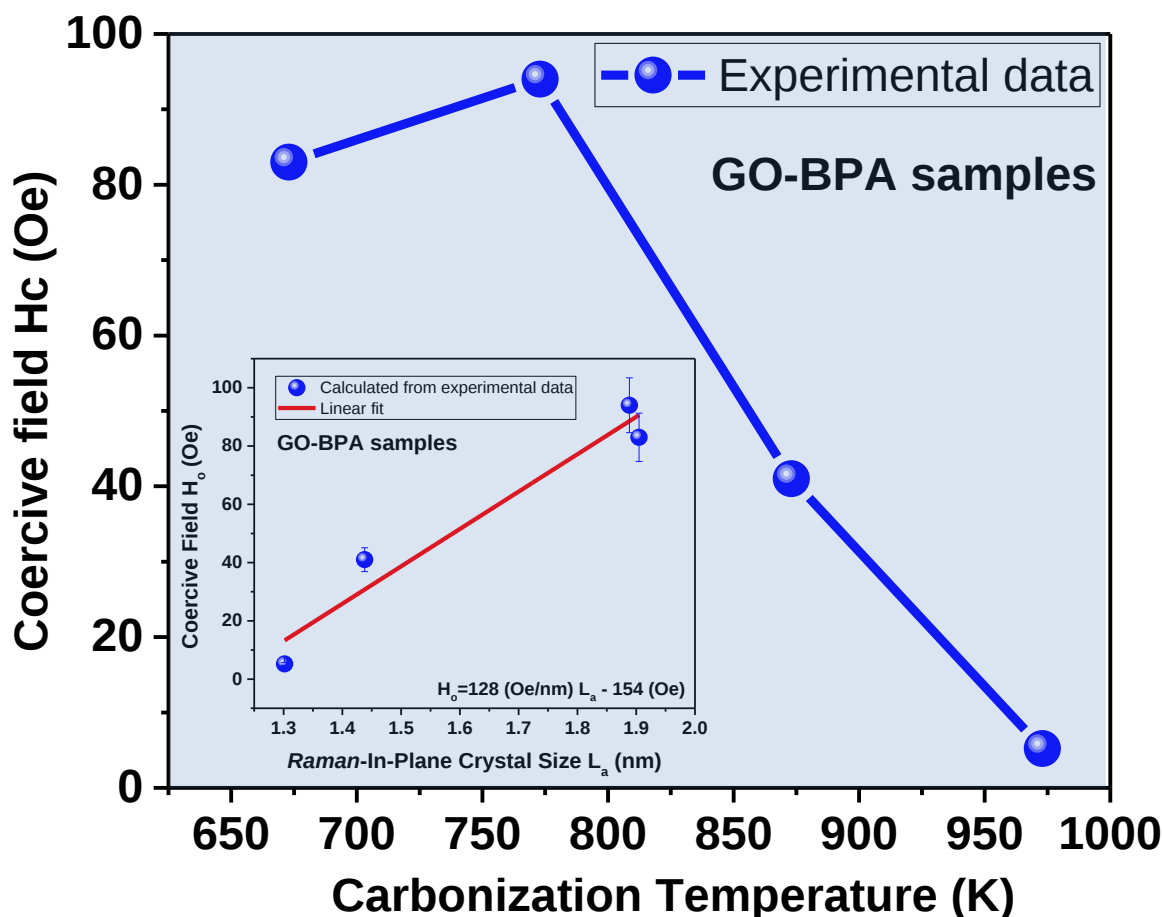


Figure 4.35. H_c as a function of T_{CA} in GO-BPA samples. Inset is the effect of Raman-in-plane crystal size in H_c (blue circles) and linear fit (red solid line) obtained as correlation behavior (more details in section 4.3).

Figure 4.36. shows the effect of T_{CA} in M_r of GO-BPA samples and it was found that decreased T_{CA} increased M_r ; this behavior can be attributed to the effect of Raman in-plane crystal size in M_r involved in FM order exhibited by the samples, as presented in the inset:

the effect of Raman-in-plane crystal size in M_r (blue circles) and the respective linear fit (red solid line) obtained as correlation behavior (more details in section 4.3).

It is possible to observe that increased crystal size increased magnetic remanence possibly due to the magnetization that remains in our samples after an external magnetic field is eliminated, which increases with increased crystal size and favors the appearance of magnetic domains in GO-BPA samples, also, this behavior occurs in GO-BPA samples when T_{CA} decreases, as presented in Figure 4.17.

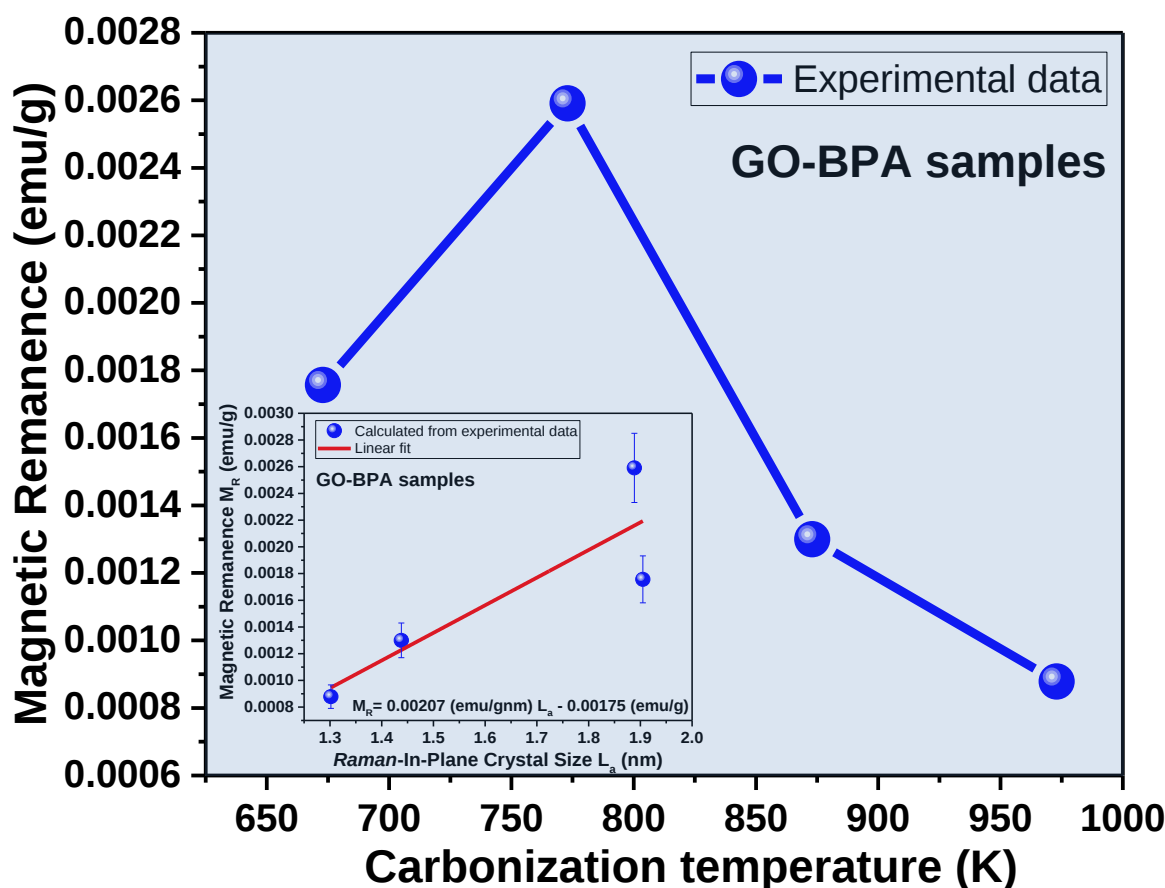


Figure 4.36. M_r as a function of T_{CA} in GO-BPA samples. Inset is the effect of Raman-in-plane crystal size in M_r (blue circles) and linear fit (red solid line) obtained as correlation behavior (see section 4.3).

The linear fit to the experimental data of crystal size dependence on M_r (blue circles, by considering 5% error) is shown in the inset of Figure 4.36. (red solid line). It was found that the linear approach proposed in this investigation describes the experimental data and offers information about the slope value of $2.07 \cdot 10^{-3} \text{ emu/gnm}$ as shift-ratio of the remanence affected by nanometer increments in crystal size and intercept value of $-1.75 \cdot 10^{-3} \text{ emu/g}$ as minimum possible M_r when the GO-BPA samples exhibit very low crystal sizes.

The FM order observed at RT in GO-BPA samples can be induced by defects present in the samples with magnetic hysteresis-loop described by H_c and remanence, both depending on crystal size.

Magnetic mechanisms exhibited by GO-BPA samples have been illustrated; henceforth, we will discuss basic results about the identification of main physical correlations in results related with the elucidation of physical transport mechanisms in GO-BPA samples.

4.3 Possible Physical Correlations

In order to explore different physical effects that can affect the transport properties in GO-BPA samples, these materials were characterized by different fine characterization techniques and these permitted studying morphological, structural, elemental, vibrational, electrical, and magnetic properties. However, it is necessary to explain possible correlations among the physical properties studied in this work. This section presents the results of the possible physical correlations (as possible effects) among XRD carbon out-plane and magnetism, Raman defects and magnetism, XRD carbon out-plane and Raman defects, XRD carbon out-plane and oxygen coverage, Raman crystal size and H_c , Raman crystal size and M_r of the GO-BPA sample.

To corroborate the physical correlation, Pearson correlation coefficient matrices were evaluated and presented in this section [69, 70]. Also, as a first theoretical approach, all possible physical correlations were confirmed by using the Pearson statistical method and described by using linear behavior or the order contributions, non-linear contributions (second- and third-order terms, as possible contributions) were not contemplated because more experimental data was required to reduce errors [69, 70].

This aspect opens future work in basic and technological physical studies in the samples mentioned. Magneto-transport results were presented and discussed in this section.

XRD Carbon Out-Plane effect on FM exhibited by GO-BPA samples. Figure 4.37. presents the effect of the XRD carbon out-plane in M_s in GO-BPA samples (blue circles), considering 10% error in experimental data and its linear fit (red solid line). It was found that increased carbon out-plane distance from 2.1 to 4.4 pm increased M_s from 2.0 to $3.9 \cdot 10^{-3} \text{ emu/g}$; this behavior can be attributed to disorder that affects M_s by increasing high localization of electrons, which produce magnetic dipoles, as physically expected in any ferromagnetic material.

The respective analysis of the linear fit parameters yields $9.3 \cdot 10^{-3} \text{ emu/gpm}$ as positive slope related with the shift-ratio M_s affected by picometer associated to changes in carbon out-plane distances, and negative intercept of $5.9 \cdot 10^{-3} \text{ emu/g}$ as minimum possible M_s when the GO-BPA samples exhibit very low carbon out-plane distances. This linear approximation behavior was corroborated by determining the Pearson correlation coefficient matrix, as shown in Table 4.9. It was found that linear description of the effect of carbon out-plane in M_s presents correlation as described by the 1 value in the diagonal values of the Pearson matrix and sigma values <20%, which is related with the data deviation of linear behavior.

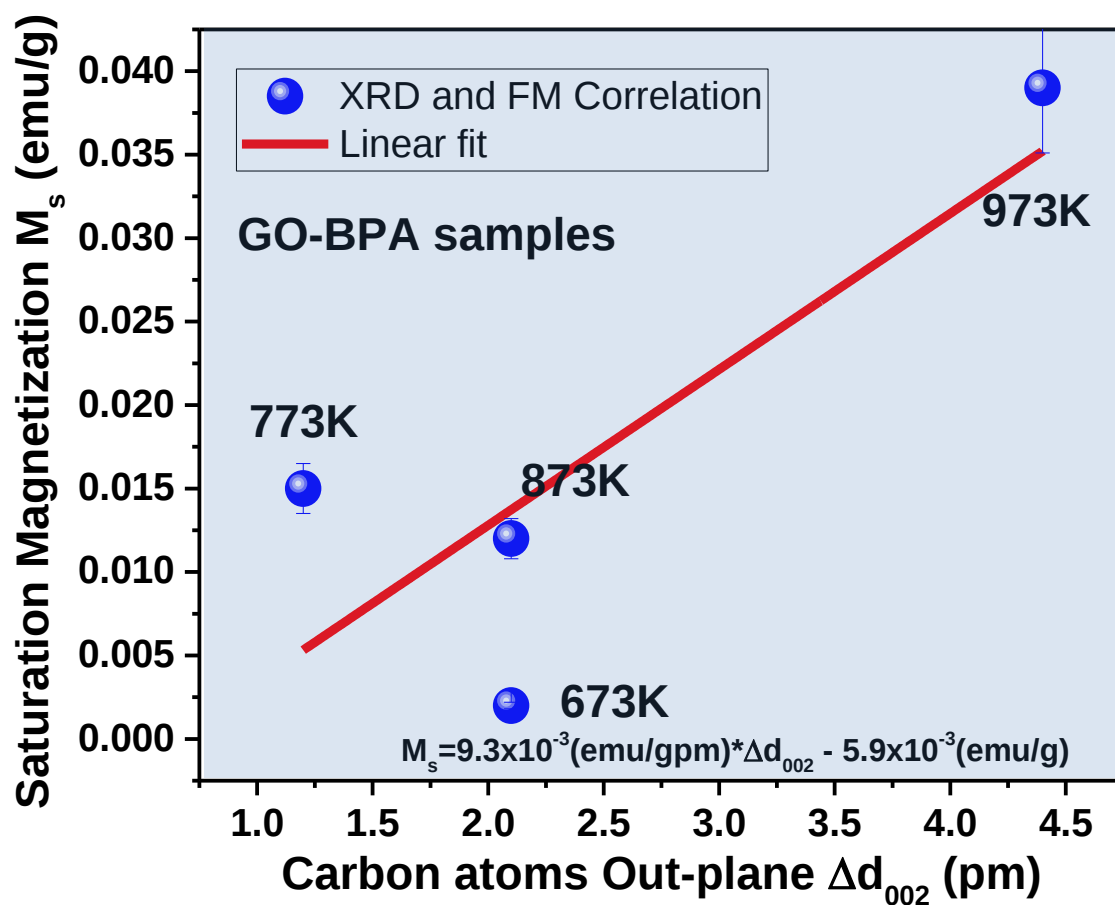


Figure 4.37. XRD carbon out-plane influence in M_s of GO-BPA samples (blue circles) by considering 10% error, and linear fit (red solid line).

Table 4.9. Pearson correlation matrix between M_s and XRD carbon out-plane data, as presented in **Figure 4.37**.

Coefficient	M_s	Δd_{002}
Pearson correlation	1	0.81437
Sigma	----	0.18563
Pearson correlation	0.81437	1
Sigma	0.18563	----

The FM order observed at RT in GO-BPA samples can be induced by disorder mainly due to defects present (as shown in [Figure 4.38.](#)) in the samples with magnetic hysteresis-loop.

Raman Defect Density Effect on Magnetism of GO-BPA samples. [Figure 4.38.](#) presents the effect of the Raman defect density in M_s of GO-BPA samples (dark cyan circles) and their linear fit (orange solid line). It was found that increased defects from $4.98 \times 10^{-4} \text{ cm}^{-2}$ to $6.03 \times 10^{-4} \text{ cm}^{-2}$ increased M_s from 2.0 to $3.9 \times 10^{-3} \text{ emu/g}$; this behavior can be explained by defect presence that affect directly the M_s due to increased number of localized magnetic dipoles.

Defects present in GO-BPA samples induced the FM order observed experimentally at RT. The respective analysis of the linear fit parameters yields $23 \times 10^{-3} \text{ emu/gcm}^{-2}$ as positive slope; it is related with the shift-ratio M_s affected by the unit of defects density, and negative intercept of $103 \times 10^{-3} \text{ emu/g}$ as a minimum possible M_s when the GO-BPA samples exhibit very low defect density.

By comparing the intercept magnitudes obtained from linear analysis in the experimental data presented in [Figures 4.37](#) and [4.38.](#), It is possible to observe that defects density produced a value of $103 \times 10^{-3} \text{ emu/g}$ greater than the $5.9 \times 10^{-3} \text{ emu/g}$ associated to the disorder effect; therefore, these results suggest that defects density affects FM order more than disorder, but disorder contribution is not negligible (only 5.7% contribution).

This linear approach behavior was corroborated by calculating the Pearson correlation coefficient matrix, as presented in [Table 4.10.](#)

It was found that linear description of the effect of defects on M_s presents correlation, as described by the 1 value in the diagonal values of Pearson matrix and sigma values <23%, which is related with the data deviation of linear behavior.

The FM order observed at RT in GO-BPA samples can be induced mainly by boundary defects density in the samples with magnetic hysteresis-loop, as expected from theory and presented in [Table 2.5](#) section 2.3. by high magnetic moment values and as expected experimentally for the RGO material and presented in [Table 2.4.](#)

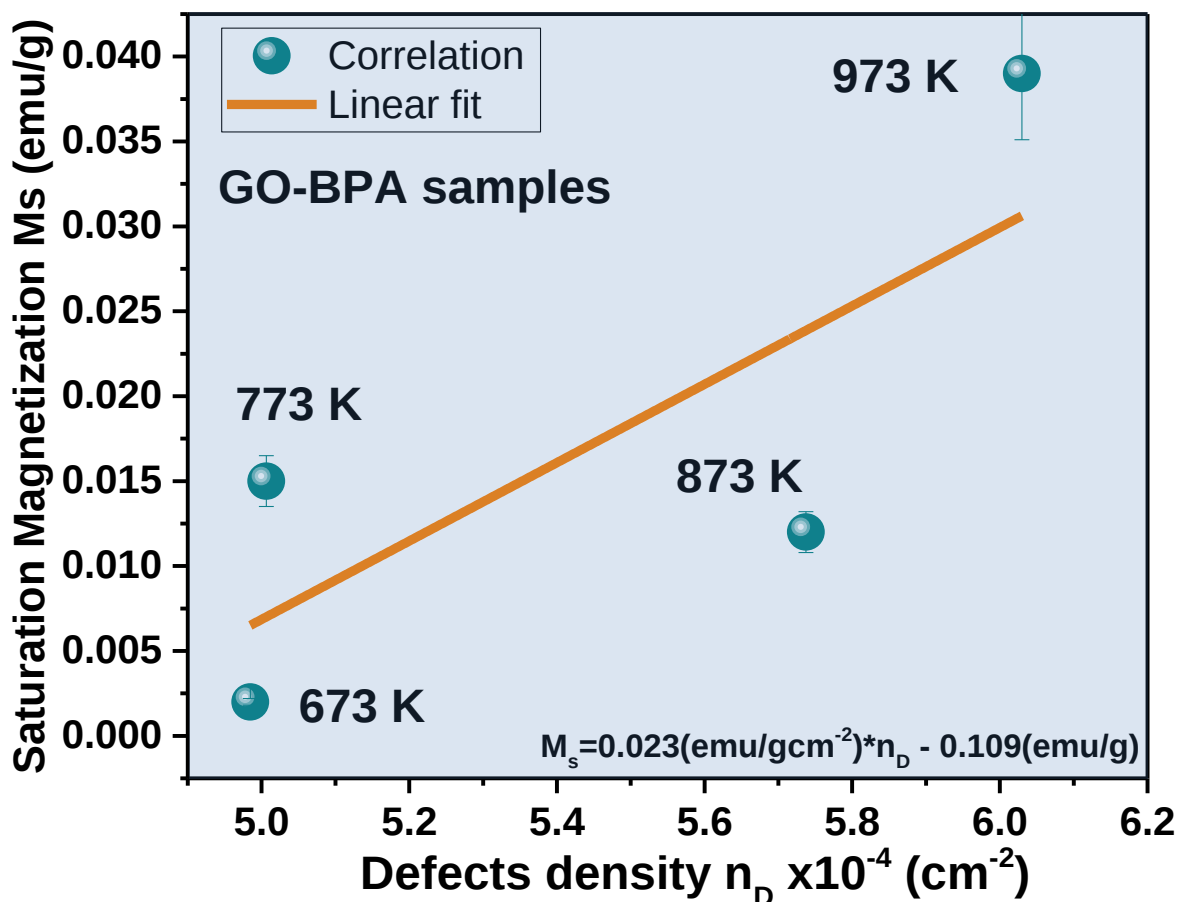


Figure 4.38. Influence of the Raman defects on M_s in GO-BPA samples (dark cyan circles) with 10% error and linear fit (orange solid line).

Table 4.10. Pearson correlation matrix between M_s and Raman defects data, as presented in **Figure 4.38**.

Coefficient	M_s	Δd_{002}
Pearson correlation	1	0.77445
Sigma	----	0.22555
Pearson correlation	0.77445	1
Sigma	0.22555	----

Effect of the XRD Carbon Out-plane on Raman Defects and XPS Oxygen Coverage of GO-BPA samples. Figure 4.39. shows the carbon XRD-out-plane distance influence on Raman defects of GO-BPA samples (dark cyan circles) and their linear fit (orange solid line). It was found that increased carbon out-plane distance from 2.1 to 4.4 pm increased defects density from $4.98 \times 10^{-4} \text{ cm}^{-2}$ to $6.03 \times 10^{-4} \text{ cm}^{-2}$. This behavior can be explained by defects also producing disorder in the GO-BPA samples. The inset presents the influence of carbon out-plane distance in XPS-oxygen coverage (dark cyan circles), and its linear fit (orange solid line). It was found that decreased carbon out-plane distance increased oxygen coverage and its respective fit. It was observed that carbon out-plane affects directly defects density. The respective analysis of the linear fit parameters involved on dependence of the Figure 4.39. yields $0.31 \times 10^{-4} \text{ cm}^{-2}/\text{pm}$ as positive slope, which is related with the shift-ratio of defects density affected by picometer unit in carbon out-plane distance, and positive intercept of $0.31 \times 10^{-4} \text{ cm}^{-2}$ as minimum possible defects density when the GO-BPA samples exhibit very low carbon out-plane distances.

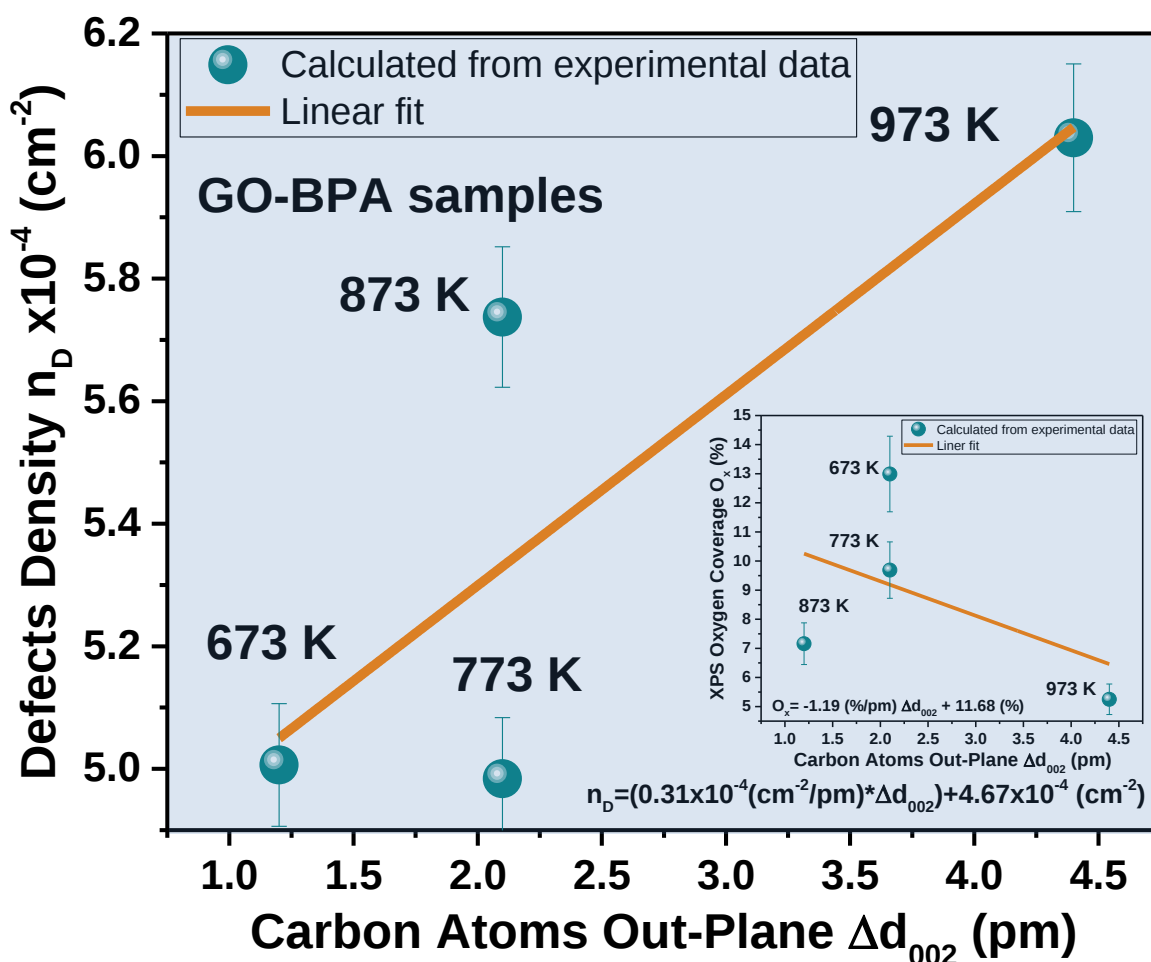


Figure 4.39. XRD carbon atoms out-plane influence on Raman defects density of GO-BPA samples (dark cyan circles), considering 10% as experimental error and linear fit (orange solid line). Inset is the variations of the oxygen percentage (from XPS results) by carbon atoms out-plane (calculated from XRD results) (green circles) and its linear fit (orange solid line).

This linear approach behavior was corroborated by calculating the Pearson matrix of correlation coefficients, as shown in **Table 4.11**. It was found that linear description of the effect of carbon out-plane distance in M_s presents correlation, as described by the 1 value in the diagonal values of the Pearson matrix and sigma values <20%, which is related with the linear deviation of the experimental data. This behavior suggests that the FM order observed at RT in GO-BPA samples can be induced by defects density in the samples with magnetic hysteresis-loop.

Table 4.11. Pearson correlation matrix between Raman defects density and XRD carbon atoms out-plane data, as presented in **Figure 4.39**.

Coefficient	Δd_{002}	n_D
Pearson correlation	1	0.80885
Sigma	----	0.19115
Pearson correlation	0.80885	1
Sigma	0.19115	----

Raman Crystal Size effects on H_c and M_r of GO-BPA samples. **Figure 4.40.** presents the effect of the Raman crystal size in H_c of GO-BPA samples (blue circles), and its linear fit (red solid line). It was found that increased crystal size from 1.30 to 1.90 nm increased H_c from 5.2 to 83 Oe, one order of magnitude difference. This behavior can be explained by expansion of the crystal size that produces an increment of the coercive magnetic energy required by the FM order observed in the GO-BPA samples. It was observed that crystal size affects directly the H_c .

The respective analysis of the linear fit parameter involved in crystal size dependence with the H_c yields 128 Oe/nm as positive slope that signifies direct proportionality between both correlated variables, and it is a value related with the shift-ratio of H_c affected by nanometer unit in expansion of the crystal size, finding a negative intercept of 154 Oe as a minimum possible H_c when the GO-BPA samples exhibit very low crystal size.

This linear approach behavior was corroborated by determining the Pearson matrix of correlation coefficients, as presented in **Table 4.12**. It was found that linear description of the effect of crystal size on H_c presents correlation as described by the 1 value in the diagonal values of the Pearson matrix and sigma values <3%, which is related with the linear deviation of the experimental data. This behavior suggests that the FM order observed at RT in GO-BPA samples can be induced by defects density in the samples with magnetic hysteresis-loop described by H_c depending on crystal size, as presented in the inset of **Figure 4.35**.

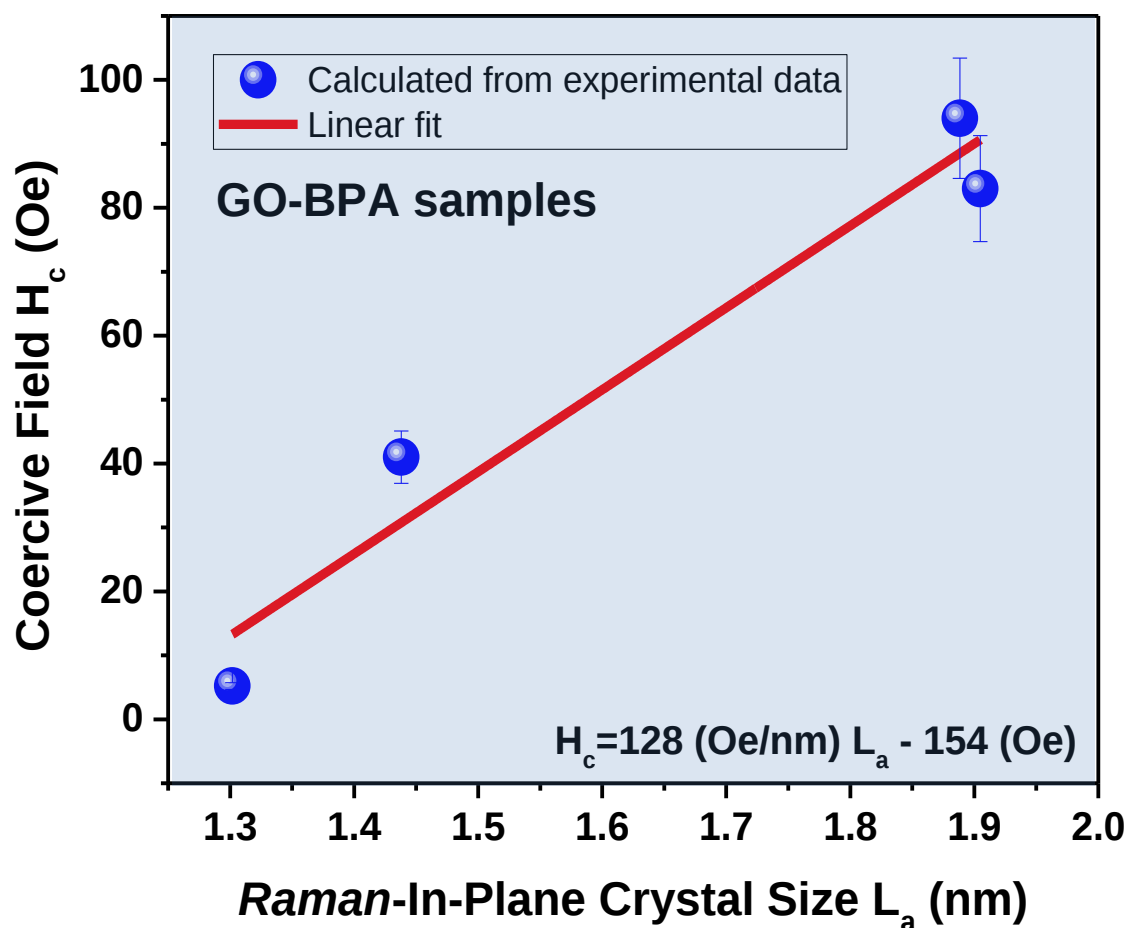


Figure 4.40. Effect of the Raman in-plane crystal size on H_c of GO-BPA samples (blue circles), considering 10% error and linear fit (red solid line).

Table 4.12. Pearson correlation matrix between Raman in-plane crystal size and H_c data, as presented in **Figure 4.40**.

Coefficient	L_a	H_c
Pearson correlation	1	0.97368
Sigma	----	0.02632
Pearson correlation	0.97368	1
Sigma	0.02632	----

Figure 4.41. shows the Raman crystal size influence on M_r in GO-BPA samples (blue circles), and their linear fit (red solid line). It was found that increased crystal size from 1.30 to 1.90 nm increased remanence from 0.87 to 1.76 10^{-3} emu/g, one order of magnitude difference. This behavior can be explained by expansion of the crystal size that produces an increment in remanence possibly due to the magnetization that remains in our samples after an external magnetic field is eliminated, which increases with the increase in crystal size and favors the appearance of magnetic domains in GO-BPA samples. It was observed that crystal size affects M_r directly.

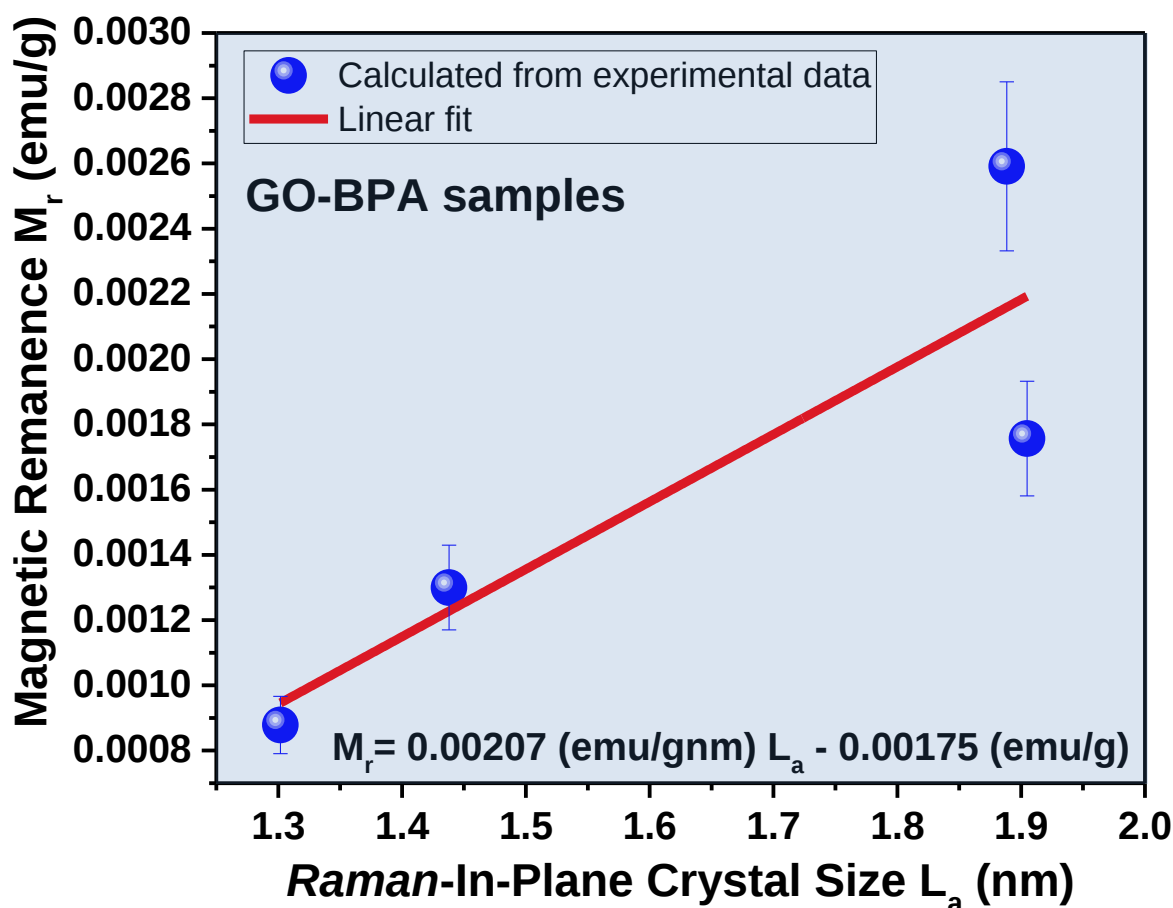


Figure 4.41. Raman in-plane crystal size effect on M_r of GO-BPA samples (blue circles) and linear fit (red solid line).

The respective analysis of linear fit parameters involved in crystal size dependence on remanence yields $2.07 \cdot 10^{-3}$ emu/gnm as positive slope, meaning direct proportionality between both correlated variables, and it is related to the shift-ratio of M_r affected by unit of nanometer in expansion of crystal size, finding a negative intercept of $1.75 \cdot 10^{-3}$ emu/g, as a minimum possible remanence when the GO-BPA samples exhibit very low crystal size.

This linear approach was corroborated by calculating the Pearson matrix of correlation coefficients, as presented in **Table 4.13**. It was found that linear description of the effect of crystal size in remanence shows correlation, as described by the 1 value in the diagonal values

of the Pearson matrix and sigma values <13%, related with the linear deviation of the experimental data. This behavior suggests that the FM order observed at room temperature in GO-BPA samples can be induced by defects density in the samples with magnetic hysteresis-loop to describe by remanence, also, depending on crystal size, as presented in the inset of [Figure 4.36](#).

Table 4.13. Pearson correlation matrix between Raman in-plane crystal size and M_r data, as presented in [Figure 4.41](#).

Coefficient	L_a	M_R
Pearson correlation	1	0.87197
Sigma	----	0.12803
Pearson correlation	0.87197	1
Sigma	0.12803	----

This behavior suggests that the FM order observed at RT in GO-BPA samples can be induced by defects density in the samples with magnetic hysteresis-loop described by H_c and M_r depending on crystal size, as presented in inset of [Figures 4.35.](#), and [4.36](#).

The physical correlation results discussed until here are important for basic comprehension of magnetism behavior exhibited by the GO-BPA samples as carbon based material and for the first time this work represents the first theoretical approach to describe the local FM order observed experimentally at RT in our samples.

Magnetoresistance at different temperatures in the GO-BPA sample. [Figure 4.42.](#) shows the magnetoresistance measurements in the GO-BPA sample synthesized at $T_{CA} = 973$ K for different temperatures from 300 to 400 K. It was found that external field increases from 0 to 40 KOe and magnetoresistance exhibits re-entry magneto-transport behavior, according to the variation in the temperature from 300 to 400 K. It was observed that increased temperature from 300 to 400 K and re-entry magnetoresistance exhibited by the sample, takes maximum positive value of 2.7% at 300 K and minimum value of -5.7% at 400 K.

To explain these complex behaviors, considering that the temperature effect in the electrical behavior of the GO-BPA sample was described by 3D-VRH mechanism as a narrow semiconductor material and discussed in section 4.2., the magnetoresistance is

directly proportional to the hall resistance [71-73], as discussed in section 2.3. Therefore, for moderate external applied magnetic fields, the Hall resistance is given by [74]:

$$R_H = \frac{p\mu_h^2 - n\mu_e^2}{e(p\mu_h + n\mu_e)^2} \quad (4.14)$$

Here, n is the electron concentration, p is the concentration of holes, μ_e is the electron mobility, μ_h is the holes mobility, and e is the elementary charge. Expression (4.14) shows that the Hall resistance takes positive values if current is conducted mainly by holes (sample is mainly p-type) and expression (4.14) yields negative values of the Hall resistance if current is conducted by electrons (sample is mainly n-type).

To gain further insight on describing the physics involved in the results presented in **Figures 4.42. and 4.43.**, the following interpretations are based on the energy conservation law by assuming that in all magnetoresistance experiments, the charge carrier in the samples can be influenced simultaneously by: (1) thermal energy (due to temperature), (2) internal magnetic energy (due to H_c effect originated by nano-crystal size and FM order induced by defects), (3) external applied magnetic field, and (4) external applied electrical field. It was considered that increased temperature increased thermal energy and decreased internal magnetic energy due to H_c dependence on crystal size, as discussed and presented in **Figures 4.20. and 4.40.**

Consider that thermal energy affects more electrons than holes and internal magnetic energy affects more holes than electrons due to differences in mobility, as reported by Toshiyuki Kobayashi *et al.*, [75].

These four energy contributions affect the type of charge carrier that dominate magnetoresistance, as observed experimentally and explained by following phenomenological descriptions:

(1) At 300 K, the GO-BPA sample synthesized at $T_{CA} = 973$ K exhibits positive magnetoresistance and by considering expression (4.14), this behavior can be attributed to current conducted mainly by holes, then, the sample exhibits electrical behavior as p-type semiconductor, and the externally applied electrical field accelerates mainly holes; under these physical conditions, the electrons are accelerated in internal magnetic domains of the sample more than holes due to thermal energy gained by electrons not being sufficient to escape from localized internal magnetic domains induced by defects and crystal size, then, the holes dominate current conduction being faster than electrons, this results agree with the expected mobility behavior in RGO reported by Toshiyuki Kobayashi *et al.*, [75] in which hole mobility takes average values from 0.25 to 0.62 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, and electron mobility exhibits values from 0.03 until 0.08 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, one order of magnitude difference, as observed here; therefore, it is expected that in GO-BPA as RGO material, the holes present greater mobility than electrons, reaching maximum value at 2.7% of magnetoresistance, as observed in **Figure 4.42.** Also, the GO-BPA samples exhibit hole-electron pairs, as observed via DFT computational simulation presented and discussed in **Figure 4. 28. (b) and (c).**

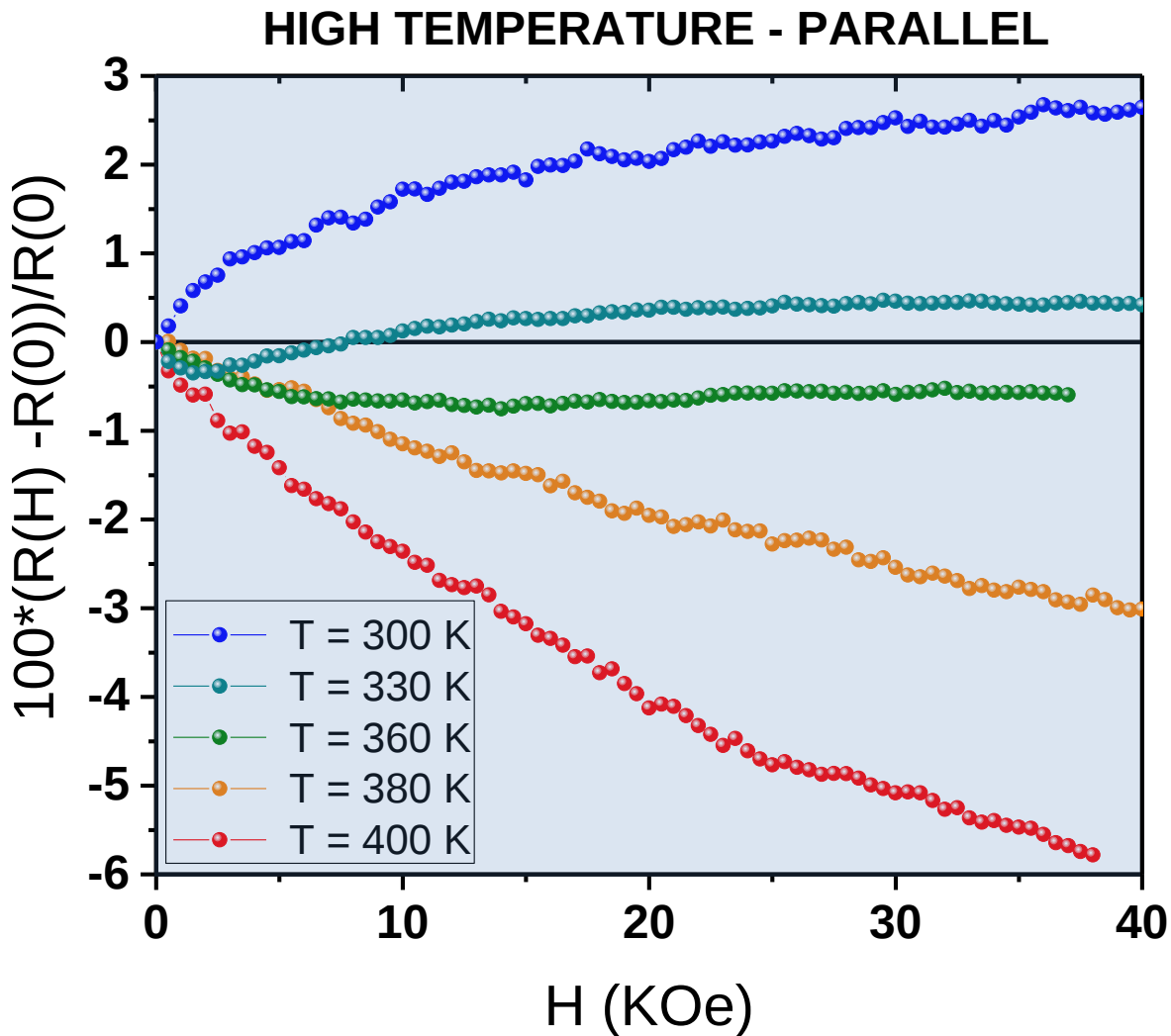


Figure 4.42. Magnetoresistance measurements in the GO-BPA sample synthesized at 973 K for different temperatures from 300 to 400 K.

(2) At 330 K, the sample exhibits re-entry magnetoresistance behavior in which the electrons dominate the current conduction for values of external applied magnetic field < 10 KOe, and the sample exhibits n-type semiconductor behavior and a minimum value of -0.4% as magnetoresistance. This change in the charge-carrier type can be explained by increased temperature, increased thermal energy, decreased internal magnetic energy and, therefore, electrons gain enough thermal energy to escape from confinement by localized internal magnetic field effects.

However, when the external applied magnetic field increased from 10 to 40 KOe, the internal magnetic domains order increased and the electrons again are accelerated around these localized magnetic dipoles induced by defects in the samples, as demonstrated in section 4.2. of this thesis; under these physical conditions, holes again dominate the current conducted and the sample exhibits p-type semiconductor behavior and maximum value of 0.4% as magnetoresistance.

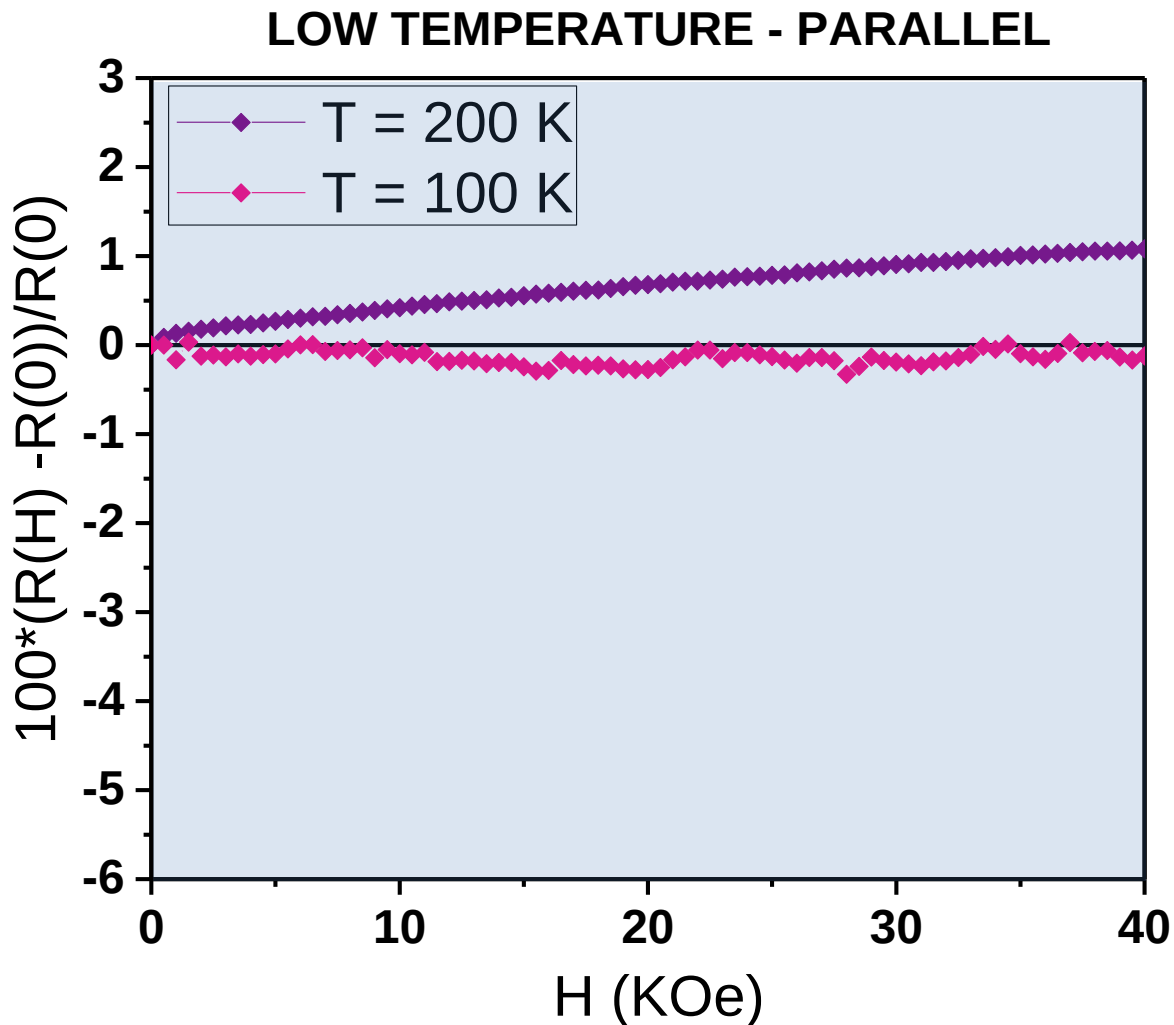


Figure 4.43. Magnetoresistance measurements in the GO-BPA sample synthesized at 973 K for low temperatures at 100 and 200 K.

(3) At high temperatures from 360 to 400 K, the electrons gained enough thermal energy to escape from magnetic effects by internal and external contributions and dominate the current conduction; therefore, the sample exhibits n-type semiconductor behavior and a minimum value of -5.7% as magnetoresistance. This value agrees with the value of -2.5% at 5 K reported in RGO material by Sai Qin *et al.*, [76].

(4) At low temperatures from 200 to 300 K, as presented in [Figure 4.43.](#), the behavior is similar to that in point (1) and the sample exhibits p-type behavior as narrow semiconductor and a value of 1% as a maximum magnetoresistance.

(5) At a lower temperature of 100 K, as presented in [Figure 4.43.](#), the GO-BPA sample exhibits -0.4% as a magnetoresistance average value and the sample is mainly n-type semiconductor material. In this case, decreased thermal energy increased internal magnetic energy that produces more confinement acceleration in holes than electrons because their

mobility is reduced at low temperatures, as reported in mono-, bi- and tri-layered graphene by G. Wenjuan Zhu *et al.*, [77].

Identification of the main physical correlations to describe transport mechanisms in GO-BPA samples was discussed; now, we will explore future applications of GO-BPA samples in electronics.

4.4 Future Application of GO-BPA Samples in Electronics

The main propose of this investigation was to identify basic transport mechanisms involved in GO-BPA samples synthesized through the DTD method. However, elemental comprehension of these physical mechanisms have technological implications and open research fields in applied physics. For these reasons, this section provides an overview of different possible future applications of GO-BPA samples in electronics and discusses some important results from applied physics that offer support of these applications in electronics.

In 2010, as suggested by Nobel Prize laureate in physics Konstantin Novoselov *et al.*, [78], the main focus in graphene-driven revolutions in information communication technology (ICT) is based on opportunities, such as: power management, hybrid electronics, flexible electronics, and energy. Consequently, the following potential applications of graphene in electronics have been suggested [45, 78]: ink and paste as conductive or coating ink; barrier as chemical sensors; heat spreader as LED lighting; composites for automobile and airplane components; energy as solar cells; batteries and supercapacitors; flexible displays and touch panels; and semiconductors as high speed transistors, RFIC and sensors, among others.

As found in this investigation by experimental physical evidence and results analysis described in section 4.2. and Table 4.14., the GO-BPA samples synthesized by DTD method at low oxygen coverage regime, exhibit chemical and physical properties similar to RGO materials (as carbon based material) and these results suggest that GO-BPA samples have the same application opportunities in electronics as the graphene material mentioned, with the advantage of having multifunctional oxides in their structure and their thermal stability.

These future technological applications of GO-BPA materials in electronics include possible selective contacts for solar cells, as reported by our group [50]; infrared emitter or heater devices, as reported by our group [12]; field-effect transistor (FET) devices; blood glycemia FET biosensors, as reported by our group [12, 82, 83]; batteries, as reported by our group [82]; and light emitter devices by incandescence effect, as reported by our group [82]. Table 4.14. illustrates a summary of the main physical transport mechanisms in GO-BPA samples identified in this thesis work and their possible technological implications mentioned. Considering only the room temperature case, GO-BPA synthesized via DTD method has the following basic physical properties and applied physics opportunities:

(1) Thermal properties are described only by phonon-phonon interaction, characterized by relaxation times from 4.1×10^{-15} to 7.8×10^{-15} s, this main result suggests applications in electronics as infrared emitter or heater devices by the Joule effect.

(2) Electrical properties are described only by carrier-impurity interaction, characterized by relaxation times from 1.2×10^{-16} to 4.5×10^{-16} s, band-gap energy tuned by oxides from 0.11 to 0.30 eV, and electrical conductivities from 63.7 to 2.3×10^3 s/m as p-type semiconductor; these results suggest applications in electronics, as field effect transistors (FET), batteries, biosensors, optoelectronics, MIR-emitter and UV-VIS detectors.

(3) Magnetism described as ferromagnetism induced by defects with coercive and M_r affected by crystal size, characterized by M_s from 2×10^{-3} to 3.9×10^{-2} emu/g, H_c from 5.2 to 94 Oe, and M_r from 0.9×10^{-3} to 2.6×10^{-3} emu/g; these results suggest possible applications, as magnetic biosensors, electromagnetic isolators, and cosmetic products.

(4) Magnetoresistance described by the type of majority charge carrier, which depend on the compromise between thermal energy and internal magnetic energy (coercive energy), characterized by positive magnetoresistance from 0.5% to 2.5% and current conduction by holes; these results suggest applications, as p-type semiconductors and contact-point diodes, among others.

Table 4.14. Summary of transport mechanisms in GO-BPA samples identified in this investigation and their future application in electronics.

Summary of Transport Mechanisms				
Property	Temperature	Physical variable	Mechanism	Possible application
Thermal Described only by phonon contributions	T < 190 K	Relaxation time τ (s): 7.8×10^{-15} s	Phonon-defects and Phonon-impurity interactions	Thermal Isolators
	190 K < T < 325 K	Relaxation time τ (s): 4.1×10^{-15} - 7.8×10^{-15} s	Phonon-phonon-interaction	Infrared heaters and emitters
Electrical Described only by charge-carrier contributions	T = 300 K	Relaxation time τ (s): 1.2×10^{-16} - 4.5×10^{-16} s E _g : 0.11 - 0.30 eV σ : 63.7- 2.3×10^3 s/m	Charge-carrier impurity interaction Carrier-impurity interaction	Field effect transistors (FET), batteries and biosensors Optoelectronics MIR-emitters and UV-VIS detectors
	And 3D-VRH 20 K < T < 290 K	Electrical resistivity: 8.6 - 0.1 Ω m	3D-Variable Range Hopping	Temperature sensors
Magnetism FM at room temperature induced by defects with H _c and remanence affected by crystal size	T = 300 K	M _s : 0.4×10^{-3} - 2.0×10^{-3} emu/g H _o : 5.2-94 Oe M _r : 0.9×10^{-3} - 2.6×10^{-3} emu/g	FM soft induced by defects, disorder and crystal size	Magnetic biosensors, electromagnetic isolators and cosmetic products
Magnetoresistance Type of majority charge carrier depends on the compromise between thermal energy and internal magnetic energy.	T < 190 K	NMR: -0.25%	Negative MR	n-Type
	200 K < T < 360 K	PMR:	Positive MR	p-Type
	360 K < T < 400 K	0.5%-2.5% NMR: -0.5%,-5.5%	Negative MR	Diode n-Type

GO-BPA Films/Quartz as Possible Selective Contact for Solar Cells. **Figure 4.44. (a)** shows the schematics of a two-step process involved in the DTD method used for synthesis of GO-BPA/Quartz thin films. This large-scale production of thin films was carried out in a first carbonization process at $T_{CA} = 973$ K to obtain BPA, which was deposited on quartz by roll-coating technique and the second carbonization process at different carbonization temperatures in roll coated BPA on quartz as precursor until synthesizing GO-BPA thin films. **Figure 4.44. (b)** displays a photograph of the GO-BPA thin film mechanical transfer on flexible adhesive polymer and synthesized over rigid quartz substrates. It is possible to observe the light transparency exhibited by the thin films, which demonstrate the low thickness exhibited by our samples.

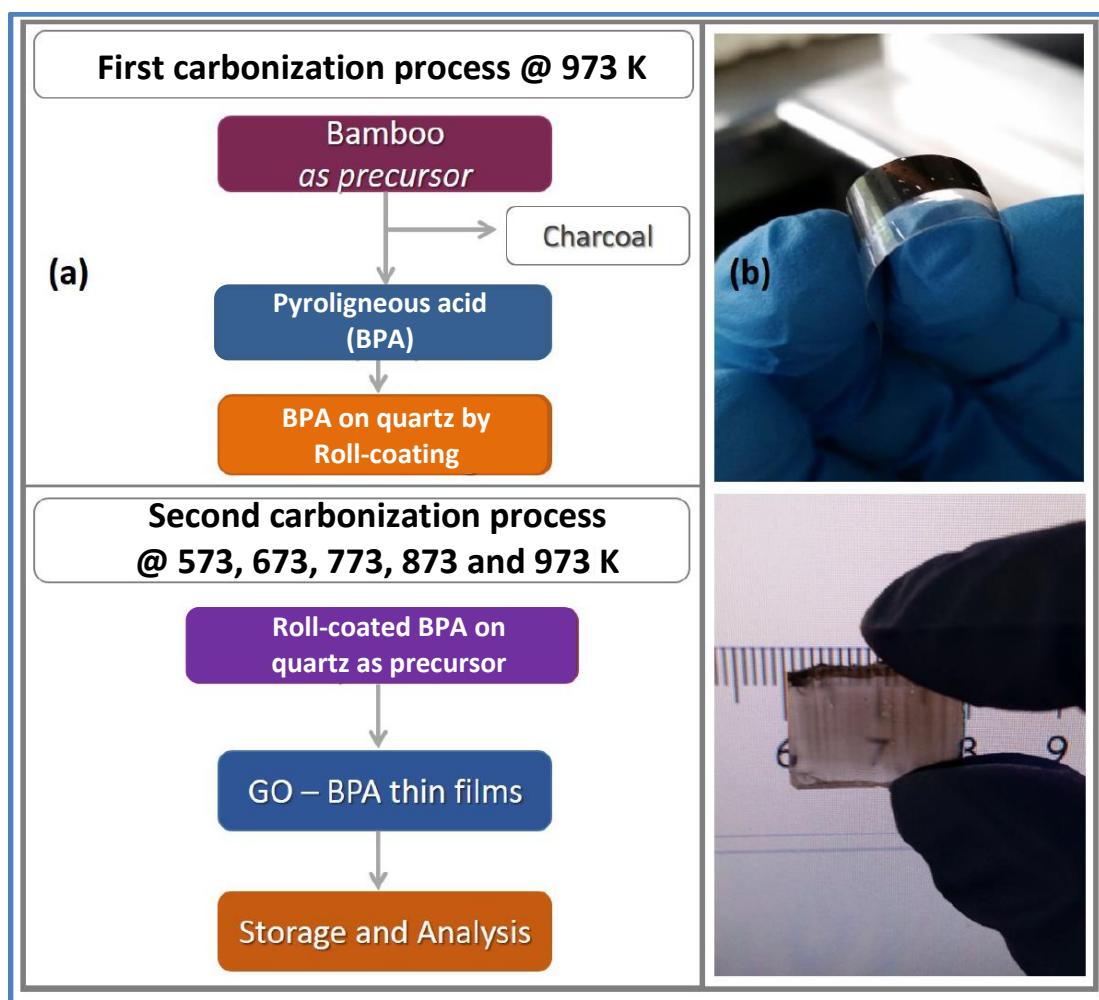


Figure 4.44. (a) Schematics of the two-step process used for synthesis of GO-BPA/Quartz thin films. **(b)** Digital images of the GO-BPA thin films on flexible and rigid substrates. Taken and adapted from our group reference [50].

As proposed by C. Chung *et al.*, [79], inverted planar solar cells based on Perovskite/Graphene Oxide Hybrid Composites present advantages, like: (1) enhanced charge separation, (2) decreased charge recombination, (3) balanced charge mobility, and (4) increased power conversion efficiency from 12.3% to 15.2%. For these reasons, this work

studied the optical properties of GO-BPA samples, seeking to identify the optical response that demonstrates the possible use of these samples as selective contact for inverted planar solar cells, as shown in **Figure 4.45**.

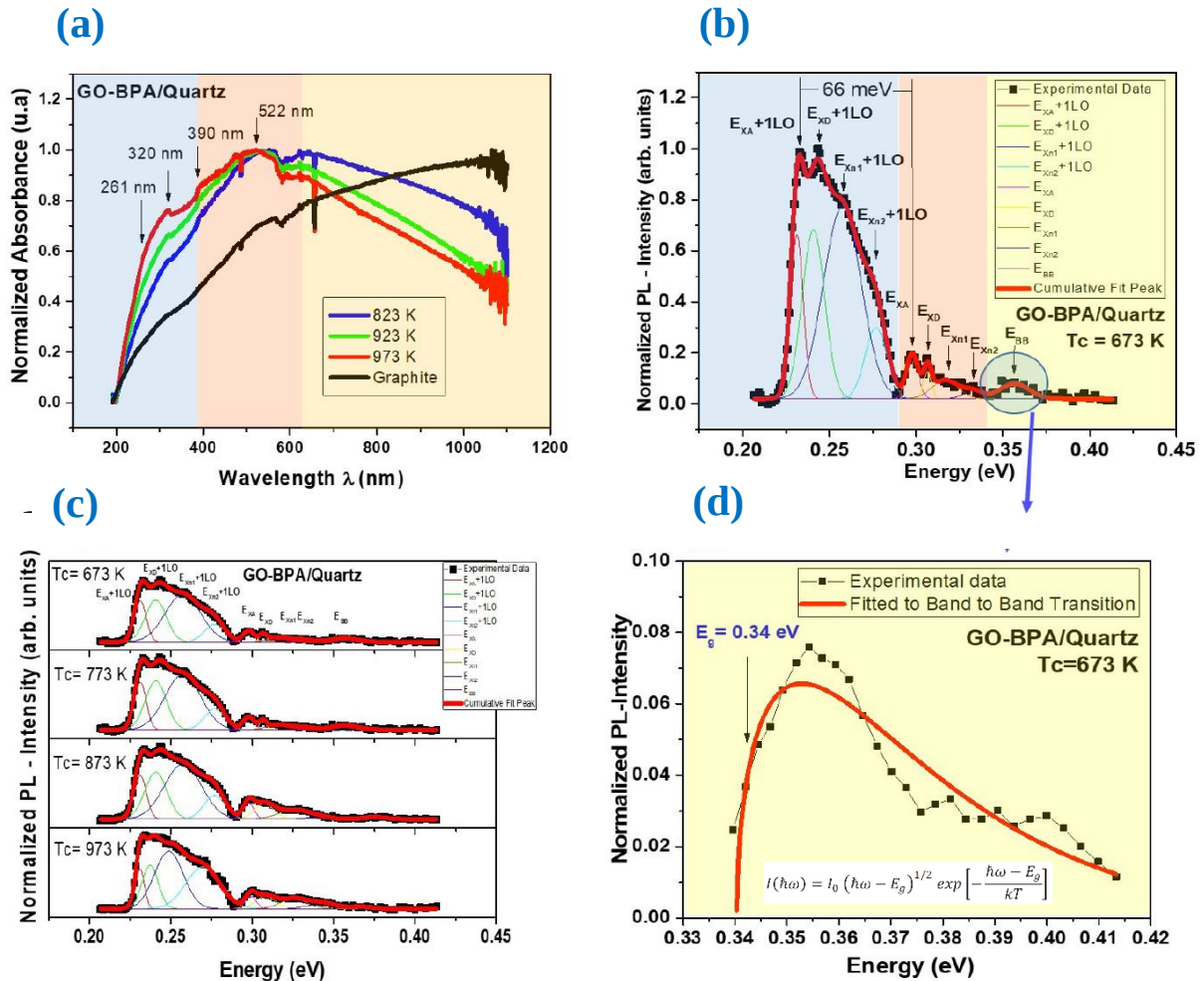


Figure 4.45. (a) UV-VIS absorption spectra of GO-PA/quartz for different T_{CA} . (b) MIR-PL spectra analysis in GO-BPA at $T_{CA} = 673$ K. (c) MIR-PL spectra in GO-BPA and analysis for different T_{CA} . (d) MIR-PL spectra analysis of the band-to-band transition region in GO-BPA at $T_{CA} = 673$ K (black point) and fitted by using the band-to-band model shown in the inset equation (red solid line). Taken and adapted from reference [50].

The absorption properties in the UV-visible range spectra of BPA-GO/Quartz at RT is shown in **Figure 4.45. (a)**. The measurements provide evidence of a broadband light absorption from 200 to 1100 nm for all T_{CA} . Interestingly, increasing T_{CA} results in a blue-shift of the absorption and agrees with results from **Figure 4.1**. Broadening of the blue-shift in the absorbance spectrum can be correlated with the large size distribution of the graphitic nano-crystals of the samples, as confirmed via Raman, XRD, and HR-TEM measurements, as presented in **Figure 4.2. (c)** and **(d)** [12, 18]. The study of the optical properties of GO-BPA materials is an important aspect for their application in photonics. The presence of

oxygen functional groups causes the formation of graphitic islands in GO, producing a disruption of the π -network and, thus, opening a band gap in the electronic structure. **Figure 4.45. (b)** shows the MIR-PL spectra of GO-BPA/quartz obtained at 673 K of T_{CA} and its respective fitting lines by using deconvolution of eight Gaussian functions, as contributions associated with phonon-exciton coupling, exciton emissions, and band-to-band transition (**Figure 4.45. (c)**).

As observed, three characteristic regions can be distinguished: Region (1) at lower energies, in a range of 0.20 – 0.30 eV, different phonon-exciton (LO, longitudinal optical phonon) emissions ($E_{XA}+1LO$, $E_{XD}+1LO$, $E_{Xn1}+1LO$, and $E_{Xn2}+1LO$) were identified; from here, a binding energy of 66 meV was obtained, expected for a narrow gap semiconductor [81]. Region-(2) at an energy range of 0.30 – 0.34 eV, where excitonic radioactive transitions (as acceptor (E_{XA}), donor (E_{XD}), E_{Xn1} and E_{Xn2} ;) could be identified. Region-(3) at an energy range of 0.34 – 0.37 eV, where band-to-band radioactive transitions are observed.

In order to obtain the band-gap value belonging to the third region, as presented in **Figure 4.45. (d)**, we used the expression for band-to-band transition given by [81]:

$$I(\hbar\omega) = I_0 (\hbar\omega - E_g)^{1/2} \exp \left[-\frac{\hbar\omega - E_g}{kT} \right] \quad (4.14)$$

Where $\hbar\omega$ is energy measured by the MIR-PL system used (eV as unit), E_g is the band-gap energy value of the material studied (eV as unit), k is the *Boltzmann* constant, T is the temperature; at room temperature, thermal energy given by kT is 26 meV and I_0 is an experimental constant attributed to the transfer function of the MIR-PL system. Considering the latter values a band-gap energy value of 0.34 eV was determined for this sample. **Figure 4.45. (d)** presents the MIR-PL spectra's in GO-BPA films/Quartz for different T_{CA} . In general, GO-BPA PL spectra show slight modifications by varying the T_{CA} .

Additionally, PL at VIS-NIR measurements were performed; in this regime, the intensity of light emission was very low and signals measured were quite noisy (not shown). These optical responses show very good absorption and emission in UV-VIS and MIR spectral ranges, respectively, and suggest that GO-BPA thin films can be employed as possible selective contact in solar cells. Part of this work was carried out through an internship in Institute of Materials for Electronics and Energy Technology (i-MEET) at Friedrich-Alexander Universität Erlangen, Nürnberg during three months and directed by Prof. Dr. Christoph J Brabec.

Hereinafter, we will explore IR- emitter devices, another important alternative proposed in this investigation.

Infrared emitters or Heater Devices Based on GO-BPA Samples. Considering the vibrational response obtained in our GO-BPA-973 K platelets, this sample implements an electrically controlled IR emitter or heater device. The configuration and development of the device proposed is presented in **Figure 4.46. (a)** and **(b)**, respectively [12]. Fabrication of the IR emitter device was carried out by using the multilayered configuration presented

schematically in **Figure 4.46. (a)**. The GO-BPA thin pellet (437 nm of thickness) is located between two circular Al foils and attached with silver paste; Au-wires were electrically contacted to the Al foil using silver paste.

The electrical measurements were carried out by using the two-point I–V curves method. **Figures 4.46. (c)** shows the ohmic response in the IR emitter device. This behavior can be explained by the Joule effect, related with the heat produced in the IR emitter device by an electric current through the GO-BPA sample. Given that a DC polarization is applied between device terminals, electrons begin to flow through the device, atomic vibrations in the GO-BPA platelets increase and, therefore, the GO-BPA sample's temperature increases. The phonon population (associated with the atomic vibrations) increases from the sample to the Al foil, where the atomic vibrations are emitted as infrared radiation by the Al foil.

The heater device uses Al foil painted with carbon to guarantee maximum emissivity and polymeric seal to avoid the loss of the GO-BPA platelets. The thermal behavior of the IR emitter or heater device can be associated to the first-order response of a thermal system (characterized by transient and steady states), as observed in **Figure 4.47 (a)**. When the IR emitter device is polarized with a I–V fixed value, the current is around 10 mA, the device temperature increases from room temperature to 31.6 °C, during 30 s. In this steady state, the electric power consumption is around 10 mW, which is the lowest value of electric power consumption compared to other IR emitters, for example IR-diodes (15 mW, polarized at 1.5 V and 10 mA). **Figure 4.47 (b)** and **(c)** presents the thermographic images when the heater device is off and on, respectively.

The thermal emission can be clearly observed. According to the results obtained on the IR emitter or heater device presented in this work, we suggest considering it in the following potential applications: optical barriers for production of IR radiation; its size (1 and 0.1 cm for diameter and thickness, respectively) make it suitable for implementation in thermal clothing, motoring, and green houses with low energy consumption. Other implementation areas include medical and biological science for localized heat production, as required in muscle relaxation therapies, therapies for skin stimulation, and dilation of blood vessels. In flexible electronics, like electrically controlled heat sources with high portability, among other potential uses.

Some aspects of IR-emitters or heater devices were seen here; now we will explore GO-BPA samples as FET device configuration, other important alternative uses of our samples.

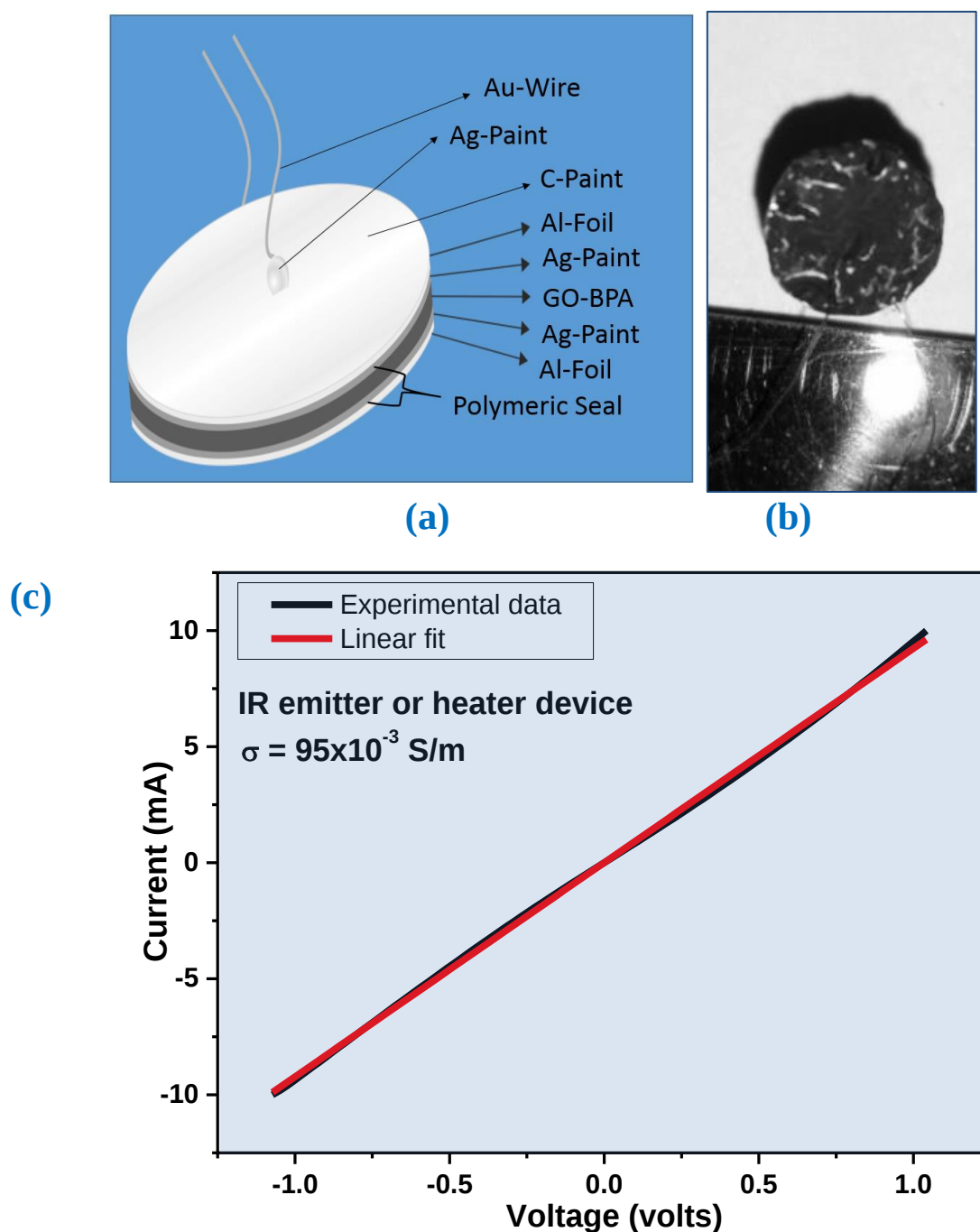
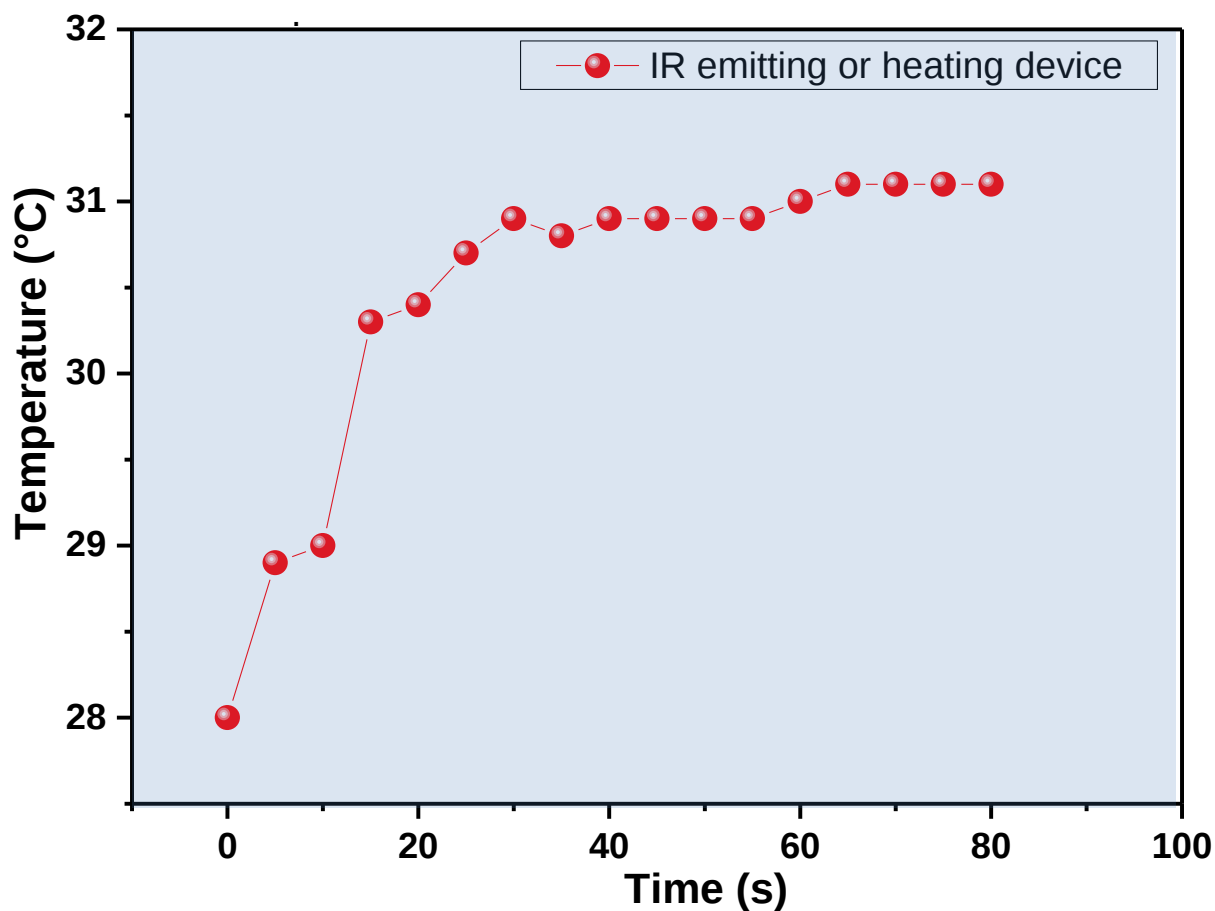
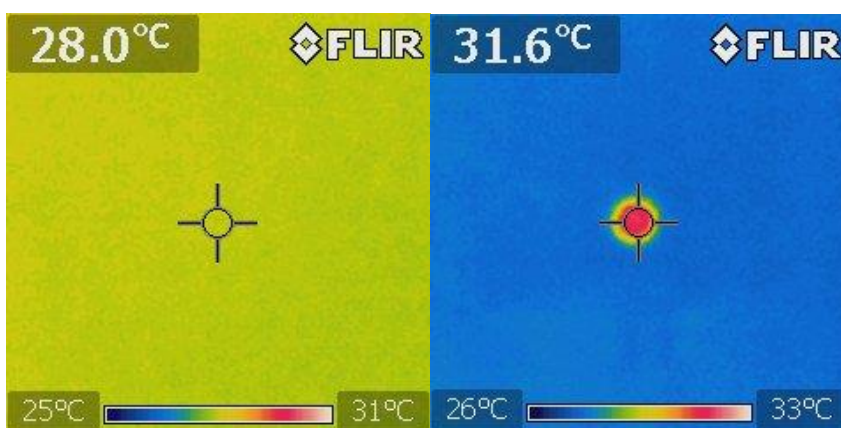


Figure 4.46. IR emitter or heater device configuration proposed in this investigation: (a) configuration. (b) Digital image of the IR emitter device developed. (c) Electrical characterization. The electrical conductivity value of the GO-BPA-973 K sample agrees with the order of magnitude expected for semiconductor materials. Reported by our group in reference [12].



(a)



(b) (c)

Figure 4.47. (a) Temperature evolution in IR emitter or heater device when this device uses fixed polarization voltage at 1 V and current at 10 mA. The steady state was achieved within 30 s on the device. Thermographic images in IR emitter or heater device for the power states: (b) off and (c) on. Taken and adapted from our group reference [12].

Field Effect Transistor (FET) Device Based on GO-BPA Sample. **Figure 4.48.** (a) presents schematic representation of the field-effect transistor (up-gate) configuration proposed in this investigation. It is possible to observe that drain, source, and up-gate (over adhesive tape/GO-BPA) terminals to be deposited over the GO-BPA sample synthesized at $T_{CA} = 973$ K via evaporation technique by using Ag as electrical contact, masks, current at 150 A, voltage at 3 V, and vacuum at 2×10^{-4} bar.

Also, this work proposed that Gate terminal can be formed by Ag/Adhesive tape/GO-BPA sample, the adhesive tape was employed as isolator material with electrical resistance at approximately 10 M Ω . This alternative device was considered for first time in our group reference [82].

Figure 4.48. (b), (c), and (d) shows images of GO-BPA FET developed in this work, with rear, zoom, and front socket circuit, respectively. the socket circuit was developed to guarantee stability in the coupling of impedances between the GO-BPA FET devices elaborated in this work and the electrical characterization equipment.

Figure 4.49. (a) presents an image of GO-BPA flexible FET with up-Gate configuration proposed in this investigation. It is possible to observe the front side showing Ag electrodes and the white arrow indicates the Up-Gate configuration terminal. **Figure 4.49. (b)** shows an image of the rear side of GO-BPA flexible FET presenting the GO-BPA platelet mechanically transferred over adhesive tape as flexible substrate.

The inset shows a systematic low-shift current when increasing Gate voltage from 0 to 30 V; this behavior can be attributed to the effect of electrical field in the acceleration of charge carriers in the device, as expected for an FET device. **Figure 4.50. (b)** presents the Gate-Source voltage influence on the drain current (black circles) and its respective fit by using the Shockley FET model.

It was observed that increased Gate-Source voltage from 0 to 6.0 V increased drain current from 0 to 5 mA; this is a typical electrical behavior of input-curves of the FET device that can be described by using the Shockley model and demonstrate the effect of the electric field in the modulation of the charge-carriers that dominate the drain current. From the respective analysis, we obtained the known FET theory to describe the FET experimental data.

The FET forward current constant at $K_F = 0.2 \times 10^{-3} \text{ A.V}^{-2}$, this value agrees with the typical value at $0.3 \times 10^{-3} \text{ A.V}^{-2}$ for commercial FETs, off-threshold voltage at $V_{th} = 1.2$ V agrees with the values from 0.3 to 18 V for commercial FETs and exponent parameter with a value of $n = 1.71$ that agrees with the value at 2.0, which is a typical value exhibited by commercial FETs.

These results demonstrate the important electric-field effect in the devices based on GO-BPA samples synthesized by DTD method and proposed in this investigation. It also opens an interesting research field in applied physics.

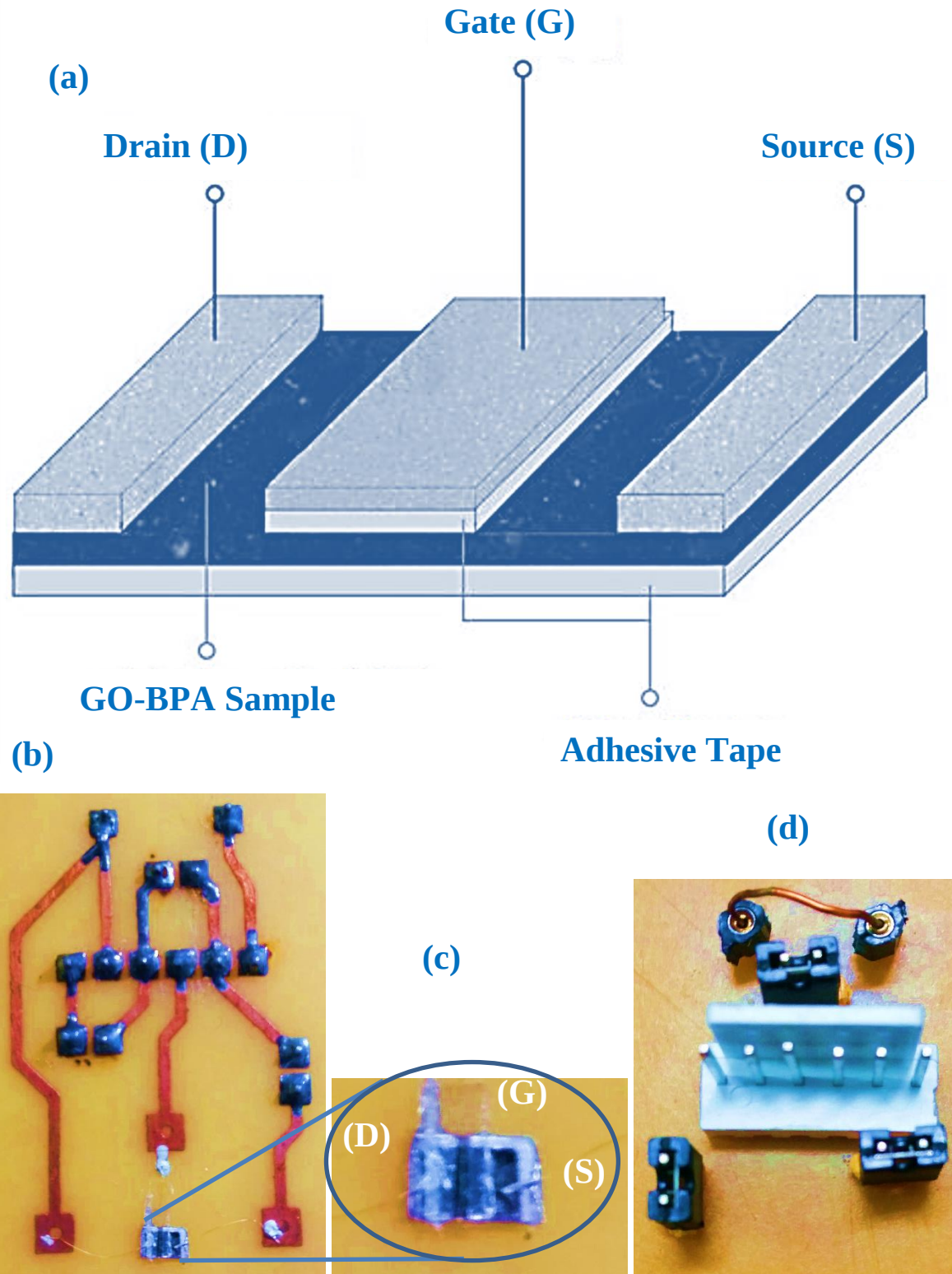


Figure 4.48. (a) Field-effect transistor (up-Gate) configuration proposed in this investigation. (b), (c) and (d) Digital images of GO-BPA FET developed with rear, zoom, and front socket circuit, respectively, as considered in our group reference [82].

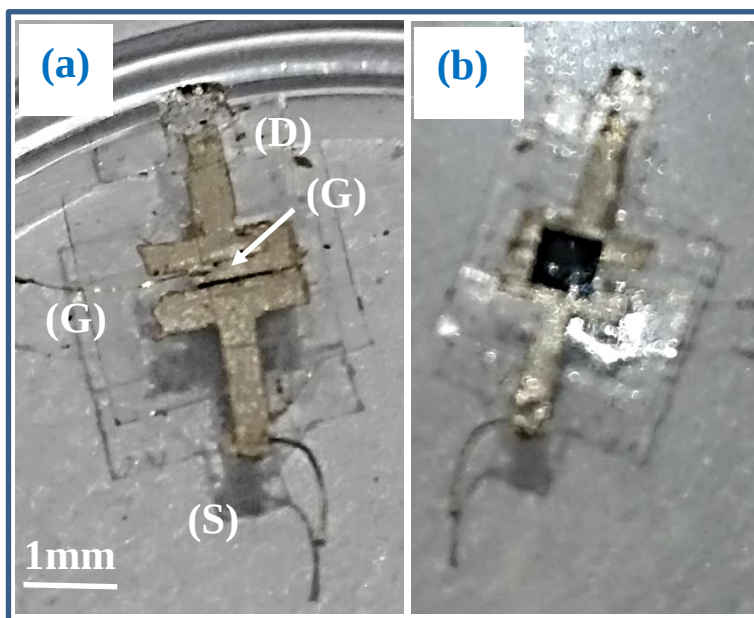


Figure 4.49. Digital images of GO-BPA flexible FET (up-gate) configuration proposed in this investigation. **(a)** Front side showing Ag electrodes and **(b)** Rear side presenting the GO-BPA platelet. As considered in our group reference [82].

Figure 4.50. (a) presents electrical characteristic output curves in FET devices based on GO-BPA samples synthesized at 973 K for different gate voltage from 0 to 30 V. It was observed that increased voltage from -3 to 3 V increased current from -0.9 to 0.9 mA with non-linear behavior, as expected for an FET device.

The important non-linear behavior exhibited by the GO-BPA FET device developed in this investigation corroborates the effect of the electric-field accelerating charge carriers in a transistor configuration and suggests that GO-BPA material can be an excellent candidate semiconductor to develop advanced electronics of sensors and devices [12, 18, 82, 83].

Figure 4.50. (a) shows the voltage drain-source influence in the drain current and its non-linear fitting by using the Shockley FET model that confirmed the FET behavior. As considered in our group reference [82].

These electrical characterization results suggest that FET configurations based on GO-BPA samples explored in this investigation open an important research field in applied physics.

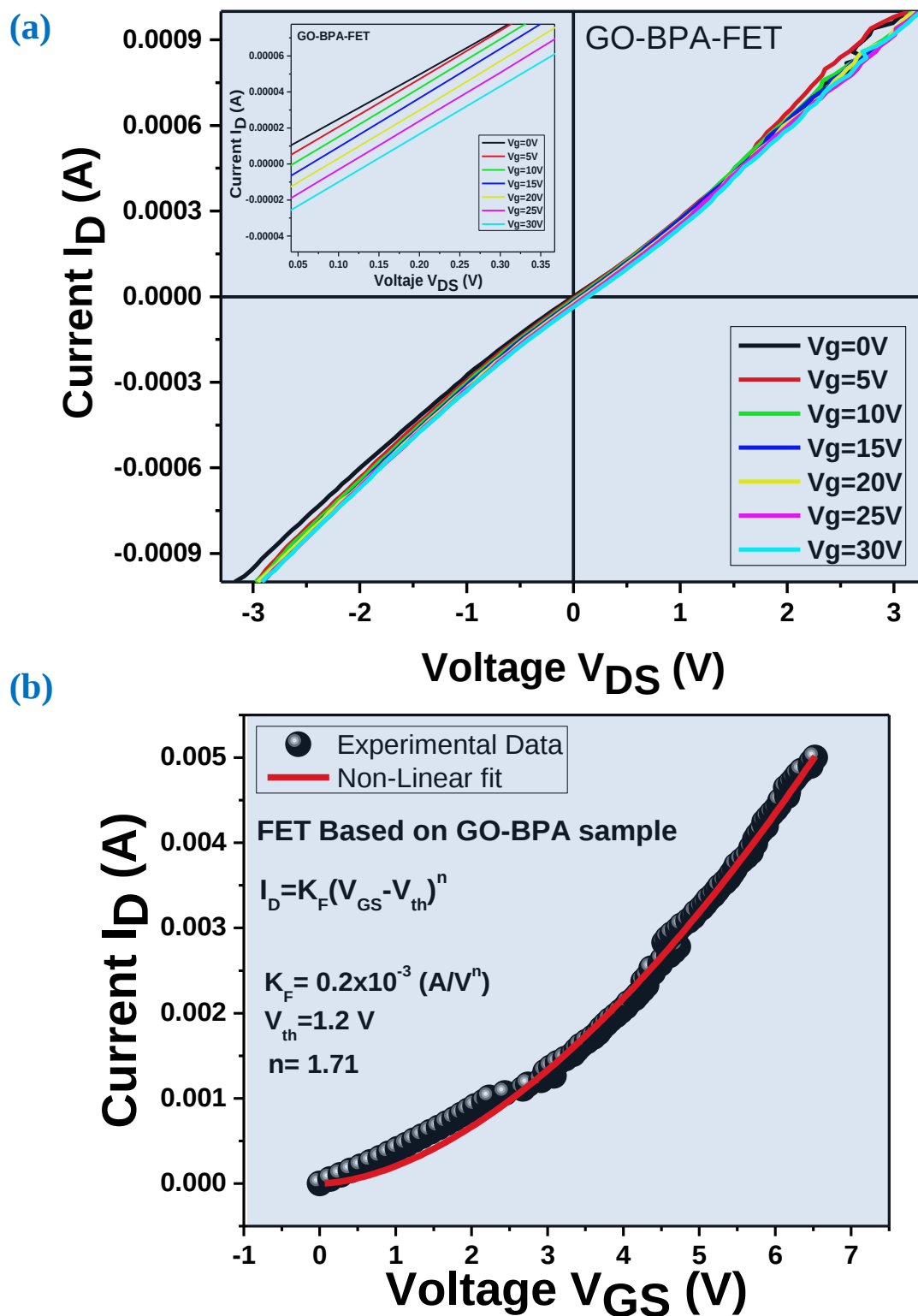


Figure 4.50. (a) Output-curves in FET device based on GO-BPA sample synthesized at 973 K for different gate voltages. Inset is a zoom around zero behavior that demonstrates the effect of the gate voltage (or electric field) in GO-BPA-FET. (b) Gate-source voltage

dependence with the drain current (black circles) fitted by using the Shockley model (red solid line).

Due to high compatibility of GO with water molecules, the GO-BPA FET configuration was explored as possible biosensor for glycemia, as presented ahead.

Blood Glycemia FET Biosensor based on GO-BPA Sample. **Figure 4.51. (a)** shows a FET Biosensor with down-Gate configuration proposed in this investigation to monitor blood glycemia. Transparent adhesive tape was used to mechanically transfer the GO-BPA film ($\sim 10\ \mu\text{m}$ of lateral dimensions). Then, indium (In 99.99%) was evaporated to be deposited in the form of two bands not connected together and having direct contact with the GO-BPA sample; these bands were denominated Drain (D) and Source (S) electrodes as terminals.

To facilitate the mechanical contact between blood and the GO-BPA film, a third indium band was built, with the same method, but this time on the back of the isolated tape and without direct contact with the GO-BPA sample; this band was called Gate (G) electrode terminal. The evaporation process was carried out in a sputtering chamber (BAE 250) connected to a mechanical vacuum pump (0.15 mbar) by using high-purity Wolfram evaporators and placing the target at 5 cm from the evaporator. Masks with rectangular 2 x 3 mm slots were used to give shape to the electrodes, as shown in **Figure 4.51. (a)**. The electrodes were welded to copper thread with silver paint and the resistance (RDS) was measured between the D and S electrodes (approx. 12.6 K Ω). These P-channel semiconductor devices are shown in **Figure 4.51. (b)**.

The electric characterization procedure of the PCS1 device, based on **Figure 4.51. (a)** corresponds to a fixed voltage in the G electrode (V_G) and produces variation in the I_D current through the D terminal, while measuring the voltage between the D and S electrodes (V_{DS}). The same method is repeated for another fixed value of V_G . **Figure 4.51. (b)** and **(c)** presents images of FET biosensors developed in this work, as flexible and rigid alternatives, respectively [83]. The rigid FET biosensor offers more stability and reproducibility than the flexible alternative configuration because it mechanically optimized the metal-semiconductor electric contact [83]. **Figure 4.52. (a)** shows I-V curves in the GO-BPA-FET Biosensor (down-Gate) configuration for different blood glycemia concentrations from 66 to 320 mg/dL, corresponding to the typical measurement range. It was found that increased glycemia concentration increased a systematic shift given by the slope of the I-V relation. This behavior can be attributed to the effect of glucose adsorption by the surface of the GO-BPA material, which increases electrical conductivity. **Figure 4.52. (b)**, presents the blood glycemia concentration dependence on the drain-source resistance.

Hence, with the drain-source resistance in GO-BPA-FET biosensors proposed in this investigation, it was observed that decreased glycemia increased electrical resistance; this behavior, as mentioned, demonstrates that glucose molecules present in blood increase the electrical conductivity, possibly associated to the high compatibility between C-OH functional groups present in the blood and GO-BPA material, as discussed in this work by FTIR spectra analysis results (**Figure 4.23.**).

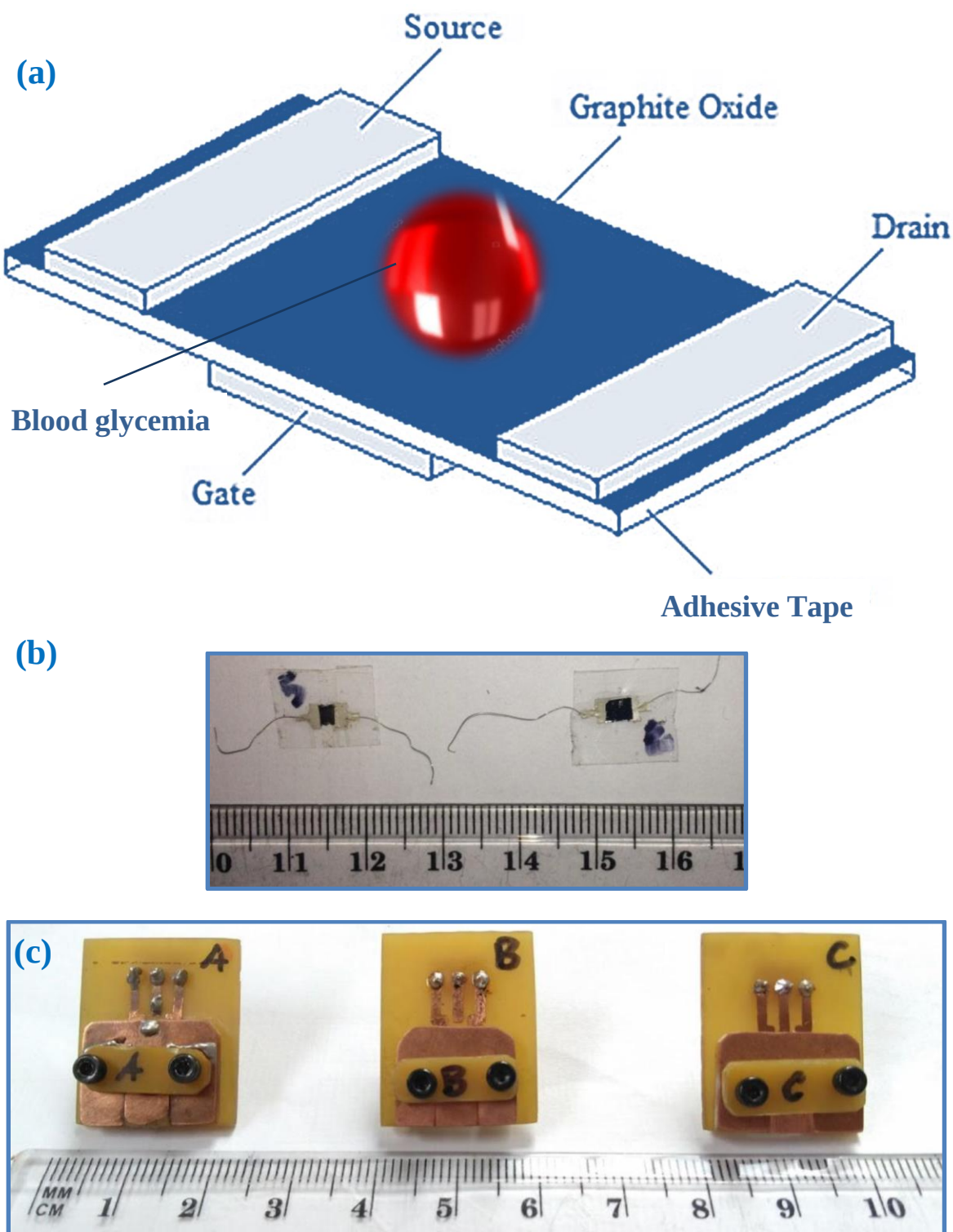


Figure 4.51. (a) FET Biosensor (down-Gate) configuration proposed in this investigation to detect blood glycemia. (b) and (c) digital images of FET biosensors developed as flexible and rigid alternatives, respectively. Taken and adapted from our group reference [83].

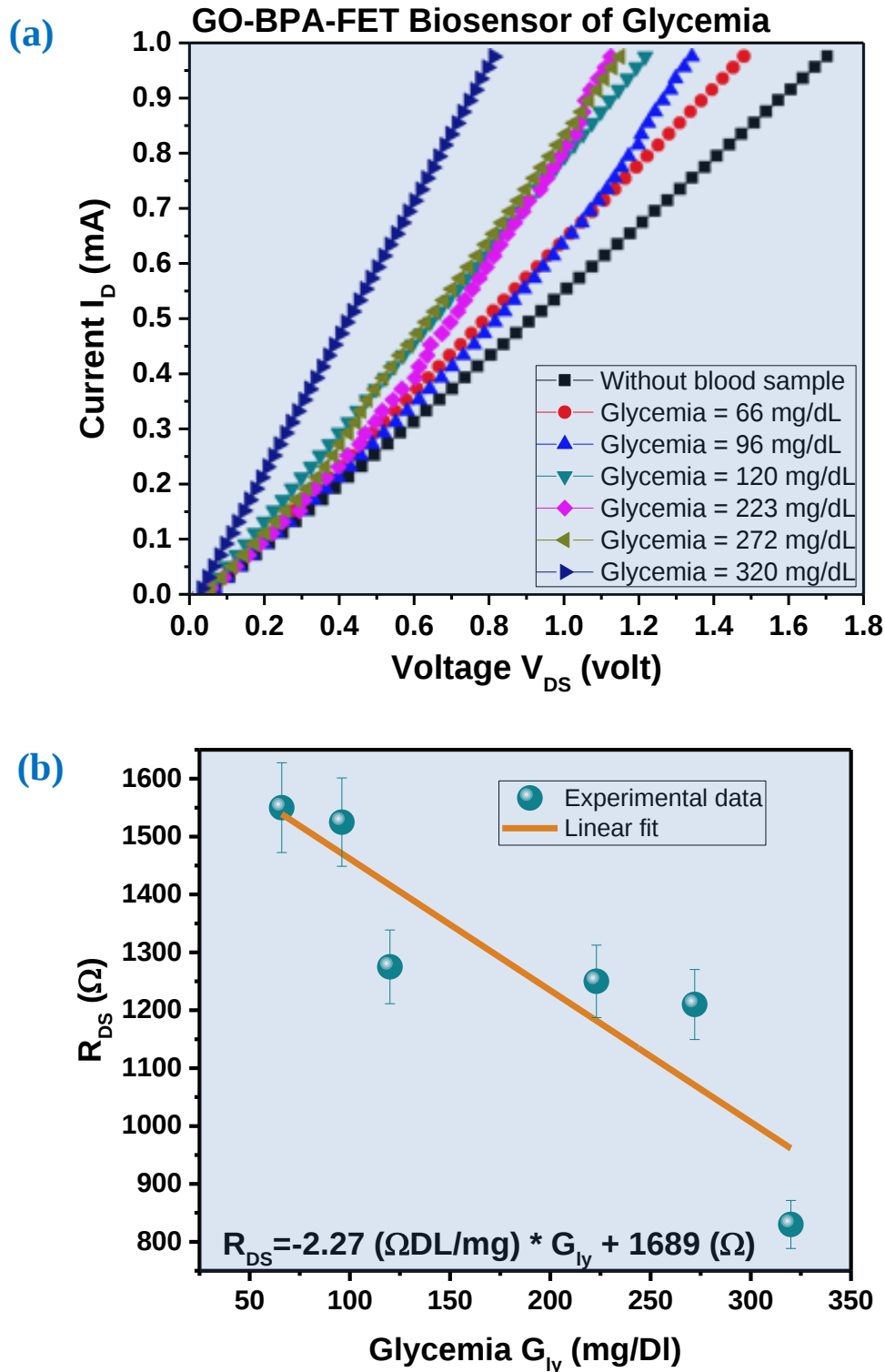


Figure 4.52. (a) I-V curves in GO-BPA-FET Biosensor (down-Gate) configuration for different blood glycemia concentrations. **(b)** Blood glycemia concentration influence on the drain-source resistance GO-BPA-FET biosensor proposed in this work at 5% error. Taken and adapted from our group reference [83].

As discussed, the GO-BPA narrow band-gap semiconductor is an excellent candidate material to develop advanced electronics for sensors and devices based on FET configurations and open an important research field in applied physics. In addition, by considering opportunities in energy, we present the first of the physical experiments in a battery source configuration based on GO-BPA material.

GO-BPA samples as Batteries. **Figure 4.53.** (a) shows a GO-BPA battery configuration proposed in this investigation. In this configuration, the GO-BPA material is placed between two different metals (copper and silver), then, due to differences between Fermi levels of the metals, the high abundance of hole-electron pairs (as found in this investigation by DFT computational simulation studies as shown in **Figure 4.28.** (b) and MIR-PL results presented in **Figure 4.45 (b) and (c)**) in GO-BPA material are polarized and the battery produces an intense internal electric field that can accelerate charge carriers in an electric circuit as a battery source, possibly due to charge-carrier re-distribution in GO-BPA samples by differences in the Fermi level by copper and silver metallic electrodes.

The GO-BPA battery functionality is based on the polarization of hole-electron pair mechanism by Fermi level differences between electrodes, which increase the internal electric field in GO-BPA platelets and produce a potential difference as voltage. **Figure 4.53.** (b) presents a photograph of the GO-BPA battery prototype developed in this work; this battery was encapsulated by using polyvinyl alcohol.

Figure 4.54. presents voltage evolution in the GO-BPA battery proposed in this investigation, it was observed that increased measurement time in the GO-BPA battery produced a stationary voltage at 650 mV between its connection terminals. Also, the transitory or steady-state behavior at low measurement time was possibly due to the input impedance of the measurement instrument.

The battery exhibits output resistance at 1 M Ω . Calculation of the energy density gives average values at approximately 5 Wh/Kg, this is a very low value compared with the value of 10³ Wh/Kg exhibited by the commercial battery; however, until now, we have yet to consider the effect of employing lithium or sodium as electrolytes. For this reason, these results suggest the optimization of these prototypes by using electrolytes and opens an interesting research field in applied physics of batteries based on GO-BPA material as host for different electrolytes.

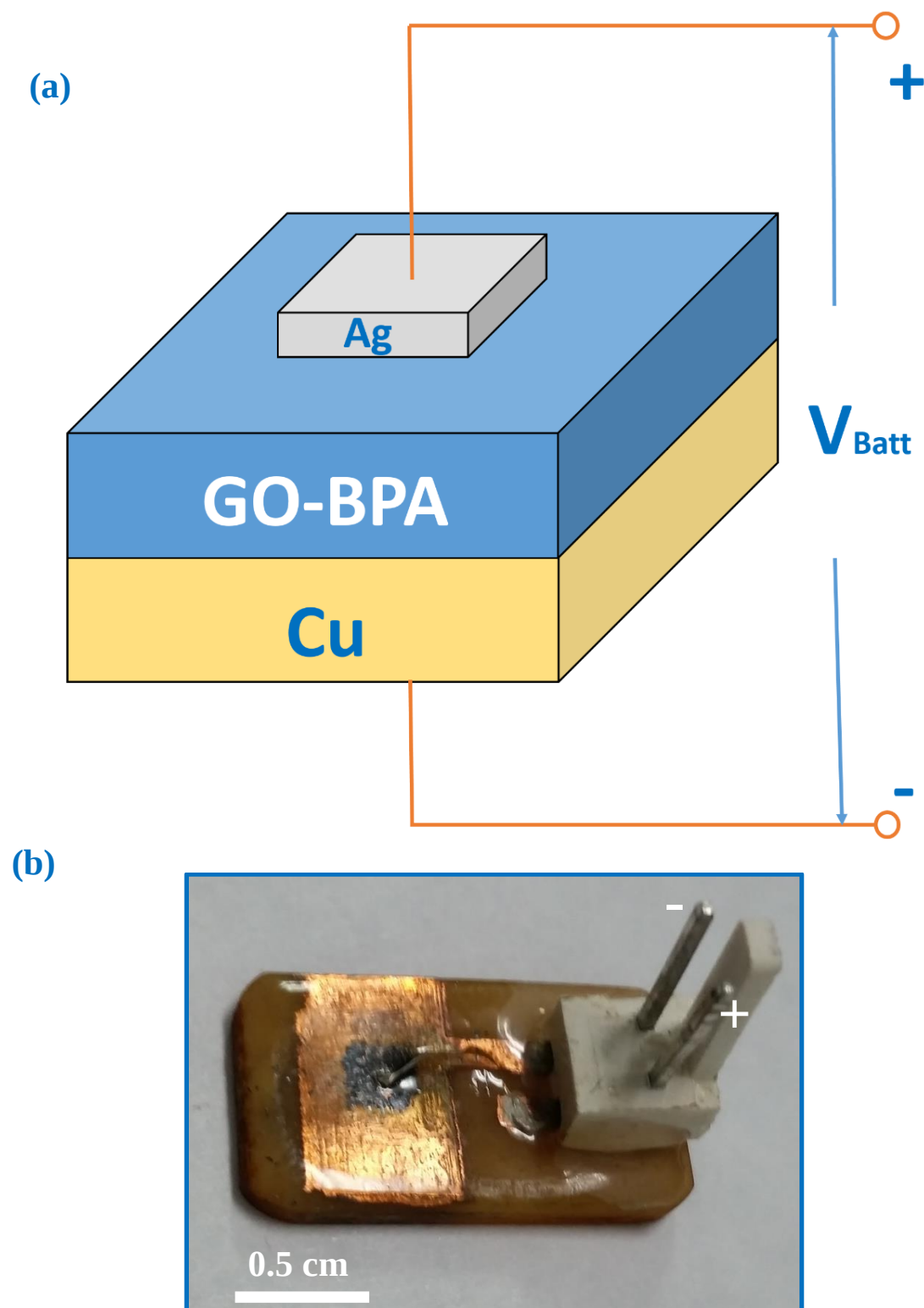


Figure 4.53. (a) GO-BPA battery configuration proposed in this investigation. (b) Photograph of the GO-BPA battery developed in this investigation.

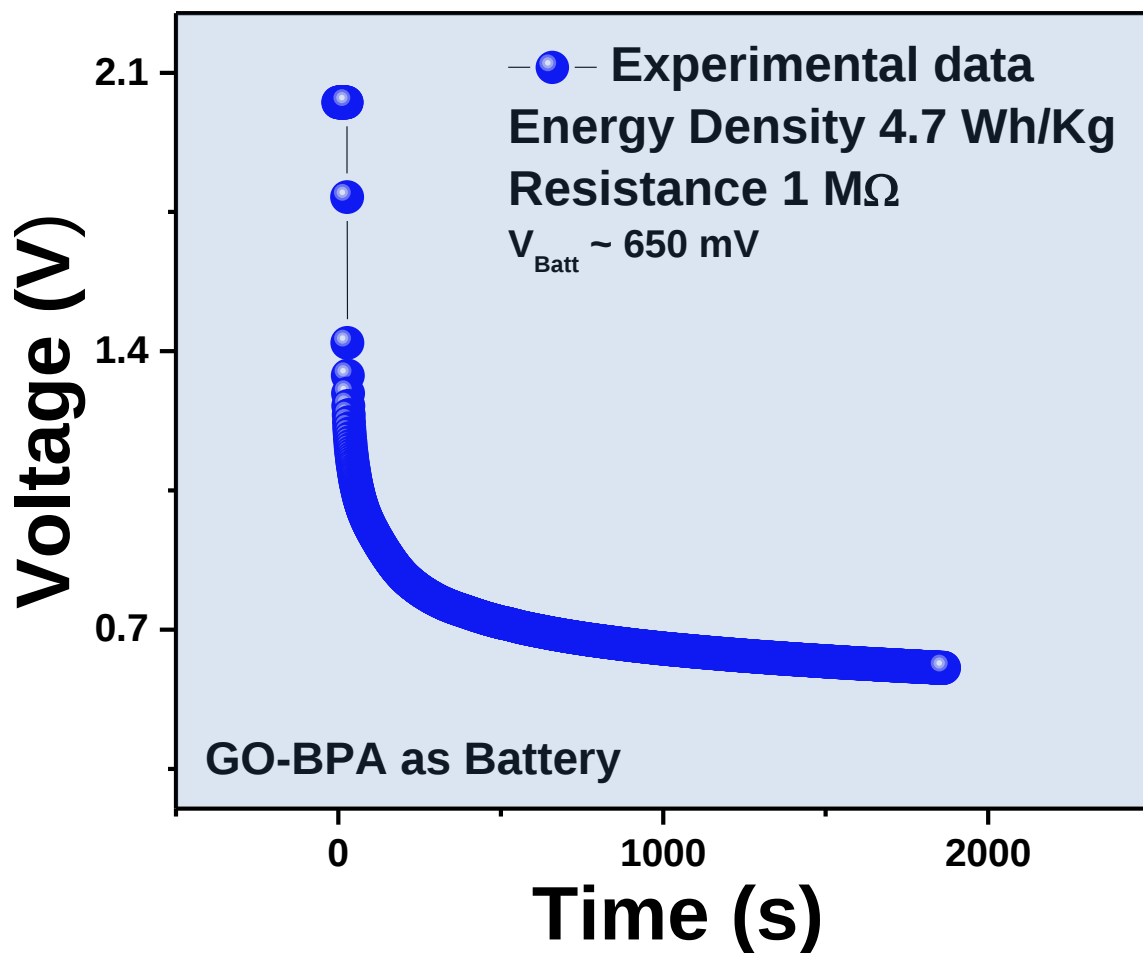


Figure 4.54. Voltage evolution in the GO-BPA battery proposed in this work without load.

Another important alternative of electronic devices explored in this investigation was the light emitter based on GO-BPA material and described ahead.

GO-BPA as light emitter. Figure 4.55. shows the configurational diagram of the GO-BPA light emitter device proposed in this investigation. The GO-BPA material synthesized via DTD method at 973 K, to be mechanically transferred to rigid or flexible substrates and located over two parallel-path films of evaporated silver as electrical contact with a substrate-separation distance of 100 μm and then the electrical contacts are elaborated by using Ag paint and Au at 25 μm diameter.

When the external electric field is applied, the charge carriers in the GO-BPA material are accelerated until producing high molecular vibration of its structure and producing light through the incandescence effect.

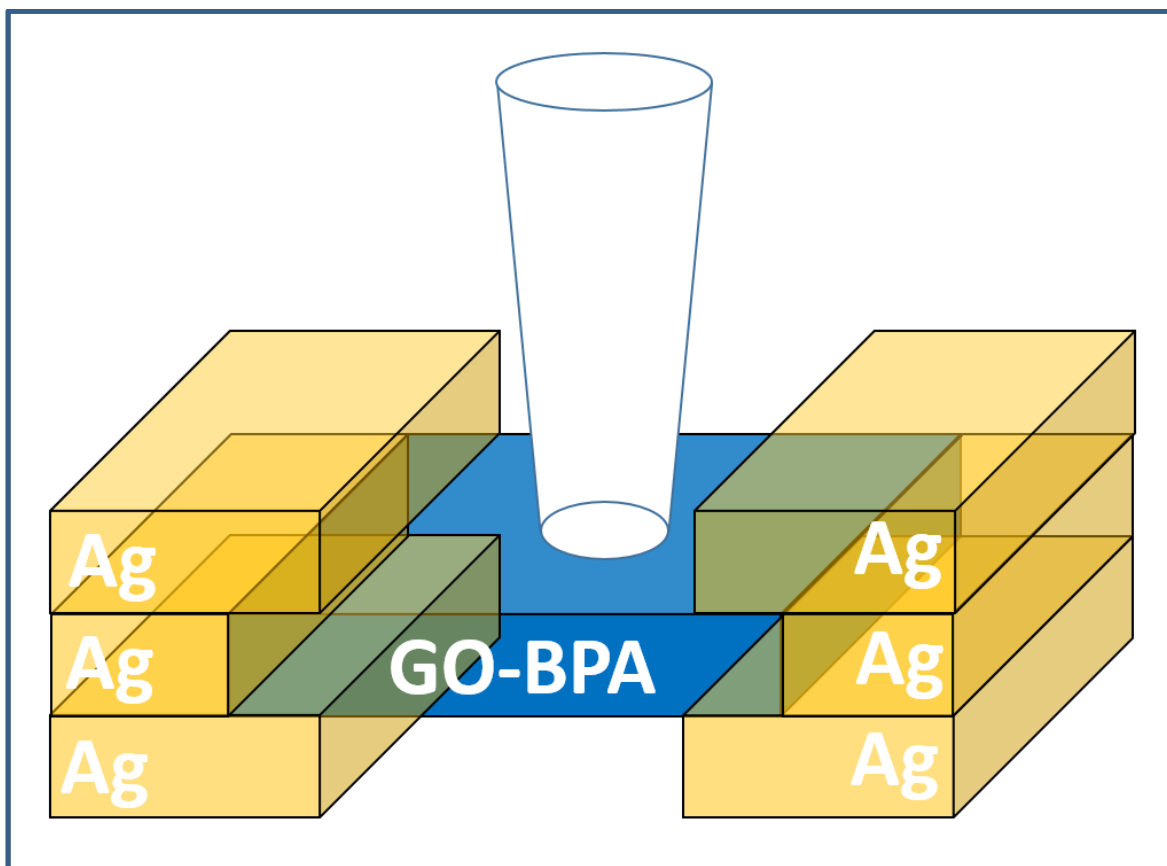


Figure 4.55. Configurational diagram of the GO-BPA light emitter device proposed in this investigation.

Figure 4.56. presents the photographs of the GO-BPA light emitter device developed in this investigation at 100 μm scale. The Ag path films were deposited by evaporation technique under the following conditions: masks with parallel patch, electrical current at 150 A, voltage at 3 V, and vacuum at 2×10^{-4} mbar.

Figure 4.56. (a) shows the light emitter device elaborated and proposed in this work for the case with power off. No light emission was observed, as expected. **Figure 4.56. (b)** presents the emission of intense white light originated by incandescence effect in the GO-BPA material when the device is polarized with an electrical source in power-on state at 10 V and 8 mA. The device was encapsulated by using polyvinyl alcohol.

Figure 4.56. (c), (d), and (e) presents the deconvolution calculus of the digital image, as shown in **Figure 4.56. (b)**, note the RGB (Red-Green-Blue) color components of the white light observed experimentally. This device requires optimization in the conditions to control white light emission; however, it is a good first step and opens an interesting vast field of research in optoelectronics and applied physics.

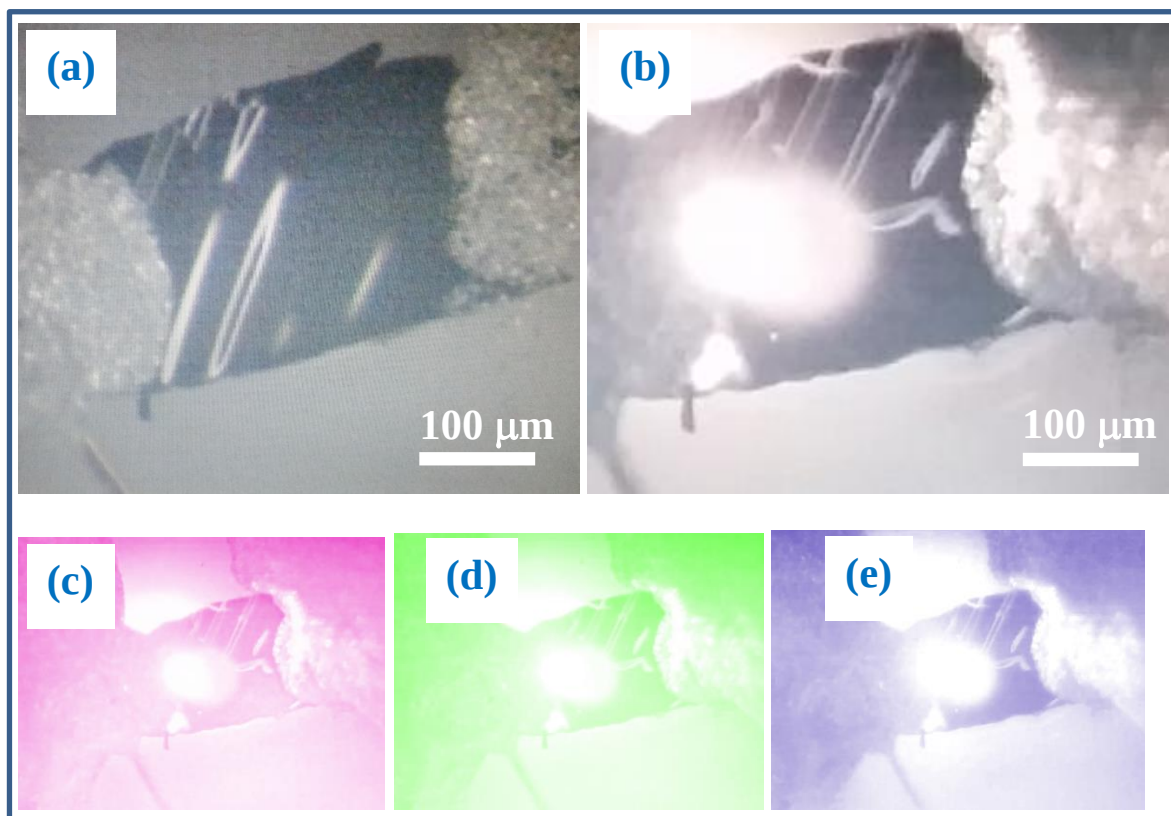


Figure 4.56. Digital picture of the GO-BPA light-emitter device developed in this investigation: **(a)** with power-off state. **(b)** with power-on state (at 10 V and 8 mA) and emission of the white light by incandescent effect was observed. **(c)**, **(d)**, and **(e)** correspond to the RGB (Red, Green, and Blue colors) deconvolution of the image presented in **(b)**, respectively.

We have, thus far, explored the physics experimental results on the study of transport mechanisms in GO-BPA platelets synthesized via DTD method employing bamboo as source; furthermore, we discussed some technological implications of these physical mechanisms in future applications in electronics and these important results suggest that GO-BPA materials can be excellent candidate materials to develop advanced electronics for sensors and devices. Chapter 5 will provide the conclusions and outlook of this original and collaborative doctoral work in Physics.

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Chapter 5

5. Conclusions and Outlook

The main goal in this thesis was to elucidate and understand the main transport mechanisms of GO-BPA samples obtained from bamboo, through systematic study of their transport properties, as well as discuss some technological implications of these transport mechanisms in possible future applications in electronics, seeking to optimize synthesis processes. Experiments with different GO-BPA samples and experimental methods has led to diverse theses. In the following, we will sum up the main results of this thesis and discuss the future of these specific results and the more general future of transport mechanisms in graphene oxide multilayers.

5.1 Summary

Graphene has attracted much attention due to its extraordinary properties and impact upon science and technology. One of the alternative and scalable methods of its synthesis is based on the physical-chemical exfoliation and reduction of graphite oxide (GO). This thesis, by means of an original and collaborative work in physics, has for the first time explored the new method, the so-called DTD-method for synthesis of GO-BPA samples, and studied the morphological, structural, elemental, thermal, electrical, and magnetic properties of GO-BPA samples; thus, elucidating the main transport mechanisms present in the GO-BPA samples synthesized via DTD-method and discussing some possible future technological impacts.

In the first part of this thesis, we proposed and implemented a new simple, cost-effective and eco-friendly DTD synthesis method to obtain GO-BPA samples from bamboo at different carbonization temperatures (T_{CA}), varying from 673 to 973 K and under controlled nitrogen atmosphere. The GO-BPA obtained via DTD method shows physical-chemical behavior similar to reduced graphite oxide, given the thermal decomposition of the phenol groups present in BPA. The GO-BPA samples were synthesized by using bamboo (*Guadua angustifolia* K., macana biotype), which is a natural, inexpensive, highly renewable, and abundant material available as waste products from the bamboo industry. In addition, the influence of the T_{CA} synthesis condition on the morphological, structural, elemental, thermal (vibrational), electrical, and magnetic properties was investigated.

At room temperature it was found that increased carbonization temperature in the GO-BPA samples leads to the following behaviors:

Morphologically, increased T_{CA} increases disordered graphitic clusters and stacking disorder in graphite oxide-type formations, with nanoplatelets geometry characterized by lateral dimensions of 5 – 100 μm and thicknesses of 25 – 100 nm, observed via TEM, HR-TEM, SEM, and AFM techniques in single GO-BPA nanoplatelets.

Structurally, increased T_{CA} increases low-shift of the diffraction angle at 002 direction, attributed to increased stacking disorder by carbon atoms out-plane (Δd_{002}), varying from 1.2 to 4.4 pm and due to the presence of defects in a polycrystalline structure with average values at 3.402 Å of interlayer d-spacing, 6.650 Å for nano-crystallite thickness, three layers, density of 2.24 g/cm³, and 77.03% of graphitization degree, which were determined by using XRD technique. The HR-TEM and EELS analyses provided a complete structural and chemical description of the GO-BPA samples. We have shown that by varying the carbonization temperature, we can obtain single GO-BPA nanoplatelets with oxygen content below 17% and modify their local atomic structure. Nanoplatelets synthesized at the highest temperature of 973 K show lower oxygen content with a short-range crystalline order and a carbon environment that is mainly in sp^2 bonding configuration (sp^2 fraction of 87%) and present greater stacking disorder due to boundary defects present. Nanoplatelets synthesized at the lowest temperature of 673 K have higher oxygen content and a disordered crystal structure with a mix of sp^2 and sp^3 characters (sp^2 fraction of 66%); these values were determined by using EELS technique.

Elementally, increased T_{CA} increases carbon conversion, varying from 85.71% to 94.00% and decreases oxygen coverage from 12.99% to 5.25%, both measured through XPS and EDS techniques.

Thermally, increased T_{CA} increases the density of boundary Raman defects and decreases crystal size due to desorption of multifunctional oxides and organic compounds by thermal decomposition of BPA, established by using Raman and FTIR spectroscopies.

Electrically, increased T_{CA} increases electrical conductivity, starting from $6.4 \times 10^1 \text{ S m}^{-1}$ and reaching a value of $2.3 \times 10^3 \text{ S m}^{-1}$ at the lowest oxidation degree. This difference of two orders of magnitude in electrical conductivity, varied by the influence of oxygen content and estimations of bandgap energy, showed variations from 0.30 to 0.11 eV by decreasing oxygen content from 17% to 5% as a narrow band gap semiconductor; these were determined by using I-V curves of electrical characterization at four contacts.

Magnetically, increased T_{CA} increases saturation magnetization by one order of magnitude from 2 to $40 \times 10^{-3} \text{ emu/g}$, attributed to increased density of the boundary defects from 4.98×10^{-4} to $6.03 \times 10^{-4} \text{ cm}^{-2}$, and decreases coercive field by one order of magnitude from 83 to 5.2 Oe and remanence magnetization from 1.76 to $0.87 \times 10^{-3} \text{ emu/g}$, both associated to diminished crystal size from 1.90 to 1.30 nm in the sample. Ferromagnetism order induced by boundary defects was observed at room temperature in the GO-BPA samples and characterized by magnetic hysteretic loop behavior, measured by using VSM technique and corroborated via MFM.

Secondly, the temperature influence in the main thermal and electrical transport mechanisms were investigated, finding that:

In thermal transport mechanisms, for a temperature range of $190 \text{ K} < T < 325 \text{ K}$, the main thermal scattering process was attributed to phonon-phonon interaction with relaxation times varying from 4.1×10^{-15} to $7.8 \times 10^{-15} \text{ s}$, low times possibly attributed to the effect of the stacking disorder by boundary defects that can modify the local anharmonicity and volume

of the GO-BPA sample. For low temperatures, $T < 190$ K approximately, the main thermal scattering processes were attributed to phonon-defect and phonon-impurity interactions with relaxation time at 7.8×10^{-15} s. They were explained by using Raman spectroscopy analysis.

In electrical transport mechanisms, at room temperature of $T = 300$ K, the main scattering process was attributed to charge carrier-impurity interaction with relaxation times varying from 1.2×10^{-16} to 4.5×10^{-16} s for variations in oxygen coverage from 17% to 5%, respectively. Low times were possibly attributed to the effect of the stacking disorder that can modify the charge-carrier effective mass and/or local screening effect. Additionally, oxygen coverage dependence on the band gap energy was estimated from experimental measurements of the electrical conductivity and determined theoretically via DFT computational simulations through the graphene oxide molecular configuration model proposed in this work, finding that the theory of this molecular model proposed agrees with the experimental data; charge-carrier distribution simulations show abundance of hole-electron pairs. Also, estimations of temperature dependence on the band gap energy in a single GO-BPA nanoplatelet at 5% oxygen coverage was well-described by the Varshni model and we determined values at 0.292 eV, 6.70×10^{-4} eV/K, and 33.62 K of extrapolated band gap energy at 0 K, and alpha and beta Varshni fit parameters, respectively, corroborating the semiconductor behavior of the single GO-BPA nanoplatelet. These values agree with the values reported for other narrow band gap semiconductor systems, like InAs, InSb, and others. All these results were obtained by using the I-V curves method in the electrical characterization at four contacts.

Third, the physical correlations among some vibrational, structural, and magnetic properties were studied and we found direct influence of the density of Raman boundary defects and XRD carbon atoms out-plane in saturation magnetization. Raman-crystal size also directly influences coercive field and remanence magnetization. Re-entry magnetotransport at different temperatures in the GO-BPA sample synthesized at 973 K of T_{CA} was observed and we found that the type of majority charge-carrier depends on the compromise between thermal energy and internal magnetic energy. At a temperature range of $360 \text{ K} < T < 400 \text{ K}$, the sample exhibited negative magnetoresistance at values varying from -0.5% to -5.5% and showed n-type semiconductor behavior because electrons gain thermal energy to escape from magnetic domains and lead current conduction. At a temperature ranges of $200 \text{ K} < T < 360 \text{ K}$, the sample presented positive magnetoresistance varying from +0.5% to +2.5% and exhibited p-type semiconductor behavior because electrons are trapped in magnetic domains and holes lead the current conduction. At temperatures of $T < 190 \text{ K}$, the sample showed negative magnetoresistance around -0.25% and displayed n-type semiconductor behavior because at low temperatures internal magnetic energy increases by increments of coercive field, then, holes are trapped in magnetic domains and electrons lead the current conduction. Magnetoresistance measurements were carried out by using a PPMS system.

Fourth, we finally discussed some technological implications of these transport mechanisms in possible future applications in advanced electronics as sensors and devices and we proposed that this thesis opens research fields in applied physics, particularly in GO-BPA films/quartz as possible selective contact for solar cells; infrared emitter or heater device based on GO-BPA samples; field-effect transistor (FET) devices based on GO-BPA samples;

blood glycemia FET biosensors based on GO-BPA samples; GO-BPA samples as batteries; as well as GO-BPA samples as light emitter devices.

5.2 Outlook

This work reveals the great potential of the GO-BPA samples for basic research and technological applications. Their morphological, structural, elemental, thermal, and electrical behavior is comparable to the reduced graphene oxide sheets obtained through more sophisticated methods. Also, these GO-BPA samples offer future opportunities to obtain 2D materials, like graphene oxide, by using an environmentally sustainable and commercially feasible synthesis method from renewable natural resources, as proposed by our group in the references in Annex 2. This work opens basic and applied physics research in the following directions:

Theory.

- How to describe the basic physical properties in terms of the random periodicity and disorder exhibited by the GO-BPA samples?
- How does stacking disorder affect the thermal and electrical relaxation times in the GO-BPA samples? – This requires the support of XRD experiments at low temperature in GO-BPA samples.
- Are there charge carriers, like Fermions, with mass and/or massless Dirac Fermions in graphitic clusters observed in the GO-BPA samples? – This requires support of Hall Effect (HE) and Quantum Hall Effect (QHE) experiments at low temperature in the GO-BPA samples.
- What is the quantum energy Hamiltonian of interaction between magnetic moments and spins in the ferromagnetism order observed at room temperature in the GO-BPA samples?
- What is the theoretical modeling of the magnetic hysteretic loop at room temperature and low temperature?
- What is the theoretical modeling of the re-entry magneto-transport observed in the GO-BPA samples?
- How do the effective mass and local screening of impurities distributed randomly affect the carrier-impurity interaction in single GO-BPA nanoplatelets?
- How to demonstrate that the GO-BPA samples exhibit hyperuniformity by random distribution of O-H functional groups (water) present?
- What is the physical correlation between structural and transport properties at low temperature in the GO-BPA samples?
- DFT computational simulation of the physical properties in the GO-BPA molecular model, as proposed in this investigation.
- What happens if the T_{CA} in the GO-BPA samples is above 973 K?

Experimental.

- Direct measurements of thermal and electrical relaxation times in the GO-BPA samples.

- XRD and FTIR experiments at low temperature in the GO-BPA samples.
- Thermal conductivity, diffusivity, and capacity measurements in the GO-BPA samples.
- Hall Effect (HE) and Quantum Hall Effect (QHE) experiments in the GO-BPA samples.
- Direct measurements of band gap energy in single GO-BPA nanoplatelets at room temperature and low temperature.
- Direct measurements of internal quantum efficiency in the GO-BPA samples.
- Direct measurements of magnetization versus external applied magnetic field M (H), as experiments at low and high temperatures, and to determine the Curie temperatures in the GO-BPA samples.
- Electrical impedance experiments in the GO-BPA samples.
- Study of the optical properties in the GO-BPA samples.
- Study of mechanical properties in the GO-BPA samples.
- Piezoelectric characterization of the GO-BPA samples.

This thesis also opens research fields in applied physics in the following directions.

- Create a spin-off company dedicated to developing technology products based on GO-BPA materials.
- Conductive and coating inks based on the GO-BPA samples obtained at carbonization temperatures >973 K, like RF circuits for internet of things (IOT).
- Chemical sensors based on GO-BPA samples, including optimization of the GO-BPA-FET blood glycemia sensor proposed in this work.
- IR emitter or a heating device based on GO-BPA samples to integrate into clothing for continued optimization of the IR emitter device proposed in this investigation.
- White light emitter device, IR emitter, and UV-VIS detector based on GO-BPA samples and their optimizations.
- Optical barrier devices based on GO-BPA samples and their optimizations.
- Produce composites based on GO-BPA samples for spintronics.
- Selective contacts and conductive inks for solar cells.
- Batteries and supercapacitors based on GO-BPA samples and their optimizations.
- Electronic advanced keyboards and touch panels based on GO-BPA samples and their optimizations.
- Transistor devices and RF circuit stickers based on GO-BPA samples and their optimizations.
- Logic transistor gates based on GO-BPA samples and their optimizations.

This work also suggests the following optimization alternatives of the DTD-method used in this work to synthesize GO-BPA samples:

- Optimize the DTD-method proposed in this work for temperatures above 973 K.
- Optimize the DTD-method proposed in this investigation by controlling simultaneously temperature, nitrogen atmosphere, and pressure. With this optimization of the DTD method, we hope to synthesize the GO-BPA for

different nitrogen contents at fixed carbonization temperatures and it is possible to increase the band gap energy of the samples.

- Optimize the DTD method proposed in this work by using an external applied magnetic field. We hope that this optimization meets synthesis of the GO-BPA samples with particular boundary defect orientation and increases magnetic response of the samples.
- Large-scale production of thin films on different substrates by using the DTD-method and considering the uses of different solvents in the roll coating process.

Scientific Contributions

1. International Publications

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Acronyms Used

AFM	Atomic Force Microscopy
BPA	Bamboo Pyroligneous Acid
BE	Bose-Einstein
CCD	Charged-Coupled Device
CENM	Center of Excellence in Nobel Materials
Co	Oxide Coverage
EELS	Energy Electron Loss Spectroscopy
Df	Defects
DFT	Density Functional Theory
DNA	Deoxyribonucleic Acid
DTD	Double Thermal Decomposition
ED	Electron Diffraction
EDS	Energy-Dispersive X-Ray Spectroscopy
EELS	Energy Electron Loss Spectroscopy
FEBID	Focused Electron Beam Induced Deposition
FET	Field Effect Transistor
FIBID	Focused Ion Beam Induced Deposition
FM	Ferromagnetism
FTIR	Fourier Transform Infrared
GNP	Graphene Nanoplatelet
GO	Graphite Oxide
GONP	Graphite Oxide Nanoplatelet
GP	Graphene
HE	Hall Effect
HOMO	Highest Occupied Molecular Orbital
HOPG	Highly Ordered Pyrolytic Graphite
HQE	Hall Quantum Effect
HR-TEM	High Resolution Transmission Electron Microscopy
IR	Infrared
ISO	International Organization for Standardization
I-V	Current-Voltage
LUMO	Lowest Unoccupied Molecular Orbital
MFM	Magnetic Force Microscope
MIR	Mid Infrared
MR	Magnetoresistance
Ox	Oxide atomic percentage
PC	Polycrystalline
PID	Proportional-Integral-Derivative
RGB	Red, Green and Blue
RGO	Reduced Graphene Oxide
RS	<i>Raman</i> Spectroscopy
RT	Room Temperature
SE	Secondary Effect
SEM	Scanning Electron Microscope

SPM	Scanning Probe Microscopy (
STM	Scanning Tunneling Microcopy (
TEM	Transmission Electron Microscopy
UV-VIS	Ultraviolet-Visible
VRH	Variable Range Hopping
VSM	Vibrating Sample Magnetometer
XPS	X-ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

ANNEX 1

XPS and EDS characterization in GO-BPA samples (in digital format)

ANNEX 2

**Scientific Contributions
(in digital format)**

Doctoral Program in Physical Sciences

