Decoration of graphene sheets with metal and metal oxide nanostructures by low-pressure plasma deposition

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Introduction and aim of the thesis

Graphene has got exceptional attention in the field of science and technology, regarding its remarkable, mechanical, electrical and electronic properties. Graphene has prominent potential to be next conducting materials to substitute the electrode materials in optoelectronic devices. With the increased demand in energy resources and other kinds of applications, pronounced effort has been dedicated to achieve advanced energy conversion and storage systems. Graphene and its composite have much pronounced attention for the energy storage system, because it’s unique properties such as chemical stability, superior thermal and electrical properties and large surface area. A wide range and different variety of graphene based materials were prepared for potential applications in sensing, catalysis, electronics, magnetic and energy storage. Graphene presents unique properties when modified by means of metal (M) and metal oxide (MO) nanostructures decoration. Recently different research activities were done for hydrogen storage in graphene based materials. It is well established that the decoration of graphene with well dispersed M nanostructures improved hydrogen uptake capacity at ambient conditions. More over graphene has been used as a burgeoning support to accommodate well-dispersed semiconductor MO nanostructures to enhance the photocatalytic and magnetic properties.

The main objective of the current work was to decorate graphene sheets with M and MO nanostructures for improvement of some properties of graphene. The main target of this work was related to decorating graphene sheets with M and MO nanostructures for hydrogen storage, photocatalytic activity and the study of the magnetic properties of the graphene and metal/metal oxide composite. It is well known that decoration of graphene sheets with M and MO nanostructures not only enhances graphene properties but also displays novel properties resulting from the interaction between M and MO nanostructures with the graphene sheets. However the
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decoration method of metal and metal oxide nanostructures which are nontoxic, environmentally friendly and fast is very challenging and important. Because the size and the distribution of the M and MO nanostructures onto graphene sheets are affected the efficiency of the prepared composite, which are difficult to control. In this thesis, the decoration of graphene powder with three kinds of materials Nb$_2$O$_5$, TiO$_2$ and Mg deposited by radio frequency sputtering techniques was studied. The low-pressure plasma deposition is a clean compatible, scalable and widely used technique in industry. Moreover using RF sputtering technique for the decoration with MO of graphene sheets can degrade the layers of graphene due to the interaction of the plasma species and high-energy sputtered atoms. These sputtered atoms and plasma species induce disorders and defects in the graphene layers which can degrade graphene. The interaction of the plasma species with graphene was not studied for hybrids material obtained by low-pressure plasma deposition till date. Based on the unique properties of the graphene effort will be made to decorate graphene sheets with TiO$_2$ nanostructures using low-pressure plasma deposition for the improvement of the photo- catalytic activity. Nb$_2$O$_5$ is an n-type semiconductor used widely as a catalyst, gas sensing, energy storage, and other applications. Magnesium based hybrid materials are promising candidates for the hydrogen storage, because Mg has high volumetric and gravimetric hydrogen storage capacities. It is believed that graphene which has high surface area serves as an ideal support for anchoring well-dispersed Mg nanoparticles for the improvement of its catalytic action toward the hydrogen dissociation.

My dissertation is composed of seven chapters, which are organized as follows: the chapter #1 gives an overview of the interaction of M and MO with graphene sheet and the application of the decorated graphene with M and MO nanostructures will be discussed. The Chapter#2 describes the experimental details used for the decoration of graphene sheets with M and MO
nanostructures. The basic principles of the growth and characterization techniques along with the analytical conditions are presented in this chapter. The chapter #3 describes the effect of the Nb₂O₅ nanostructures on the structural, chemical and electronic properties of graphite nanoplatelets (GNPs). Chapter # 4 focuses on the study of Nb₂O₅ effect on the structural, magnetic and chemical properties of graphene powders. Chapter # 5 describes the effect of crystalline Mg nanoparticles and crystalline film on the structural and chemical properties of graphene powder. Chapter # 6 deals with the influence of TiO₂ effect on the structural, chemical properties of graphene powders. In Chapter # 7 an exploration of potential applications of the deposited M and MO nanostructures onto graphene sheets is reported. Concluding remarks and future prospective are presented at the end of the thesis.
Chapter #1 Background and literature survey

Chapter # 1

Background and literature survey

1 Introduction
This chapter presents the basics of graphene which include band structure and some physical properties of graphene. The preparation methods of graphene based composite with M and MO nanostructures and types of defects induced in the structure of graphene by the interaction of metal and metal oxide nanostructures will be presented. The applications graphene based composite with M and MO will be discussed at the end of this chapter.

1.1 Graphene
Graphene is a 2D one-atom-thick planar sheet of sp² carbon bonded, which is organized in a honeycomb lattice structure. Graphene is one of the thinnest materials in the world. The structure of single layer graphene is hexagonal [1]. Graphene and diamond is an allotropic form of carbon, even though both have different physical properties. When single layer graphene wrapped, it forms 0D fullerenes and rolled it form 1D nanotube. Graphene layers can be stacked together to form crystal lattice of graphite and the stacking order of layers of graphene can be found in the form of highly ordered pyrolytic graphite (HOPG) or even the core of a pencil [2] as shown in Fig 1.1. In single carbon atom consist of four electrons in the outer shell. The graphene structure contains three sigma σ bonds and one π bond. The sp² hybridization present in sigma σ bonds with a mixture of the orbitals (s px, p_y), these orbitals providing a strong bonding force to a neighbor carbon atom. The fourth electron of the carbon is called pz electron and it makes the π bond. This pz electron are responsible for the half-filled band that allows free moving electron, due to this free moving electrons graphene exhibit the metallic characteristic [3].
Graphene surface can be modified with oxygen or hydrogen to form “graphane” or other carbonic materials respectively. Graphene displays astonishing properties. Graphene is more conductive than copper and stronger than diamond and having high flexibility than rubber. Due to the remarkable properties of graphene electrical, thermal and optical properties of graphene has attracted much attention in the field of science and technology \(^{[4,5,6]}\). Graphene also presents the anomalous quantum phenomena \(^{[7]}\) at room temperature, such as relativistic quantum Brownian motion, Klein tunneling \(^{[8-9]}\) and the quantum Hall effect (QHE) \(^{[10]}\). For
these phenomena graphene have also drawn much attention in the field of quantum engineering \cite{11, 12}

### 1.2 Band structure of graphene

Generally, for the semiconductor the electronic band is a parabolic shape with non-zero energy gap separated valence and conduction band \cite{13, 14}. It is well understood that the band structure of the graphene cone like structure and there is no space between the valance and conduction band and this point is called Dirac point \cite{15, 16}. Therefore, electrons can be excited from the valance band to the conduction band by means of small thermal fluctuation or with the application of small electric field \cite{17}. The Fermi level of the graphene can increase or decrease with a variation of the applied electric field and due to this, the graphene displays metallic characteristics. More importantly, due to the zero band gap of graphene, there is the limited application of the graphene in semiconducting devices \cite{18}. Consequently, the band gap opening of the graphene is the most significant assignment in making graphene transistor become a practical example. For this purpose, several approaches were made to create the gap in graphene in deformed structures of bi-layer graphene to work as a transistor channel \cite{19, 20}. Moreover, recently it is well established that graphene oxide (GO) can provide a small band gap opening \cite{21}. There are also so many other possibilities to open the band gap of graphene, it includes either physical strain or by bending of the graphene sheet and the schematic representation is illustrated in Fig 1.1. It is well established that, band gap property depends upon the width alignment of the graphene allotrope. The band gap of graphene can be opened by using chemical doping or either generate the defects in the structure of graphene as explained by Coletti et al. \cite{22} and Terrones et al. \cite{23}
The sigma bond is one most strong bond, the addition of the M and MO is mostly placed onto the graphene sp$^2$ domains instead of replacing the carbon atom itself. Then dopant generates the defects and these defects can vary the electronic property of the graphene. Many dopants were used to modify the band structure of the graphene and the band structure can be controlled by means of dopant concentration. Some common dopants include gold, sulphur and many other metals.

Fig 1. 2 Schematic diagram of the band structure of graphene and band opening

The mostly common and key compound for the band gap creation in graphene is Boron nitride (BN). Fet et al. have been described that, with random doping of BN onto graphene surface which is capable to modify the band structure and opening of the band gap [24]. The distribution of the surface charges (electron in $\pi$ bond configuration) being modified with doping and subsequently a small gap is formed. Contrary the doping in graphene is sometimes not simple to
control [25]. However, Liu et al. reported a new route for the doping method, which is simpler and stable in term of opening the band gap [26].

1.3 Physical properties of graphene

1.3.1 Electrical Conductivity of graphene

The mobility of the graphene is depending on the interaction of the type material and interaction with substrate. It has been reported that mobility values after the annealing exfoliated graphene can reach upwards 200,000 cm² V⁻¹ s⁻¹ in defects free structure of graphene [27, 28, 29]. This measured valued of graphene is around double with respect to the value obtained for the conductance quantum wire [30]. This indicates that the charge carrier in graphene may execute long range (ballistic) transport without much scattering at all even at room temperature [31, 32]. Due to the strong resistance against the destruction and high elasticity of graphene, it is very useful material for the electronics application. For the graphene the Young’s modulus value is around 1TPa. Graphene is one of the strongest material in the world, which is around 100 time stronger than steel [33]. More importantly the monolayer graphene can be stretched and bent rather easily.

1.3.2 Thermal Conductivity

Thermal conductivity of the material can be defined as the heat flux per unit area, (in W/m²) to the temperature gradient, \( Q'' = -\kappa \nabla T \). The thermal conductivity of suspended graphene is generally carried out by the ballistic phonons, it was found by using the high-resolution vacuum scanning thermal microscopy [34]. Accordingly, due to the number of scattering channels increase with substrate the thermal conductance of the graphene degrades significantly. It means that the heat may lose to the substrate. It is also well established that with increasing number of graphene layers the thermal conductance also decreased [35]. The value of thermal conductivity
Chapter #1 Background and literature survey

of graphene on the silicon dioxide substrate around 600 Wm$^{-1}$K$^{-1}$ is reported by Prasher et al [36], which much higher than copper. The in-plane thermal conductivity of the graphene is even higher values in order of 1,000 Wm$^{-1}$K$^{-1}$ [37, 38]. The dissipation of the heat flow between the graphene and the substrate can be influenced thermal of conductivity graphene. The acoustic phonon is responsible for the heat transport in plane of graphene. Though, the heat transport between the graphene and substrate interface in the cross plane direction is currently unidentified as described by Koh et al. [39].

1.3.3 Optical properties of graphene

Single layer graphene is almost transparent and absorbed only mere $\pi \alpha \approx 2.3\%$ of visible light (where $\alpha = 1/137$ is the fine structure constant [40]. This indicates that the graphene is highly transparent and the transparency of the single layer graphene is 97.7 %. The absorption of graphene is almost independent of wavelength range. Therefore, graphene is a suitable material for the photonic devices. Due to the high transparency of the graphene in the visible range, it can be used to make small screen devices. Additionally, for the same scenario the graphene has a true potential to use it in opto-electronics devices, which is explained by Nair et al. [41]. Moreover, the optical luminance property was also observed in graphene by Stoehr et al. [42]. They described that the luminescence property arises in graphene due to the electron-hole recombination when it is created in a broad energy range [43].

1.4 Overview method of preparation of graphene and metal oxide composites

The role of graphene in the graphene-based composite as a supporting material for the metal or metal oxide or acts as a functional component. The large surface areas and the conductive strong structure of graphene frequently enable the charge transfer, redox reaction, as well as strength the mechanical properties of resulting of the interaction of metal oxide graphene composites.
Therefore, anchoring of metal and metal oxides nanostructures onto graphene sheet improve the various kinds of properties of graphene in terms of storage of energy, catalytic energy conversion, and magnetic properties etc.\cite{44,45,46,47,48,49}. In this study, we mainly focus on recently developed methods for synthesis or decoration of high-quality graphene and metal oxide composite.

1.4.1 Solution-based methods of graphene and metal oxide composites

The solution-based method is the efficient and direct method used for the preparation of the metal oxide and graphene composites. The solution-based method is a widely used method to prepare the graphene- metal oxide (MO) composite. Peak et al synthesized graphene and SnO$_2$ composite by solution mixing. They prepared the SnO$_2$ sol by hydrolysis of Sncl$_4$ with NaOH, and subsequently, the graphene was dispersed with SnO$_2$ sol in ethylene glycol to achieve the composite\cite{50}. The following strategy was also applied for the preparation of the Graphene–TiO$_2$ composites by Williams, et al. They mixed the commercialized TiO$_2$ nanoparticles with Nafion–coated graphene to assemble dye sensitized solar cell, the role of the Nafion as ‘glue’ to join the graphene and TiO$_2$ nanoparticle (P25) \cite{51}. Likewise the TiO$_2$ nanoparticles were mixed using ultra sonication, then followed with ultraviolet-assisted photo catalytic reduction of GO to synthesized graphene–TiO$_2$ composites \cite{52}.For the preparation of graphene–TiO$_2$ composite Akhavan et al. followed the same strategy \cite{53}.

1.4.2 Graphene and metal oxide composites prepared by Sol–gel method

Sol gel is one of the most efficient methods for the synthesis of metal oxide nanostructures and films. TiO$_2$ and Fe$_2$O$_3$ nanostructures were synthesized onto graphene sheet by sol gel method reported in the literature \cite{54,55,56,57,58}. The generally used precursor for the TiO$_2$ nanostructures are TiCl$_4$, titanium butoxide \cite{59} and titanium isopropoxide \cite{58}, the result of these precursor
comes in nanoparticles, nanorods, mesoporous nanostructures of the TiO$_2$, which is highly depending on the different experimental conditions applied for the synthesis of TiO$_2$ nanostructures. Two step methods are used to obtain the TiO$_2$ nanocrystals onto graphene oxide sheet. In the first step of synthesis the amorphous TiO$_2$ nanostructures were decorated by hydrolysis and subsequently, the TiO$_2$ anatase nanocrystals were obtained by hydrothermal treatment. Due to the strong interaction of the graphene with TiO$_2$ nanostructure, the composite displays various applications, which includes photocatalysis and energy storage $^{[60]}$. The graphene/mesoporous silica composite was established using the sol-gel approach to prepared 2D sandwich composite was reported by Mullen group $^{[61]}$. Additionally, the mesoporous Co$_3$O$_4$ graphene composite was synthesized using the template of the mesoporous silica sheet by means of nano casting method. The key advantage of synthesis of graphene and MO composite by using the sol-gel method is that the graphene oxide or reduced graphene oxide offer reactive and anchoring sites for the nucleation and support the nanoparticles and as a result, the chemical bond between the graphene and metal oxide establish on the surface of GO/RGO.

1.4.3 Preparation of graphene and metal oxide by Hydrothermal/ solvothermal method

For the preparation of the organic nanocrystals structure material mostly Hydrothermal/solvothermal methods are used. The main advantage of the preparation of graphene and MO composite of the hydrothermal over the sol-gel is that the hydrothermal method is operated at evaluated temperature in a confined volume to produce large pressure. The one-pot hydrothermal/solvothermal route can give growth to nanostructures martial with high crystallinity without any calcination or post-synthetic annealing. Additionally, this method is also used to reduce graphene oxide. Many MO graphene composite prepared by using the hydrothermal or solvothermal method. Shen et al. prepared the graphene and TiO$_2$ composit
by using the hydrothermal method. They used the reduced graphene oxide and TiO2 composite in water and the graphene oxide used as a precursor for the reduced graphene oxide and the precursor used for the TiO2 is tetra butyl titanate under hydrothermal condition \[^{62}\]. More importantly the hydrothermal process is very simple and can be compatible for the industry applications. The crystal defects in the graphene- TiO2 composite can be controlled by means of varying the experimental parameters such precursor concentration solution and time of reaction. The hydrothermal method can be used to synthesize the other metal oxide nanostructures onto graphene sheet such Fe\(_2\)O\(_4\), Co\(_3\)O\(_4\), and SnO\(_2\) nanostructures. The porous and very thin nanostructure arrays of the Co\(_3\)O\(_4\) onto graphene sheet have been developed by using the facile hydrothermal process \[^{63}\]. More likely, the compositions, grain size and surface area of the graphene and MO composites can be tuned by controlling the hydrothermal treatment parameters or annealing processes. The prepared graphene and MO composite can be used in different kinds of application such as the lithium-ion batteries and energy conversion etc. Huang et al used a one-step solvothermal synthesis of graphene and SnO\(_2\) composites \[^{64}\]. They distributed the SnO\(_2\) nanocrystals uniformly on the graphene sheet by means of the solvothermal method. Some authors also reported the MO graphene composite other than the mention of the method \[^{65}\].

1.5 Decoration of graphene with metal oxide by Atomic layer deposition

The Atomic layers deposition (ALD) is one of the efficient and capable techniques used to deposit ultrathin layers or mostly MO, metal (M) and other coating materials onto the substrate surface. Due to the precise film thickness obtained by means of ALD technique has got much attention in many technological, academic researcher and industrial applications. For the most of the nanoelectronic devices very thin layers and controlled deposition of the uniform, layers are required. For this purpose, the ALD is the suitable technique to produce such kind of ultra-thin
layers films. Several research group was used the ALD technique for the deposition of the metal oxide thin film onto graphene sheet. Meric et al deposited the HfO$_2$ layers onto graphene by using the ALD technique [66]. The deposition metal oxide film onto graphene sheet is not very easy because there are no dangling bonds on the graphene surface by using ALD process. Moon et al also deposited a very thin layer of Al$_2$O$_3$ onto graphene directly by ALD process and they used the obtained composite for the top gated device to present good performance [67]. Wang et al also used the ALD technique to deposit 2 nm thin layers of Al$_2$O$_3$ onto exfoliated graphene sheets and the exfoliated graphene sheets were cleaned in Argon atmosphere at 600 °C. They used the vapor of trimethylaluminum (TMA; Al(CH$_3$)$_3$) and water used as a precursor to obtained thin layer of Al$_2$O$_3$ on graphene at 100 °C [68]. A similar strategy was also applied to deposit the Al$_2$O$_3$ and HfO$_2$ thin layer onto the surface of Highly Ordered Pyrolytic Graphite (HOPG) by Xuan et al. They obtained large number of nanoribbons of Al$_2$O$_3$ more than 50 μm in length and with the dimensions of 5 - 200 nm in width [69].

1.6 Choice of the materials for the decoration of graphene sheets.

1.6.1 Properties of Nb$_2$O$_5$

Recently Nb$_2$O$_5$ has got much attention in scientific area of research due to its excellent chemical stability with respect to the other oxides [70]. Nb$_2$O$_5$ is a wide band gap semiconductor having band gap of 3.2 eV[71]. Therefore, Nb$_2$O$_5$ has much potential to replace other oxide semiconductor in the different kinds of application. In this scenario, Nb$_2$O$_5$ based materials have presented substantial concern in the field of gas sensing and catalysis [72, 73]. Nb$_2$O$_5$ is also one of the impotent material for its desirable properties, which includes high refractive (n = 2.4 at 550 nm), high transparency and low absorption in the UV-vis –NIR and for this Nb$_2$O$_5$ is a widely used material in solar cell and bright windows [74]. It is also used for improving the
optical performance of optical devices such as waveguide based optics and optical filters \([75, 76]\). Beside these properties, Nb\(_2\)O\(_5\) present good electrical and magnetic properties and these properties can be improved by the addition of foreign impurities \([77, 78]\). Recently it is reported that Nb\(_2\)O\(_5\) used for the electrode material in electrochemical applications \([79]\).

### 1.6.2 Characteristic of TiO\(_2\)

Due to the astonishing physical and chemical properties of the TiO\(_2\), it is a widely used material in different kinds of application. TiO\(_2\) is extensively studied material in many scientific fields, which includes photocatalysis, electrolysis and photovoltaic cells \([80, 81]\), where the TiO\(_2\) is taken as active part for the solar energy conversion. TiO\(_2\) has a high refractive index and it makes it a suitable candidate for the transparent conducting oxide and other optical applications \([82, 83]\). TiO\(_2\) has also many potential applications in the field of ceramics and medical application. In the medical perspective, the TiO\(_2\) plays a vital role in the biocompatibility of bone implants \([84]\). Due to the chemical stability at high temperature, TiO\(_2\) shows good sensing characteristics toward the CO \([85]\), Hydrogen \([86]\), methane and ethanol \([87, 88]\). TiO\(_2\) nanostructures show good magnetic properties with some metal doping \([89]\). TiO\(_2\) is also widely used as an anode material for the lithium ions batteries \([90]\).

### 1.6.3 Properties of Mg nanostructure

A useful substitute for the safe and efficient source of energy carrier is much needed to use as fossil fuels \([91]\). In this scenario, light metal hydrate, such as MgH\(_2\) is one the most prominent candidates used for the hydrogen storage application, because of its high volumetric and gravimetric hydrogen storage capacity (7.6 wt % H\(_2\) and 110 kg H\(_2\)/m\(^3\) for MgH\(_2\))\([92]\). Though, due to the slow kinetics and operating at high temperature for hydrogen absorption/desorption the practical use of MgH\(_2\) are limited. To solve this issue regarding of slow kinetic and improve
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the hydrogen sorption properties at minimum temperatures, the nanoscale sizes Mg nanoparticles will be prepared. Recently, the enhancement of the hydrogen storage capacity and more rapid kinetics have been reported for the prepared Mg nanoparticle and nanocomposites [93]. Moreover, the reaction between Mg and hydrogen is one of most extensively used reaction for the hydrogen storage.

1.7 Review of the preparation study of transition metal oxide and graphene composite.

As discussed in the above section, MO and graphene composite can be prepared by wet chemistry methods and physical vapor deposition techniques. It has been reported that transition MO have got much attention in the field of organic electronic devices, because of its high work function values when it is inserted between the anode and organic layers would decrease the interfacial hole injection barriers [94, 95, 96]. Mostly used transition metal oxides for the hole injection layers (HILs) in organic electronic devices are V_{2}O_{5}, WO_{3}, and MoO_{3} [97, 98, 99, 1317]. Jens Meyer et al deposited the molybdenum trioxide (MoO_{3}) layers onto graphene sheet by thermal evaporation and used the graphene and (MoO_{3}) interface for Efficient Organic Light Emitting Diodes [100]. Qi-Hui Wu et al is also studied the graphene and (MoO_{3-x}) interface for the Efficient Organic Light Emitting Diodes [101]. Recently very few studies have been done for the preparation of the transition Nb_{2}O_{5} and graphene composite for the numerous kind of application. Jussara F. Carneiro et al prepared the Nb_{2}O_{5} and reduced graphene oxide by using the hydrothermal method for the H_{2}O_{2} electro generation [102]. They prepared the graphene oxide from the graphite flakes by modified hummer’s method, subsequently the graphene oxide reduction and the synthesis of Nb_{2}O_{5} nanoparticles supported on the reduced graphene oxide by hydrothermal method. Mahmood Jamil et al also prepared graphene-Nb_{2}O_{5} composite material by hydrothermal method for the dye sensitized solar cell (DSSCs) [103]. Similar method was also
employed by the Paulraj Arunkumar et al for the graphene and Nb$_2$O$_5$ nanoparticles composite for the electrochemical storage. They synthesized Nb$_2$O$_5$ nanoparticles of size 50 nm and decorated onto graphene sheets homogenously. They used very low content of graphene sheets of (4.5 wt. %) with high conducting Nb$_2$O$_5$ composite prepared by hydrothermal method. They used the prepared composite for the electrochemical characterizations, which include cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic charge/discharge [104]. Luyuan Paul Wang et al used the graphene and Nb$_2$O$_5$ composite for the High-performance hybrid electrochemical capacitor[105]. Litao Yan, et al is also prepared graphene and Nb$_2$O$_5$ composite by using the hydrolysis method for the application of high performance sodium ion battery[106].

1.8 Review of the preparation study of Mg and graphene based hybrid materials,

As discussed in the above section that, Mg is one of vital element for the solid state hydrogen storage application. It is already discussed that, the graphene has high surface area and have potential to support metal nanostructures for the improvement of their catalytic activity. The majority reported data for the preparation of the M and carbon materials are via ball milling or chemical wet chemistry method or solidification [107]. However, the preparation of the M and carbon based materials via ball milling process intrinsically produced unwanted morphological structures, chemical in-homogeneity in properties, which can reduce the performance of the composite. Therefore, new methods are required for the preparation of the metal and carbon based material for the improvement of the catalytic activities. Recently Eun Seon Cho et al synthesized the reduced graphene and Mg nanocomposites via a simple solution based co-reduction method. They used the Mg$^{2+}$ precursors dispersed onto graphene oxide sheets and subsequently reduced the graphene oxide by using the lithium naphthalenide. The synthesized
composite were used for the hydrogen storage application and they found hydrogen storage capacity was 6.5 wt. % and 0.105 kg H₂ per liter in the total composite at 200 °C and 250 °C at 15 bar [108]. Jun Zhang et al studied the hydrogen adsorption in Mg doped graphene oxide by using density functional theory calculation. They described that; hydroxyl group from the graphene oxide surface can be reduced by the addition of Mg. Theoretically; they found that eight H₂ molecules are adsorbed on each side of Mg-doped graphene oxide and obtained hydrogen storage capacity was 5.6 wt % at a temperature of 200 K [109]. Recently Guanglin Xia et al used chemical method for the well dispersed MgH₂ nanoparticles onto reduced graphene oxide sheets. They discussed that, by reducing the particles size of Mg onto graphene sheets, the hydrogenation and dehydrogenation kinetics can be increased notably. They also found that by reducing the particles size of Mg nanoparticles, the kinetic of hydrogenation and dehydrogenation could achieve 85.5 % and 57.3 % of the theoretical value for the Mg nanoparticles [110]. Xiuyi Lin et al is also simultaneously dispersed Mg and Cl onto graphene oxide by using chemical route method for the improvement of the mechanical dielectric and electrical properties of the composite [111].

1.9 Review of the preparation TiO₂ and graphene based hybrid materials

Recently the TiO₂ nanostructure and graphene sheet were extensively studied for the high performance of the photo catalytic of graphene TiO₂ composite and also to improve other properties of graphene. Different chemical and physical approaches were used to prepare the nano size TiO₂ structure onto graphene sheet. Md. Selim Arif Sher Shah et al used one step hydrothermal method for the composite of reduced graphene oxide and TiO₂ nanostructure without using reducing agent [112]. They measured the photo catalytic activities of the prepared composite for the degradation of rhodamine B dye. They also observed that composite can
degrade colorless dye such as benzoic acid under visible light. Lanbing Gu, et al adopted the same method for the preparation of graphene and TiO$_2$ nanostructure composite, but followed some modification with facile glucosamine assisted hydrothermal strategy in alkaline conditions, the obtained results indicate that with addition of glucosamine, which play an important role for the dispersion of the TiO$_2$ nanoparticles onto graphene$^{[113]}$. They measured photo catalytic performances of the prepared composite for the degradation of three kinds of dyes, which include the rhodamine B (RhB), methylene blue (MB) and methyl orange (MO) under UV light irradiation. Wan-Sheng Wang et al used one step solvothermal method for the graphene and high quality anatase ultrathin TiO$_2$ nanosheets$^{[114]}$. They observed that the prepared composite of graphene and ultrathin TiO$_2$ nanoparticles present high photo catalytic activity with respect to pure TiO$_2$ and P25. Nguyen-Phan et al illustrates that the hydrogenated graphene and TiO$_2$-x nanocomposites used as phtocatlayst for the production of H$_2$ and O$_2$ from water, without any assistance of noble metal co-catalyst $^{[115]}$. The charge transfer phenomenon between the graphene and TiO$_2$ composite has been explained by Aijun Du, etal$^{[116]}$. They described by using the ab inntio calculation and observed the charge being transferred from graphene to TiO$_2$ as the consequence of large work function difference, which lead to significant hole doping in graphene. Yaxin Zhang et al using the hydrothermal method for the preparation of the TiO$_2$ and graphene composite, this exhibits that, the prepared composite shows high photo catalytic activity for the degradation of the sodium pentachlorophenol $^{[117]}$. Zahra Gohari Bajestani et al prepared graphene with different concentration levels of TiO$_2$ nanoparticles by simple chemical method. They used the prepared composite for the hydrogen storage application at room temperature and pressure upto 10 bars. The reported hydrogen capacity for the graphene and TiO$_2$ composite was measured upto 0.39 wt% at room temperature $^{[118]}$. Surajit Kumar Hazr et al
used the TiO$_2$ and graphene composite for the chemical sensor [119]. Ying-Na Changa et al adopted a simple chemical method for the preparation of the TiO$_2$ and graphene composite for the magnetic and antibacterial properties under solar irradiation. They reported that magnetic graphene oxide and TiO$_2$ composite displayed a high antibacterial activity against Escherichia coli[120].

1.10 Defects in Graphene structure

Generally, defects in materials are measured to be unfavorable to the properties of materials and device based on such materials. However, defects in materials can also be useful in providing the dopant control both their carrier concentration and whether the carriers are n-type or p-type [121, 122]. Commonly one can refer to that defect in graphene that breaks the symmetry of the sp$^2$ bonded carbon atom in honeycomb lattice. The symmetry of graphene plane structure can break with the defects induced in the plane of graphene, which includes point defects, such as vacancies [123, 124, 125] substitutionally impurities, [126, 127] interstitial impurities$^{128, 129}$ and the impurity can be a chemical impurity or an isotopic impurity [130, 131]. Mostly grain boundary defects were observed in graphene by using the chemical vapor deposition method for its preparation and the grain boundary defects also occur, when the graphene was mechanically, exfoliated but there are some differences found by comparing the two of graphene[132]. The grain boundaries of the graphene or edge defects also break the symmetry of graphene and these boundaries serve as scattering centers for electron and phonons.[133, 134]. Accordingly, also some defects present in the interlayer spacing when the graphene sheets were synthesized for the specific application, such as stacking faults within interlayer stacking, different chemical arrangement and the arrangement of the isotopic interplaner. Various kind of experimental techniques are used to understand the influence of the different defects in the graphene system,
for the information driven from the atomic level structural of graphene characterized by high-resolution transmission electron microscopy\cite{135}, spectroscopic information derived from Raman and scanning tunneling spectroscopies \cite{136}. It is well known that, the structural defects are associated with both naturally occurring imperfections and growth induced defects. The structural defects which induced in the structural of graphene include cluster defects \cite{137}, boundaries or edges and point defects and these defects lowering the symmetry of the graphene crystal. The point defects occur in the plane of graphene in the form lattice vacancies and impurity atoms. These impurities onto graphene plane can be either in interstitial or substitutional and these impurities can be in the form of isotopic impurities \cite{131,138}. These impurities normally perturb the phonon spectra. Impurities, which are in the form of foreign dopant (species), tend to generate strain and local electric fields, because of the small size of the carbon atoms in graphene planes relatively to all other dopant species. The size of boron atom is smaller than the size of carbon, which is spherical impurity atom that establishes a normal p-type dopant for graphene. Interestingly, Fluorine or hydrogen mostly either to physisorb onto graphene sheets in the defects site \cite{139} and when fluorine is added to graphene in high concentration its forms covalent bond with graphene. Additionally, the defects can strongly influence the properties of graphene and defects can vary with the preparation and production methods.

1.11 Applications of graphene hybrid based materials

1.11.1 Graphene and TiO$_2$ based photo catalytic application

In the above section, we discussed different approaches for the preparation of graphene and TiO$_2$ nanocomposites for the enhancement of the photo catalytic properties. The access of the purifying water for the human and other domestic uses has become a current issue around the
world. Huge amount of the organic pollutants are introduced by various commercial and agricultural activities, which are regularly unrestricted into the eco-system. These organic pollutants are commonly toxic and can cause seriously health and environmental problems. In the past, much research has been done on these issues to remove these organic pollutants from the wastewater, which include biological treatment, coagulation, ultrafiltration and ion exchange. These approaches have some advantages, but these methods are not very efficient for a number of applications. Semiconductor photocatalysts have been got much attention toward the enhancement of the photocatalytic activity.

![Fig1.3 Schematic diagram of TiO\textsubscript{2} and graphene based material for photocatalytic application](image)

Titanium dioxide (TiO\textsubscript{2}) is a very important and suitable semiconductor, which has been an extensively, used materials for the improvement of the photocatalytic properties due to its
nontoxicity, low cost and high chemical stability. However the large band gap of the anatase TiO$_2$ (3.2 eV) restricts its photocatalytic properties to the limit range of the ultraviolet (only about 3–5% of total sunlight). In this situation the electrons and holes can easily recombine before emigrates to the photocatalyst surface, which considerably reduced the photocatalytic efficiency. Recently, it has been well established that, graphene has high potential for the improvement of the photocatalytic activity due to its unique properties, such as high surface area, high transparency, huge electrical conductivity and good interfacial contact with adsorbents \[140,141\]. Due to this large surface area of graphene can modify the surface properties of graphene, and then graphene is an anticipated material for the heterogeneous growth for the guest material. It is also a well interesting fact that, the surface function groups onto graphene sheets such as hydroxyl group act as favorable nucleation sites for the guest materials. The viable growth of nucleated clusters onto graphene sheets may modify the size and the structure of the final nanoclusters. More importantly, the well dispersed growth of the anatase TiO$_2$ nanoparticles onto graphene sheets is also a big challenge, however in some cases of nucleating nanoparticle or nanocrystals onto graphene sheets has been described \[140,142\]. Furthermore, due to the high electrical conductivity of the graphene is one most suitable material in promoting electron transfer in photocatalytic reactions and electrochemical process. Therefore, the well dispersed nanosized mesoporous anatase TiO$_2$ nanoparticles onto graphene sheets are well appropriate composite for the improvement of the photocatalytic activity and application and the result is presented in Fig 1.3 \[143\].

1.11.2 Magnetic properties of graphene based hybrid materials

In the above section, we discussed that graphene has numerous exceptional properties in wide range of field, which includes microelectronics, sensor and superconductor energy storage and
other so many. Several observations have been reported about the existence of ferromagnetic in long range of ordering in carbon based materials \[^{144, 145, 146, 147}\]. Induced ferromagnetic behavior in highly oriented graphite is related to the lattice imperfection, as reveal that graphite has shown the ferromagnetic behavior by proton irradiated and also the ferromagnetic signal enhanced in prepared pyrolytic graphite, which contained high defects concentration. In addition ferromagnetic behavior has been also observed in other carbon based materials, which includes carbon nanofoams \[^{148}\] , proton-irradiated thin carbon films \[^{149}\] and carbon-ion-implanted nanodiamond \[^{150}\]. All these observations indicate that, the carbon based materials possess ferromagnetic behavior \[^{151}\]. Recently, it is well established that magnetism was observed in doped or defective graphene and graphene oxide \[^{152, 153, 154}\]. It was observed by Wang, Y. et al. that graphene shows a ferromagnetic behavior at room temperature. They explained that the very few contaminations such as (Fe, Ni) are responsible for the ferromagnetic behavior of the graphene at room temperature \[^{154}\]. Generally, different types of defects are responsible for the magnetic properties in the carbon based materials. However, the magnetic behavior details can be varied for different structures such as (graphene nanotubes, fullerenes and graphite based composite). Commonly, structural defects, which occurred in graphene based materials, are vacancy, atom at the edges, and adatoms. These structural defects induced the magnetic behavior in the graphene sheets. Moreover, the structural defects give rise to localized electronic states, a net magnetic moment, and an increase in the density of states at the Fermi level, and eventually to the development of magnetic order. Largely, the d and f elements are mostly used magnetic materials in the present technological applications. Additionally, the magnetic nanoparticle has got much attention in various sectors of applications, such as data storage \[^{155}\] , catalysis \[^{156}\] and magnetic resonance imaging \[^{157}\]
etc. In current scenario, the good dispersion of magnetic nanoparticles onto reduced graphene oxide sheets potentially provides a new path to develop unique catalytic, electrode and magnetic materials \[158\]. For the nanoscience and nanotechnology, the magnetic nanomaterials are the most forefronts and fast emerging fields in many fields of applications. Besides, it is also reported theoretically, that the atomic scale defects induced in graphene based material by foreign impurities and vacancies in the graphene can generate the magnetic moment of about one Bohr magneton, \(\mu B\) \[156,159\]. Additionally, the prospect of the long range magnetic ordering of graphene based material is established by the randomly dispersed grain boundaries and point defects \[160,161\], and the ferromagnetism of the bi layer graphene was proposed by the spontaneous many-body system \[162\].

1.11.3 Hydrogen storage in graphene based material

For the renewable energy storage, hydrogen is one of the environmentally friendly energy sources and has pronounced potential to substitute the non-renewable other hydrocarbons for the energy carrier and transport application. For the replacement of the hydrocarbons, hydrogen is one of the best ‘green’ fuels, due to its light weight, very simple structure, nontoxic and one of abundant elements in the world. Hydrogen is a clean energy source and the high energy density with no emission of \(\text{CO}_2\) gas. Compared to the other commonly used fuels, hydrogen has highest energy density by mass. The heating value of hydrogen is 140 MJ.\(\text{kg}^{-1}\), which is three times greater than that of the gasoline. \[163\]. However, two simple steps are required to employ the molecular hydrogen as energy carrier, so called hydrogen storage and hydrogen production. First to describe the hydrogen production, in the universe less than \((1\%)\) isolated hydrogen \(\text{H}_2\) exists. \(\text{H}_2\text{O}\) is the main source for the production of hydrogen and also found some other compounds such as ammonia \((\text{NH}_3)\), or hydrocarbons. Now secondly, appropriate material or surfaces are
still needed for the reversible hydrogen storage and also become economically feasible for all intended applications. Carbon based materials such as carbon nanotubes, metal organic frameworks graphite nanofibers are the most favorable candidates for the hydrogen storage application, because of its many remarkable properties such as high specific area, stability for the large scale production, fast kinetics, which can tune the pore structure, low density and these material are mostly studied for hydrogen storage application. Big challenge for the hydrogen storage media in carbon based material is to find a structure, whereas the structures can tunable porosity and having high surface area and also provide a feasible surface for the absorption of hydrogen, which is thermodynamically stable and not to strongly so that reversible fast kinetics are possible \[^{164}\]. Recently, graphene got much attention for the hydrogen storage application due to it remarkably properties such as unique 2D structure, high surface area which is theoretically measured about to 2630 m\(^2\)/g a much higher surface area with respect to the other carbon based structures.. More importantly, in order to improve the hydrogen storage capacity at feasible condition, different approaches were studied theoretically for the functionalization of graphene. The most appropriate effort has been devoted to examine the role of the functionalized elements to improve the hydrogen storage capacity at viable pressure condition and room temperature. Several other theoretically methods were studied to improve both binding and gravimetric/volumetric storage capacity, because there is weak interaction between the graphene and molecular hydrogen. One approach for the enhancing of the hydrogen storage capacity is the chemical decoration of the alkali metals onto graphene sheets, such as Li, Na and K. It was found that decoration of graphene with Li nanostructure, which can adsorb four hydrogen molecules and reached the gravimetric hydrogen storage density above 10 wt\% \[^{165}\]. Moreover, a remarkable experimental result was achieved by the reduction of graphene oxide with decorated
palladium atom. An enhancement of the gravimetric density at room temperature from 0.6% to 2.5% at 30 bars was obtained and the hydrogen molecules were dissociated to a spillover mechanism through Pd atoms followed by H passage onto the graphene sheet \[^{166}\].
1.12 References

Chapter #1 Background and literature survey


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2.1 Introduction
The main goal of this chapter is to describe the characterization techniques, tools and the sample preparation methods used to deposit the metal and metal oxide nanostructure onto graphene sheets. In the first section of this chapter will be described the method of the preparation of the samples. The first section also following to cover the RF sputtering technique and deposition parameters were used for the deposition of the metal and metal oxide nanostructure onto graphene sheet. In the second section of the thesis will describe, different characterization techniques used to understand the fundamental structural, chemical, electronic and the interface properties of the decorated graphene with metal and metal oxide nanostructures. The techniques used for the characterization of the graphene composite include, X-ray diffraction (XRD), Raman, X-ray photoelectron spectroscopy (XPS), synchrotron x-ray photoelectron spectroscopy transmission electron microscopy (TEM), Magnetometer and photo catalytic activity. The following properties; crystal structure, grain size, surface morphology, chemical bonding position and the stoichiometry of deposited oxide nanostructures onto graphene sheet were measured by using the above stated techniques.

2.2 Samples preparation
The graphene powder samples for the deposition were prepared in the glove box. The graphene powder and deposited M and MO onto graphene was protected from the moisture in the glove box and the other kind of the contaminations. Especially in case of metal deposition onto graphene sheet, subsequently oxidized, when it was exposed to the air moisture. A special kind of sample holder was designed to protect the graphene powder from the air exposure and other kind contaminations. Moreover the atmosphere inside the glove box contains an inert gas
(Argon). There are two analyzers in the glove box one is the O\textsubscript{2} analyzer and the other H\textsubscript{2}O analyzer, which are used to measure the amount of oxygen and water molecules inside the glove box. The powder samples were prepared in the glove box and subsequently the graphene powders are protected from the air by using the special kind substrate holder as shown in Fig. 2.1.

**Fig 2.1 Glove box and substrate holder used for the samples preparation**

### 2.3 Plasma for material synthesis and RF Sputtering technique

The electrical discharge of an inert gas is mostly used for the generation of plasma for material synthesis by PVD. This process is performed by the introduction of inert gas (like Ar) into the process chamber, while maintaining a specific base pressure (In our work, the base pressure is maintained below \(10^{-5}\) Pa). The process chamber comprises an electrode pair, one each for cathode and anode. The target serves as a cathode and is usually connected with negative potential whereas the sample holder acts as anode. The acceleration of charged particles achieved by the potential difference of cathode and anode is vital for the transfer from neutral gas to the plasma. The (inelastic) collision of free electrons and neutral gas atom is initiated. The free
electrons are accelerated to an energy level greater than the ionization energy of the neutral gas. The process of inelastic collisions results in ionization and excitation of gas atoms [34].

$$\text{Ar}^0 + e^- \rightarrow \text{Ar}^+ + 2e^-, \quad (2.1)$$

Every ionization collision results in two free electrons and in case of sufficient kinetic energy also induce the ionization of gas atoms and these ionized gas species accelerating towards the cathode. As a consequence, the sputtering process ejects the target atoms and also the secondary electrons from target surface. The process eventually leads with the cascade of free electrons and ions. The resultant plasma discharge is self-sustained and occurs due to the continuous supply of secondary elections, which ensures regeneration of enough secondary elections during the sputtering process due to production of enough Ar+ ions. The process also includes diffusion to the wall in order to compensate the loss of charged particles. On the basis of the applied potential and the obtained discharge current density, a plasma discharge occurred into numerous regimes [3]. This thesis is related about the deposition of the metal (M) and metal oxide (Mo) onto graphene by low pressure plasma. In the plasma deposition, the discharge potential and current density rising with increasing RF power values, until the surface of the target completely cover by the ionized gas species. Furthermore, by raising RF power values leads to the arc discharge regime, which is categorized by an exceptionally high current density at the target surface, in this case the plasma density reached at a value of $10^{21} \text{m}^{-3}$ [3].

It is well established that plasma is supposed be to quasi-neutral, therefore this characteristic is essentially related to the bulk plasma. Some nonconformity, such as charge disparity can occur at the wall of the chamber or at the plasma boundaries where the plasma species interrelates with other kinds of particles or may be wall of the chamber. The main reason of this case is due to the fact that mobile ions are heavier than electrons and diffuse very fast to the wall of the chamber,
subsequently they leave the bulk plasma at a potential (which is called plasma potential) higher as compared to the grounded chamber wall. Usually the plasma potential is in the range of couple volts \([2]\). Furthermore, any other isolated electrode working in the plasma process will be at slightly negative potential (floating potential) as compared to the ground potential, which is also an effect of the faster electrons. Generally, the region where the interaction takes place by the plasma species with other surface, in these region ions will outnumber the electrons. This space or region is known as plasma sheath \([167]\). The plasma sheath is a non-neutral region in contrast to the bulk of the plasma. The following is the expression for the sheath thickness and the Debye length, \(\lambda_D\), and which is given as \([167]\),

\[
\lambda_D = \left(\frac{e_e T_e}{\varepsilon_0 n_0}\right)^{1/2}
\]

In the above equation \(\varepsilon_0\) is the constant of electric permittivity, \(T_e\) is represented the electronic temperature, \(e\) is related to the fundamental charge and where \(n_0\) represent to the density of the plasma under the equilibrium condition \((n_i = n_e = n_0)\). The Debye length is related to the length of the scale in which a substantial leaving from charge neutrality can be sustained \([24]\).

Sputtering is a physical phenomenon, in which the atoms are ejected from the source material called target by means of incident energy and transfer of momentum \([34]\). When the vacuum chamber is evacuated to an anticipated level, a sputtering gas is introduced in the chamber. Generally inert gas is frequently used in the deposition process. Mostly the argon gas is used for the sputtering process. The sputtering gas is usually in the Pa range. A suitable negative potential is applied to cathode (Target) and the anode (substrate) is coupled to the chamber walls and to the ground or itself at fixed potential. The electrons are ejected from the target surface and
accelerating through the potential difference having high kinetic energy. The ejected electrons are colliding with gas molecules and ionized the gas molecules. Then plasma is generated by means of electric discharge of an inert gas. Plasma contains of electrons, gas species, ions and neutral atoms.

Fig 2. 2 Schematics of the sputtering process

The positive ions from the plasma reach to the target surface due to the large negative potential of the target and the electric fields are generated between the target and anode (substrate) by the influence of large negative potential of the target. The positive ions hitting the target surface part of energy of the positive ions is transferred to heating and remaining part of energy is transferred to the other particles. These particles eventually get enough energy and leave the target surface and reach the substrate. Different types of the particles are emitted from the surface of targets, which include negative ions, photon, and neutral atoms and the secondary electrons and the sputtered species will reach onto substrate and start growth of the film. These secondary electrons further ionize the gas molecules and the positive ion interacted with target and so on.
Chapter #2  Experimental methods

For the maintained the plasma inside the chamber the high yield of secondary electrons are needed. Different ion-solid surface interaction arises by the impact of the ion interaction on the target surface. Based on the incident energy of the ions, the sputtering process is occurred into three regimes, the first regime is related to the low energy regime (< 1keV) called single knock on, second regime is named linear cascade (moderate energy regime, 1-50 keV) and the third regime called spike ((high energy regime, >50 keV).

The DC and RF sputtering are most commonly used sputtering techniques for the industry purposes. But RF sputtering is more useful sputtering technique over the DC sputtering, because of limitation of the DC sputtering technique. In the RF sputtering process, the potential of the target is changed continuously according to the voltage frequency. The electrons of the plasma travel to the electrode when target voltage is turn positive and argon ions accelerates towards the target surface when it turns negative. It indicates that, for each part of the cycle, the target acts as a cathode and anode. Due to the differences of masses of the electrons and the ions, electrons reach the surface of the target much faster than the ions, therefore the duration of the target as the anode is much shorter than the time when it is negative (the cathode)\(^\text{168}\). The negative self-bias (DC voltage) is developed at the surface of the target during the deposition process and the argon ions have accelerated the target and the extract the atoms from the surface of the target. Generally, 13.56 M Hz frequencies are used for the industrial purpose. The extracted atoms are settled on the substrate and build the film.

2.3.1 Decoration of graphene sheets with Metal and Metal oxide (Piezoelectric shaker).
In the present study, the radio frequency (13.56 MHz) sputtering was used to deposit the metal and metal oxide nanostructures onto the graphene sheets. The deposition chamber for the decoration of graphene with metal and metal oxide nanostructures is shown in schematic diagram in Fig 2.3. Our deposition chamber consists of vacuum gauges, wave generator (piezoelectric shakers), cathode rays oscilloscope, gas flow controller, power supply, substrate holder and target.

Fig 2. 3 A schematic of the RF sputtering system

Three different targets (TiO$_2$, Mg and Nb$_2$O$_5$) with diameters of 5 and 10 cm were used for the deposition. The high vacuum inside the deposition chamber was introduced by means of the rotary pump and turbo molecular pump. The flow of gas and deposition pressures was tuned by means of mas flow controller. A special setup was designed for the powder shaking during the
deposition process. The setup consists of special kind of prepared sample holder contained the graphene powder and piezoelectric shaker. In the present study, this piezoelectric shaker is playing an important role in our deposition process. The input signal (voltage) will transform to the piezoelectric shaker, and the piezoelectric shaker starts the vibrating motion with desired amplitude. Three parameters, vibration amplitude, frequency and input voltage can be changed for the piezoelectric shaker during the deposition process. The schematic diagram of the piezoelectric shaker is used during the deposition process is illustrated in Fig 2.4.

![Image of vibrating stage for the decoration of the sample](image.png)

**Fig 2.4 Vibrating stage for the decoration of the sample**

The wave generator was used to give the vibration to the piezoelectric shaker, the square waveform is generated into the shaker and this waveform can be tune according to their frequency, amplitude and shape. The oscilloscope is used for the measurement of the amplitude of the square shape waveform. The powder vibration frequency can play a significant role in the uniform decoration of metal and metal oxide nanostructures on the surface of graphene sheet compared to without powder vibration frequency. The metal and metal oxide nanostructures
Chapter #2 Experimental methods

were deposited onto moving graphene powder during the deposition process and the deposition process are described below.

2.3.2 Decoration of GNPs with Nb$_2$O$_5$ nanoparticle.

Nb$_2$O$_5$ nanoparticles were deposited onto graphite nanoplatelets by using RF sputtering (13.56 MHz) technique. A high purity (99.99%) and commercially available Nb$_2$O$_5$ with 10 cm diameter was used as sputtering target. Four different deposition process, RF power, process pressure, powder vibration frequency and deposition time parameters were varied for the deposition of Nb$_2$O$_5$ nanoparticles onto GNPs. The experimental detailed will be explained in their corresponding chapter.

2.3.3 The deposition of Mg nanoparticle onto graphene sheet.

Mg nanoparticles were deposited onto graphene by employing the RF sputtering (13.56 MHz) technique. Mg target which has high purity (99.99 with 5 cm diameter was used a sputtering target. Different amount of Mg nanoparticles were deposited by using three deposition process parameters variation. The base pressure was kept constant at 3 \times 10^{-5} \text{ Pa} foe each deposition and the deposition of Mg nanoparticles onto graphene sheet was carried out 6 \text{ Pa} process pressure with constant flow rate at 21 sccm.

2.3.4 Decoration of graphene powder with TiO$_2$ nanoparticles

The graphene powder was decorated with TiO$_2$ nanoparticles by using RF sputtering technique. TiO$_2$ target (99.99 % high purity) with 5 cm diameter (Good fellow) was used as a sputtering target. The different level of anatase nanoparticles were obtained by employing three deposition process parameters. The RF power, deposition time and powder vibration frequency parameters were used to deposit the TiO$_2$ nanoparticles.
2.5 Thin Films Characterizations
2.5.1 Structural Properties: X-Ray Diffraction:

X-ray diffraction (XRD) is a non-destructive and useful technique used to investigate the structural properties of the crystalline solid materials. The crystalline and semi-crystalline structures produce the diffraction patterns upon the interaction of the X-ray. Different features such as crystalline size, graphite basal planes; interplaner distance can be measured from the X-ray diffraction patterns of the crystalline materials.

Fig 2.5 Interaction of X-ray with crystalline materials according to the Bragg’s law

The mono or multiphase crystalline sutures can be identified from the diffraction patterns of the crystalline materials. It is well known that in the crystalline materials the arrangement of the atoms are in periodic order and the atoms are spaced by atomic distance $d$. The diffraction patterns will be occurred by the incident of X-ray on the crystalline material, if it is fulfill the condition of the following equation.

$$2d \sin \theta = n\lambda$$

$(2.1)$
The equation 2.1 is known Bragg equation, where \( d \) is the distance between the lattice planes, \( n \) is an integer, \( \lambda \) is wavelength and \( \theta \) is the incident glancing angle. The equation 2.1 exhibits that the diffraction pattern will be occurred from the planes of the crystalline material, if the path difference from the atomic planes is equals to the integral multiple of \( \lambda \). In this case the coherent diffraction peak will be appeared on the spectrum from the reflection of the atomic planes. However no diffraction peak will be appeared in the spectrum if the Bragg condition is not fulfilling. Generally two conventional configuration are used for the acquiring the X-ray diffraction patterns. One is called the Bragg-Brentano and other one is grazing angle configuration. For the Bulk material the Bragg-Brentano configuration is extensively used. But Bragg-Brentano geometry is not useful for the very thin film due to the poor signal and the existence of inquisitive effect of the substrate. However the grazing angle configuration is used for the very thin films without penetration depth of x-ray incidence. In present work the influence of the metal and metal oxide nanostructures on the structural properties of the graphene sheets were investigated using a Seeman–Bohlin (Bragg Brentano) X-ray diffractometer. The measurements were carried out by using CuK\( \alpha \) radiation (\( \lambda = 0.1541 \text{nm} \)) in steps of 0.02 operated at 40 kV and 30 mA. The effect of the Nb\(_2\)O\(_5\) concentration onto graphite nanoplatelets were studied by using XRD analysis and measured the average crystalline thickness of the GNPs, interlayer spacing of graphene, degree of graphitization from the diffraction peak of GNPs and in the last strain induced in the planes of the GNPs by the interaction of the sputtered and plasma species. The Williamson hall plot was used for the determination of the crystalline thickness of the graphite nanoplatelets. Additionally the crystalline size of the decorated graphene with Mg nanoparticles were calculated using the using the Scherrer’s formula. The silicon powder x-rays diffraction was use as standard for the instrumental broadening correction and the expression
B = \sqrt{B_F^2 - B_S^2} \text{ where } B_F \text{ and } B_S \text{ are the FWHM of the lines from the film and the standard, respectively.}

### 2.5.2 Raman Spectroscopy studies

Raman spectroscopy is a non-distractive and spectroscopic technique used to measure the inelastic scattering of the monochromatic light, usually from a laser source. The Raman spectroscopy is based on the inelastic scattering. The frequency of laser light is changed with the interaction of the sample. The schematized illustration of the Raman frequency shift is presented in Fig 2.6

---

**Fig 2.6** Energy level diagram for Raman scattering; Stokes and anti-Stokes Raman scattering
When the monochromatic light is interacted with molecule or crystal, mostly photon is scattered with same frequencies as the time of incident means that photon are the elastically scattered, this process is called Rayleigh scattering. However, small friction of monochromatic light (approximately 1 in $10^7$ photons) is scattered in-elastically and having different frequency than the incident photon, generally photon is shifted up or down in of the incident photon frequency. This phenomenon is called the Raman scattering and this Raman shift can change the vibrational, rotational or electronic energy states of the molecule. Then the Raman shift gives the information about the vibrational, rotational and other low vibration modes of the molecules. The Raman scattering phenomenon was discovered by Indian scientist named V. C. Raman in 1928. Raman spectroscopy is also used for the identification of the molecule and minerals.

In present study, Raman spectroscopy was used for the decorated graphene with M and MO nanostructures. It can be used to identify the disorderness and for measuring strain, electronic properties of multilayer graphene and single layer graphene. The Raman spectrum was taken at room temperature with a Labram Aramis micro spectrometer. To avoid the heating effect a low power at 10 mW was used to characterize the decorated graphene sheets with M and MO. The laser spot measured the area less than 2 $\mu$m$^2$ and the spectral resolution was better than 1 cm$^{-1}$.

2.5.3 X-Ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy is widely and useful surface analysis technique to evaluate the elemental composition and the chemical state of the material. The working principle of XPS is based on the photoelectric effect phenomenon. The electrons form the atomic shell is ejected by the interaction of the X-ray photon. The emitted electrons from sample are called photoelectrons.
Chapter #2  Experimental methods

The emissions of these photoelectrons escape from atomic orbital of the samples to the vacuum level. The kinetic energy of the emitted photoelectrons and binding energy core level with respect to Fermi level of the material can be measured by using the following expression.

\[ K.E = h\nu - B.E - \Phi_s \quad (2.4) \]

In the above equation the \( h\nu \) is the characteristic X-ray energy, B.E is the binding energy of the sample and \( \Phi_s \) is the represent the work function of the sample.

Fig 2. 7 Schematic of XPS and "Photoelectric Effect"

The XPS spectrum consists of the intensity plot as function of the irrespective of the binding energy value and the scheme is presented in Fig 2.7. Each element has a specific and characteristic binding energy peak. The electrons which are emitted from the shell originate XPS peaks. The attenuation length of the XPS probes is very small and emits only the photoelectron at the few layers of the samples. The electrons only emit and escape elastically from the top
layers of the sample. In addition to XPS core-level peaks, the XPS spectra consists Auger electron peaks.

X-ray photoelectron spectroscopy was used to determine the elemental composition and the component interaction of the prepared samples. X-ray photoelectron spectroscopy was carried with a Scienta ESCA 200 spectrometer with a monochromatic Al Kα x-ray source (1486.6eV). The XPS data were analyzed with the R Studio software. No special surface treatments were carried out for any of the samples. The spectra have been fitted with a Gaussian peak shape, after a Shirley-type background subtraction. The chemical composition and stoichiometry have been derived by applying Scienta sensitivity factors for the core levels.

3.5.4 Transmission Electron Microscopy

The transmission electron microscopy is widely used technique to investigate the structural, surface morphology and the crystallinity of the composite material. The average size of the particle and particles nature of the prepared or synthesized sample can be measured by employing transmission electron microscopy (TEM). A high resolution transmission electron microscopy can measure the sample having size in the range of 1 nm due to the shortening in de Broglie wavelength of the high energetic electron beam. This gives us useful information about to measure the crystalline or amorphous structures and also can be used to find the structural defects such as lattice expansion or dislocation within nanoparticles. Other information can be examined by employed the TEM analysis such as the atomic spacing distance, growth direction of the nanostructures material and the crystalline planes orientation. The schematic diagram of TEM components are presented in Fig 2.45. The working principle of the TEM is like this, the high energy electrons are accelerating by applying the high voltage up to 300 kV. The speed of accelerating electrons has nearly equal to the speed of light and these electrons behave like a
wave front having wavelength shorter than the light waves. The electron are scattered with interaction of the thin specimen of the material. The electromagnetic lenses are used to focus the electron beams to the sample. With interaction of the electron beam onto the sample the transmission takes place. The electrons beam is further focused to the objective lens into the image which is then passed through the intermediate and projector lenses, and then projected on the fluorescent screen.

Fig 2. 8 Schematic diagram for TEM analysis [169]
Chapter #3

The influence of Nb\textsubscript{2}O\textsubscript{5} deposited by RF sputtering on the structural chemical and electronic properties of graphite nanoplatelets

3.1 Introduction:

The aim of this chapter is to reconnoiter an approach to decorate graphite nanoplatelets with layers of Nb\textsubscript{2}O\textsubscript{5} using deposition process parameters. For this intention, different deposition process parameters (RF power, process pressure and powder vibration frequency were varied to decorate graphite nanoplatelets with layers of Nb\textsubscript{2}O\textsubscript{5} film in Ar plasma. Based on the variation of deposition parameters used, this chapter is divided into four sections.

In the 1\textsuperscript{st} section, we will present the results of the decoration of graphite nanoplatelets with Nb\textsubscript{2}O\textsubscript{5} layers by varying the RF power and discuss the chemical, structural, morphological and electronic properties of the interface between the graphene sheets and Nb\textsubscript{2}O\textsubscript{5} layers.

In the 2\textsuperscript{nd} section, the influence of Nb\textsubscript{2}O\textsubscript{5} concentration on the structural and chemical properties of graphite nanoplatelets studied by varying the process pressure will be discussed.

In the 3\textsuperscript{rd} section, the effect of Nb\textsubscript{2}O\textsubscript{5} concentration on the structural and chemical properties of graphite nanoplatelets studied by varying powder vibration frequency will be presented.

In the last section, the decoration of graphite nanoplatelets with Nb\textsubscript{2}O\textsubscript{5} layers by varying the deposition time will be described.

3.2 Experimental details:

Nb\textsubscript{2}O\textsubscript{5} thin films were deposited on fine graphite nanoplatelets (GNPs) powder with specific surface area-80 m\textsuperscript{2}/g, purity 99.2% and average flake thickness 12 nm (30-50 monolayer graphene) by Radio frequency (13.5 MHz) sputtering. The graphite nanoplatelets powder was provided by Graphene Supermarket. A commercially available high purity Nb\textsubscript{2}O\textsubscript{5} disc (99.99%)
with 10 cm diameter was used as a sputtering target. Typically a base pressure of about $2 \times 10^{-5}$ Pa was established before each deposition. The distance was fixed 50 mm between the target and substrate. For the uniform distribution of the Nb$_2$O$_5$ nanostructures onto graphene surface a powder vibration system was developed. The sputtered particles were deposited on the vibrating powder; the powder vibration frequency is an important parameter and plays a vital role for uniform decoration. More specific details are given below:

- For the results presented in section I, in order to obtain different amounts of Nb$_2$O$_5$ on the GNPS surface, the power applied to the Nb$_2$O$_5$ target was varied from 40 W to 100 W. The total pressure and powder vibration frequency were fixed at 10 Hz (with amplitude of 32 µm) and 6 Pa respectively. The deposition time was fixed at 15 min.

- For the results reported in section II, the GNPs powders were decorated with Nb$_2$O$_5$ layers deposited with a range of process pressure of (2 Pa - 8 Pa). The self-bias voltage and power applied to the target was fixed at -72 V and 40 W respectively. The powder vibration frequency and deposition time were kept constant at 10 Hz and 15 min respectively.

- For the results described in section III. We decorated the GNPs with Nb$_2$O$_5$ layers deposited with powder vibration frequencies $0 \leq \omega \leq 100$ Hz with vibrating amplitude of 32 µm. The process pressure and power applied to Nb$_2$O$_5$ target were fixed at 40 W and 6 Pa respectively. The deposition time for each sample was kept as 15 min.

- For the results presented in section IV, in order to obtain different amounts of Nb$_2$O$_5$ contents on the surface GNPs powder, the GNPs powder was decorated with Nb$_2$O$_5$ layers deposited by stepping up the deposition time from (10 to 45 min) at a constant power. The powder vibration frequency and power applied to Nb$_2$O$_5$ target were kept
constant at 10 Hz and 40 W respectively. The decoration of GNPs powder with Nb₂O₅ layers was performed at 6 Pa process pressure in Ar plasma.

### 3.3 The influence of Nb₂O₅ concentration on the properties of graphite nanoplatelets deposited by varying the RF power

Different Nb₂O₅ concentrations on the surface of the GNPs were obtained by varying the power applied to Nb₂O₅ target. In this section the interaction of high energy sputtered particles with GNPs will be discussed. These energetic plasma species and sputtered particles generated defects in the structure of GNPs. The structural defects and disorderness were characterized by using the Raman spectroscopy and X-ray diffraction (XRD) techniques. The surface morphology of the decorated Nb₂O₅ layers was investigated by Transmission Electron Microscope (TEM). The chemical state and composition of the deposited Nb₂O₅ layers were evaluated by using X-ray photoelectron spectroscopy (XPS). Furthermore the detail process parameters are presented in table 3.1.

#### Table 3.1 the process condition of decorated GNPs with Nb₂O₅ films

<table>
<thead>
<tr>
<th>Sample #</th>
<th>RF Power (W)</th>
<th>Process pressure (Pa)</th>
<th>Deposition Time (min)</th>
<th>Powder vibration frequency (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40</td>
<td>6</td>
<td>15</td>
<td>10</td>
</tr>
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<td>60</td>
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<td>15</td>
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<td>10</td>
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<tr>
<td>4</td>
<td>100</td>
<td>6</td>
<td>15</td>
<td>10</td>
</tr>
</tbody>
</table>

#### 3.3.1 XPS analysis of pristine GNPs and Nb₂O₅ decorated GNPs at different RF powers

The C 1s and Nb 3d core-level spectra shown in Fig 3.1 were used for the chemical analysis of the GNPs before and after the decoration by Nb₂O₅ at different RF power values. The C 1s spectrum de-convoluted by using Gaussian peak was performed after performing a Shirley
background correction. The C 1s signal of GNP s is shown in Fig 3.1 (a) the de-convolution of the C 1s spectra yields three peaks. In addition to the strong peak at 284.69 eV attributed to the graphitic carbon \(^{[170, 171]}\), a peak around 285.40 eV corresponds to defect structure arising from C-H related \(sp^3\) hybridized structure or hydrocarbon contamination \(^{[172, 173, 174]}\), and a peak around 286.3 eV related to C-O bonding, probably from adsorbed impurities is also observed \(^{[175]}\). Interestingly the C 1s binding energy for Nb\(_2\)O\(_5\) decorated GNP s is shifted toward lower values relatively to that of pristine GNP s as shown in Fig 3.1(a).

![XPS spectra](image)

Fig 3.1 XPS spectra of GNP s with incrementally increased of Nb\(_2\)O\(_5\) contents through RF power variation (a) (a) Shift in the C 1s core levels position upon Nb\(_2\)O\(_5\) deposition (b) Nb 3d core level spectra with positions of the Nb\(^{5+}\) peaks. [Process pressure = 6 Pa, Time=15 min, Frequency = 10 Hz]

The downshift in the C 1s core level could be due to the interface charge transfer between the of the graphene sheets and metal oxide nanostructures, even there is no chemical bonding between the graphene sheets and metal oxide nanostructure, in this scenario charges are expected to be
transferred between the interface of the graphene sheets and metal oxide nanostructures in order to align the Fermi levels. In XPS measurement, Fermi level is the reference energy level for core level binding energy. Consequently a shift in the Fermi level is the origin of an equal shift in the C 1s core level binding energy.

The shift of the C 1s core level of Nb$_2$O$_5$ decorated GNPs relative to the C 1s core level in GNPs is understood as an equivalent shift of the Fermi level of GNPs. It can be seen that C 1s peak position shifts gradually toward the lower binding energies after deposition of Nb$_2$O$_5$ layers with the increasing RF power values. The maximum down shift was observed in the C 1s peak of 0.33 eV after the decoration of Nb$_2$O$_5$ onto GNPS at 100 W. Subsequently the shifts of C 1s peak suggest that Fermi level shift downward due to p type doping of GNPs due to charge transfer from GNPs to Nb$_2$O$_5$ layers. Charge transfer can be explained by the work function difference between the Nb$_2$O$_5$ and GNPs. Because Nb$_2$O$_5$ has a much higher electron affinity (3.90 eV) and work function (4.70 eV) than GNPs (1.26 eV and 4.33 eV) [176, 177], electrons are expected to transfer from GNPs to the Nb$_2$O$_5$. Similar phenomenon has been reported in a previous work concerning the deposition of MoO$_3$-x on graphene surface [100, 101].

Figure 3.1 (b) shows the Nb 3d XPS spectra with Nb$_2$O$_5$ layer deposited on GNPs at different RF power values. The binding energy values for Nb 3d at 208.1 eV and 210.12 eV correspond to Nb 3d$_{5/2}$ and Nb 3d$_{3/2}$ peak of Nb$^{+5}$ [178]. XPS analysis confirmed that only one chemical state has been observed for the Nb. In addition, we observed a shift of 0.36 eV in the Nb$^{+5}$ 3d$_{5/2}$ states toward lower binding energies values with increasing Nb$_2$O$_5$ contents through RF power variation from 40 W to 100 W. It is another indication that the electrons transfer from the GNPs to the metal oxide i.e. a p-type doping of GNPs. It suggest that by increasing Nb$_2$O$_5$ layer thickness with rising RF power values the valance band edge of the metal oxide moves 0.36 eV.
closer to the Fermi level which can be attributed to band bending. A similar phenomenon has been explained by Meyer, J. et al [100].

Fig 3.2 (a) presents the O 1s spectrum of the decorated GNPs with Nb$_2$O$_5$ films at 100 RF power value in Ar plasma. The O 1s spectrum were de-convoluted into three components due the presence of the asymmetric components towards the higher binding energy (BE) with respect to main component (O I), which suggest that oxygen exist in different chemical state. The peak is de-convoluted into three peaks: the first and main peak at lower B.E (530.84 eV) indicated as OI can be attributed to the O 1s core peak of O$^2$ bound to Nb$^{+5}$ [179], whereas a second component (OII) located at 531.82 eV, may arise due to the oxygen contribution in possible C=O or C-O-C [180]. A 3rd component (O III) at higher BE of 533.62 eV is from C-O bonding in O-C=O [181].

Fig 3.2 (a) O 1s core peak and its de-convolution  (b) variations of Nb/C and OI/Nb atomic ratio with RF power

The OI/Nb ratios were measured for the all samples on the basis of the area under the main component of the oxygen (OI) and the area under the Nb 3d$_{5/2}$ component. The calculated values of the OI/Nb are presented in Fig 3.2 (b). It was found that the OI/Nb ratio decreased from 2.48 to 2.26, when the Nb$_2$O$_5$ were deposited onto GNPs in a ratio of 1.37 at. %. The Nb/C sp$^2$
increases steadily with the rising RF power values the results are presented in Fig 3.3 (b). This suggests that with rising RF power values the sputtered particles energy increased and reached at the surface of the GNPs with high kinetic energy. These high energy sputtered particles generated the oxygen vacancies in the lattice of Nb$_2$O$_5$ structure during the deposition process. The oxygen vacancy formation mechanism can be explained as follows, as already discussed in the above text, with increasing RF power values the sputtered particles and plasma species gain more kinetic energy during the deposition process. These energetic sputtered particles may direct remove the oxygen from the lattice of the Nb$_2$O$_5$ or might be due to the high collision of the sputtered particles with the high energetic plasma species induced the oxygen vacancy in the lattice of Nb$_2$O$_5$ during the deposition process.

### 3.3.2 XRD analysis of pristine GNPs and Nb$_2$O$_5$ decorated GNPs at different RF power values

The XRD patterns of the pristine GNPs and Nb$_2$O$_5$ decorated GNPs at different RF power values (40 to 100 Watt) are shown in Fig 3.3 (a). The peak positions in XRD patterns at 26.44°, 42.41°, 44.53°, 54.62°, 77.63° and 83.43° are assigned to reflections of the planes (002), (100/101), (004), (110) and (112) respectively [182]. The strongest intensity of the (002) diffraction peak indicates a preferred oriented hexagonal graphitic polycrystalline structure [183]. There is no extra peak observed in the XRD spectra related to Nb$_2$O$_5$ impurities due to low concentration or more likely to an amorphous state due to the low temperature growth. The enlarged view of peak (002) inset as shown in Fig 3.4 (a) shows that by the deposition of the low amount of Nb$_2$O$_5$ onto the GNPs produced notable change in the structure of GNPs. In the XRD patterns for the low Nb$_2$O$_5$ content sample (Nb/C $sp^2$=0.48 at. %) obtained with a 40 W power the peaks slightly broadened indicating a deterioration of the crystallinity of the GNPs. Higher contents Nb/C $sp^2$ = 1.37 at.
% obtained at 100 W produced a further increase of the FWHM and an intensity reduction of the peaks. We observed a shift in the position of the (002) peak toward lower angle values with increasing contents of Nb$_2$O$_{5-x}$ in GNPs through rising RF power as shown in Fig. 3.3 (b). It shows that the interlayer d spacing between the layers of graphene is increased.

The interplaner spacing d values of un-decorated GNPs and Nb$_2$O$_5$ decorated GNPs powders were calculated for the (002) plane using Bragg’s relation.

\[ d_{002} = \frac{\lambda}{2\sin \theta} \]  

Where \( \lambda \) is the wavelength of X-ray radiation (equal to 0.1541 nm) and \( \theta \) is the diffraction angle.

The calculated d spacing evaluation with the increasing Nb/C sp$^2$ is shown in Fig 3.6.

The increasing d spacing of GNPs for samples with Nb/C sp$^2$ indicates that Nb$_2$O$_{5-x}$ molecules induced stress in the layers of GNPs [184]. This caused the lattice distortion and expansion.
According to the hexagonal symmetry the lattice constants can be evaluated using the following equation,

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2)$$

Where a and c are the lattice parameters h, k and l are the Miller indices of the plane and $d_{hkl}$ is the inter-planar spacing. The lattice parameters “a” and “c” of undoped GNPs and Nb$_2$O$_5$ doped GNPs were calculated from the reflection of the planes (100) and (002) using equation (2). Fig.3.4 shows the evolution of the lattice parameters (“a” and “c”) of the GNPs when changing the Nb/C (sp$^2$) through increasing the RF power. A small Nb$_2$O$_{5-x}$ amount of introduction changed the “c” and “a” parameters. “The maximum elongation along ‘c’ axis is about 0.071 Å from 6.734 Å (for 0 % Nb) to 6.797 Å (for Nb/C of 1.37 at. %).
More likely reason for the expansion along the c axis is that, by the deposition of Nb$_2$O$_5$ onto graphene sheet with increasing RF power values the sputtered particles interacted with GNPs sheets more energetically and generates the stress in the layers of GNPs. With interaction of the sputtered particles and plasma species the planes of the GNPs are distorted, which might be cause e caused the expansion of the lattice of the GNPs or it might be due to the large difference between ionic radii of the Nb (0.70 Å) compared to the spacing between the layers of graphene (3.35 Å), which Nb intercalated randomly in the first two layers of GNPs.

Generally XRD is the bulk analysis technique; it gives the information about whole GNPs structure. The low expansions along “c” axis of GNPs after the deposition of the Nb$_2$O$_{5-x}$ onto GNPs sheets might be due to the intercalation of Nb in the first two layers of GNPs. Consequently it can be considered that Nb atoms are randomly intercalated in the first two layers of GNPs, which might be cause the expansion along the c axis. Moreover Nb$_2$O$_{5-x}$ deposition onto GNPs had also an observable influenced on the lattice parameter ‘a’. The lattice parameter ‘a’ is also expanded with increasing of Nb/C atomic ratio (%) (sp$^2$).

Microstrain (\(\varepsilon\)) and crystalline size \(L_c\) (the crystalline coherence length in the 002 direction) of un-decorated GNPs and Nb$_2$O$_5$ decorated GNPs were calculated using Williamson Hall equation \(^{185}\).

\[
\beta_{hkl} \cos \theta = \frac{K \lambda}{L_c} + 4 \varepsilon \sin \theta \ldots \ldots \ldots \ldots \ldots (4)
\]

Where \(\beta_{hkl}\) is represented the FWHM (the full width at half-maximum) of the 002 peak of the GNPs, \(\theta\) is the Bragg angle and \(L_c\) is the average crystallite size of GNPs, \(K\) is approximately equal to 0.9 \(^{186}\). Here the peak widening (\(\beta_{hkl}\)) is considered to be induce by both the strain and the crystallite size.
Using this equation a plot of $\beta \cos \theta$ in a function of $4 \sin \theta$ was applied to the peaks (002), (004) and (112). The crystallite size was extracted from y-intercept and microstrain from the slope of linear fit. Fig 3.5 shows that the crystallite size linearly decreased with the increase of Nb/C (Sp$^2$). The crystalline size $L_C$ of pristine GNPs before decoration by Nb$_2$O$_5$ was (12.9±0.32) nm and the basal planes of graphene were stacking in order. The decrease of the crystalline size of GNPs after the decoration for Nb$_2$O$_5$ might be due to the basal plane bending or dislocations. Similar result was also reported in previous work by Zhang, B. et al [187]. The possible explanation for this is that the sputtered particles interact with GNPs, reduce the orientation and stacking order of the basal planes along c axis. From this, it is concluded that the crystalline size $L_C$ of GNPs decreases due to the deprivation of ordered of basal planes or less graphitization part due the higher Nb$_2$O$_5$ contents on the GNPs. Similar result is also reported by Anjana Asthana using the neutron irradiation on highly oriented pyrolytic graphite [188].

Fig 3.5 Crystallite size and strain of undoped GNPs with Nb$_2$O$_5$ doped GNPs in function of Nb/C atomic ratio as obtained by varying the RF power during the deposition [Process pressure = 6 Pa, Time=15 min, Frequency = 10 Hz RF power value (40 W to 100 W).]
Chapter #3 The influence of Nb₂O₅ concentration on the structural chemical and electronic properties of GNPs

The shifts in the 2θ values for GNPs corresponding to the (002) peak are well reflected in the variation of the residual strain with Nb/C (Sp²) as shown in Fig 3.5. This can be correlated with the variation of the cell volume of the undoped GNPs and Nb₂O₅ doped GNPs as shown in Fig 3.4. It is observed that the strain in Nb₂O₅-doped samples was higher than that of undoped GNPs. Also the strain increased as the dopant amount increased.

The graphitization index is used to describe quantitatively the degree of similarity between a carbon material and a perfect single crystal of graphite. The higher graphitization index indicates a more ordered graphitic structure.

![Graph of d spacing and graphitization index vs Nb/C atomic ratio]

Fig 3.6 Degree of graphitization and d spacing of undoped GNPs with Nb₂O₅ doped GNPs through RF power values variation [Process pressure = 6 Pa, Time=15 min, Frequency = 10 Hz RF power value (40 W to 100 W)].

The graphitization index derived from the average interplaner spacing between two successive graphite layers according to the equation [189].

\[
G_{\text{XRD}} = \frac{3.440 - d_{002}}{3.440 - 3.354} \quad \text{...(3)}
\]
The interplaner spacing ($d_{002}$) of undoped GNPs and Nb$_2$O$_5$ doped GNPs calculated from equation (1), where 3.440 is interplanar spacing in carbon with a turbostratic structure, and 3.354 interplanar spacing in a defect-free single crystal of graphite.

Graphitization indices ($G_{xrd}$) and d spacing of the GNPs and decorated GNPs with Nb$_2$O$_5$ by varying RF powers are shown in Fig 3.6. The interlayer spacing $d_{002}$ gradually increased with rising Nb/C ($sp^2$). The graphitization index ($G_{xrd}$) of GNPs before the Nb$_2$O$_5$ decoration was 0.85, which suggest that the stacking layers of the GNPs were well ordered. However, after decoration with Nb$_2$O$_5$ the degree of graphitization of GNPs decreased with increasing Nb/C ($sp^2$). It shows that with increasing of Nb/C ($sp^2$) through RF power variation, the large amount defects were induced onto GNPs, due to induced defects the basal plane of the GNPs loss their initial ordering, decreasing the degree of graphitization. This shows that high Nb/C ($sp^2$) atomic ratio values transformed the ordered GNPs structure to disordered GNPs structure.

3.3.3 TEM analysis of undoped and Nb$_2$O$_5$ doped GNP at 100 W RF power value

The surface morphology of the undoped GNPs and Nb$_2$O$_5$ deposited onto GNPs surface were examined using Transmission electron microscopy (TEM) to determine average size of the Nb$_2$O$_5$ layer on the GNPs. TEM images in Fig.3.7 (A–B, C-D) show the undoped and Nb$_2$O$_5$ deposited at 100 W onto GNPs surface. Fig 3.7 (C, D) depicts a GNPs surface decorated with uniform layers of the Nb$_2$O$_5$ nanoparticles. Around 5 to 10 nm homogeneously distributed nanoparticles were successfully deposited onto GNPs surface and these nanoparticles make aggregates on the surface of GNPs. High coverage of the Nb$_2$O$_5$ layers was obtained onto GNPs by using high deposition rate. As discussed in above text, with increasing the power values the deposition rate increased and more sputtered particles are deposited onto GNPs. The sputtered particles were agglomerated onto GNPs with increasing RF power values. However, a certain
amount of agglomeration of Nb$_2$O$_5$ was observed. A highly dispersed Nb$_2$O$_5$ layer on the GNPs surface with large surface area is favorable to promote their interfacial contact. A uniform decoration of the Nb$_2$O$_5$ layer on the GNPs surface has potential advantage in catalytic activity and other application.

![Fig 3. 7 TEM images (A-B) undoped GNPs and (C-D) Nb$_2$O$_5$ doped GNPs at 100 W](image)

### 3.3.4 Raman study of undoped GNPs and Nb$_2$O$_5$ doped GNPs

The Raman spectra of Nb$_2$O$_5$ deposited at different RF powers shown in Fig. 3.8 (a) consist of four peaks. The so called D, G, D’ and 2D peaks appear around 1330 cm$^{-1}$, 1580 cm$^{-1}$, 1610 cm$^{-1}$ and 2675 cm$^{-1}$ respectively. The G peak corresponds to the E$_{2g}$ phonon at the Brillion zone
The G-band is highly sensitive to strain effects in sp\(^2\) systems. The D band is a sign of either the existence of the disorder or the presence of any type of defects such as vacancy defects and the edges of the crystallite (i.e., the boundaries of the crystallite)\(^{190,191}\). The 2D peak is originates in the process of the double resonance in which momentum conservation is accomplished by two phonon which are opposite wave vectors. Generally, 2D peak is always present in Raman spectra and it’s required no defects to be originated. 2D peak is very sensitive to the electronic structure and the stacking order along the c-axis\(^{192}\). The Raman spectra of undoped GNPs and Nb\(_2\)O\(_5\) doped GNPs at different RF power values are shown in Fig 3.8 (a).

The G and 2D peaks of Nb\(_2\)O\(_5\) doped GNPs shifted to lower frequencies compared to undoped GNPs. The shift in G and 2D modes towards lower wavenumbers increased with rising of Nb/C sp\(^2\) through RF power variation as shown in Fig 3.8 (b). The highest red shift is 10.8 cm\(^{-1}\) and 24.68 cm\(^{-1}\) for G and 2D peaks, respectively. There are several possible reasons reported in the literature for the shift of Raman peaks, including the effects of doping\(^{193}\) and strain\(^{194}\). The electron/hole doping in GNPs can affect the transition across the band gap with the interactions of optical phonons\(^{195}\). Hence the G band shows softening as well as bandwidth sharpening with doping\(^{196}\). G and 2D bands shift caused by charge doping through phonon-electron coupling in GNPs were reported by Kim et al\(^{197}\).

In case of a charge doping the shift in G band should be greater than the shift in 2D band\(^{198}\). Therefore, the red shift of G and 2D peaks observed in our case cannot be explained by charge doping and there should be other mechanisms. Tensile stress is reported to cause the red shift in graphene sheets\(^{199}\). The tensile strain lowering the vibration frequency of the phonon of GNPs due to the elongation of the elongation of C-C bonds\(^{200}\). More importantly lattice of the GNPs were distorted by the deposition of Nb\(_2\)O\(_5\)-x. Consequently by the deposition Nb\(_2\)O\(_5\)-x layers onto
GNPs the lattice constants of GNPs were enlarged, which lead to tensile strain in GNPs layers, which is in good agreement with the XRD results.

Fig 3.8 (a) Raman spectra of undoped GNPs and (b) positions of the G and 2D peaks vs Nb/C (sp2) at.ratio Nb2O5 doped GNPs at different RF powers

It is well established that the \( I_D/I_G \) peak ratio is used to measure the level of disorder, which is directly related to the diameter of the crystalline cluster (La) in the graphite system. For low disorder \( I_D/I_G \) ratio is known to be proportional to \( 1/L_a \) and to \( L_a^2 \) for high disorder. Ferrari and Robertson introduced a three-stage model of disorder in carbon materials, which allows to simply evaluating the disorder in carbon \(^{201}\). The first stage leads to nanocrystalline graphite (nc-G phase) from crystalline graphite. The second stage is related to the transformation of the nanocrystalline graphite into low sp\(^3\) amorphous carbon (a-C phase), and third stage is lead to low sp\(^3\) amorphous carbon (a-C phase) to high sp\(^3\) (tetrahedral) amorphous carbon. In the following, we refer to these three stages to quantify the impact of deposition of Nb\(_2\)O\(_5\) on the structural quality of GNPs.
The first stage of disorder graphene sheets Raman spectrum can be explained as follow \([^{124,136}]\). \(I_D/I_G\) increases and D band appears b) all peaks broaden. In the case of graphite, the D and 2D peaks lose their doublet structure \([^{202,203}]\). However in the second stage of disorder graphene sheets can be evolved as follows \(^{204}\) a) the G peak position decreases b) Tuinstra and Koenig relation fails and \(I_D/I_G\) decreases. Tuinstra and Koenig relation is used for the measurement of in plane crystallite size \(/(1/L_a)\) from the \(I_D/I_G\) ratio \([^{205}]\).

Fig.3.9 plots the ratio of the integrated area of the D and G peak for GNPs as function of Nb/C (sp\(^2\)) obtained by the RF power. The intensity ratio of D band to G band \((I_D/I_G)\) can serve as a convenient measurement of the amount of defects in graphitic materials \([^{206}]\). It is noticeable that \(I_D/I_G\) ratio gradually decreased with increasing Nb/C (Sp\(^3\)) atomic ratio (%). This corresponds to the second stage at which \(I_D/I_G\) ratio decreases as a function of increasing defects, which can be ascribed to a steady evolution from the sp\(^2\) -bonded carbon found in graphene sheets into amorphous carbon with low sp\(^3\) bonding \([^{207,208}]\). It can be explained as follows; with an increasing number of defects on the surface of GNPs through sputtered particles and plasma species interaction, hexagons in the honeycomb lattices are more distorted. More importantly with the interaction with the sputtered particles the I\(_D\) peak begins to attenuate with respect to I\(_G\) as a function of increasing defects and disorderness. Thus, with the loss of sp\(^2\) rings, I\(_D\) will decrease and the \(I_D/I_G \propto 1/L_a\) relation will no longer hold \([^{208}]\).

It means that the decrease of \(I_D/I_G\) is due to the main disordering related to the decrease in the number of sp\(^2\) ordered rings \([^{136}]\). Furthermore we can exclude the possibility of high sp\(^3\) bonding formation because in our case \(I_D/I_G\) does not go to zero and remain in the range 0.31 to 0.18 even for the highest RF power values. Also the FWHM of the G peak is found to be in the range
between ~ 24.1 cm\(^{-1}\) and 18.4 cm\(^{-1}\), whereas the amorphous carbon with high sp\(^3\) content would give a FWHM of 200-300 cm\(^{-1}\)[209, 210].

<table>
<thead>
<tr>
<th>Nb/C atomic (%)</th>
<th>FWHM (G)</th>
<th>(I_D/I_G)</th>
<th>(I_{2D}/I_G)</th>
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<tbody>
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<td>0.3</td>
<td>21.6</td>
<td>0.325</td>
<td>0.300</td>
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<td>0.6</td>
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<td>0.300</td>
<td>0.275</td>
</tr>
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<td>18.0</td>
<td>0.275</td>
<td>0.24</td>
</tr>
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<td>1.2</td>
<td>16.2</td>
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<td>1.5</td>
<td>14.4</td>
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<td>0.18</td>
</tr>
</tbody>
</table>

Fig. 3.9 Variation of Raman peak intensity ratios of \(I_D/I_G\), \(I_{2D}/I_G\) and FWHM of the G peak plotted against the Nb to C atomic ratio (%).

Fig. 3.9 shows the changes of \(I_{2D}/I_G\) with the increase of Nb/C (sp\(^2\)). As can be seen, \(I_{2D}/I_G\) decreased almost linearly with the increasing of Nb/C (sp\(^2\)). In GNPs, the ratio \(I_{2D}/I_G\) decreases strongly with increasing doping level due to the additional electron-electron scattering contribution [211]. The intensity of 2D peak is strongly affected by the electron/hole and electron defects scattering rate. The defects generated into the lattice of GNPs with deposition of Nb\(_2\)O\(_5\)-x may increase the electron scattering rate and hence the intensity of 2D peak may decrease with the increase of defect/dopant concentration. Therefore, the \(I_{2D}/I_G\) decreases with increasing doping by Nb\(_2\)O\(_5\) contents, i.e. defect density. Recent theoretical calculation predicted that...
resonant scattering of electrons with short-range defects in GNPs dramatically increase the scattering cross section $^{[212]}$. Such resonant scattering of electrons may arise in GNPs with high Nb$_2$O$_5$ doping, where the short-range defects are induced in GNPs by Nb$_2$O$_5$ doping.

The structural disorderness in disorder carbon can be measured by evaluating the FWHM of the G peak and the topological disorder can be measured by evaluating the shift in the position of the G peak $^{[213]}$. More over the structural disorderness in graphene structure arises from the distortion of C-C bond length and bond angle. Topological disorder arises from the size and shape distribution of sp$^2$ clusters. FWHM (G) of the undoped GNPs and Nb$_2$O$_5$ doped GNPs as a function of Nb/C sp$^2$, are shown in Fig 3.9. It is found that FWHM (G) decreased from 23.63 cm$^{-1}$ and reached 19 cm$^{-1}$, when the Nb$_2$O$_5$ were deposited onto GNPs in a ratio Nb/ C sp$^2$=1.37 atomic ratio (%). Meng et al is also reported that FWHM of GNPs decreased with charge doping$^{[184]}$. This indicates that with deposition of Nb$_2$O$_5$ onto GNPs not only induced tensile strain in the plane of GNPs but also shows the doping behavior with deposition of the Nb$_2$O$_5$ layers.

**3.4 The influence of Nb$_2$O$_5$ concentration on the structural and chemical properties of graphite Nanoplatelets deposited by varying the process pressure**

In the section 3.3, the Nb$_2$O$_5$ were deposited onto GNPs surface by varying the RF power values and the deposition of Nb$_2$O$_5$ were carried at a constant process pressure value (6 Pa). It was found that defects were generated in the GNPs structure by the interaction of the high energy sputtered particles and plasma species. The process pressure one of the important deposition process parameter was used to deposit the Nb$_2$O$_5$ onto GNPs. The main goal of this section is to study the effect of the Nb$_2$O$_5$ concentration obtained on the surface of the GNPs by the variations of the process pressure. It is well established that the sputtered particles that are extracted from
the target adopt straight route during the deposition or either they are scattered in the plasma by single or multiple collisions with gas particles. In this perspective Nb$_2$O$_5$ were deposited onto GNPs surface at range of process pressures values from 2 Pa to 8 Pa. It was found that at low process pressure more defects and disorderness are induced in the structure of the GNPs compared to high process pressure. The defects and disorderness of decorated GNPs with Nb$_2$O$_5$ were characterized by Raman, XRD and XPS. Moreover the process parameters are described in table 3.2

Table 3.2 the process condition of decorated GNPs with Nb$_2$O$_5$ films

<table>
<thead>
<tr>
<th>Sample #</th>
<th>RF Power (W)</th>
<th>Process pressure (Pa)</th>
<th>Deposition Time (min)</th>
<th>Powder vibration frequency (Hz)</th>
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<td>2</td>
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<td>10</td>
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</tr>
<tr>
<td>6</td>
<td>40</td>
<td>8</td>
<td>15</td>
<td>10</td>
</tr>
</tbody>
</table>

3.4.1 XPS analysis of undoped GNPs and Nb$_2$O$_5$ doped GNPs at different process pressure values

Fig. 3.10 presents the XPS spectra of GNPs before and after deposition of Nb$_2$O$_5$ at different plasma process pressure values. The main peak with a binding energy 284.69 eV is attributed to carbon in C-C bond with sp$^2$ hybridization. Two other small components which have binding energies of 285.34 eV and 286.20 eV correspond to C-H /C-C bond with sp$^3$ hybridization and C-O bond respectively. A shift toward the lower binding energy in the C 1s core level was
observed after the deposition of Nb$_2$O$_5$ onto GNPs at different process pressure values. The downshift of the C 1s core level increased with deposition of the Nb$_2$O$_5$ onto GNPs at low process pressure.

![XPS spectra of GNPs with incrementally increased Nb$_2$O$_5$ contents through process pressures variation](image)

**Fig 3.** 10 XPS spectra of GNPs with incrementally increased of Nb$_2$O$_5$ contents through process pressures variation (a) Shift in the C 1s core levels position upon Nb$_2$O$_5$ deposition (b) Nb 3d core level spectra with positions of the Nb$^{+5}$ peaks. [Process pressure = 6 Pa, Time=15 min, Frequency = 10 Hz].

The downshifts in the C 1s core level were further increased with increasing of Nb$_2$O$_5$ concentration onto GNPs surface with variation of the process pressures values. The C 1s core level were further shifted to lower binding energy by 0.23 eV with respect to the undoped GNPs, when the Nb$_2$O$_5$ were deposited onto GNPs at 4 Pa process pressure in a ratio Nb/C sp$^2$=0.53 at. %. The downshift of the C 1s core level after the deposition of the Nb$_2$O$_5$ layers onto GNPs is the indication of the p-type doping of graphene, where the electrons are transferred from the GNPs to Nb$_2$O$_5$ layers at interface. The maximum downshift of the C 1s core level after the deposition
of Nb$_2$O$_5$ layers onto GNPs at 4 Pa could be in agreement with increasing structural disorderness due to the disruption in the sp$^2$ carbon framework upon the deposition of Nb$_2$O$_5$. The similar phenomenon has been explained by the C. Coletti$^{22}$. They described that the structural defects and disorderness is also shift the Fermi level from its position.

Figure 3.11 (b) shows the Nb 3d XPS core level for Nb$_2$O$_5$ layer deposited on GNPs at different process pressure values. The binding energy of the Nb 3d$_{5/2}$ and 3d$_{3/2}$ were 207.89 and 210.72 eV respectively, which corresponds to the Nb$^{5+}$ state. Nb 3d peaks were shifted to the lower binding energies values by the deposition of the Nb$_2$O$_5$ onto GNPs at different process pressure values. The maximum downshift of 0.26 eV was observed in the Nb 3d core level with deposition of Nb$_2$O$_5$ onto GNPs at 4 Pa. The downshift of the Nb 3d core level suggests that the charge is transferred from graphene to the Nb$_2$O$_5$ layer due to the difference of the work function. The band of the Nb$_2$O$_5$ bends towards the interface after the charge accumulation in the band of Nb$_2$O$_5$.

Fig 3.11 (a) shows the O 1s peak deposited at 4 Pa process pressure. After the deposition of the Nb$_2$O$_5$ the O 1s spectra has been de-convoluted into three components. The component OI which has a BE of 530.973 eV is assigned to oxygen bonded with Nb (O-Nb). A second component OII having a BE energy of 532.18 eV, may arise due to the oxygen contribution in possible C=0 bond$^{[180]}$. The 3rd component (O III) at higher BE 533.62 eV is from C-O bond$^{[181]}$.

Furthermore, the oxide stoichiometry of deposited Nb$_2$O$_5$ on GNPs surface and atomic ratio of Nb/C (Sp2) is also assessed form the XPS analysis and the values are presented in Fig 3.11 (b). It can be seen that OI/Nb are in the range 2.18 -2.39 corresponding to the stoichiometry of Nb$_2$O$_{5-x}$. It was found that the calculated OI/Nb ratio at low process pressure values (2 Pa to 4 Pa) was in the range of 2.18 to 2.24 and the evaluated OI/Nb ratio for the high process pressure values (5 to
8 Pa) was in the range (2.28 to 2.42). This shows that more oxygen vacancies are generated in the lattice of Nb$_2$O$_{5-x}$ with respect to high process pressure values.

![Graph showing O1s core level and OI/Nb variations](image)

**Fig 3.11** (a) De-convolution of the O 1s core level (b) Variations of Nb/C and OI/Nb with respect to process pressure

This can be elucidated by the fact that at low process pressure values the sputtered particles and the plasma species interacted with layers of graphene more energetically generating oxygen vacancies in the lattice of Nb$_2$O$_5$. Also the Nb/C ratio at low process pressure values (2 Pa to 4 Pa) was obtained onto the GNPs surface in a ratio from (0.51 to 0.53 at. %) and for the high process pressure values (5 to 8 Pa) the Nb/C ratio was obtained in the (0.38 to 0.25 at. %).

**3.4.2 XRD analysis of undoped GNPs and Nb$_2$O$_5$ decorated GNPs at different working pressure values**

Fig 3.12 (a) shows the XRD patterns of undoped and Nb$_2$O$_5$ doped GNPs at different working pressure values. The XRD spectra shows that the crystal structure is hexagonal for all diffraction peaks that are indexed to the peaks of graphite (hexagonal) structure (ICDD card # 65-6212)
with lattice constants \( a = 2.464 \, \text{Å} \) and \( c = 6.71 \, \text{Å} \). We observed significant changes in the XRD patterns with \( \text{Nb}_2\text{O}_5 \) doping into the GNPs at different working pressures. The enlarged view of (002) peak of undoped GNPs and \( \text{Nb}_2\text{O}_5 \) doped GNPs shows two different behaviors with working pressure variation. One is at low working pressures (2-4 Pa), in which the (002) diffraction peak for the \( \text{Nb}_2\text{O}_5 \) doped GNPs was shifted towards the lower angle values with respect to the undoped GNPs. The second is at high working pressures (5 - 8 Pa), in which the (002) the peak shift is less pronounced with respect to lower pressure range (2-4 Pa) as shown in Fig 3.12 (b). These two behaviors can be explained as follows; in plasma process sputter deposition plasma is used as the source of charged species (electrons, ions). These high energetic ions extract few clusters and atoms from the target during the sputtering process, which are subsequently deposited on substrate [40]. The said scenario successfully explained the so-called Keller-Simmons (K-S) formula, a well-known empirical equation \[^{214}\].

\[
r = r_o \left(1 - \frac{K}{P} \exp\left\{-\frac{p}{K}\right\}\right) \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldOTS
\[ \phi \propto (E + U)^{-3} \cos \theta \] with the kinetic energy \( E \), the surface binding energy \( U \) and the emission angle \( \theta \) [215, 216].

Fig 3.12 (a) XRD patterns Nb\textsubscript{2}O\textsubscript{5} doped GNPs  (b) Variation of the 2\( \theta \) angle of the (002) at different working pressure peak with different working pressure process pressures

This indicates that sputtered particles are highly directed in the direction perpendicular to the cathode with high kinetic energies. In this way, equation (5) satisfies two main contributions i) the arrival of sputtered atoms which have conserved their original kinetic energy and directionality at the substrate surface, and ii) the arrival of sputtered atoms that have been thermalized by the plasma gas. Our XPS results showed that the deposition rate of Nb\textsubscript{2}O\textsubscript{5-x} was higher at low working pressures, (ratio of Nb/C is higher). At low pressure, the rate of deposition increases with total pressure until 4 Pa, where a maximum was reached. For higher pressure, the deposition rate decreases with pressure. The impact of the energetic sputtered particles does not only lead to a change in the deposition rate, but also has a noticeable influence on the structure of GNPs. The enlarged view of the (002) peak (inset) shows that the FWHM of (002) peak at low
working pressure broadened, indicating deterioration of the crystallinity of the GNPs. Also at low working pressures, the (002) peak intensity of GNPs became weaker, implying an increase of the disorder in GNPs. Furthermore, the bombardment of the sputtered particles and plasma species induced a significant strain in the GNPs, (as it will be described in the next section). At last we can conclude that the XPS result show that the Nb/C (sp²) increased at low working pressures. Also from the XRD analysis results it was observed that the disorderness increased at low working pressure.

The lattice parameters “a” and “c” of undoped and Nb₂O₅ decorated GNPs at different process pressure were calculated from the reflection of the planes (100) and (002) using equation (2). Fig. 3.13 shows the dependence of the calculated lattice parameters (‘‘a’’ and ‘‘c’’) of the GNPs with Nb₂O₅-x amount obtained by varying working the pressure values. The lattice parameter c’ and ‘a’ of GNPs linearly increased with rising Nb/C (sp²). The maximum elongation along ‘c’ axis is about 0.081 Å when Nb₂O₅-x incorporated to the lattice of GNPs in an atomic ratio (0.58 %) to C (sp²) at low working pressure. The possible reason for the elongation along ‘c’ and ‘a’ axis is that at low working pressure the plasma species and sputtered particles interacted with layers of GNPs more energetically. More possible reason for the elongation of the of ‘c’ and ‘a’ axis are that, by interaction of the GNPs with high energetic species and sputtered particles strain were induced in the planes of the GNPs.
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Fig 3. 13 Lattice parameters “a” “c” and cell volume V of GNPs with various Nb₂O₅-doping levels through variation of process pressure (the dashed line indicate a, c, and v values of bulk graphite).

3.4.3 Raman study of undoped GNPs and Nb₂O₅ doped GNPs at different process pressure values

Fig 3.14 (a) shows the Raman spectra of undoped GNPs and Nb₂O₅ doped GNPs at different working pressure values. The working pressure had a strong influence on the structure of GNPs. Two different behaviors were observed in Raman spectra (inset shown in Fig 3.14 (a) for the deposition of Nb₂O₅ₓ onto GNPs by varying the process pressure. At lowest process pressure values (2 to 4 Pa), for lower process pressers values the G and 2D bands of the decorated GNPs with Nb₂O₅ are shifted toward lower wavenumbers with respect to the undecorated GNPs. The Nb/C (sp²) ratios increased from 0.50 at. % and reached 0.58 at. %, when the Nb₂O₅ deposited onto GNPs at lower process pressure values (2 to 4 Pa). The shift in G
and 2D for the decorated graphene with Nb$_2$O$_5$ layers as a function of Nb/C sp$^2$ are presented in 3.15 (b).

![Raman spectra of undoped GNPs and Nb$_2$O$_5$ doped GNPs at different working pressure](image)

Fig 3.14 (a) Raman spectra of undoped GNPs and (b) position of the G and 2D peaks vs Nb/C (%)

**Nb$_2$O$_5$ doped GNPs at different working pressure**

The highest red shift of G and 2D are 16.53 cm$^{-1}$ and 30.5 cm$^{-1}$ respectively, when Nb$_2$O$_{5-x}$ deposited on GNPs in a ratio of Nb/C equal to (0.58 at. %) obtained at low working pressure values. This high red shift can be explained as follow, at low working pressures the mean free path $\lambda$ for the sputtered particles, which accounts for the typical average distance covered by the sputtered atoms in the plasma gas species, is longer. Consequently, the sputtered particles undergo less-frequent collisions with plasma species and these sputtered particles deposited on the GNPs surface with higher energy [217]. Deposition of the Nb$_2$O$_5$ onto GNPs at low process pressure values generates the stress in the layers of GNPs due to the interaction of energetic plasma species and sputtered particles. As already discussed that at low process pressure values
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the sputtered and plasma species are less frequent collision during the deposition process. Direct interaction of the energetic sputtered particles and plasma species with GNPs layers induced the stress the in the lattice of the GNPs. Accordingly by the interaction of the energetic sputtered particles with layers of the GNPs, the tensile strain was established in the planes of GNPs and eventually breaks the A-B symmetry of GNPs, which could effectively change the electronic band structure of GNPs. Likewise for higher working pressure values from (5 Pa to 8 Pa), the red shift for G and 2D bands are 6.81 cm$^{-1}$ and 15.5 cm$^{-1}$ respectively, when Nb$_2$O$_{5-x}$ contents was deposited onto GNPs in ratio of (0.25 at. %) to C (sp$^3$). This behavior can be explained by the fact that with increasing the working pressure, thermalization mean free path $\lambda$ for the sputtered species was decreased. The sputtered species undergo many collisions inside the plasma and as a result, fewer low energy sputtered particles arrive at the surface of GNPs produced less red shift in G and 2D modes compared to low working pressure (2-4 Pa). These consequences are consistent with the XRD results.

3.5 Effect of Nb$_2$O$_5$ concentration on the structural and chemical properties of graphite nanoplatelets decorated by varying powder vibration frequencies

In the above two sections (3.3-3.4), the influence of Nb$_2$O$_5$ concentration onto GNPs by varying RF power values and process pressure values were discussed. In both sections Nb$_2$O$_5$ films were decorated on the surface of the GNPs with low vibration frequency of the powders. The powder vibration frequency is an important parameter and plays a vital role for the uniform decoration. The main objective of this work was to study the decoration of the Nb$_2$O$_5$ layer onto GNPs surface and the influence of the Nb$_2$O$_5$ concentration by varying different powder variation frequencies during the deposition process. For this purpose a sample holder stage previously designed to vibrate GNPs powder during the deposition process was used. In this context, Nb$_2$O$_5$
layers were deposited onto GNP s surface with powder vibration frequencies $0 \leq \omega \leq 100$ Hz with constant amplitude of 32 µm. It was found that with high powder vibration frequencies, more sputtered particles were deposited on the GNP s with respect to the deposition of Nb$_2$O$_5$ onto GNP s without moving the GNP s powder. The detailed structural and chemical properties were studied using XRD, Raman and XPS techniques. Moreover the process parameters are presented in table 3.3.

Table 3.3 the process condition of decorated GNP s with Nb$_2$O$_5$ films

<table>
<thead>
<tr>
<th>Sample #</th>
<th>RF Power (W)</th>
<th>Process pressure (Pa)</th>
<th>Deposition Time (min)</th>
<th>Powder vibration frequency (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40</td>
<td>6</td>
<td>15</td>
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<tr>
<td>4</td>
<td>40</td>
<td>6</td>
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3.5.1 Chemical analysis of undoped GNP s and Nb$_2$O$_5$ doped GNP s deposited at different powder vibration frequencies

The high resolution XPS spectra of undecorated graphene and decorated graphene with Nb$_2$O$_5$ layers at different powder vibration frequencies are illustrated in Fig 3.15. Fig.3.15 (a) shows de-convolution of the C1s peak of the GNP s and decorated GNP s with Nb$_2$O$_5$ films deposited at different powder vibration frequencies.

The C 1s core level were de-convoluted the three Gaussian peaks one centered at BE 284.69 eV corresponding to C-C Sp$^2$ hybridized carbon, the other peaks centered at binding energy at 285.32 eV to sp$^3$ hybridized carbon (C-C)/C-H $^{[218]}$ and at 286.24 eV are attributed to C-O bonding configurations due to oxidation from the moisture
Fig. 3.15 (b) shows the high resolution XPS spectra of Nb 3d for Nb$_2$O$_5$ decorated on GNP’s surface at different powder vibration frequencies. To study the chemical state of Nb$_2$O$_5$, the peaks of the Nb 3d$_{5/2}$ and Nb 3d$_{3/2}$ core levels are at binding energies of 208.07 eV and 210.72 eV respectively. This suggests that one chemical state has been observed for the Nb which is designated to Nb$^+$[210].

The O 1s XPS spectrum of decorated GNP’s with Nb$_2$O$_5$ films deposited at 100 Hz powder vibration frequency is presented in Fig 3.16 (a). The O 1s core level was de-convoluted into three components. The component OI which has BE energy of 530.92 eV corresponds to bond O-Nb. The second component has a BE energy position of 532.182 eV, it may arise due to the oxygen
contribution in possible C=O \[^{65}\] . The 3rd component (O III) at higher BE 533.96 eV is from C-O bonding \[^{65}\]. The OI/Nb and ratio was measured for all samples on the basis of the area under the main component of the oxygen (OI) and the area under the Nb5/2 component and sensitivity factors. The evaluated OI/Nb ratio as a function of powder vibration frequencies is presented in Fig 3.16 (b). The stoichiometry of the deposited Nb2O5-X lowers than ideal value (2.5), which suggests that, the deposited Nb2O5 layers onto GNPs were under stoichiometric. Also Nb/C sp\(^2\) ratios as function of the powder vibration frequencies are also presented in Fig 3.16 (b). It was found that the Nb/C sp\(^2\) ratio increased with rising powder vibration frequencies.

![Fig 3. 16 (a) De-convolution of the O 1s core level](image)

![Fig 3. 16 (b) variations of Nb/C and OI/Nb as a Function powder vibration frequencies](image)

### 3.5.2 Structural analysis of undoped GNPs and Nb2O5 doped GNPs at different powder vibration frequencies

Fig.3.17 (a) depicts the XRD patterns of undoped and Nb2O5 decorated onto GNPs with different powder vibration frequencies. The characteristic peaks of the undoped GNPs at position 26.44°, 42.41°, 44.53°, 54.62°, 77.63° and 83.43° correspond to the reflections of the planes (002), (100/101), (004), (110) and (112) respectively. It can be seen that with high powder vibration...
frequency noticeably variation was observed in the intensity of GNPs peaks with respected to without moving GNPS powder. Here we compared the impact of the Nb$_2$O$_5$ on the moving GNPs powder and without moving GNPs powder during the deposition. The (002) peak became broader and less intense for the powder vibration frequency of 100 Hz, which indicates a less graphitic ordered of GNPs. However the enlarged view of the peak (002) in the inset in Fig 3.17 (a) shows that the peak is more shifted toward lower angle values with high powder vibration frequencies compared to undoped GNPs.

Fig 3. 17 (a) XRD patterns Nb$_2$O$_5$ doped GNPs (b) Variation of the 2θ angle of the (002) at different powder vibration frequencies peak with through varying powder vibration frequencies (RF power =40 W deposition time =15 min and process pressures =6 Pa)

This suggests that the interlayer d –spacing of the GNPs increased with raising the Nb$_2$O$_5$ concentration. Significant enhancement in the deposition rate was observed for the high powder vibration frequency with respect to the case without moving GNPs powder. At $\omega =0$ Hz (no vibration to the GNPs powder) the sputtered particles were deposited at certain areas of the GNPs flakes. For the low vibration frequency at $\omega =10$ Hz, the GNPs powder starts vibration
motion with respect to the sputtered particles by means of fixed amplitude of 32 µm during the deposition process. Consequently there is more possibility for the sputtered particles to deposit at large surface area of the GNPs with respect to the case of without moving (0 Hz) GNPs powder. It should be noted that, in both process of deposition the same deposition parameters were used to deposit Nb$_2$O$_5$ films onto GNPs. But the Nb$_2$O$_5$ films were coated only the surface powder and the beneath surface of the GNPs flakes were not covered with sputtered particles in case of without moving (0 HZ) GNPs powder. With high powder vibration frequency (100 Hz) the sputtered particles coated the whole GNPs surface. High surface area of the GNPs exposed to the sputtered particles during the deposition process. The above mentioned phenomenon can be explained as follows, our XPS analysis shows that by increasing the powder vibration frequencies more Nb$_2$O$_5$ concentration were obtained onto GNPs., XPS is a surface technique and gives the information of the coated surface of the GNPs upto 100 nm. Therefore, it can be considered that, the decoration of the GNPs with Nb$_2$O$_5$ films by means of high powder vibration frequency, the sputtered particles anchored over larger area of the GNPs surface with respect to the case without moving GNPs powders. These observations indicate that with deposition of Nb$_2$O$_5$ onto GNPs by increasing powder vibration the planes of GNPs are more distorted with increasing powder vibration frequencies.

The calculated lattice parameters “a” and “c” of undoped GNPs and Nb$_2$O$_5$ doped GNPs at different powder vibration frequencies from the reflection of the planes (100) and (002) are presented in Fig.3.18. The lattice parameters “a” &“c” increased linearly with rising of Nb/C (sp$^2$). The increase of lattice parameters values suggest that, with interaction of the sputtered particles the planes of the GNPs were distorted and the tensile strain were established in the plane of GNPs.
Fig 3. 18 Lattice parameters “a” “c” and cell volume V of GNPs with various Nb2O5-doping levels through varying powder vibration frequencies

Microstrain (ε) and crystalline size (Lc) (the crystalline coherence length in the 002 direction) of undoped GNPs and Nb2O5 decorated onto GNPs at different powder vibration frequencies were calculated using equation (4).

The crystallite size of undoped GNPs and Nb2O5 films decorated onto GNPs at different powder vibration frequencies are presented in Fig.3.19. The crystallite size of the GNPs deceased with rising of Nb/C (sp²) atomic ratio (%). The decrease of the crystallite size can suggest that with decoration of the GNPs by Nb2O5 at different powder vibration frequencies the more sputtered particles and plasma species interact to the basal plane of the GNPs. During the deposition process the sputtered particles and plasma species interacted with basal planes of the GNPs. These plasma species and sputtered particles degraded basal plane of the GNPs. Consequently, due to the degradation of order of the basal plane the crystallite sizes of decorated GNPs along
the c-axis decreased. Moreover the strain induced in the lattice of the GNPs after the deposition of Nb$_2$O$_5$ films onto GNPs.

Williamson Hall plot confirmed that the Nb$_2$O$_5$ induced a tensile strain in the lattices of the GNPs. This suggests that after decoration of Nb$_2$O$_5$ films the lattice constant of the GNPs increased. From the Fig 3.20 it can be seen that strain increases with rising of Nb/C (sp$^2$). It is correlated with cell volume of the GNPs. The cell volume of the GNPs increases with rising of the Nb/C (sp$^2$).

3.5.3 Raman study of undoped GNPs and Nb$_2$O$_5$ doped GNPs at different powder vibration frequencies

Fig 3.20 (a) presents the Raman spectra of undoped GNPs and Nb$_2$O$_5$ deposited on GNPs with different powder vibration frequencies The deposition of Nb$_2$O$_5$ with variation of the powder vibration frequencies strongly affected the structural and electronic properties of GNP, as the Raman spectra show that with high powder vibration frequencies the D, G and 2D bands
position, intensity and FWHM drastically changed. We observed a red shift in G and 2D bands after the deposition of Nb₂O₅ on GNPs using high powder vibration frequencies. Also this red shift increases with rising of Nb₂O₅-x, when varying the powder vibration frequencies as shown in Fig 3.21 (b).

![Graph showing Raman shift vs. Nb/C (%)](image)

**Fig 3. 20 (a) Raman spectra of undoped GNPs and Nb₂O₅ doped GNPs at different sample vibration frequencies.**

The red shift in G and 2D were also observed for the decorated GNPs with Nb₂O₅ without moving powder (0 Hz). But the red shift observed in the G and 2D in case of without moving GNPs powder was less than with respect to the red shift observed for the decorated graphene with Nb₂O₅ by means of high powder vibration frequency (100 Hz). The maximum red shift of G and 2D in the case without moving powder was 6.80 cm⁻¹ and 9 cm⁻¹ with respect to undoped GNPs. However in the case of high powder vibration frequency (100 Hz), the maximum red shift in G and 2D was 8.5 cm⁻¹ and 16.4 cm⁻¹ observed., This high red shift in G and 2D peaks for
GNPs bands with high powder vibration frequencies compared to the case without moving powder vibration (0 Hz) could be due to the more Nb$_2$O$_5$ deposited onto the GNPs. As explained in the XPS section with high powder vibration more sputtered particles are decorated on the surface of the GNPs. This high redshift of the G and 2D in case of high powder vibration frequencies can be explained as follows, by the deposition of Nb$_2$O$_5$ films onto GNPs at different powder vibration frequency generates the structural defects in the plane of the GNPs and theses structural defects modified the lattice of the GNPs, which could change the electronic properties of the GNPs. Accordingly, the crystal phonon energy of the lattice of GNPs with interaction of Nb$_2$O$_5$ films is lowered due to the due the enlarged the lattices of GNPs.

3.6 Effect of Nb$_2$O$_5$ concentration on the structural and chemical properties of graphite nanoplatelets decorated by varying deposition time

The influence of the Nb$_2$O$_5$ contents onto GNPs studied by the variation of the sputtered ions energies and plasma species by varying RF powers and process pressures was studied in the above section. Also we concluded that the high energy sputtered particles induced large disorderness in the structures of the GNPs. In this section the Nb$_2$O$_5$ films were deposited onto GNPs by keeping constant ion energy at constant RF power value and only increased the amounts of the Nb$_2$O$_5$ onto GNPs surface. The different amounts of Nb$_2$O$_5$ onto GNPs were obtained by stepping up the deposition time. The structural disorderness and the defects were characterized by XRD and Raman techniques and the chemical analysis of decorated graphene with Nb$_2$O$_5$ was characterized by XPS analysis. The condition of the process parameters are presented in table 3.4

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<th>Sample #</th>
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<th>Process pressure (Pa)</th>
<th>Deposition Time</th>
<th>Powder vibration frequency (Hz)</th>
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Table 3.4 the process condition of decorated GNPs with Nb$_2$O$_5$ films
Chapter #3 The influence of Nb$_2$O$_5$ concentration on the structural chemical and electronic properties of GNPs

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3.6.1 Chemical analysis of undoped GNPs and Nb$_2$O$_5$ doped GNPs at different time of deposition

Fig 3.21 depicts the XPS core levels of undecorated GNPs and decorated GNPs with Nb$_2$O$_5$ films at different times of deposition. The high resolution C 1s core level of the undecorated GNPs and decorated GNPs with Nb$_2$O$_5$ films at different times of deposition are presented in Fig 3.21 (a).

![XPS spectra](image)

Fig 3.21 XPS spectra of GNPs with incrementally increased Nb$_2$O$_5$ contents through different times of deposition  (a)a) Shift in the C 1s core levels position upon Nb$_2$O$_5$ deposition (b) Nb 3d core level spectra with positions of the Nb$^{+5}$ peaks. (RF power =40 W deposition time =10 min to 45 min) process pressures =6 Pa, Powder vibration= 10 Hz)
The C 1s core level of the undoped and Nb$_2$O$_5$ doped GNPs samples were de-convoluted into three components. The binding energies of the components of the undecorated GNPs C 1s spectrum are 284.69, 285.23 and 286.2 eV respectively, which are attributed to C-C (sp$^2$), C-H/C-C (sp$^3$) and C-O bonds respectively.

Nb 3d XPS spectra of Nb$_2$O$_5$ layers deposited on GNPs at different times of deposition are shown in Figure 3.21 (b). The binding energy values for Nb 3d at 208.1 eV and 210.12 eV represent the Nb 3d$_{5/2}$ and Nb 3d$_{3/2}$ states of Nb$^{+5}$. It is confirmed from the XPS spectra that only one chemical state has been observed for the Nb.

Fig 3.22 (a) shows the O 1s XPS core level of Nb$_2$O$_5$ decorated on GNPs at 45 min of deposition in Ar plasma. The Gaussian line function was used to de-convolute the O 1s core level. The O 1 core level was de-convoluted into three components. The component OI which has BE energy of 530.92 eV corresponds to bond O-Nb. The second components OII BE position at 532.16 eV allocated to the oxygen contribution in possible C=O. The 3rd component (O III) at higher BE of 533.62 eV is from C-O bonding.
Additionally, the stoichiometry and concentration of the decorated Nb$_2$O$_5$ onto GNPs surface at stepping up the deposition time were evaluated from the XPS analysis and the results are shown in Fig.3.22 (b). It can be seen that the Nb/C ($sp^3$) ratio increased with stepping up deposition time however the OI/Nb ratio linearly decreased with rising of the deposition time. This indicates that the decorated Nb$_2$O$_5$ is under stoichiometric with respect to the ideal of 2.5.

### 3.6.2 XRD analysis of undoped GNPs and Nb$_2$O$_5$ doped GNPs at different times of deposition

Figure 3.23 (a) depicts the XRD patterns of undoped and Nb$_2$O$_5$ deposited on GNPs at different times of deposition. In this case the amount of Nb$_2$O$_5$ onto GNPs increased by stepping up deposition time. The peaks are identified as (002), (100)/(101), (004) (110) and (112) planes of hexagonal graphite.

**Fig 3.23** (a) XRD patterns Nb$_2$O$_5$ doped GNPs (b) Variation of the 2θ angle of the (002) at different time of deposition

With increasing of Nb$_2$O$_5$ concentration onto GNPs the intensity of the (002) peak was attenuated. The full width at half maximum of (002) peak became higher by increasing the Nb$_2$O$_5$ concentration onto GNPs. The shift in (002) peak of the GNPs toward lower angle values...
increased with stepping up the deposition time and the results are presented in Fig 3.24 (b). This indicates that the interplaner spacing between the layers of GNPs is increased. The increase in the lattice spacing between the layers of graphene suggests that the planes of the GNPs are distorted with interaction of the sputtered particles and plasma species.

Furthermore the lattice parameters “a” and “c” of undoped GNPs and Nb2O5 deposited onto GNPs at different times of deposition were calculated from the reflection of the planes (100) and (002) using equation (2)

![Graph showing Nb/C atomic ratio (%) vs. lattice parameters](image)

**Fig 3.24** Lattice parameters “a”, “c” and cell volume V of GNPs in function of Nb/C at. ratio

Fig. 3.24 shows the dependence of the calculated lattice parameters (“a” and “c”) of the GNPs when changing the Nb2O5 concentration by stepping up deposition time. The “c” and “a” parameters increased, when a small amount of Nb2O5 was deposited onto GNPs in atomic ratio Nb/C (sp2) =1.2 %. The enhancement of the “c” and “a” parameters can suggest that, the
planes of GNP's were distorted with deposition of the Nb$_2$O$_5$ and the tensile strain were developed in the planes of GNP's with interaction of the plasma species and sputtered particles. Due to the tensile strain the lattice parameters of the GNP's increased.

Moreover, to characterize the similarity between the GNP's and perfect single crystal graphite the Mering–Meire (G$_{\text{xrd}}$) index was used $^{[220]}$.

Fig 3.25 shows the graphitization indices (G$_{\text{xrd}}$) and d spacing of the GNP's and decorated GNP's with Nb$_2$O$_5$ by stepping up the deposition time. With raising of Nb contents to the C (Sp$^2$) the interlayers spacing d$_{002}$ is increased.

\[
\begin{array}{c}
\text{G (xrd) of the GNP's before the decoration was 0.85, this suggest that the basal planes were well aligned. However after the decoration of Nb$_2$O$_5$ the graphitization index of GNP's decreased from the 0.85 to 0.5, when the Nb$_2$O$_5$ layers were deposited onto GNP's sheets with a Nb/C (sp$^2$)= 1.2 atomic ratio (%). It can be explained like as follows; by increasing the deposition time more sputtered particles were deposited and plasma species interacted with}
\end{array}
\]
GNPs sheet generates the structural defects in the planes of the GNPs. The stacking orders of basal planes were degraded with interaction of the sputtered particle and plasma species. Due to the degradation of the stacking order of the basal planes of GNPs gradually loss their initial ordering, decreasing the degree of graphitization.

3.6.3 Raman study of undoped GNPs and Nb$_2$O$_5$ doped GNPs with different times of deposition

We have further studied the Raman analysis of undoped and decorated GNPs with Nb$_2$O$_5$ films deposited by varying the deposition time. Three main peaks corresponding the D, G and 2D bands dominated all the spectra. The enlarged view of the position G inset shows that G peak shifted to lower wavenumber with increasing the deposition time as shown in Fig 3.26 (a). The position of the G peak started at 1572.1 cm$^{-1}$ before the Nb$_2$O$_5$ deposition and decreased up to 1567.06 cm$^{-1}$ after the deposition of Nb$_2$O$_5$ for 45 min. Similarly the position of the 2D peak shifted to a lower wavenumber from 2666.7 to 2651.3 cm$^{-1}$ after deposition of Nb$_2$O$_5$ for 45 min as shown in Fig 3.26 (b). Literature survey points to several possible explanations for this red shift in GNPs. This includes the effects of charge doping [221] and mechanical strain [222]. The relatively shift in G and 2D bands gives us information whether the shift due to charge transfer or strain effect dominates [223,224]. The shift in G and 2D band will be due to charge transfer if shift G band is stronger than that of 2D band [225, 226]. However if the shift in 2D band is greater than G bands then the mechanical strain dominates. Therefore downshift of G and the 2D bands of Nb$_2$O$_5$ doped GNPs are attributed to tensile strain [227]. This effect can be explained as follows, when the C-C bond length and angles of sp$^2$ ring are modified through tensile strain, the hexagonal symmetry of the graphene layers is broken due to the enlarging of the lattice constants and the lowering of vibration frequency of the crystal phonon [200]. This is in good agreement
with XRD findings in which lattice constants of GNPs increased after decoration of Nb$_2$O$_5$. Hence, for increasing tensile strain in GNPs both pos (G) and Pos (2D) shifted to lower wavenumbers [68].

More importantly the level of defects and disorderness induced in the planes of GNPs by the interaction of the Nb$_2$O$_5$ were evaluated using the intensity ratios of D and G peaks. As in the section (3.3.4) it has been explained that, there are two regimes in the defected GNPs structures. One is low density defect regime where $I_D/I_G$ ratio increased with respect to the high defects density and for this regime the lattice phonon scattered elastically. The second regime is related to the high defects density, whereas $I_D/I_G$ begins to attenuate as a function of increasing the defects density, this regime can be attributed to a gradual evolution from the sp$^2$–bonded carbon found in graphene sheets into amorphous carbon with low sp$^3$ bonding [207]. The $I_D/I_G$ ratio of the decorated GNPs with Nb$_2$O$_5$ films as a function of Nb/C (sp$^2$) atomic ratio (%) is illustrated in

Fig 3. 26 (a) Raman spectra of undoped GNPs and Nb2O5 doped GNPs at different time of deposition. (b) position of the G and 2D peaks vs Nb/C (%)
Fig. 3.27. It can be seen that $I_D/I_G$ ratio gradually decreased with rising of Nb/C (Sp²) atomic ratio (%). This can be attributed to the second regime of the defects at which $I_D/I_G$ ratio decreases as a function of induced defects in GNPs structures, whereas the sp² bonded carbon of the GNPs is transformed into low sp³ amorphous carbon (a-C phase). This effect can be explained like this, when the sputtered particles and plasma species interacted with GNPs surface, they generate the structural defects in the structure of the GNPs. Also these defects on the surface of the GNPs increased with stepping up the deposition time. This is confirmed from XPS analysis, with stepping up deposition time more sputtered particles deposited on the surface of the GNPs.

The $I_{2D}/I_G$ ratio of the decorated GNPs with Nb₂O₅ as a function of Nb/C (%) ratio is presented in Fig 3.27(c). $I_{2D}/I_G$ ratio is very sensitive to the doping level GNPs. From the Fig.3.28 (c) it can
be seen that with raising Nb/C (Sp\(^2\)) by stepping up the deposition time the I_{2D}/I_G ratio decreased. According to the previous reported data suggest that the I_{2D}/I_G ratio decreases with increasing doping concentration due the additional electron-hole or electron-defect scattering contribution. As discussed in the section 3.3 that the intensity of the 2D bands strongly depend on the doping concentration and also affected with extra electron/hole or electron defects scattering rate. In our case the defects induced in the structure of the GNPs with interaction of sputtered particle and plasma gas species. The intensity of the 2D bands more affected with these defects with respect to G peak. More importantly the defects increased on the surface of GNPs with rising of deposition time. The intensity of 2D of the GNPs attenuated with these short range defects induced by Nb_2O_5 contents. Furthermore the full width at half maximum (FWHM) of the G peaks of GNPs decreased as a function of changing Nb/C (sp\(^2\)) with rising deposition time are presented in Fig 3.28 (a). The FWHM of the GNPs is very sensitive to the doping level due to the reduction of the Kohn anomaly \([228]\). The reduction of the FWHM of the GNPs after the interaction of the Nb_2O_5 could be due to charge doping at the interface. Actually the sharpening of FWHM (G) of the GNPs could be decaying into electron-hole pair due to the Pauli Exclusion Principle. Addition to this reduction of the FWHM of the G peak occurred when the electron hole gap becomes higher than the phonon energy, then phonons is decayed \([229]\).

**3.7 Concluding Remarks**

In this chapter we presented the experimental study results about Nb_2O_5 deposition on GNPs by the variation of the deposition process parameters. Based on the variation of deposition parameters used, this chapter is divided into four sections (i) the decoration of the GNPs with Nb_2O_5 at different RF power values have been discussed. (ii) The structural disorderness of the
decorated GNP\textsuperscript{s} with Nb\textsubscript{2}O\textsubscript{5} by varying process pressures was studied. (iii) The powder vibration frequencies were used to decorate the GNP\textsuperscript{s} powder with Nb\textsubscript{2}O\textsubscript{5} films uniformly and the structural and chemical are presented. (iv) Different amounts of Nb\textsubscript{2}O\textsubscript{5} nanoparticle were deposited by varying the deposition time.

In section 3.3, decoration of the Nb\textsubscript{2}O\textsubscript{5} onto GNP\textsuperscript{s} by varying the RF power values (40 -100 W) was presented. The structural, chemical properties and morphological investigations were carried out of the decorated samples. It was found from the XRD investigations that tensile strain was developed in the planes of the GNP\textsuperscript{s} with deposition of Nb\textsubscript{2}O\textsubscript{5}. Also with interaction of the high energy sputtered particles and plasma species the defects on the surface of the GNP\textsuperscript{s} are increased. Raman studied revealed that the frequencies of the GNP\textsuperscript{s} G and 2D modes were found to undergo red shifts with decoration of Nb\textsubscript{2}O\textsubscript{5}. We explained the red shift of GNP\textsuperscript{s} from the Raman frequencies in terms of tensile strain and doping induced by Nb\textsubscript{2}O\textsubscript{5}. TEM images demonstrated that GNP\textsuperscript{s} decorated with around 5 to10 nm uniform layer of Nb\textsubscript{2}O\textsubscript{5} at 100 W on their surface were successfully fabricated. From the XPS analysis it was confirmed that, by increasing Nb\textsubscript{2}O\textsubscript{5} layer thickness on the GNP\textsuperscript{s} surface with rising RF power values downshift in C 1s peak suggests a p-type doping of GNP\textsuperscript{s} due to charge transfer at the interface as a consequence of the higher work function difference between the Nb\textsubscript{2}O\textsubscript{5} (4.70 eV) and GNP\textsuperscript{s} (4.3 eV).

In section 3.4, the structural disorderness of the Nb\textsubscript{2}O\textsubscript{5} decorated onto GNP\textsuperscript{s} by varying process pressure has been discussed. It was noted from the Raman and XRD result that at low working pressure values the high energy of sputtered particles and plasma species bombardment onto GNP\textsuperscript{s}, induced large disorder onto graphene layers. Also at low working pressure more sputtered
particles were deposited on the GNPs surface, these sputtered interacted with basal plane of the GNPs more energetically, which degraded stacking order of the basal planes of GNPs.

In section 3.5 for the uniform decoration of the GNPs with Nb$_2$O$_5$ film the powder vibration was used. From the XPS analysis it has been confirmed that with high powder vibration frequency more sputtered particles deposited on the surface of the GNPs compared to the case without moving powder. Furthermore the Raman and XRD studied reveal that with powder vibration the tensile strain was induced in the lattice of GNPs.

In section 3.6 the structural defects of the decorated GNPs with Nb$_2$O$_5$ at different times of deposition were discussed in detail. The XRD results shown that, the introduction of low concentration of Nb/C ($sp^3$) led to a significant lattice distortion along the c-axis and a-axis, which reveals that Nb$_2$O$_5$ generated a tensile strain in and between the planes of GNPs. The stacking order of the basal plane and the crystalline thickness of the GNPs along c-axis were degraded upon the deposition of Nb$_2$O$_5$. The redshift in G and 2D peak of GNPs after the decoration of Nb$_2$O$_5$ is due to the tensile strain induced in the plane of GNPs with increasing the Nb$_2$O$_5$ concentration.

Concluding, decoration of Nb$_2$O$_5$ onto GNPs powders by the variation of RF parameters were discussed in detail. In this chapter, the interaction of the Nb$_2$O$_5$ concentration with GNPs which consist of 30 to 40 layers of graphene sheets was presented. The interaction of the graphene flakes (1.6 nm) consisting of average three to five layers of graphene sheet in average with Nb$_2$O$_5$ nanoparticles will be discussed in next chapter #4 and the interface between the graphene flakes and Nb$_2$O$_5$ nanoparticles will be presented.
Chapter # 4

Effect of Nb₂O₅ concentration on the structural electronics and chemical properties of graphene powder

4.1 Introduction:
The main aim of this work is to study the interaction of graphene powder with Nb₂O₅ nanoparticles deposited by RF sputtering technique. In chapter # 3 the effect of Nb₂O₅ concentration on the structural and chemical properties of graphite nanoplatelets (consist of 30 to 40 layers of graphene) by varying deposition process parameters, like RF power, powder vibration frequency and process pressure was presented. It was found that, the tensile strain was established into the GNPs planes upon the deposition of the Nb₂O₅. The tensile strain in the planes of the GNPs increased with rising of Nb₂O₅ concentration. The tensile strain and doping were confirmed from the XRD, Raman study and XPS analysis. In this chapter the interface between graphene powder and deposited Nb₂O₅ nanoparticles by RF sputtering technique will be discussed. Different deposition parameters were adjusted during the deposition process to achieve the uniform distribution of the Nb₂O₅ nanoparticles onto graphene sheets. Interface between the graphene powder and a dissimilar material is needed for different kinds of applications [230,231] Moreover the influence of Nb₂O₅ concentrations on the chemical, structural and electronic properties of graphene will be described in this chapter. Based on the study of the decoration of Nb₂O₅ on the surface of graphene powder with different deposition process parameters, this chapter is divided into three sections:

- For the results presented in section I, the structural chemical and electronic properties of the decorated graphene with Nb₂O₅ nanoparticles will be discussed. In this study, no vibration frequency was given to the graphene powder during the deposition process.
• For the results reported in section II, different amounts of Nb$_2$O$_5$ nanoparticles were obtained onto graphene by increasing the deposition time. A powder vibration frequency of 10 Hz was used to deposit the Nb$_2$O$_5$ nanoparticles onto graphene powder. The influence of Nb$_2$O$_5$ concentration on the structural, chemical and electronic properties of GNP will be presented.

• For the results described in section III, the influence of Nb$_2$O$_5$ nanoparticles on the structural, chemical, morphological and electronic properties of graphene will be studied.

4.2 Experimental details
The Nb$_2$O$_5$ nanoparticles were deposited onto graphene powder by varying three different deposition parameters. The Powder vibrations frequency, RF power and deposition time parameters were used to deposit the Nb$_2$O$_5$ nanoparticles onto graphene powders. The other deposition parameters like substrate to target distance base pressure and target used for the deposition are the same as described in chapter#3. More specific details for each section are given below:

• In order to obtain different amounts of Nb$_2$O$_5$ contents on the surface graphene powder, the graphene powder was decorated with Nb$_2$O$_5$ nanoparticles deposited by stepping up the deposition time (8 to 32 min). The Nb$_2$O$_5$ nanoparticles were deposited onto graphene surface without moving powder. The RF power and process pressure values were kept constant at 6 Pa and 40 W respectively.

• The graphene powders were decorated with Nb$_2$O$_5$ nanoparticles at different time of deposition (8 to 32 min). In this study, 10 Hz powder vibration frequency with fixed amplitude of 32 µm was used to deposit the Nb$_2$O$_5$ nanoparticles onto graphene sheets. The self-bias voltage and power applied to Nb$_2$O$_5$ target was fixed at -72 V and 40 W
respectively. The total process pressure for the decoration of Nb$_2$O$_5$ nanoparticles onto graphene surface was fixed at 6 Pa.

- In order to obtain different concentration of Nb$_2$O$_5$ on the graphene surface power applied to Nb$_2$O$_5$ target was varied from 40 W to 100 W. The total pressure and powder vibration frequency were fixed at 10 Hz and 6 Pa respectively. The deposition time were fixed at 15 min.

4.3: The influence of the Nb$_2$O$_5$ concentrations on the properties of graphene deposited by RF sputtering technique on static graphene powders:

The main objective of this work is to investigate the influence of Nb$_2$O$_5$ concentrations on the structural, chemical and magnetic properties of graphene powder. The different amount of Nb$_2$O$_5$ concentrations were obtained on the graphene surface by stepping up the deposition time. It is well established that due to the presence of numerous topological defects graphene shows a weak ferromagnetic behavior in long range ordering [232, 233]. By the deposition of Nb$_2$O$_5$ onto graphene powder structural defects were generated in the plane of graphene and the structural defects and disorderness increased with rising of Nb$_2$O$_5$ contents onto graphene powder. These structural defects enhanced the ferromagnetic property of the graphene. The ferromagnetic property of the decorated graphene with Nb$_2$O$_5$ nanoparticles will be presented in chapter # 7. The structural defects, ferromagnetic behavior and chemical composition of decorated graphene with Nb$_2$O$_5$ nanoparticles were characterized by X-ray diffraction (XRD), Raman spectroscopy, vibrating sample magnetometer from PPMS (Dyna Cool) and X-ray photoelectron spectroscopy (XPS). Moreover the process parameters are presented in table 4.1.
Table 4.1 the process condition of decorated graphene with Nb$_2$O$_5$ nanoparticles

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<th>Sample #</th>
<th>RF Power (W)</th>
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4.3.1 XPS Analysis of undoped graphene and Nb$_2$O$_5$ doped graphene:

XPS is a potential technique for exploring the chemical composition, element states, and the nature of heteroatom functionalized or doped graphene supported nanocomposites. The C 1s and Nb 3d XPS spectra of the undecorated graphene and decorated graphene with Nb$_2$O$_5$ nanoparticles at different times of deposition are illustrated in Fig.4.1. The high resolution C 1s XPS spectra of undecorated graphene and for the decorated graphene with Nb$_2$O$_5$ nanoparticles at different times of deposition are shown in Fig.4.1 (a). The C 1s core levels spectra were deconvoluted into three components. The XPS C 1s spectra of the undoped graphene has characteristic peaks at 284.81, 285.58 and 286.72 eV respectively that correspond to sp$^2$ carbon bonded (C-C) [233,234] sp$^3$ hybridized carbon (C-C)/C-H [235] and C-O bonding configurations due to oxidation from the moisture. It is interesting to see that after the decoration of Nb$_2$O$_5$ nanoparticles on the surface of graphene the C 1s peak shifts toward the lower binding energies. The downshift in C 1s peak can be explained as, when graphene make interface with weakly interacting material like Nb$_2$O$_5$, the charge are expected to transfer across the interface in order align the Fermi level of the contacted material. The downshift of the C 1s peak increased with
stepping up the Nb$_2$O$_5$ concentration. The maximum downshift was observed in the C 1s peak about 0.10 eV after the decoration of Nb$_2$O$_5$ onto graphene at 32 min of deposition.

Fig 4.1 XPS spectra of graphene powder with incrementally increased Nb$_2$O$_5$ contents by varying the deposition time (a) Shift in the C 1s core levels position upon Nb$_2$O$_5$ deposition (b) Nb 3 d core level spectra with positions of the Nb$^{+5}$ peaks. [Process pressure = 6 Pa, Time= 8 to 32 min, Frequency = 0 Hz RF power= 40 W]

Actually the downshift of the C 1s core level binding energy is equal shift in the Fermi level. However the Fermi level shift is the consequence of the charge transfer between interfaces of the two materials. Therefore, the downshift in the C 1s core level of the graphene is due to p doping upon the deposition of Nb$_2$O$_5$ nanoparticles, whereas the electrons are transferred from graphene to Nb$_2$O$_5$ nanoparticles due to difference of work function between the graphene and Nb$_2$O$_5$.

Fig 4.1 (b) depicts the high resolution XPS spectra of Nb 3d for decorated graphene surface with Nb$_2$O$_5$ nanoparticles by stepping up the deposition time. To study the chemical state of Nb$_2$O$_5$, there are two main peaks of the Nb 3d$_{5/2}$ and 3d$_{3/2}$ core level centered at 208.14 eV and 210.68
Chapter #4 Effect of Nb$_2$O$_5$ concentration on the structural and chemical properties of graphene powder

eV respectively, which designates that the peaks are originated from Nb$^{5+}$ state \[^{236}\]. The binding energies of these photoelectrons are characteristic of Nb$_2$O$_5$ \[^{237}\]. The downshifts in the Nb 3d were observed with the increasing of Nb$_2$O$_5$ concentration on the surface of graphene by stepping up deposition time. The maximum downshift of 0.12 eV was noted upon the deposition of Nb$_2$O$_5$ nanoparticles onto graphene at 32 min. The downshift of the Nb 3d core level upon the deposition of Nb$_2$O$_5$ nanoparticles suggest that, the band of Nb$_2$O$_5$ bending toward the interface with accumulation layers of the electrons from the graphene.

The O1s XPS spectrum of decorated Nb$_2$O$_5$ nanoparticles on graphene surface in Ar plasma is presented in Fig. 4.2 (a). The O 1s peak is de-convoluted into three components the first peak OI at lower binding energy (BE), 530.91 eV can be ascribed to the O1s core peak of O$^{2-}$ bound to Nb$^{5+}$ in graphene sheets. Whereas the other two peaks at higher BE located at 532.13 eV, and 534.15 eV may probable come from the (C=O, COO) and from C-O bonding \[^{238}\].

Fig 4.2 (a) De-convolution of the O 1s core level  (b) variations of Nb/C and Stoichiometry with respect to different time of deposition
The OI/Nb ratio was evaluated for the decorated graphene with Nb$_2$O$_5$ nanoparticle to determine the oxygen vacancy. The measured OI/Nb ratios for the decorated graphene with Nb$_2$O$_5$ nanoparticles at different times of deposition are presented in Fig 4.2 (b). The calculated value of the OI/Nb ratios indicates that the deposited Nb$_2$O$_5$ nanoparticles are under stoichiometric. The Nb/C sp$^2$ ratio increased by rising the deposition time and the results are shown in Fig 4.3 (b). The Nb/C sp$^2$ ratio increased from 0.63 and reached to 1.37 atomic ratios (%), when the decoration time was varied from 8 min to 32 min.

### 4.3.2 XRD analysis of undoped Graphene and Nb$_2$O$_5$ doped graphene

X-ray diffraction was used to characterize the undoped graphene and Nb$_2$O$_5$ decorated graphene powders. Fig.4.3 (a) shows the XRD patterns of undoped graphene and Nb$_2$O$_5$ decorated graphene powder by stepping up deposition time. There is strong influence of the Nb$_2$O$_5$ concentration onto the structure of the graphene.

By the deposition of Nb$_2$O$_5$ onto graphene sheets, the FWHM and position of the graphene plane was drastically changed. A broad and low intensity of (002) peak was observed for the...
undecorated graphene and decorated graphene with Nb$_2$O$_5$ nanoparticles, which suggests that graphene flake consist of very few layers of graphene [239]. The (002) peak of the graphene gradually shifted toward the lower 2θ values by increasing the deposition time as shown in Fig (a) (enlarged view). This indicates that the interlayer distances of graphene sheet increased with rising of the Nb$_2$O$_5$ concentration. The measured values of the d –spacing as a function of Nb/C sp$^2$ is presented in Fig 4.4 (b). The d-spacing values of graphene increased from the 0.351 nm to reach 0.355 nm, when the graphene were decorated with Nb$_2$O$_5$ nanoparticles in a ratio Nb/C sp$^2$=1.31 at. %. Furthermore, the FWHM of the (002) peak for the undecorated graphene and decorated graphene with Nb$_2$O$_5$ nanoparticles were evaluated using the Lorentzian line function. It was found that the FWHM of the (002) peak of graphene became broadened with increasing the Nb$_2$O$_5$ concentration. The evaluated FWHM of graphene as function of Nb/C sp$^2$ are depicted in Fig 4.4

![Graph](image_url)

Fig 4.4 Variation in the FWHM of the (002) peak and crystallite thickness as function of Nb/C sp2 atomic ratio

The FWHM of the (002) peak for graphene increased from the 4.85 to 5.20 with the deposition of Nb$_2$O$_5$ nanoparticles in a ratio Nb/C sp$^2$=1.31 at. %. The broadening of the FWHM of
Chapter #4 Effect of Nb$_2$O$_5$ concentration on the structural and chemical properties of graphene powder

graphene upon the deposition of Nb$_2$O$_5$ nanoparticles suggest that the defects were pronounced in the plane of the graphene. The crystalline thickness of the graphene was calculated using the Scherer equation [240].

\[
D = \frac{K\lambda}{\beta \cos \theta} \tag{1}
\]

Where D is the average crystalline thickness of the graphene, λ is the wave length of the X-ray source, \( \beta_{hkl} \) is the full width at half-maximum (FWHM) of the peak considered (in rad), θ is the Bragg angle. The crystalline size of the graphene flakes as a function of Nb/C sp$^2$ are shown in fig 4.4. The crystalline thickness decreased from 1.76 nm to 1.62 nm with deposition of the Nb$_2$O$_5$ nanoparticles onto graphene sheet in a ratio Nb/C sp$^2$=1.31 at. %. The reduction of the crystalline thickness of the graphene sheet indicates that the stacking order of the graphene sheet was reduced due to the interaction of the sputtered particles and plasma species.

4.3.3 Raman analysis of undecorated graphene and decorated graphene with Nb$_2$O$_5$ nanoparticles

Raman spectroscopy is a powerful tool to extract the identification about the graphitic systems including the defects, strain and disorderness present in the graphitic material [194]. The Raman spectra of undoped graphene and Nb$_2$O$_5$ decorated graphene at stepping up the deposition are shown in Fig 4.5(a). We can see characteristic bands for all samples. Four characteristic bands for the undecorated graphene and decorated graphene with Nb$_2$O$_5$ nanoparticles were observed.

The bands around at 1585.89, 1327, 2636 and 2920 cm$^{-1}$ are attributed to the G-band, D-band, 2D band and D+G band respectively. The G peak arises at the Brillouin zone center and corresponds to the E$_{2g}$ phonon. The D peak which is related to the breathing modes of sp$^2$ atoms and defects are required for its activation. The 2D peak is the second order of the D peak it
appears around 2646 cm\(^{-1}\) and originates in the process of the double resonance in which momentum conservation is accomplished by two phonon in opposite wave vectors. The D+G band is the combination band originated in the presence of disorderness in the system \(^{241}\). It is interesting to note that blue shifts were observed in the G and 2D of graphene after the deposition of the Nb\(_2\)O\(_5\) nanoparticles. The upshift in G and 2D bands were observed upon the deposition of Nb\(_2\)O\(_5\) nanoparticles onto graphene. The upshift in the G and 2D increased by rising the deposition time the results are shown in Fig 4.5 (a) (enlarged view). The maximum upshifts of 5.8 cm\(^{-1}\) and 4.5 cm\(^{-1}\) in the G and 2D were noted, when the Nb\(_2\)O\(_5\) nanoparticles were deposited onto graphene in a ratio Nb/C sp\(^2\)=1.31 at. % and the results are illustrated in Fig 4.5 (b). Several possible explanations were reported in the literatures related to the shift in G and 2D bands. It includes charge doping, mechanical strain and disorderness generated in the plane of the graphene. The shift in G and 2D bands in the Raman spectra due to the charge transfer has been explained by Ferrari et al \(^{210}\)

![Raman spectra](image)

**Fig 4. 5** (a) Raman spectra of undoped graphene and Nb2OS doped GNPs at different times of deposition

(b) positions of the G and FWHM (G) vs Nb to C (%)

Intensity (a.u) vs Raman shift (cm\(^{-1}\))
It can be considered that with deposition of Nb$_2$O$_5$ onto graphene the strain is established in the plane of graphene. Our XRD result demonstrates that tensile strain was developed into the plane of graphene upon the deposition of Nb$_2$O$_5$ nanoparticles. The shift in the G and 2D bands due to the tensile strain is also reported by Elena del Corro et al \[^{242}\]. But in our case, less than 2 % strain was established in the plane of the graphene. It is also well established in the literatures that, the upshift in G and 2D band of graphene with metal oxide interaction is due to the p doping \[^{243}\]. With deposition of the Nb$_2$O$_5$ nanoparticles onto graphene sheet the upshift in G band is greater than the shift in 2D band. Phan Thanh Luan et al also reported that the upshift of the G and 2D is due to the p doping \[^{244}\]. This suggest that the upshift in G and 2D band is not due to the strain, but doping phenomenon was dominates. Therefore, the upshifts G and 2D bands position of graphene after the decoration of Nb$_2$O$_5$ corresponds to the charge transfer between the graphene and Nb$_2$O$_5$ nanoparticles, where electrons being transferred from graphene to Nb$_2$O$_5$ nanoparticles. Consequently it is a clear that Nb$_2$O$_5$ nanoparticles interacted with graphene sheet the charge transfer from graphene to Nb$_2$O$_5$ nanoparticles. This result is good agreement with XPS analysis.

Moreover the full width half maximum (FWHM) of the G peaks of graphene were evaluated by means of Gaussian line of shape. The evaluated FWHM of the G peak as function of Nb/C sp$^2$ are presented in Fig 4.5 (b). It was observed that, the FWHM of the G peak decreased from 78.7 cm$^{-1}$ to 73.8 cm$^{-1}$, when the Nb$_2$O$_5$ nanoparticles were introduced in a ratio in a ratio Nb/C sp$^2$=1.31 at. %. The reduction in FWHM (G) of graphene after the interaction of Nb$_2$O$_5$ nanoparticles are attributed the charge doping. The sharpening of the FWHM is actually decayed into electron-hole pairs due to the Pauli Exclusion Principle. Magdalena Onyszko et al is also reported the similar phenomenon and explained that with decoration of the reduced graphene
oxide with metal oxide nanoparticles, the FWHM of G peak decreased upon the doping of graphene with metal oxide nanoparticles \[^{245}\].

The defects and disorderliness induced in the graphene structure with the interaction of the sputtered particles and plasma species were evaluated by using the \( I_D/I_G \) ratio \[^{246}\]. Generally, the \( I_D/I_G \) is used to measure the density of defects in disorder graphene. The estimated \( I_D/I_G \) ratio of undecorated graphene and decorated graphene with \( \text{Nb}_2\text{O}_5 \) nanoparticles as function of \( \text{Nb}/\text{C} \) sp\(^2\) are depicted in Fig. 4.6. The \( I_D/I_G \) ratio increased from 1.65 and reached 1.75 with deposition of \( \text{Nb}_2\text{O}_5 \) nanoparticles onto graphene sheet in a ratio \( \text{Nb}/\text{C} \) sp\(^2\)=1.31 at. %. This shows that, the structural defects were enhanced in graphene plane with deposition of the sputtered particles.

Furthermore, the \( I_D/I_G \) ratio is also used to measure the in-plane crystalline size of the graphene.

\[
\begin{align*}
\text{Fig 4.6 Variation of Raman peak intensity ratios of } I_D/I_G \text{ plotted against the Nb to C atomic ratio (\%)}
\end{align*}
\]

The in-plane crystallite size of undecorated graphene and decorated graphene with \( \text{Nb}_2\text{O}_5 \) nanoparticles were calculated by using the Tuinstra - Koenig relation \[^{247}\].
\[ La(nm) = 2.4 \times 10^{-10} Z^4 \left( \frac{I_D}{I_G} \right)^{-1} \] ..........(2)

The calculated in-plane crystallites sizes of the undecorated graphene and decorated graphene with Nb₂O₅ nanoparticles as a function of Nb/C sp² are shown in Fig 4.6. The in-plane crystallites size of graphene flakes decreased from 23.2 to 21.4 nm, when the Nb₂O₅ nanoparticles were deposited onto graphene sheet in a ratio Nb/C sp²=1.31 at. %. The reduction of the in-plane crystalline size of the graphene upon the deposition of Nb₂O₅ nanoparticles suggests that, the sp² domain of the graphene were broken. As already discussed before, structural defects increased by stepping up deposition time. It is well proven that, when the structural defects increased to the sp² domain, the hexagon of the graphene were more distorted with increasing defects density. Therefore, the reduction of the sp² domain size of the graphene upon the deposition of Nb₂O₅ nanoparticles could be increasing the structural defects.

4.3.4 TEM analysis of decorated graphene at 16 and 32 min.

The morphology and size distributions of the decorated Nb₂O₅ nanoparticles on the graphene powder were examined by TEM analysis. Fig. 4.7 (a-d) shows graphene sheets decorated with Nb₂O₅ nanoparticles at 16 and 32 minute of depositions. The distribution of Nb₂O₅ nanoparticles onto the graphene sheets and their intimate contact can be seen clearly from the TEM images. Fig 4.8 (a-b) shows the decoration of Nb₂O₅ on the graphene surface at 16 min of deposition. The dispersion of the Nb₂O₅ nanoparticles on the graphene sheets are uniformly distributed even at low decoration of time. Fig 4.8(c-d) depicts that, Nb₂O₅ nanoparticles were deposited onto graphene sheet for 32 min of deposition. The deposited Nb₂O₅ nanoparticles were made aggregates onto graphene sheet. As discussed in the above text that, the graphene sheets were decorated with Nb₂O₅ nanoparticles onto static graphene flakes. The sputtered particles were deposited onto graphene sheets at specific area of flakes and make aggregates onto graphene.
sheets. The agglomerations of the deposited Nb$_2$O$_5$ nanoparticles were increased with high deposition time. The size of the decorated Nb$_2$O$_5$ nanoparticles on the graphene sheet is around 15 to 20 nm.

Fig 4. 7 TEM images (A-B) decorated graphene at 16 min of deposition and (C-D) Nb$_2$O$_5$ decorated graphene at 32 min of deposition
4.4: The effect of the Nb$_2$O$_5$ concentration on the structural and chemical properties of graphene powder via given 10 Hz vibration to the graphene powder

In the section 4.1 we discussed the deposition of Nb$_2$O$_5$ nanoparticles on the graphene without moving powder during the deposition process and studied the interaction of the graphene with Nb$_2$O$_5$ nanoparticles. In this section, we presented the decoration of graphene with Nb$_2$O$_5$ nanoparticles via given 10 Hz vibration with amplitude of 32 µm to the graphene powder. The powder vibration plays important role in the uniform decoration of the Nb$_2$O$_5$ nanoparticles on the surface of graphene powders. To see the influence and interaction of the sputtered particle on the moving graphene powder various characterizations techniques were used. The structural defects, chemical composition of decorated graphene with Nb$_2$O$_5$ nanoparticles were characterized by X-ray diffraction (XRD), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) Moreover the process parameters are presented in table 4.2.

Table 4.2 the process condition of decorated graphene with Nb$_2$O$_5$ nanoparticles

<table>
<thead>
<tr>
<th>Sample #</th>
<th>RF Power (W)</th>
<th>Process pressure (Pa)</th>
<th>Deposition Time (min)</th>
<th>Powder vibration frequency (Hz)</th>
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<td>4</td>
<td>40</td>
<td>6</td>
<td>32</td>
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</tbody>
</table>

4.4.1 XPS analysis of undoped graphene and Nb$_2$O$_5$ doped graphene

Fig 4.8 (a) (b) shows the XPS signal of C 1s and Nb 3d core level were measured for undecorated graphene and decorated graphene with Nb$_2$O$_5$ nanoparticles deposited by stepping up the deposition time. The C 1s core levels of the undoped graphene were de-convoluted into three components which described into above section 4.8 (a). It is important to note that after the
interaction of graphene with Nb$_2$O$_5$ nanoparticles the C 1s core levels shifts toward the lower binding energy values. Graphene can be doped with electron if the work function of the dopant is lower than graphene, otherwise it will be doped with hole under the opposite condition. The shift in the C 1s core level toward the lower binding energies increased as by the raising of Nb$_2$O$_5$ concentrations. The maximum downshift in the C 1s core level of 0.11 eV was observed after the deposition Nb$_2$O$_5$ nanoparticles onto graphene powders at 32 min of deposition. The downshift of the carbon C 1s core level is clear indication of the p-type doping of graphene due to the electron being transferred from the graphene to Nb$_2$O$_5$ nanoparticles at the interface in order to align the Fermi level of the contacted materials.

![Graphene XPS spectra](image)

Fig 4.8 XPS spectra of graphene powder with incrementally increased Nb$_2$O$_5$ contents by varying the deposition time (a) Shift in the C 1s core levels position upon Nb$_2$O$_5$ deposition (b) Nb 3d core level spectra with positions of the Nb$^{5+}$ peaks. [Process pressure = 6 Pa, Time= 8-32 min, Frequency = 10 Hz, RF power = 40 W]
The composition of the decorated Nb$_2$O$_5$ nanoparticles were examined by using the XPS measurements and the results are presented in Fig 4.9 (b). The binding energies of Nb 3d$_{5/2}$ and 3d$_{3/2}$ core level were 208.14 eV and 210.68 eV respectively. The spin-orbit splitting between Nb 3d$_{5/2}$ and 3d$_{3/2}$ core level was 2.6 eV, which perfectly matched the reported values for Nb$_2$O$_5$ [248]; thus, this result suggested that the chemical state of the decorated nanoparticle is in the Nb$^{+5}$. The similar shift of the 0.16 eV were observed in the in the Nb 3d$_{5/2}$ peak towards the lower binding energies with increasing of Nb$_2$O$_5$ concentration which suggests that electron transfer from graphene to the Nb$_2$O$_5$, i.e. a p-type charge transfer doping of graphene. This can be explained as follow, the band of Nb$_2$O$_5$ move closer to the Fermi level with accumulation of the electrons from the graphene in the bands of the Nb$_2$O$_5$. As discussed in chapter #3 the band of the Nb$_2$O$_5$ bends toward the interface after the charge is transferred from graphene to Nb$_2$O$_5$. Therefore, the Nb 3d core level shifted toward the lower binding energy due to the band bending of the Nb$_2$O$_5$ upon interface with graphene sheets.

A Gaussian fit was performed on the O 1s peaks of deposited Nb$_2$O$_5$ nanoparticles onto graphene at 32 min of deposition and three components centered at ~530.92 eV (OI), ~532.4 eV (OII) and ~533.80 eV (OIII), respectively are displayed in Fig 4.9 (a). The OI sub peak is attributed to O$^{2-}$ bound to Nb$^{+5}$, while the two other components OII and OIII at higher binding energy values, 532.13 eV, and 534.15 eV, may come from the (C=0, COO) and from C-O bonding.

Additionally, the oxide stoichiometry (OI/Nb), and Nb/C (%) atomic ratios were also estimated from the XPS analysis. The measured the OI/Nb as function of deposition time is presented in Fig 4.9 (b). The measured values of OI/Nb indicate that the deposited Nb$_2$O$_5$ nanoparticles onto graphene sheets are under stoichiometric with respect to the ideal value of Nb$_2$O$_5$, which is 2.5
As expected Nb/C sp\(^2\) atomic ratio increased from 0.93 and reached 1.51 atomic ratio %, when the decoration times of the Nb\(_2\)O\(_5\) nanoparticles onto graphene powder was varied from 8 min to 32 min. It was found that with decorated graphene Nb\(_2\)O\(_5\) nanoparticles with 10 Hz is that, more Nb/C atomic ratio % was obtained with respect to the case of without moving graphene powder (0 Hz). This is described in section 4.1.1.

**Fig 4.9 (a) De-convolution of the O 1s core level (b) variations of Nb/C and Stoichiometry with respect to different time of deposition**

### 4.4.2 XRD analysis of undecorated Graphene and Nb\(_2\)O\(_5\) doped graphene

Fig 4.10 (a) illustrates the XRD patterns of the undecorated graphene and decorated graphene with Nb\(_2\)O\(_5\) nanoparticles at different times of deposition. Fig4.11 (a) shows a broad diffraction peak around 25.11° which corresponds to the (002) diffraction peak of few layer graphene. The weak peak intensity suggests that the graphene sheets consist of less than 5 layer of graphene. The inset of Fig 4.11 (a) depicts that (002) peak of graphene sheet was shifted toward lower 2θ values after Nb\(_2\)O\(_5\) deposition. This shows that the d-spacing of the graphene sheet increased
upon the deposition of Nb$_2$O$_5$ nanoparticles. The calculated d-spacing values in accordance with 2θ values are 0.354, 0.355, 0.356, 0.3564 and 0.357 nm respectively. This can suggest that distortions in the lattice of graphene induced with increasing of Nb$_2$O$_5$ concentration. Moreover the XRD patterns show linear trend in the full width at half-maximum (FWHM) of (002) peak as a function of Nb/C ($sp^2$). The evaluated of the values of the (FWHM) of the 002 peak of the graphene as function of Nb/C ($sp^2$) ratio are presented in Fig 4.10 (b). The FWHM of the (002) peak increased from 4.54 and reached 4.92 with deposition of Nb$_2$O$_5$ nanoparticles in a ratio Nb/C ($sp^2$) = 1.51 at.ratio (%).The broadening of the (002) peak indicates that, structural defects were pronounced in the structure of graphene with decoration of Nb$_2$O$_5$ nanoparticles onto graphene sheets.

The notable feature in the XRD pattern is that 002 peak shifted more towards lower angles values with respect to the decorated Nb$_2$O$_5$ nanoparticles without moving graphene powder, which have been discussed above in section( 4.1.2). The same deposition times were used in both
cases. The more likely reason of this high shift is due to fact that with vibration of graphene powders more Nb$_2$O$_5$ contents are deposited to the graphene rings, which generates more distortion in the plane of graphene.

4.4.3 Raman Spectroscopy of Nb$_2$O$_5$ decorated graphene via given vibration to graphene powder

The Raman spectra of undecorated graphene and Nb$_2$O$_5$ decorated graphene by rising deposition time are shown in Fig 4.11 (a). In the previous section (4.1.3) we presented the Raman spectra of decorated graphene with Nb$_2$O$_5$ nanoparticles without moving the graphene powder during the deposition and discussed the upshift of G and 2D peaks upon the deposition of the Nb$_2$O$_5$ nanoparticles. Now in this section 10 Hz powder vibration frequency with 32 µm amplitude was given to the graphene powder during the deposition.

![Raman spectra of undoped GNPs and Nb$_2$O$_5$ doped GNPs at different time of deposition](image)

Fig 4.11 (a) Raman spectra of undoped GNPs and (b) positions of the G and FWHM (G) vs Nb to C (%) Nb$_2$O$_5$ doped GNPs at different time of deposition
Again four peaks were observed for all samples, which correspond to the D, G, 2D and D+G bands respectively. More likely, strong variation in the FWHM and position of the G and 2D were observed of graphene powder after the deposition of Nb$_2$O$_5$ nanoparticles.

The upshift in the G and 2D were detected after the deposition of the Nb$_2$O$_5$ nanoparticles. The upshift in the G and 2D increased with the stepping up the deposition time. The maximum upshift in the G and 2D of 9.21 cm$^{-1}$ and 7.8 cm$^{-1}$ were observed after the deposition of the Nb$_2$O$_5$ nanoparticles onto graphene powder in a ratio Nb/C (sp$^2$) = 1.51 at.ratio (%). The upshift of G and 2D bands after the deposition of Nb$_2$O$_5$ nanoparticles suggest that, there is strong electronic interaction between the graphene and Nb$_2$O$_5$ nanoparticles due to which the bands of graphene shifted to higher wavenumbers. Based on the reported observation about the upshifted of the G and 2D bands are due to the hole doping and opposite for the electronic doping. Accordingly, the upshift in the G and 2D bands of the graphene upon the deposition of Nb$_2$O$_5$ nanoparticles are due to p doping, whereas the electrons being transferred from graphene to the Nb$_2$O$_5$ nanoparticles and this result is well consistent with XPS analysis.

Additionally, it is interesting to note that the FWHM (G) peak decreased with rising of Nb/C (sp$^2$) atomic ratio (%) and the results are presented in Fig 4.11 (b). The FWHM of G peak decreased from 79.7 cm$^{-1}$ and 73.43 cm$^{-1}$, after the deposition of Nb$_2$O$_5$ nanoparticles in ratio Nb/C (sp$^2$) = 1.51 at.ratio (%). It is well understood that doping has major influence on the Raman spectra. Doping in graphene shifts the Fermi level away from the Dirac point, which decreased the probability of the excited charge carrier recombination [$^{207}$]. It is also well established that the lattice strain can also modify the FWHM of the G peak. Zhen Hua Ni, et al reported that the FWHM of G peak varied with both compressive and tensile strain [$^{249}$]. For the compressive strain the FWHM of the G peak increased and opposite for the tensile strain[$^{228}$]. In
addition to this it has been also reported that the FWHM (G) decreases and the G peak position increases for both electron and hole doping. The FWHM (G) sharpening is due to Pauli blocking of phonon decay into e−h pairs when the e−h gap is higher than the phonon energy \[^{250, 251}\]. Therefore, it can be considered that the reduction FWHM of the G peak is not only due to the doping, but might due to the tensile strain induced in graphene by decoration of Nb_2O_5 nanoparticles.

Generally the intensity ratio of D to G peak I_D/I_G can be used to measure the level of disorder and defects in graphitic materials. It is noticeable that the intensity of the D peak becomes very strong after the deposition of Nb_2O_5 nanoparticles. This indicates that after interaction of graphene with Nb_2O_5 nanoparticles the symmetry of the graphene was broken and which induced the structural defects in the graphene.

Fig 4. 12 Variation of Raman peak intensity ratios of I_D/I_G plotted against the Nb to C atomic ratio (%).
Fig 4.12 shows $I_D/I_G$ the intensity (area) ratio of the decorated graphene with Nb$_2$O$_5$ nanoparticles as a function of Nb/C (sp$^2$) atomic ratio (%). The $I_D/I_G$ ratios are linearly increased with rising of Nb/C (sp$^2$). The $I_D/I_G$ ratios values increased 1.76, when Nb$_2$O$_5$ nanoparticles were deposited onto graphene sheets with a ratio Nb/C (sp$^2$) = 1.51 at.ratio (%) to the value obtained for undoped graphene $I_D/I_G$ 1.64. This suggests that with deposition of the Nb$_2$O$_5$ nanoparticles onto graphene sheets the structural defects in the sp$^2$ framework were enhanced. The in-plane crystalline size was calculated for the decorated graphene with Nb$_2$O$_5$ nanoparticles by using the equation (1). The in-plane crystalline size as a function of Nb/C (sp$^2$) is presented in Fig 4.12. By increasing the Nb/C (sp$^2$) ratio the in-plane crystalline size of graphene decreased. The in-plane crystalline size decreased from the 23.2 nm to 21.2 nm, when the Nb$_2$O$_5$ nanoparticles deposited in a ratio Nb/C (sp$^2$) = 1.51 at.ratio (%)

### 4.5 Effect of Nb$_2$O$_5$ nanoparticles on the structural and chemical properties of graphene powder deposited by varying the RF power values

In the above two sections, the interaction of the sputtered particles with graphene by keeping constant the sputtered particles energy with constant RF power value was presented. The structural defects induced in graphene plane with interaction of the sputtered and plasma species. The main goal of this work is to study the interaction of the Nb$_2$O$_5$ nanoparticles with graphene sheet deposited by varying the RF power values. By changing the RF power values to Nb$_2$O$_5$ target different amounts of Nb$_2$O$_5$ nanoparticles were obtained on the graphene sheets. The Raman and X-ray diffraction techniques were used to investigate the structural defects. The chemical analysis of the decorated graphene with Nb$_2$O$_5$ nanoparticles were performed by using XPS. Moreover the process parameters are presented in table 4.3.
Table 4.3 the process condition of decorated graphene with Nb$_2$O$_5$ nanoparticles

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<thead>
<tr>
<th>Sample #</th>
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<th>Powder vibration frequency (Hz)</th>
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4.5.1 Chemical analysis of undoped graphene and Nb$_2$O$_5$ doped graphene at different RF power

XPS analysis was performed for the decorated graphene with energetic sputtered Nb$_2$O$_5$ nanoparticles. Fig 4.13 depicts the XPS spectra of decorated graphene with Nb$_2$O$_5$ nanoparticles deposited at different RF power values. The high resolution XPS spectra of the undecorated graphene and decorated graphene at different RF power values are presented in Fig 4.13 (a). The C 1s peak is asymmetric with a long tail extending to the high binding energy region. The C 1s core levels were de-convoluted into three components. The characteristic and features of the de-convoluted components are similar to those which are explained in the section of 4.3.1. More importantly, downshifts in the C 1s core levels of graphene were observed after the deposition of Nb$_2$O$_5$ nanoparticles. The downshift in the C 1s core levels of graphene increased by the increasing the RF power values. The maximum downshift of 0.18 eV of C 1s core level was observed upon the deposition of Nb$_2$O$_5$ nanoparticles in a ratio (Nb/C sp2= 2.09 at. %), at 100 W RF power value. Literature surveys suggest that, when graphene interacted with metal oxide the charge is expected to transfer at the interface between the contacted materials due to the difference of work function. Using the C 1s peak of undoped graphene as a reference for the
neutral charge transfer graphene, then the shift of 0.18 eV to lower binding energy after the interaction of Nb$_2$O$_5$ corresponds to a p type doping of graphene. The doping of graphene by metal oxide at interface is well established phenomena [23]. Consequently the charge transfer between the Nb$_2$O$_5$ and graphene due to the difference of the work function.

![Graphene XPS spectra](image)

**Fig 4.13** XPS spectra of graphene powder with incrementally increased Nb$_2$O$_5$ contents by varying the RF power values (a) (a) Shift in the C 1s core levels position upon Nb$_2$O$_5$ deposition (b) Nb 3d core level spectra with positions of the Nb$^{5+}$ peaks. [Process pressure = 6 Pa, Time=15 min, Frequency = 10 Hz]

Fig 4.13 (b) shows XPS spectra of the Nb 3d peaks for the Nb$_2$O$_5$ nanoparticles decorated graphene surface with rising RF power values. The Nb3d$_{3/2}$ and Nb3d$_{5/2}$ peaks are located at 207.89 eV and 210.64 eV, respectively. The binding energies of these photoelectron peaks are characteristic of Nb$^{4+}$ states. It is interesting to note that, the Nb 3d core level shifted toward the lower binding energy by increasing the RF power values. The maximum downshift of 0.24 eV in the Nb 3d$_{5/2}$ was observed after the deposition of Nb$_2$O$_5$ nanoparticles at 100 W. More likely
reason for the downshift of the 3d_{5/2} is that, charge transfer between the graphene and Nb_{2}O_{5} nanoparticles are occurred at the interface. Due to the difference of the work function between graphene (4.3 eV) and Nb_{2}O_{5} nanoparticles (4.70 eV) electrons are transferred from the graphene to Nb_{2}O_{5} band. Therefore, in order to align the band between the graphene and Nb_{2}O_{5} the band of Nb_{2}O_{5} bend towards the interface happened and the binding energy values of the Nb_{2}O_{5} decreased.

The O1s XPS core level of decorated Nb_{2}O_{5} nanoparticles on graphene surface at 100 W are presented in Fig. 4.14 (a). The O 1s core level displays an asymmetric shape at higher binding energy values. The O 1s peak was fitted by three Gaussian components. The main component (OI) located at binding energy (530.89 eV) is assigned to the O^{2-} bound to Nb^{5+}. Two shoulder components towards the higher binding energies values located at 532.12 eV and 533.3 eV can be assigned to the C=O and C-O bonds respectively.

More interestingly, OI/Nb ratios for the decorated graphene with Nb_{2}O_{5} nanoparticles at different RF power values were estimated from the XPS analysis. The measured values of the OI/Nb ratio as a function of RF power values are depicted in Fig 4.14 (b). The OI/Nb ratio decreased from 2.47 and reached 2.26, when RF power values were varied from 40 W to 100 W. Also the Nb/C sp^{2} atomic ratio (%) increased from 0.69 and reached to 2.09 atomic ratios (%) upon the deposition of Nb_{2}O_{5} nanoparticles at 100 W. These results indicate that by the deposition of Nb_{2}O_{5} nanoparticles the oxygen vacancies generates into the lattice of Nb_{2}O_{5}. The oxygen vacancies in the lattice Nb_{2}O_{5} increased by raising the RF power values. To address this point, the vacancy formation mechanisms involve direct removal of oxygen from Nb_{2}O_{5} lattice by the interaction plasma energetic species.
4.5.2 XRD of undoped Graphene and Nb$_2$O$_5$ decorated graphene at different RF power

The XRD patterns of undoped graphene and decorated graphene with Nb$_2$O$_5$ films deposited by varying the RF power values are presented in Fig 4.15 (a). The undoped graphene powder shows a broad and low intensity peak centered at $2\theta = 25.36^\circ$ which corresponds to the few layers graphene planes. The $2\theta$ position of (002) of graphene powder gradually shifts toward the lower angle value by increasing the RF power values. The evaluated values of the undecorated graphene and for the decorated values as a function of Nb/C sp$^2$ are presented in Fig 4.15 (b). The shift of (002) peak toward the lower angle values after the deposition of the Nb$_2$O$_5$ nanoparticles suggest that, the d spacing of the graphene sheets increased by raising the Nb/C sp$^2$. The calculated d-spacing values in accordance with $2\theta$ values are 0.351, 0.3524, 0.3526, 0.353 and 0.355 nm respectively. More importantly the XRD patterns show systematic changes in the full width at half-maximum (FWHM) of the (002) peak as a function of Nb/C (Sp$^2$) are depicted in Fig 4.15 (b). The broadening of (002) peak of graphene powder after the interaction
of Nb$_2$O$_5$ nanoparticles deposited by varying the RF power values indicates that the defects are
pronounced in the graphene framework.

![XRD patterns of the undoped graphene](image)

![Variation of the 2θ angle of the (002) and Nb2O5 and doped graphene at different RF Power](image)

**Fig 4.15** (a) XRD patterns of the undoped graphene (b) Variation of the 2θ angle of the (002) and Nb2O5 and doped graphene at different RF Power

**4.5.3 Raman Spectroscopy of undoped graphene and Nb$_2$O$_5$ doped graphene at different RF power values.**

Fig 4.16 (a) present the Raman spectra of the undecorated graphene and decorated graphene with Nb$_2$O$_5$ nanoparticles deposited at different RF power values. In all Raman spectra, the characteristic G and 2D bands of graphene (centered at ≈1586 cm$^{-1}$ and ≈2646 cm$^{-1}$, respectively) are present. The D and D+G bands (≈1330 cm$^{-1}$ and ≈2920 cm$^{-1}$, respectively) are also present in the spectra and typically suggest the presence of defects in the graphene lattice like edges and disordered carbon.

It is reported that significant changes occur in the properties of graphene, in specific its electronic structure and phonon frequencies when holes or electron are added by the interaction
with metal or metal oxide \(^{26}\). It was recently revealed that due to the charge transfer mechanism the Fermi level of graphene modulated \(^{252}\). The charge transfer between the graphene and metal oxide interaction is a well-known phenomenon \(^{253}, \, 254\). The induced charge transfer between the graphene and metal oxide which modifies the electronic properties of graphene can be understood by using characteristic Raman spectra of graphene. The confirmation of the charge transfer between the graphene and metal oxide can be identified by measuring the position of D, G or 2D bands or their ratios. It is also well established that the, the G and 2D bands of the graphene was shifted to higher frequency upon the p doping graphene with metal oxide \(^{255}\). A low blue shift of 4 cm\(^{-1}\) and 3 cm\(^{-1}\) were observed upon the deposition of Nb\(_2\)O\(_5\) nanoparticles at 40 W RF power values. The upshifts in G and 2D bands increased with raising RF power values. The maximum upshift of G and 2D by 11.5 cm\(^{-1}\) and 9.5 cm\(^{-1}\) were observed, when the Nb2O5 nanoparticles were deposited onto graphene sheets in ratio Nb/C sp\(^2\)=2.09 atomic ratio (\%) at 100 W RF power value. The blue shift in G and 2D peaks of graphene after the decoration of Nb\(_2\)O\(_5\) nanoparticles suggest that, the charge are transferred between the graphene and Nb\(_2\)O\(_5\) nanoparticles, where the electron being transferred from graphene to Nb\(_2\)O\(_5\) nanoparticles. It is therefore clear that Nb\(_2\)O\(_5\) films interact with graphene as electron accepter and the charge is the transfer between the graphene and Nb\(_2\)O\(_5\) nanoparticles.

Interestingly the FWHM of G peak decreased with interaction of Nb\(_2\)O\(_5\) nanoparticles. Further the doping confirmation can be extracted from the FWHM of G peak. It has been reported that the FWHM of G peak decreases with electrons and holes doping. Fig 4.16 (b) depicts the FWHM of G peak as a function of the Nb/C sp\(^2\) atomic ratio. The FWHM of G peak is decreased as a function of increasing Nb/C (sp\(^2\)) by varying the RF power values. The FWHM of G peak
decreased from 78.68 and reached to 71.8 cm$^{-1}$ when the Nb$_2$O$_5$ nanoparticles were deposited in a ratio of Nb/C (sp$^2$) = 2.09 % to C (Sp$^2$).

Fig 4.16 (a) Raman spectra of undoped GNPs and (b) positions of the G and FWHM (G) vs Nb to C (%) Nb$_2$O$_5$ doped GNPs at different RF powers

The sharpening of the FWHM of G peak after the interaction Nb$_2$O$_5$ films corresponding to the doping. In the section 4.4.3, we discussed that the FWHM of G peak decreased, when the tensile or compressive strain was developed in the lattice of graphene sheets. Our XRD results demonstrate that with deposition of the Nb$_2$O$_5$ nanoparticles onto graphene sheets the tensile strain was established in the lattice of graphene sheets. From these observations, it can be considered that the reduction of FWHM of G peak not only doping also might be due to the tensile strain induced in graphene sheets.
It is well known that the intensity ratio of D band to G band ($I_D/I_G$) was used to quantify the level of defects and disorderliness in the structure of the graphene. The $I_D/I_G$ is directly related to the diameter of the crystalline cluster (La) in the graphite system. Fig. 4.17 presents the $I_D/I_G$ ratios as a function of the Nb/C (sp2), when Nb$_2$O$_5$ nanoparticles were deposited onto graphene sheets by increasing the RF power values. 

![Graph showing ratio vs. Nb/C atomic ratio](image)

**Fig 4.17** Variation of Raman peak intensity ratios of $I_D/I_G$ plotted against the Nb to C atomic ratio (%).

The $I_D/I_G$ ratio of the increased from 1.66 and reached to 1.82, when the Nb$_2$O$_5$ nanoparticles were deposited in a ratio Nb/C (sp$^2$) = 2.09 atomic ratio (%). This can suggest that with interaction of sputtered particles and energetic plasma species induced defects in the sp$^2$ framework of graphene. To address this point, it has been well established that by increasing RF power values the sputtered particles and plasma species gain more kinetic energy during the deposition and interact with graphene surface more energetically. Due to the interaction of the energetic plasma species and sputtered particles with graphene the defects are introduced in the
graphene rings. The defects are increased with interaction of the high energetic species and sputtered particles.

4.6 Conclusion Remarks:

In summary, the influence of the Nb$_2$O$_5$ concentrations on the structural, chemical, morphological and magnetic properties of graphene deposited by varying the deposition process parameters were investigated. Based on the variation of Nb$_2$O$_5$ concentrations by varying the deposition process parameters the chapter was categorized in three sections.

In section 4.3, the effect of Nb$_2$O$_5$ concentrations on the structural, chemical and magnetic properties were studied. The Nb$_2$O$_5$ nanoparticles were deposited on the surface of graphene by varying the deposition time via no vibration given to graphene powders. The structural properties of the decorated graphene were investigated using X-ray diffraction and Raman spectroscopy. From the X-ray diffraction analysis it was observed that by decoration of graphene with Nb$_2$O$_5$ nanoparticles the lattice of graphene distorted and the d-spacing of the layers of graphene increased. Raman study revealed that that the frequency of the G band undergoes blue shift after the interaction of Nb$_2$O$_5$ nanoparticles. The blue shift can suggest that Nb$_2$O$_5$ nanoparticles interact with graphene as an electron acceptor and the charge transfer from graphene to Nb$_2$O$_5$ nanoparticles. Also defects and disorderness in the graphene were increased after the decoration of Nb$_2$O$_5$ nanoparticles. X-ray photoelectron spectroscopy analysis shows that electron transfer from graphene to Nb$_2$O$_5$ nanoparticles is responsible for the p-type doping of graphene. The morphology and size distributions of the decorated Nb$_2$O$_5$ nanoparticles on the graphene powder were confirmed by transmission electron microscopy (TEM). The size of the decorated Nb$_2$O$_5$ nanoparticles on the graphene sheet is around 15 to 20 nm. The magnetic data indicate that
formation of Nb₂O₅ nanoparticles anchored to the graphene matrix. The ferromagnetic behaviors of graphene are significantly changed by the interaction of Nb₂O₅ nanoparticles.

In section 4.4, the influences of the Nb₂O₅ nanoparticle on the structural and chemical properties of the graphene were discussed. The interactions of the graphene with Nb₂O₅ nanoparticle deposited by RF sputtering via given 10 Hz vibration to the graphene powder during the deposition process were investigated by X-ray diffraction (XRD), Raman spectroscopy and X-ray photoelectron spectroscopy. The XRD result demonstrates that the d-spacing of the graphene sheets increased with the interaction of the Nb₂O₅ nanoparticle. The strong p-doping effect was clearly evident in the Raman spectroscopy data where the positions of the G of graphene progressively upshifted after the increasing the Nb₂O₅ concentrations. Increasing intensity of the D peak of graphene after the interaction of Nb₂O₅ nanoparticles suggest that the defects and disorderness were induced in the structure of graphene. The chemical environment of the surface composition of the decorated graphene with Nb₂O₅ nanoparticles was recorded by X-ray photoelectron spectroscopy. By stepping up the deposition time the Nb percentage in host graphene was regulated ranging 0.48 to 1.51 %.

In section 3.5 the graphene powders were decorated with Nb₂O₅ films by varying the RF power values ranging from (40-100 W). Different amount of Nb₂O₅ concentrations were obtained on the graphene surface by varying the RF power value to Nb₂O₅ target. It has been reported that by increasing the RF power values during the plasma deposition, more sputtered particles extracted from the target having high kinetic energies. The interaction of the high energetic sputtered particle with graphene sheet induced structural defects. The chemical and structural properties of
decorated graphene with energetic sputtered particles were characterized by Raman spectroscopy; X-ray diffraction X-ray photoelectron spectroscopy. The XRD investigation shows that with the interaction of the energetic sputtered particles the lattice of the graphene was distorted. The d spacing of graphene was linearly increased with interaction of the energetic sputtered particles. Raman study revealed that with interaction of the graphene with Nb$_2$O$_5$ films blue shift of the G band observe, which are consistent with p-type doping. Finally, XPS measurements of the graphene/Nb$_2$O$_5$ interface suggest p-type doping of graphene due to charge transfer at the interface as a consequence of the high work function of Nb$_2$O$_5$.

Concluding this chapter, the interface between Nb$_2$O$_5$ nanoparticle and graphene sheets were presented. The detailed structure, chemical, morphological and electronic properties were discussed. In next chapter # 5, the structural, chemical, morphological and electronic properties of the decorated graphene sheets with Mg nanoparticle will be presented.
Chapter # 5

Effect of Mg crystalline nanoparticles and crystalline film on the structural and chemical properties of graphene powder

5.1 Introduction:
Recently, owing to the exceptional material’s properties, a remarkable research attention has been focused on graphene. Meanwhile it is believed that the graphene, which has high surface area, serves as an ideal support for anchoring well-dispersed nanoparticles for the improvement of its catalytic action toward the hydrogen dissociation. It has been reported that Magnesium based hybrid materials a promising candidates for the hydrogen storage, because of their high gravimetric and volumetric hydrogen storage capacities. In this chapter we demonstrate different approaches to employ graphene as hydrogen storage materials. First, strategy is to decorate the graphene with very small Mg nanoparticles to enhance the hydrogen sorption. In parallel, different RF process parameters will be varied to achieve the well dispersed nanoparticles onto graphene sheets in the range in the range of 5-10 nm. On such scale, quantum size effects enter at play lowering the \( \text{H}_2 \) desorption temperature from 350°C typical of bulk Mg hydrides to 140°[256]. In order to achieve the small Mg nanoparticles on the surface of graphene powder different depositions process parameters like RF power, Powder vibration frequency and deposition time were varied. Based on the deposition conditions used, this chapter is divided into three sections; this is categorized like this;

❖ For the results described in section I, the chemical structural and electronic properties of decorated graphene with Mg nanoparticles will be discussed.

❖ For the results reported in section II, different levels of Mg nanoparticles were obtained onto graphene sheets by increasing the deposition time. The structural, chemical and electronic properties of the decorated graphene with Mg nanoparticles will be displayed.
For the results described in section III, Mg nanoparticles were decorated onto graphene sheet by varying the powder vibration frequencies. Structural analysis was investigated by Raman and x-ray diffraction and chemical analysis were performed with XPS analysis.

5.2 Experimental details

The crystalline Mg nanoparticles and crystalline films were deposited onto graphene powders by radio frequency sputtering in Ar plasma. A high purity Mg disc (99.99%) with 5 cm diameter was used as a sputtering target. Powder vibrating stage was developed for the uniform distribution of Mg nanostructures onto graphene surface. More specific details for each section are given below:

- To obtain different levels of Mg content onto graphene sheets the power applied to the Mg cathode was varied from 30 to 75 W, corresponding to self-bias voltage ranging between -157 to -273 V. The powder vibration frequency and deposition time was fixed at 10 Hz and 18 min respectively. The total process pressure was fixed at 6 Pa.

- In order to achieve different amounts of the Mg nanoparticles onto graphene, the graphene powder was decorated with Mg nanoparticles deposited by stepping up the deposition time (6 to 27 min). The self-bias voltage and power applied to Mg target was fixed at -158 V and 40 W respectively. The total process pressure and powder vibration frequency for each deposition were kept at 6 Pa and 10 Hz respectively.

- The Mg nanoparticles were deposited onto graphene sheets by using different powder vibration frequencies. For the well-distributed Mg nanoparticles onto graphene sheet the powder vibration frequency was varied from 0≤ω≤100 Hz with constant amplitude of 32 μm. The process pressure and power applied to Mg target were fixed at 6 Pa and 40 W respectively. The deposition time were kept constant at 27 min.
5.3 The effect of crystalline Mg nanoparticles on the properties of graphene powder deposited at different RF power values

The main goal of this work is to decorate graphene with well dispersed Mg nanoparticle and study the interaction of the energetic sputtered particles deposited by increasing RF power values. Different amount of Mg concentrations were obtained by changing the RF power values. By increasing the RF power values the energy of the sputtered ions were increased and reached at surface of the graphene with high kinetic energy. The influence of the energetic sputtered particles and plasma species on the structural and chemical properties of the graphene will be discussed in this section. Different characterization techniques were used to investigate the structural defects induced in graphene by the interaction of the energetic sputtered particles. The Raman and XRD were used to study the structural defects and for the chemical analysis XPS was used. The morphology of the deposited Mg nanoparticles onto graphene was examined by TEM analysis. Moreover the process parameters are presented in table 5.1.

Table 5.1 the process condition of decorated graphene with Mg nanoparticles

<table>
<thead>
<tr>
<th>Sample #</th>
<th>RF Power (W)</th>
<th>Process pressure (Pa)</th>
<th>Deposition Time (min)</th>
<th>Powder vibration frequency (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>6</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>45</td>
<td>6</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>6</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>6</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>75</td>
<td>6</td>
<td>18</td>
<td>20</td>
</tr>
</tbody>
</table>
5.3.1 TEM analysis of graphene sheets decorated with Mg nanoparticles at 27 min of deposition.

The surface morphology of the decorated graphene with Mg nanoparticles was investigated using Transmission electron microscopy (TEM). Fig 5.1 (a, b) presents the TEM micrographs of the deposited Mg nanoparticles onto graphene 27 min of deposition. TEM micrograph of Mg/graphene composite shows that Mg nanoparticles are uniformly distributed onto graphene sheet. These nanoparticles were deposited at powder vibration frequency (10 Hz). Fig (b) shows that the deposited particles distributed uniformly onto graphene sheets. However, the deposited Mg nanoparticles made aggregates onto graphene sheets. Moreover the deposited Mg nanoparticles are in spherical shape and having an average particles size of 20-25 nm.

![Fig 5.1 TEM images (A-B) of Mg decorated onto graphene at 27 min of deposition](image)
5.3.2 XPS analysis of undoped graphene and Mg doped graphene at different RF power values

To evaluate the influence of energetic sputtered particles onto graphene X-ray photoelectron spectroscopy (XPS) measurements were performed. Fig 5.2 (a) shows the XPS spectrum of the C 1s core level of the undoped graphene and decorated graphene with Mg nanoparticles deposited at different RF power values. The high resolution C 1s XPS spectra of the undoped graphene were de-convoluted into three components. The de-convoluted components of the undecorated graphene are centered at 284.45, 285.23 and 286.2 eV, which are assigned to the C-C (sp²), C-H/C-C (sp³) and C-O bonds respectively.

![Fig 5.2 (a) XPS spectra acquired on graphene powders with incrementally increased Mg contents by varying the RF power values](image)

![Fig 5.2 (b) Mg 2p core level spectra](image)

**Fig 5.2 (a)** XPS spectra acquired on graphene powders with incrementally increased Mg contents by varying the RF power values (a) Shift in the C 1s core levels position and the shift of this position upon Mg deposition (b) Mg 2p core level spectra (RF power =30 to 75 W, Process pressure=6 Pa, Time= 18 min and powder vibration frequency= 10 Hz)
More interestingly, the C 1s core level of graphene shifted towards the lower binding energy values upon the deposition of the Mg nanoparticles onto graphene. The downshift of the C 1s core level of the graphene toward the lower increased after increasing the RF power values. The downshift of C 1s peak about 0.13 eV were observed after the deposition of Mg nanoparticles onto graphene at 75 W of deposition. The shift in the C 1s core level is the consequence of the charge transfer (n-type or p-type) between interfaces of the graphene and nanostructure. It is also revealed that for the doping, the charge is transferred between the various nanostructures and graphene due to the difference of work function values. It is well understood that the work function of the metal is dramatically changed by the unintentional metal oxidation, when it was exposed to the air and also to change the doping type i.e from n-type to p-type doping or vice versa [257]. The reported work function value for the Mg is 3.68 eV and further increased to 4.94 eV due to the native surface oxide [258, 259]. From the XPS analysis it was found that, the deposited Mg nanoparticles onto graphene sheets are oxidized by exposed to the air moisture. Consequently the downshift of C 1s core level of the deposited Mg nanoparticles onto graphene sheets suggests that graphene is p doped with Mg nanoparticles upon the surface oxidation of the Mg nanoparticles, where the electrons are transferred from graphene (4.33 eV) [260] to MgO due to the high work function of the MgO (4.96 eV).

The high resolution spectra of the Mg 2p peak for the decorated graphene with Mg nanoparticles deposited by increasing the RF power values are presented in Fig 5.2 (b). The Mg 2p spectra were de-convoluted into two components, located at 50.93 eV and 52.85 eV respectively. The peak located at 51.43 eV belongs to the Mg-O bond [261, 262], and the component which is located at 52.85 eV is assigned to the Mg-OH bond [263], meanwhile no metallic Mg peak was observed in the XPS spectra. This suggests that the deposited Mg nanoparticles were surface oxidized due
to exposing to the air. The peak position of Mg 2p, C 1s and the O 1s spectra and chemical composition for the decorated graphene with Mg nanoparticles are shown in table 1. The composition of the Mg-O and Mg-OH component for all the decorated graphene sheets with Mg nanoparticles at different RF power values were determined on the basis of the area under the whole component of the Mg-O (I) and area under the component of Mg-(OH) (II) of the Mg 2p spectrum and the results are presented in table 1. It can be seen that, with increasing RF power values, the composition of Mg-O and Mg-(OH) gradually increased. This suggests that as deposited Mg nanoparticles are mainly consisting of MgO and as well as few residual OH group adsorbed from the air moisture.

The O 1s high resolution XPS spectrum of Mg nanoparticles deposited onto graphene in Ar plasma is shown in Fig 5.3 (a).

![Image](image1.png)

**Fig 5.3** (a) O 1s core peak and its de-convolution (b) variations of Mg/C sp2 atomic ratio with RF Power

It is shown that after the deposition of Mg nanoparticles onto graphene the O 1s spectra become asymmetric toward the higher binding energy side. The O 1s spectrum is de-convoluted into two
components. The main component at lower B.E 531.09 eV is assigned to O\(^{-2}\) bound to Mg\(^{+2}\)\[264\], whereas toward the higher B.E 533.45 eV is attributed to the Mg-OH bond \[265\]. Moreover the O/Mg ratio was calculated to estimate the stoichiometry of oxidized Mg nanoparticles onto graphene sheet. The stoichiometries of the decorated graphene with Mg nanoparticles at different RF power values are present in table 1.

The OI/Mg ratio OI which bonded to Mg (I) in the Mg 2p spectrum for the deposited samples were estimated on the bases of the area under the Mg components and area under the OI component of the O 1s spectra. The measured OI/Mg(I) ratios were found between 0.99 and 0.94 (see Table 1) and 1 is the ideal values for the MgO crystal. This shows that deposited Mg nanoparticles on graphene surface under-stoichiometry; this might be due to the adsorbed of (OH) group. Moreover, the Mg/C sp\(^2\) as a function of the RF power values is presented in Fig 5.3 (b). The Mg/C sp\(^2\) ratio increased from 13.5 atomic ratios (%) and reached to 28.37 atomic ratios (%), when the RF power values varied from 30 W to 75 W for the deposited of Mg nanoparticles onto graphene sheets.

**Table 1:** Binding energy values of C 1s and Mg 2p core-levels, O/Mg atomic ratio, MgO and Mg(OH)\(_2\) concentration for increasing power applied Mg target

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>BE (C 1s) (eV)</th>
<th>BE (Mg-O) (eV)</th>
<th>OI/Mg(I)</th>
<th>MgO (%)</th>
<th>Mg(OH)(_2) (%)</th>
<th>Mg(OH)(_2)/MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>284.45</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>284.40</td>
<td>51.43</td>
<td>0.96</td>
<td>8.62</td>
<td>0.71</td>
<td>0.082367</td>
</tr>
<tr>
<td>45</td>
<td>284.39</td>
<td>51.26</td>
<td>0.95</td>
<td>8.97</td>
<td>1.2</td>
<td>0.133779</td>
</tr>
<tr>
<td>50</td>
<td>284.39</td>
<td>51.22</td>
<td>0.95</td>
<td>9.20</td>
<td>1.26</td>
<td>0.136957</td>
</tr>
<tr>
<td>60</td>
<td>284.38</td>
<td>51.11</td>
<td>0.94</td>
<td>11.21</td>
<td>1.86</td>
<td>0.16132</td>
</tr>
<tr>
<td>75</td>
<td>284.32</td>
<td>50.98</td>
<td>0.92</td>
<td>13.05</td>
<td>2.87</td>
<td>0.219923</td>
</tr>
</tbody>
</table>
Additionally, the obtained ratio between the MgO and Mg(OH)$_2$ are presented in table (1). It was found that the ratio between the MgO and Mg(OH)$_2$ ratio linearly increased by raising RF power values. This behavior can be explained like this, in the above text, we discussed that Mg/C sp$^2$ ratio increased and the OI/Mg(I) ratio under stoichiometric. This behavior indicates that the deviation from stoichiometry of MgO nanoparticles at different RF power values might be due the hydroxylation. Hydroxylation increased onto the surface of Mg nanoparticles by rising RF power values. Therefore, the ratio between the MgO and Mg(OH)$_2$ increased linearly by rising RF power values.

5.3.3 XRD analysis of undoped graphene and Mg doped graphene at different RF power values

The XRD pattern of the undoped graphene and decorated graphene with Mg nanoparticles deposited at different RF power values (30 to 75 Watt) are shown in Fig 5.4(a). The peak positions of the undoped graphene in the XRD pattern at 25.11$^\circ$ and 42.85$^\circ$ are assigned to the reflection of the plane (002) and (100) respectively, which corresponds to the diffraction peaks of few layers graphene [266]. On the other hand for the decorated graphene with Mg films additional diffraction peaks at 2$\theta$ = 31.83$^\circ$, 34.05$^\circ$, and 36.35$^\circ$ were also observed. These peaks can be indexed to the three reflection peaks (001), (002) and (101) planes of hexagonal Mg structure (JCPDS 04-0770) [267]. The crystalline nature of the Mg nanostructure in the Mg/graphene composite was confirmed by XRD investigation. The characteristic peak (101) plane confirmed that the Mg metal is deposited onto graphene sheet. No other impurities peaks were observed in the XRD pattern. This suggests that only Mg nanoparticles were anchored to the graphene sheet. The intensity of Mg (101) monotonically increased with gradual increase RF
power values from 30 to 75 W. The average crystallite size of the decorated Mg nanoparticles was estimated using the Scherer’s formula \[ D = \frac{K\lambda}{\beta \cos \theta} \]...

Where \( \beta_{hkl} \) is the full width at half-maximum (FWHM) of the peak considered (in rad), \( \theta \) is the Bragg angle and \( D \) is the average crystallite size where \( k \) is the shape factor and \( K \) has a typical value is approximately equal to 0.9 [12].

Fig 5.4 (a) XRD patterns of decorated graphene with Mg (b) crystallite sizes of the decorated Mg nanoparticles at different RF power values

The average crystallite size of the Mg films as a function of the RF power values are shown in Fig 5.4 (b). We observed that with increasing the RF power values from 30 W to 75 W the FWHM of the characteristic peaks were reduced and a slight increase in the average crystallites size of the Mg crystal. The crystallite sizes of the deposited Mg nanoparticles onto graphene sheet as a function of RF power values are presented in Fig 5.4 (b). It can be seen that crystallite size of deposited Mg nanoparticles increased from 15.4 nm and reached 19.44 nm, when the RF
power values varied from 30 W to 75 W. It is well presumed that by increasing the RF power values the more sputtered particles were extracted from the target. Addition to this the energy of the sputtered particles increased with rising RF power values. Also it is well known that the deposition rate increased with rising RF power values. The improvement of the crystallite size of the deposited Mg nanoparticles can be explained as follows, by increasing RF power values the plasma species gain more kinetic energy and interacted with target with high kinetic energy and extracted larger particles from target with respect to lower RF power values, or it might be with increasing RF power values more Mg nanoparticles were deposited onto graphene sheets and these nanoparticles made aggregation onto graphene sheet. Consequently with increasing RF power values the growth of the Mg nanoparticles was enhanced.

The (002) peak of the graphene gradually shifted toward lower 2θ values after the deposition of Mg nanoparticles at different RF power values as shown in Fig 5.5. This shows that d spacing of graphene sheets increased by raising the Mg concentration onto graphene sheets. The calculated values of the d-spacing of graphene as a function of Mg/C sp² are illustrated in Fig 5.5.

**Fig 5.5** Variation of the 2θ angle position of the (002) and d-spacing as function of Mg/C at. %
The d-spacing increased from 3.54 nm and reached 3.57 nm, when the Mg nanoparticles were deposited onto graphene sheets in a ratio Mg/C \( \text{sp}^2 = 28.37 \) atomic ratio (%). The FWHM of the (002) peak for decorated graphene with Mg nanoparticles were evaluated using the Lorentzian line function. It was found that the (002) peak of graphene became broadened with rising of Mg concentration onto graphene sheets. This shows that with increasing amounts of the Mg nanoparticles onto graphene surface weak signal were detected from the (002) plane. The weak intensity of the (002) peak suggest that the crystallite thickness of graphene sheets were reduced upon the deposition of the Mg nanoparticles. The peak around \( 2\theta \) position 42.85° corresponding to (100) plane of graphene was weak peak detected after the deposition of Mg nanoparticle at 75 W, which shows that sheet of the graphene were fully anchored by Mg nanoparticles, resulting in lowered degree of graphitization. The behavior can correlate with TEM analysis; Fig 5.1 (b) shows the deposited Mg nanoparticles were anchored over the larger surface area of the graphene sheets.

### 5.3.4 Raman study of undoped graphene and Mg doped graphene at different RF power values

Raman analysis was carried out for the undoped graphene and decorated graphene with Mg nanoparticles to examine doping and mechanical strain. The Raman spectra of the undecorated graphene and decorated graphene with Mg nanoparticles at different RF power values are presented in Fig 5.6 (a). Four characteristic peaks (G, D, 2D and D+G) were detected in the Raman spectra for the undoped graphene and decorated graphene with Mg nanoparticles. The relative shift in the position of G and 2D bands can be used to evaluate the combined the effect of doping and mechanical strain induced in the graphene sheets [6-8]. For the undoped graphene the G band is at 1584.86 cm\(^{-1}\) and the 2D band position is at 2636.87 cm\(^{-1}\). After the deposition
of the Mg nanoparticles at 30 W, the G band shifts to high wavenumbers at $1589.56 \text{ cm}^{-1}$ and the 2D bands of the graphene comparatively unchanged (within standard error) at $2637.76 \text{ cm}^{-1}$. The G and 2D bands were shifted to higher wavenumber by 10.87 and 8.5 cm$^{-1}$ respectively upon the deposition of Mg nanoparticles onto graphene sheet at 75 W RF power value. These shifts could be attributed to doping or mechanical strain induced in the graphene sheets. Recently, it is reported that metal with high lattice mismatch on graphene lead to a significant shifts in G and 2D bands (due to increased strain) [6].

![Raman spectra of undoped graphene and Mg doped graphene at different time of deposition](image)

**Fig 5.6** (a) Raman spectra of undoped graphene and (b) positions of the G and FWHM (G) as a function of Mg/C (%) Mg doped graphene at different time of deposition

When mismatched lattice indices metal like Au (4.08 Å) and Ag (4.05 Å) were deposition onto graphene (2.46 Å) sheet, where (4.08 Å), (4.05 Å) and (2.46 Å) are the lattice constant values of Au, Ag and graphene. For these metals the G and 2D peak Raman shifts are attributed to the mechanical strain and doping is hard to conclude from the Raman studies [269]. In this case of study, it is reported that the shift in 2D band is always greater than the shift in G band, which indicates that mechanical strain dominates over the doping phenomenon. However by the
deposition of metal with matching lattice indices to the graphene like Co, Ni and Mg, the shifts in the G peak is larger compared to the shift in the 2D band and this comparative shift in the position suggested to a successful doping in graphene. It is also reported that the upshifted of G and 2D bands of graphene is due to p doping \[^{26}\]. Based on this observation, the upshift of G and 2D bands of graphene after the deposition of Mg nanoparticles suggests that the graphene is p doped with Mg nanoparticles. The Gaussian function line shape was used to evaluate the FWHM (G) peak of undecorated graphene and decorated graphene with Mg nanoparticles. The evaluated values of FWHM of G peak as function of Mg/C atomic ratio are presented in Fig 5.6 (b). The FWHM of G peak decreased from 78.5 cm\(^{-1}\) to 71.5 cm\(^{-1}\) upon the deposition of Mg nanoparticles onto graphene sheets at 75 W RF power values in a ratio Mg/C = 28.37 at. %. It is reported that reduction of FWHM (G) is due to the charge doping \[^{270}\].

The \(I_D/I_G\) ratio was used to quantify the defects and disorderness level induced in the graphene by the interaction of the energetic sputtered particles. The relationship between the \(I_D/I_G\) and obtained values of Mg/C (sp\(^2\)) atomic ratio by increasing RF power is shown in Fig 5.7. The \(I_D/I_G\) ratios of the decorated graphene with Mg nanoparticles increased as a function of the Mg/C atomic ratio (%). The measured \(I_D/I_G\) ratio for the undecorated graphene was 1.66, suggesting that structural defects were present in the graphene. However after the deposition of Mg nanoparticles onto graphene sheets by increasing RF power the \(I_D/I_G\) ratio were further increased. The \(I_D/I_G\) ratios values were increased to 1.76, when the Mg was deposited in a ratio Mg/C sp\(^2\) = 28.37 %), at 75 W RF power value. This suggests that the structural defects further increased by rising the Mg concentrations onto graphene sheets. The in-plane crystalline sizes of the decorated graphene with Mg nanoparticles were calculated using the using Tuinstra - Koenig relation \[^{247}\]. It was found that the in plane crystalline size of decorated graphene with Mg nanoparticles
decreased from 23.2 nm to 21.5 nm upon the deposition of Mg nanoparticles onto graphene sheets at 75 W RF power value in a ratio Mg/C sp² = 28.37%. This suggest that the sp² domain of graphene decreased by the deposition of Mg nanoparticles onto graphene sheets. The sp² domain of the graphene was distorted with interaction of the Mg nanoparticles. It is well proven that the sp² domain become smaller with increasing the structural defects to graphene plane. L. G. Canado et al reported that the sp² domain become smaller and more distorted upon the increasing the structural to graphene sheets[136].

Fig 5.7 Variation of Raman peak intensity ratios of $I_D/I_G$ and $I_{2D}$ plotted against the Mg to C atomic ratio (%)

5.4 The effect of crystalline Mg nanoparticles on the properties of graphene powder decorated deposited at different times of deposition

In the above sections (5.3) we discussed the deposition of Mg nanoparticles onto graphene by increasing RF power values. The structural defects were investigated by Raman and XRD techniques for the decorated graphene with Mg nanoparticles deposited at different RF power
values. It was found that by increasing the RF power structural defects increased. In this process of deposition we kept the sputter ion energy constant and only increase the amount of Mg nanoparticle onto graphene surface by increasing the deposition time. XRD and Raman were used to investigate the structural defects induced in the sp² framework by the deposition of Mg nanoparticles. For the chemical analysis X-ray photoelectron spectroscopy was used. Moreover the process parameters are presented in table 5.2.

Table 5.2 the process condition of decorated graphene with Mg nanoparticles

<table>
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<tr>
<th>Sample #</th>
<th>RF Power (W)</th>
<th>Process pressure (Pa)</th>
<th>Deposition Time (min)</th>
<th>Powder vibration frequency (Hz)</th>
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5.4.1 XPS analysis of graphene and Mg deposited onto graphene at different times of deposition

Fig 5.8 (a) shows the XPS spectrum of the C 1s core level of the undoped graphene and decorated graphene with Mg nanoparticles deposited at different time of deposition. The high resolution XPS spectra of the undoped graphene were de-convoluted into three components. The main peak with a binding energy 284.69 eV is assigned to carbon in C-C bond with sp² hybridization. Two other small components which have binding energies of 285.34 eV and 286.20 eV correspond to C-H /C-C bond with sp³ hybridization and C-O bond respectively. Fig 5.8 (b) shows the high resolution spectra of the Mg 2p peak for the decorated Mg nanoparticles
deposited by varying the deposition time. It can be seen that by increasing the deposition time the Mg spectra became asymmetric and broadened toward the higher binding energy side. The Mg spectrum was de-convoluted into two peaks. The following two components were observed one at 50.94 eV and the other at 53.7 eV. The peak of 50.90 eV may be ascribed to MgO and the peak of 53.78 eV correspond to Mg (OH)₂\(^2\).\(^{271,272}\).

Fig 5.8 (a) XPS spectra of graphene powder with incrementally increased of Mg contents by varying the deposition time (a) a) Shift in the C 1s core levels position and the shift of this position upon Mg deposition (b) Mg 2p core level spectra (RF power =40 W, Process pressure= 6 Pa, Time= 6 to 27 min and powder vibration frequency= 0 Hz.

Fig 5.9 (a) depicts a high-resolution spectrum of the O 1s peak of decorated graphene with Mg nanoparticles. The O 1s spectra were de-convoluted into two components. The first and main peak at lower binding energy (531.1 eV) can be attributed to the O 1s core peak of O\(^2\) bound to
Mg\(^{+2}\) \(^{[273]}\), whereas a second component (OII) is located at 533.82 eV correspond to Mg(OH)\(_2\) peak \(^{[274, 262]}\).

Additionally, the Mg/C sp\(_2\) atomic ratio was assessed from the XPS analysis. The evaluated values of Mg/C sp\(_2\) ratio as function of the different deposition times are presented in Fig 5.9 (b). It was found that Mg/C sp\(_2\) ratio increased from 6.73 and reached 18.3 atomic ratios (%), when the deposition time varied from 6 min to 27 min of deposition.

Fig 5.9 (a) O 1s core peak and its de-convolution (b) variations of Mg/C and atomic ratio with time

5.4.2 XRD analysis of undecorated graphene and Mg decorated graphene at different times of deposition

The X-ray diffraction (XRD) patterns of undoped graphene and Mg doped graphene decorated by stepping up the deposition time are shown in Fig. 5.10. The characteristic C (002) peak undoped graphene centered at \(2\theta = 25.11^\circ\) belongs to few layers graphene plane. The characteristic C (100) peak is also visible in the XRD patterns. In the case of Mg nanoparticles modified graphene three characteristic peaks were observed. The characteristic peaks are corresponding to (001), (002) and (101) planes of hexagonal structure of metallic Mg, which is
observed at 31.83°, 34.05°, and 36.35°. The average crystallite size of the decorated crystalline Mg nanoparticles was calculated using equation (1).

![XRD patterns](image_url)

**Fig 5.10** XRD patterns of the undecorated graphene and decorated graphene with Mg nanoparticles at different times of deposition

The crystallite sizes of the Mg nanoparticles onto graphene sheet were in the range of 14 to 16 nm. Addition to this 2θ position of C (002) peak is slightly shifted toward the lower 2θ values by increasing the Mg concentration to the graphene plane. The position of (002) peak of graphene as function of the Mg/C sp2 are shown in Fig 5.11. This indicates that the d spacing of graphene sheet increased by raising the Mg concentration to graphene plane. The calculated d-spacing value increased from 0.354 nm and reached 0.357 nm upon the deposition of Mg nanoparticles at 27 min of deposition in a ratio Mg/C sp2 = .18.3 atomic ratio (%). Moreover the FWHM of the (002) peak of graphene becomes broadened by the deposition of Mg nanoparticle onto graphene sheet. The broadening of (002) peak after the deposition of the Mg nanoparticles indicates the
structural defects were induced in the graphene framework. The structural defects increased by raising the Mg concentration to the graphene plane.

![Graph showing (002) peak position and d-spacing vs Mg/C (%)](image)

**Fig 5.11** Variation of the 2θ angle position of the (002) and d-spacing as function of Mg/C at. %

### 5.4.3 Raman study of undecorated graphene and Mg doped graphene at different times of deposition

Various amounts of the Mg nanoparticles were deposited on the surface of graphene to study the interaction between the Mg nanoparticles and graphene. Fig 5.12 (a) shows the Raman spectrum of undoped graphene and decorated graphene with Mg nanoparticles by increasing the deposition time. Four characteristic peaks at 1327.89, 1585.85, 2635 and 2920 cm\(^{-1}\) were observed in the Raman spectrum for undoped graphene. These peaks correspond to the G-band, D-band; 2D band and D+G band respectively. It is a well effective process for distinguishing the doping type or mechanical strain by comparing G and 2D peaks position between decorated graphene with Mg nanoparticles and undoped graphene \[^{110}\]. It is also well reported that the mechanical strain is dominates over on doping, if the shift in 2D band is larger than the shift in G band. Our XRD
results shows that the tensile strain induced in the plane of graphene, but in case of tensile strain the G and 2D band is shifted toward the lower wavenumbers. The evaluated Raman spectrum for the decorated graphene with an increasing amount of Mg nanoparticles is presented in Fig 5.12 (a) (enlarged view) with a comparison to the undoped graphene. When the amount of Mg nanoparticles increased onto graphene sheet the G peak blue-shifts gradually from 1586 to 1590.56 cm\(^{-1}\) as a function of the increasing Mg/C (sp2) are shown in Fig 5.12 (b) suggesting p-type doping. Similar result is also reported by the Xiuyi Lin etal \([^{111}]\).

**Fig 5.12 (a) Raman spectra of undoped graphene and (b) positions of the G and FWHM (G) vs Mg to C (%) Mg doped graphene at different time of deposition**

This shows that there is strong interaction between the Mg nanoparticles and graphene sheet, which change the electronic properties of the graphene upon the deposition of Mg nanoparticles. Furthermore by using the Lorentzian function to evaluate the FWHM of G peak, we found that with raising of amount of Mg contents to graphene Sp\(^2\) framework, the full width half maximum (FWHM) of the G peaks is gradually decreased as a function of increasing the Mg/C Sp\(^2\) as shown in Fig 5.12 (b). The FWHM of G peak is decreased from 79.56 to 73.6 cm\(^{-1}\) when Mg
contents were deposited in a ratio 18.3 % to C (Sp²). The sharpening in FWHM (G) of graphene after the deposition of Mg nanoparticles onto graphene is attributed to the charge doping [207]. Magdalena Onyszko et al is also explained that the FWHM of G peak of the reduced graphene oxide decreased due to the charge doping [245]. The intensity ratio of D and G (I_D/I_G) were used to quantify the degree of disorderness (including defects and edges) and average size of the Sp² domains. It was observed that the intensity of the D peak of graphene increases as function of the Mg contents.

This suggests that the symmetry of graphene was broken and induced the structural defects in the structure of graphene. The calculated intensity ratio of the D and the G band (I_D/I_G) were varied from 1.66 to 1.75 as a function of the increasing Mg/C (sp²). The evaluated values of I_D/I_G as a function of the Mg/C (sp²) are illustrated in Fig 5.13. Moreover, the in-plane crystalline size was calculated using the I_D/I_G ratio and the obtained values as function Mg/C sp2 atomic ratios are presented in Fig 5.12. It can be seen that La decreased by increasing the Mg/C atomic ratio (%).
This suggests that by the deposition of Mg nanoparticles onto graphene the size of the $sp^2$ domain decreased.

### 5.5 The influence of Mg crystalline nanoparticles on the structure and chemical properties of graphene powder via given different vibration frequencies to graphene powders

In the above two sections (5.3, 5.4), the deposition of Mg nanoparticles were discussed by varying two deposition parameters RF power and deposition time. In both processes we deposited the Mg nanoparticles onto graphene at low powder vibration frequency (20 Hz). It was found that at low powder vibration frequency, the deposited Mg nanoparticles make aggregates on the graphene sheet. Recently different chemical and physical approaches were used to decorate graphene well dispersed metal nanoparticles [275, 276, 277]. However the decorated nanoparticles onto graphene sheets were not homogeneous sizes and these nanoparticles easily tend to agglomerate due to the high surface energy of the nanoparticles onto graphene sheet and lose their catalytic activities. In this section of thesis, the well dispersed Mg nanoparticles were deposited onto graphene sheet by given high vibration frequency to graphene powder during the deposition process. A range of powder vibration frequencies from 0 to 100 Hz was used to decorate the graphene with Mg nanoparticles. The Raman and X-ray diffraction techniques were used to study the structural disorderness induced in graphene by the deposition of Mg nanoparticles. For the chemical analysis X-ray photoelectron spectroscopy (XPS) were used. The surface morphology of the deposited Mg nanoparticle was examined by TEM analysis. Moreover the process parameters are presented in table 5.3.
Table 5.3 the process condition of decorated graphene with Mg nanoparticles

<table>
<thead>
<tr>
<th>Sample #</th>
<th>RF Power (W)</th>
<th>Process pressure (Pa)</th>
<th>Deposition Time (min)</th>
<th>Powder vibration frequency (Hz)</th>
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5.5.1 TEM analysis of decorated graphene with Mg nanoparticles deposited at 0 Hz and 80 Hz

The surface morphology of the decorated Mg nanoparticles was examined by TEM. Fig 5.14 (a-d) presents the TEM micrographs of the decorated Mg nanoparticles deposited onto graphene sheet without moving (0 Hz) the graphene powder during the deposition process. Fig 5.14 (a) shows the low magnification of the decorated Mg nanoparticles. The deposited Mg nanoparticles are homogeneously distributed onto graphene sheets. The high magnification TEM micrograph, as shown in Fig 5.14 (b-c), indicates that deposited Mg nanoparticles onto graphene flake are distributed with high density. The deposited Mg nanoparticles are anchored to the graphene sheet, even after the ultra-sonication used to disperse the Mg/graphene composite for the TEM characterization. From the Fig 5.14 (d) indicates that the deposited Mg nanoparticles make aggregates by the deposition of Mg nanoparticles onto graphene sheets without moving (0 Hz) graphene powder. The average size of the deposited Mg nanoparticles are around 10-15 nm.
Fig 5. 14 TEM images (a-d) of deposited Mg nanoparticles without moving powder (0 Hz)

TEM micrographs of the deposited Mg nanoparticles onto graphene at high powder vibration frequency (80 Hz) are shown in Fig 5.15. Low magnification micrographs as shown in Fig 5.15 (a,d), indicates that the deposited Mg nanoparticles are homogeneously distributed onto graphene sheet. This shows that with high powder vibration frequency the graphene flake are almost completely covered by Mg nanoparticles. Well dispersed small Mg nanoparticles were deposited onto graphene sheets with high powder vibration frequency. Notably feature for the deposited
Mg nanoparticles at high vibration frequency is that, less agglomeration of the Mg nanoparticles was observed. This is confirmed that by the deposition of the Mg nanoparticles onto graphene with high powder vibration the sputtered particles decorated over the entire graphene sheet. The average particles size of the deposited Mg nanoparticles at high powder vibration frequency (80 Hz) from the micrographs are about 8-12 nm.

Fig 5. 15 TEM images (a-d) of deposited Mg nanoparticles at high powder vibration frequency (80 Hz)
5.3.2 XPS analysis of undoped graphene and Mg doped graphene at different powder vibration frequencies.

The C 1s spectra of the undecorated graphene and decorated graphene with Mg nanoparticles at different powder vibration frequencies are displayed in Fig 5.16 (a). The C 1s spectra of the decorated graphene with Mg nanoparticles become asymmetric toward the higher binding energy (B.E) regime. The Gaussian line shapes were used for the de-convolution of the C 1s spectra. The C 1s spectra are de-convoluted into three components. The main peak at 284.46 eV is allocated to sp$^2$ C-C bonds and other two low intensity peaks at 285.6 and 286.3 eV are assigned to defects or sp$^3$ bond (C-H/C-C) and C-O bond respectively. More importantly by the deposition of Mg nanoparticles onto graphene sheet at different powder vibration frequency the shift in the C 1s core level were observed. The C 1s core level spectra shifts towards the lower binding from the 284.45 eV to 240.41 eV after the deposition of the Mg nanoparticles onto graphene without moving powder (0 Hz). The shift in C 1s core level towards the lower the binding energy increased with raising the powder vibration frequencies. The C 1s core level is shifted 0.10 eV toward lower binding energy upon the deposition of Mg nanoparticles at 100 Hz powder vibration frequency. The peak shifts in the C 1s core-level position are strongly related to Fermi-level. The shift in the C 1s core level is equal shift in the Fermi level. But the Fermi level is shifted from its position by the charge doping. It is also reported the charge is transfer between the graphene and metal interface due to the difference of the work function. The shift in C 1s core level of the deposited Mg nanoparticles onto graphene can be explained as follow, the XPS analysis shows that the deposited Mg nanoparticles are oxidized by exposing to the air. M. Giangregorio etal is reported that the oxidation of the metal surface dramatically change the
work function of the metal. The work function of the Mg metal is 3.68 eV and increased to 4.96 eV by the unintentional oxidation \(^{[278]}\).

Fig 5.10 (a) XPS spectra of graphene powder with varying the powder vibration frequencies (a) a) Shift in the C 1s core levels position and the shift of this position upon Mg deposition (b) Mg 2p core level spectra (RF power =40 W, Process pressure=6 Pa, Time= 27 min and powder vibration frequency= (0 to 100 Hz).

The work function of metal is known to depend on its structure, crystalline orientation and oxidation state \(^{[279}, 280, 281\). The reported work function for the graphene is 4.33 eV. It would be presumed that graphene is doped with electron if the works function of graphene (WG) > work function of the metal (WM) or its oxide and doped with holes if WG < WM. Due to the surface oxidation of the Mg nanoparticles, the work function of the MgO is greater than that of graphene, the graphene is p doped with MgO nanoparticles, whereas electrons are transferred from graphene to the MgO in order to aligned the Fermi level between the interface of the two
Chapter 5 Effect of Mg concentration on the structural and chemical properties of graphene powder

composite materials. The high-resolution spectra of the Mg 2p peak for the deposited Mg nanoparticles onto graphene at different powder vibration frequencies are shown in Fig 5.16 (b). The Mg 2p peak is contained within two components located at 51.38 eV and 53.73 eV respectively. The main components at the lower binding energy side is assigned to Mg-O bond from MgO and with a chemical shift of 2.3 eV with respect to Mg-O component is attributed to Mg bonded to the –OH groups.

The Mg concentration onto the graphene surface increased with a variation of the powder vibration frequency. The obtained Mg concentration onto graphene sheet by varying the powder vibration frequency is presented in Fig 5.17 (b). At 0 Hz vibration, the Mg/C is 12.94 at. % and further increased to 32.23 at. %, when the Mg nanoparticles were deposited at 100 Hz powder vibration frequency. The same other deposition parameters were used in both cases (RF power =40 W, Process pressure=6 Pa, Time= 27 min and powder vibration frequency= (0 to 100 Hz).

With powder vibration frequency more sputtered particles were deposited onto graphene sheet compared to the case without moving powder vibration frequency (0 Hz). This phenomenon can be explained as follows, by the deposition of the Mg nanoparticles onto graphene without moving powder the sputter particles were deposited only one face of the graphene sheet. Only surface graphene flakes were coated during the deposition process. The beneath graphene powder were not decorated by the Mg nanoparticles. Also, the Mg nanoparticles not covered the whole surface area of the graphene sheet during the deposition process. However, at 100 Hz powder vibration frequency, the powder vibrated with respect to sputtered particles during the deposition process, more sputtered particles are line of sight to the graphene sheet. It can be expected that both faces of the graphene sheets were covered with Mg nanoparticles during the deposition process. It is also confirmed from the TEM analysis that; Mg nanoparticles were
uniformly distributed over the graphene sheet at high powder vibration frequency. Larger surface area of graphene sheets were covered by the Mg nanoparticles during the deposition process with using of high powder vibration frequency. As discussed in Chapter#3, XPS is a surface technique and analyzes the surface of the decorated graphene upto a few nanometers. Consequently, the XPS detects more Mg nanoparticles, when it was deposited onto graphene sheets by using high powder vibration frequency compared to the case without moving graphene powder (0 Hz). The O 1s XPS spectra of the deposited Mg nanoparticles at 100 Hz powder vibration frequency is presented in Fig 5.17 (a). The O 1s spectrum is de-convoluted into two components. The main component OI located at 531.08 eV is assigned to the Mg-O bond; with shoulder on the high binding energy side corresponding to (OII) peak is also observed, about 2.1 eV higher than the main peak (OI) at 531.08 eV. The peak located at 533.32 is attributed to the surface hydroxyl group formed by adsorption of moister on oxidized magnesium surfaces [14].

The composition of the Mg-O and Mg-OH component for all the decorated graphene sheets with Mg nanoparticles at different powder vibration frequencies were measured on the basis of the area under the whole component of the Mg-O (I) and area under the component of Mg-(OH) (II) of the Mg 2p spectrum and the results are presented an in table 2. Moreover, to measure the stoichiometry, the O/Mg was firstly evaluated using the area of whole component OI of the O 1s peak and the Mg(I) 2p component. The measured ratios for the decorated graphene with Mg nanoparticles at different powder vibration frequencies are displayed in Table 2. The calculated O/Mg ratio indicates that the oxidized Mg nanoparticles were under stoichiometric (see table 2) and 1 is the ideal values for the MgO, which is might be due to the adsorption of the OH group at the surface of the MgO. Furthermore, XPS results also demonstrate that no metallic Mg components were observed, which suggest that all the deposited Mg nanoparticles were oxidized
at the surface. Since there is no protective layer on the top of the deposited Mg nanoparticles, the MgO was further hydroxylated easily, when it was exposed to air and Mg(OH)$_2$ was formed at the surface MgO. The amount of the Mg(OH)$_2$ increased by rising the powder vibration frequencies. The evaluated ratio of the Mg(OH)$_2$:MgO as a function of the powder vibration frequencies are displayed in a table (2).

This behavior can be explained as follows, this indicates that the deposited Mg nanoparticles deviated from the stoichiometry of MgO nanoparticles might be due to the hydroxylation and the hydroxylation increased by raising the powder vibration frequency. Because by using high powder vibration frequency more Mg nanoparticles were deposited onto graphene sheets.

**Fig 5.17** (a) O 1s core peak and its de-convolution (b) variations of Mg/C atomic ratio as function of powder vibration frequencies

| Table 2: Binding energy values of C 1s and Mg 2p core-levels, O/Mg atomic ratio, MgO and Mg(OH)$_2$ concentration for the different powder vibration frequencies |
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5.5.3 XRD investigation of undoped graphene and Mg-doped graphene decorated at different powder vibration frequencies

The XRD patterns of the graphene and decorated graphene with Mg nanoparticles deposited at different powder vibration frequencies are presented in Fig 5.18 (a). The broad and dominant diffraction peak centered at $2\theta=25.11^0$ in the XRD pattern of the graphene correspond to the reflection of the (002) plane [34]. In the XRD patterns, the characteristic (002) peak is broad and low-intensity peak, which indicates that the graphene powder contained only a few layers of graphene [57]. On the other hand for the decorated graphene with Mg nanoparticles additional three diffraction peaks at $2\theta=31.83^0$, 34.05$^0$, and 36.35$^0$ were also observed. These peaks can be indexed to the three reflection peaks (001), (002) and (101) planes, which are assigned to the reflection from the hexagonal phase of Mg with lattice constant of $a = 3.234 \, \text{Å}$ and $c = 5.204 \, \text{Å}$ ([JCPDS 04-0770]). There was no other impurities peak observed in the XRD patterns. The characteristic peaks of Mg nanoparticles located at 31.83$^0$, 34.05$^0$, and 36.35$^0$ were obtained. It was observed that the (101) peak of the Mg nanoparticles deposited without moving powder (0

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<th>BE (Mg-O) (eV)</th>
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<th>Mg(OH)$_2$ (%)</th>
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(continued)
Hz) was narrower, which suggests that large nanocrystalline particles were deposited onto graphene sheet. The crystallite sizes of the deposited Mg nanoparticle were calculated using equation (1). The crystallite sizes of the deposited Mg nanoparticles decreased with increasing powder vibration frequencies and the results are presented in Fig 5.18 (b).

It can be seen in the XRD patterns, the FWHM of the (101) peak for deposited Mg nanoparticles are becoming wider as by increasing powder vibration frequencies. For comparison, the Lorentzian function was used to evaluate the FWHM of (101) peak for the deposited Mg nanoparticles without moving powder (0 Hz) and with powder vibration frequency at 100 Hz. It was found that the FWHM of the (101) peak without moving powder (0 Hz) and high powder vibration frequency (100 Hz) are 0.55 (degree) and 0.74 (degree) respectively. These results can be explained as follows, as discussed in the section 5.5.1 that, with deposition of Mg nanoparticles onto graphene sheets without moving powder (0 Hz), the sputtered particles were deposited onto graphene sheets at a certain area of the graphene surface and the graphene surface
were not completely covered by the sputtered particles. Also, it was found that the sputtered particles make aggregates onto graphene sheet. Due to the aggregation of the Mg nanoparticle on the graphene surface, the crystallite size of the Mg nanoparticles increased. However in the case of high powder vibration frequency (100 Hz) the crystallite size of the Mg nanoparticles obtained onto graphene sheet decreased with respect to that the crystallite size obtained without moving the powder (0 Hz). From the TEM image shown in Fig 5.15(a) indicates that well dispersed Mg nanoparticles were obtained onto graphene sheets by using high powder vibration frequency. The sputtered particles were anchored over the entire surface of the graphene flake. No aggregations of the sputtered particles were observed during the deposition process with high powder vibration frequency. Therefore, the crystallite size of the deposited Mg nanoparticles onto graphene sheet obtained in case of using high powder vibration was less than that of the crystallite size obtained onto graphene sheets without moving graphene powder.

Moreover the FWHM of the graphene (002) peak increased by the deposition of the Mg nanoparticles at different powder vibration frequencies and the values are presented in Fig 5.19. This suggests that the crystanality of the graphene were reduced. The reduction of the crystalline thickness of the graphene after the deposition of the Mg nanoparticles suggest that, the stacking order of the graphene plane reduced due to the high concentration of Mg nanoparticles onto graphene plane. Additionally by the deposition of graphene with Mg nanoparticles the (002) peak of graphene were gradually shifted towards the lower angle values. This indicates that the plane of the graphene was distorted with the increasing amount of Mg nanoparticles onto graphene.
Chapter 5 Effect of Mg concentration on the structural and chemical properties of graphene powder

Fig 5.19 Crystallite sizes and FWHM of undecorated graphene and decorated graphene flakes with Mg nanoparticles as a function of powder vibration frequency

5.5.4 Raman study of undoped graphene and Mg-doped graphene decorated at different powder vibration frequencies

Fig.5.20 shows the Raman spectra undoped graphene and decorated Mg nanoparticles onto graphene deposited at different powder vibration frequencies. The Raman spectra of the undoped graphene and decorated graphene with Mg nanoparticles revealed characteristic G peak originating from in-plane vibration of sp$^2$ carbon atoms and D arising from the disorder induced mode. The Raman spectra of undoped graphene and deposited Mg nanoparticles onto graphene contain D and G peaks located at 1324 and 1585.67 cm$^{-1}$ reactively. In addition to D and G peaks a broad low intensity 2D band is also observed at ~2637.23cm$^{-1}$. A change in the positions, intensities and the full width at half maximum (FWHM) of the G, 2D and D peaks were observed. It is found that the G peak of graphene upshifted after the deposition of Mg nanoparticles at different powder vibration frequencies. The G peak of the graphene was shifted
from the 1585.67 cm\(^{-1}\) to 1588.78 cm\(^{-1}\), when Mg nanoparticles were deposited onto graphene without moving graphene (0 Hz) powder.

![Raman spectra](image)

**Fig 5.20** Raman spectra of undoped graphene and Mg-doped graphene at different powder vibration frequencies

The shifts in G position toward higher wavenumbers were increased by increasing the powder vibration frequencies. The upshifts of the G peak were further increased from 1585.67 cm\(^{-1}\) to 1595.23 cm\(^{-1}\) after the deposition of Mg nanoparticles onto graphene at 100 Hz powder vibration frequency. Visible shifts in 2D bands toward the higher wavenumber were also observed after the deposition of Mg nanoparticles onto graphene as shown in Fig 5.20 (enlarged view). The 2D bands were upshifted from 2637.23 cm\(^{-1}\) to 2645.43 cm\(^{-1}\) after the deposition of Mg nanoparticles at 100 Hz powder vibration frequency. The doping type and strain can be measured from the position shift of the G and 2D bands. It is known from literature that the downshift of the 2D peak and upshift of the G peak correspond to n-doping of graphene, while
the upshift of the G band position and the upshift of the 2D band position means p-doping $^{[198, 283]}$. In our case the G band position and the of the 2D band position were shifted to higher wavenumbers by 9.81 cm$^{-1}$ and 8.2 cm$^{-1}$ respectively. This result suggest p-doping of graphene with Mg nanoparticles depositions. The blue shift of G peak in the graphene peak by the deposition of the Mg nanoparticles suggesting phonon stiffening due to charge transfer.$^{[284]}$

The $I_D/I_G$ of the decorated graphene with Mg nanoparticles as function of the Mg/C is presented in Fig 5.21. Normally $I_D/I_G$ ratio was used to measure the defect density induced in the sp$^2$ domain by the interaction of the metal or other impurities $^{[285]}$. From the Fig 5.21, it is asserted that as the Mg contents increased by increasing the powder vibration frequency, the defects in the decorated graphene were pronounced. Moreover by the deposition of the Mg nanoparticles onto graphene scattering of phonon from the defects sites were increased, the Raman spectra display the noticeable increase of the D peak intensity. Fig 5.21 shows $I_D/I_G$ of the of the deposited Mg nanoparticles onto graphene as function of the Mg/C atomic ratio. It was found that with increasing Mg/C atomic ratio obtained by increasing the powder vibration frequencies, the $I_D/I_G$ ratios increased. The $I_D/I_G$ ratios values increased to 1.767, when Mg nanoparticles were obtained in ratio Mg/C (sp$^2$) = 32.34 atomic ratio (%) at high powder vibration frequency (100 Hz). This suggests that, the structural defects were pronounced in the sp$^2$ domain with increasing of Mg concentration onto graphene sheets. The intensity ratio of the D and G bands ($I_D/I_G$) is also used to calculate the in-plane crystallite sizes (La). The in-plane crystallite size is measured by using Tuinstra - Koenig relation $^{[247]}$.

$$La(nm) = 2.4 \times 10^{-10} \lambda^4 \left(\frac{I_D}{I_G}\right)^{-1} \quad \text{(2)}$$

Where La is the in-plane crystallite size and $\lambda$ is the excitation wave length wavelength used in the Raman measurement. Fig 5.21 shows that the in-plane crystallite size decreased by increasing
the Mg/C sp². This suggests that by increasing the Mg contents to C sp² domain, the sp² domain was broken and decreased from 23.2 nm to ~21.6 nm due to the deposition of Mg nanoparticles onto graphene sheets.

![Graph](image)

Fig 5. Variation of Raman peak intensity ratios of I_D/I_G and in plane crystallites size (La) plotted against the Mg to C atomic ratio (%)

### 5.6 Concluding Remarks:

In this chapter, the influence of the Mg amount on the structural, chemical and morphological properties of the graphene are reported. The Mg nanoparticles were deposited onto graphene successfully by varying three deposition parameters RF power, deposition time and powder vibration frequency. By the variation of the deposition parameters different amounts of Mg concentration were obtained onto graphene sheet. On the bases of the variation of the deposition parameters, the following conclusions are drawn from this chapter and categorized in the following sections.

In the 5.3 section, the structural properties of the decorated graphene with Mg nanoparticles were investigated by X-ray diffraction and Raman spectroscopy. The chemical properties were
studied using the XPS technique. It was found from the XRD results, by increasing the RF power values the plane of the graphene were distorted with the interaction of high energetic sputtered particles and plasma species. Addition to this the crystalline nature of the Mg nanostructure in the Mg/graphene composite was confirmed by XRD investigation. The crystallites sizes of the deposited Mg nanoparticle were increased from (14 to 21 nm) by variation of the RF power values (30 to 75 W). Raman spectrum showed that with the interaction of graphene with Mg nanoparticles the G and 2D peak were shifted 11 cm\(^{-1}\) and 7 cm\(^{-1}\) to higher wavenumbers, suggesting p doped graphene by the deposition of Mg nanoparticles. The structural defects were increased in the graphene with interaction of Mg nanoparticle. The XPS results revealed that with the deposition of the Mg nanoparticles the C 1s core level shifts toward the lower binding energy. The charge is transferred from the graphene to the MgO due to the difference of work function.

In the 5.4 section, the interactions of graphene with Mg nanoparticles were characterized by XRD, Raman, XPS and TEM. XRD results demonstrated that by the interaction of the graphene with Mg nanoparticles the d spacing of the graphene was increased. Also the three characteristic peaks correspond to (001), (002) and (101) planes of hexagonal structure of metallic Mg were also observed. The crystallite sizes of deposited Mg nanoparticles were in the range of 14 to 16 nm. The p-doping effect was clearly evident in the Raman spectroscopy data of graphene upon the deposition of the Mg nanoparticles. The sp\(^2\) domain of graphene was decreased due to the interaction of energetic species and sputtered particles. XPS analysis showed that the deposited Mg nanoparticles were oxidized due to exposr to the atmosphere. The p doping effect was also confirmed from the XPS analysis. TEM micrograph showed that Mg nanoparticles are uniformly
distributed onto graphene sheet. The deposited Mg nanoparticles are in spherical shape and having an average particles size of 20-25 nm.

In the last section, the well dispersed Mg nanoparticles onto graphene sheet were deposited by varying the powder vibration frequencies. The deposited Mg nanoparticles onto graphene at different powder vibration frequencies were characterized by XRD, TEM, Raman, and XPS techniques. TEM micrographs revealed that the deposited Mg nanoparticles onto graphene sheet without moving powder were aggregated at certain places of the graphene sheet. However by deposition of Mg nanoparticles onto graphene at high powder vibration frequency were uniformly distributed over the entire sheet of graphene. The well dispersed Mg nanoparticles onto graphene flake were confirmed from the TEM analysis. XRD results demonstrated that with deposition of Mg nanoparticles at high powder vibration frequency the plane of the graphene were distorted due to the interaction of energetic species. The crystallite sizes of the deposited Mg nanoparticles were decreasing by using high powder vibration frequency. By the deposition of Mg nanoparticles, the intensity ratio of D and G bands $I_D/I_G$ of graphene was increased. The XPS analysis showed that with high powder vibration frequency more sputtered particles were deposited onto graphene sheet compared to the case of without moving powder.

Lastly, the structural, chemical and electronic properties decorated graphene sheets with different amount of the Mg nanoparticle were discussed in this chapter. Furthermore, the interaction of the graphene sheets with TiO$_2$ nanoparticles will be studied in next chapter# 6.
Chapter 6 Effect of TiO$_2$ concentration on the structural and electronic properties of graphene powder

Chapter # 6

The influence of TiO$_2$ concentration on the structural, chemical and electronic properties of graphene powder by plasma processing

6.1 Introduction:
Graphene 2D nanostructure can potentially serve as supporting materials to anchor semiconductor nanoparticles onto graphene sheet and improve the performance of the composite materials in optoelectronic and energy conversion devices. Additionally, the graphene surface properties could be tuned via chemical modification. For the decoration of catalytic nanoparticles onto graphene sheets can more usefulness in carrying out sensing or catalytic process. TiO$_2$ is a wide band gap semiconductor and active in its photo catalytic property under UV irradiation. The interaction of graphene with TiO$_2$ nanoparticles is capable to enhance the catalytic activity under UV irradiation $^{[60]}$. Different chemical and physical methods were used to decorate with well distributed nanoparticles graphene sheets. However, by chemical methods the nanoparticles tend to aggregate onto graphene powder, which reduces the photo catalytic activity of the composite $^{[286]}$. The main objective of this part of the work is to study the interaction of graphene with TiO$_2$ nanoparticles and the enhancement of catalytic activity of the composite. In this chapter, three different deposition parameters were used for the decoration of well dispersed TiO$_2$ nanoparticles onto graphene sheets. On the bases of variation of the deposition process this chapter is divided into three sections and following investigation are driven:

- For the results presented in the first section, TiO$_2$ nanoparticles were deposited by varying RF power values and the interaction of the energetic sputtered particles and plasma species with graphene sheet will be discussed.
For the results described in the second section, different amount of TiO$_2$ nanoparticles were obtained onto graphene by increasing the deposition time. The structural, chemical and electronic properties of the decorated graphene with TiO$_2$ nanoparticles will be studied.

For the results reported in the last section, the influence of the TiO$_2$ concentration on the structural, chemical and electronic properties of the graphene will be presented.

6.2 Experimental detail:

The anatase TiO$_2$ nanoparticles were deposited onto graphene by RF sputtering in Ar plasma. High purity (99.99%) TiO$_2$ disc with 5 cm diameter was uses as a sputtering target. The distance between the TiO$_2$ target and graphene powder were fixed at 50 mm. The powder vibration system was used to decorate the graphene powder with uniform TiO$_2$ nanoparticles. Three deposition parameters RF power, deposition time and powder vibration frequency were varied to deposit the TiO$_2$ nanoparticles onto graphene sheet and the specific details of the deposition parameters are given below.

Firstly, the TiO$_2$ nanoparticles were deposited onto graphene powder by varying the RF power values from 30 to 80 W corresponding to self-bias voltage ranging between -174 to -294 V. The total process pressure and powder vibration frequency were kept constant at 6 Pa and 20 Hz respectively. The deposition time was fixed at 40 min.

Secondly, in order to vary the amount of TiO$_2$ nanoparticles onto graphene sheet at constant RF power value, the TiO$_2$ nanoparticles were deposited by increasing the deposition time from (10 to 60 min). The RF power and self-bias voltage applied to the TiO$_2$ target were fixed at 40 W and 174 V respectively. The powder vibration frequency and total process pressures were kept constant at 20 Hz and 6 Pa.
At last, the graphene powders were decorated with well dispersed TiO$_2$ nanoparticles by varying the powder vibration frequency form 0 to 100 Hz with constant amplitude of 32 µm. The deposition time RF power and process pressure were kept at constant values of 60 min a 40 W and 6 Pa process pressure respectively.

6.3 Effect of TiO$_2$ nanoparticles on the structural, chemical and electronic properties of graphene powder deposited by varying RF power values

In this section, the results of the deposited TiO$_2$ nanoparticles onto graphene by varying the RF power values are presented. The main goal of this work is to study the interaction of graphene with TiO$_2$ nanoparticles, when the sputtered particles interact with graphene sheet with high kinetic energy. By the variation of the RF power values different amounts of TiO$_2$ nanoparticles onto graphene were obtained. The influence of the TiO$_2$ concentrations on the structural, chemical and electronic properties of the graphene is discussed in this section. The interaction of graphene with TiO$_2$ nanoparticles were characterized by the XRD, Raman, XPS and TEM techniques. Moreover the process parameters are presented in table 6.1.

Table 6.1 the process condition of decorated graphene with TiO$_2$ nanoparticles

<table>
<thead>
<tr>
<th>Sample #</th>
<th>RF Power (W)</th>
<th>Process pressure (Pa)</th>
<th>Deposition Time (min)</th>
<th>Powder vibration frequency (Hz)</th>
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<td>6</td>
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</table>
6.3.1 TEM analysis of decorated graphene with TiO$_2$ nanoparticles deposited at 80 W

The surface morphology and structure feature of the decorated graphene with TiO$_2$ nanostructures were examined by TEM analysis. Fig 6.1 (a-b) shows the decorated graphene with TiO$_2$ nanoparticles deposited at 80 W. It is observed from the TEM micrographs that very small TiO$_2$ nanoparticles anchored onto graphene. Fig (a) shows the high magnification of the decorated graphene sheet with TiO$_2$ nanoparticles. Graphene sheets were decorated with high coverage of TiO$_2$ nanoparticles and the deposited particles are well distributed over the graphene sheets. Fig (b) demonstrates the low magnification of the deposited TiO$_2$ nanoparticles onto graphene sheet, which indicates that a uniform layer of TiO$_2$ covered the graphene sheet. Due to deposition of the TiO$_2$ nanoparticles at high RF power value the small TiO$_2$ nanoparticles make aggregates onto graphene sheet and look like thin layer of TiO$_2$ nanoparticles. The sizes of the deposited TiO$_2$ nanoparticles are in the range of 5-10 nm.

![Fig 6.1 TEM images (a-b) of deposited TiO$_2$ nanoparticles onto graphene sheet at 80 W](image-url)
6.3.2 XPS analysis undoped graphene and TiO2 doped graphene deposited at different RF power values

The interaction between the graphene and deposited TiO₂ nanoparticles are studied by using the XPS analysis. The high resolution XPS spectra of the C 1s core level of the undecorated graphene and decorated graphene with TiO₂ nanoparticles deposited at different power values are shown in Fig 6.2 (a). The C 1s core level were de-convoluted into three components. The binding energies of the components of the undecorated graphene C 1s spectrum are centered at 284.45, 285.23 and 286.2 eV respectively, which are attributed to C-C (sp²), C-H/C-C (sp³) and C-O bonds respectively.

![XPS spectra for graphene powder and deposited TiO2 nanoparticles at different RF power values](Image)

Fig 6.2 (a) XPS spectra for graphene powder and deposited TiO2 nanoparticles at different RF power values

(a) Shift in the C 1s core levels position and the shift of this position upon TiO2 deposition. (b) Ti 2p core level spectra. [Process pressure = 6 Pa, Time=40 min, Frequency = 20 Hz  RF power= 30 to 80 W]

By the deposition of TiO2 nanoparticles the C 1s core level of the graphene shifted toward lower binding energies values. A low shift of 0.04 eV was observed in the C-C (sp²) bond with respect
to undoped graphene C-C (sp²) bond, when TiO₂ nanoparticles were deposited onto graphene at 30 W. The shifts in C-C (sp2) bond increased by raising the RF power values and reached 0.17 eV with the deposition of TiO₂ nanoparticles onto graphene at 80 W. Generally the photoemission spectroscopy are used to measure the core level, work function and valance band and this method is also useful for the determination of the interface band alignment. Recently it was reported that, when graphene interacted with high band gap semiconductor the C 1s core level is shifted toward the lower binding energies due to the charge transfer at the interface in order to align the Fermi level [287]. Youngkyu Chang et al demonstrated that the shift in the Fermi level is due to the difference of the work function [288]. Similar observation about the charge transfer between the interactions of graphene and TiO₂ due to the difference of work function is reported by Aijun Du et al using density function theory [116]. He described that charge is transferred from graphene to TiO₂ due to large difference in work function values between the TiO₂ (5.50 eV) and graphene (4.3 eV). In our case, after the deposition of TiO₂ nanoparticles onto graphene sheet the C 1s core level of the graphene is shifted towards the lower binding energies values. Therefore, the shift in the C 1s core level of the graphene after the deposition of TiO₂ nanoparticles is due to p doping, whereas the electrons are transferred from graphene to TiO₂ nanoparticles at the interface in order to align the Fermi level between the TiO₂ and graphene.

The high resolution XPS spectra of the Ti 2p peak for the decorated graphene with TiO₂ nanoparticles deposited at different RF power values are presented in Fig 6.2 (b). The Ti 2p XPS spectra were fitted by two components one is Ti 2p₁/₂ and the second Ti 2p₃/₂ [289]. The spin orbit split components of Ti 2p₁/₂ and Ti 2p₃/₂ is located at binding energy positions of 459.08 and 464.95 eV respectively. The separation between the Ti 2P₁/₂ and Ti 2P₃/₂ is 5.87 eV and this split
orbit coupling suggests that the oxidation state of Ti is +4 [290]. Moreover with increasing RF power values, the Ti 2p core level is shifted towards the lower binding energy values. The maximum downshift of 0.26 eV was observed, when graphene were decorated with TiO2 nanoparticles at 80 W. The downshift of the Ti core levels suggest that charge is transferred from the graphene to TiO2 due the difference of the work function of the contacted materials [291]. The band of the TiO2 bends toward the interface upon the interface of TiO2 films with graphene sheets. The band bending of TiO2 is further explained in section 6.5.1.

Fig 6.3 (a) depicts the O 1s spectra for the deposited TiO2 nanoparticles onto graphene at different power values in Ar plasma. The O 1s XPS spectra were de-convoluted into three components. The main component (OI) located at binding energy (530.69 eV) is assigned to the O²⁻ bound to Ti⁴⁺ [181] Two shoulder components towards the higher binding energies values located at 532.12 eV and 533.3 eV can be attributed to the C–OH and C–O bonds respectively [292, 180]. There was a similar shift observed in the OI components like C 1s and Ti 2p by increasing the deposition RF power values. This indicates that surface dipoles were developed due to the charge transfer between TiO2 and graphene and lead band bending of TiO2 and also decreased the binding energies of the Ti 2p and O 1s [112].

Furthermore, the atomic ratio between oxygen and metal in oxide is one of the important and useful parameter to evaluate the stoichiometry of the oxide. The TiO2 (OI/Ti) stoichiometry were measured on the basis of the area under the main component of the oxygen (OI) and the area under the Ti 2p3/2 component. The measured atomic ratio, OI/Ti, for the decorated graphene with TiO2 nanoparticles at different RF power values are displayed in Fig 6.3 (b). It can be seen that by increasing the RF power values from 30 W to 80 W, the OI/Ti ratio decreased linearly
from 1.96 to 1.86. This shows that the deposited TiO$_2$ is more oxygen deficient at high RF power values than at low power deposition.

Generally by deposition of the TiO$_2$ at higher power the ion flux and sputtered particles bombardment on the graphene powder was higher than at low power deposition. It is well known by increasing the RF power values, the sputtered particles extracted from the TiO$_2$ target having high kinetic energies and the interaction of these sputtered particles with graphene powder is more rigorously. Ti/C (sp2) atomic ratio also increased from 3.45 at. % and reached 13.37 at. %, when the RF power values varied from 30 W to 80 W. The results are presented in Fig 6.3 (b). The reduction of the OI/Ti ratio can be explained as follow, by increasing RF power values the sputtered particle and plasma species interact with lattice of TiO$_2$ more energetically generates the oxygen vacancies in the TiO$_2$ lattice.
The oxygen formation mechanism of the deposited TiO$_2$ nanoparticles onto graphene sheets at different RF power values can be explained as follows, as discussed in the above text that the sputtered particles gain more kinetic energy by increasing RF power values, these energetic sputtered particles remove the oxygen from the lattice of TiO$_2$ nanoparticles when it was deposited onto graphene sheets, or might be oxygen remove from the lattice of TiO$_2$ during the deposition process, when the sputtered particles coming from the target and collision takes place between the sputtered particles with energetic plasma species.

6.3.3 XRD analysis undoped graphene and TiO$_2$ doped graphene deposited at different RF powers

The XRD patterns of the undoped graphene and decorated graphene with TiO$_2$ nanoparticles deposited at different RF power values are presented in Fig. 6.4 (a). The XRD pattern of the undecorated graphene shows a broad peak at $2\theta = 25.11^\circ$ attributed to the (002) reflection of few layer graphene. The numbers of graphene layers were calculated using the relation $^{293}$

$$N = \frac{\text{Thickness}}{d_{(002)}}$$

The calculated number of layers from the above equation for the undoped graphene is 4.96. This shows that the graphene powder consist of very few layers of graphene. The characteristic (002) peak of the graphene is very broad, which indicates that graphene layers are not well ordered. By the decoration of graphene with TiO$_2$ nanoparticles, the (002) peak was shifted to higher $2\theta$ values and the shift in (002) gradually increased by raising the TiO$_2$ concentration. This indicates that the spacing between the layers of graphene is reduced with increasing contents of the TiO$_2$. The calculated interplaner distances of the undecorated graphene and for the decorated graphene with TiO$_2$ nanoparticles as function of Ti/C (sp$^2$) atomic ratio (%) are presented in Fig.
Moreover it is observed that FWHM of the graphene is becoming wider by increasing the TiO$_2$ concentration. FWHM of the (002) peak of all the samples were evaluated upon Gaussian shape fit. This suggests that by the deposition of TiO$_2$ nanoparticles onto graphene, the structural defects were pronounced in the graphene structure.

The crystallite thickness of undoped graphene and for the decorated graphene with TiO$_2$ nanoparticles were measured by fitting the (002) peak [294]. The crystallite thicknesses were calculated by using the Scherer equation and the crystallite thickness decreased with increasing the TiO$_2$ concentration as shown in Fig 6.5. This can be explained as follows; by the deposition of TiO$_2$ nanoparticles onto graphene the stacking order of the graphene layer was reduced with the interaction of the high energetic sputtered particles.
Chapter 6 Effect of TiO$_2$ concentration on the structural and electronic properties of graphene powder

![Graph showing variation in FWHM and crystallite size vs Ti/C ratio](image)

**Fig 6.5** Variation in the FWHM of the (002) peak and crystallite thickness as function of Ti/C atomic ratio

### 6.3.4 Raman analysis of undoped graphene and TiO$_2$ doped graphene deposited at different RF power values

Raman spectra of the undecorated graphene and decorated graphene with TiO$_2$ nanoparticles deposited by increasing RF power values are depicted in Fig 6.6. Four characteristics bands in the Raman spectrum of the undoped graphene were detected: the D band (defects band or disordered) band located at 1324 cm$^{-1}$ and the G (in-plane stretching of the sp$^2$ C-C bonds) band centered at 1586.45 cm$^{-1}$. The 2D band of the graphene centered at 2637 cm$^{-1}$ is originated from the second order zone boundary and D+G band located at 2876 cm$^{-1}$ is the combination band originated in the Raman spectra in the presence of disorders in the system. In addition, for the decorated graphene with TiO$_2$ nanoparticles, four characteristics bands of the TiO$_2$ were also observed in the Raman spectra. The peaks are centered at 154, 394, 510 and 632 cm$^{-1}$. These peaks can be attributed to the E$_g$, B$_{1g}$, A$_{1g}$ and E$_{1g}$ modes of the anatase phase of TiO$_2$, respectively [295, 296]. This is confirmed that anatase phase formation was established onto
graphene sheets. It is also shown that by the deposition of TiO$_2$ onto graphene at different RF power values, there were strong changes observed in the position, intensity and FWHM of the G, D and 2D peak respectively. The G and 2D peak were shifted by 5 and 4 cm$^{-1}$ to higher wave numbers, when the TiO$_2$ nanoparticles were deposited at 30 W. The shifts in G and 2D peaks increased with rising TiO$_2$ concentration obtained onto graphene at different RF power values. Further upshifts in G and 2D bands of 11.34 cm$^{-1}$ and 10.5 cm$^{-1}$ were observed, when the graphene was decorated with TiO$_2$ nanoparticles at 80 W and the results are presented in Fig 6.6 (enlarged view).

![Fig 6.6 Raman spectra of undoped graphene and TiO$_2$ doped graphene at different RF power values](image)

It is reported that the 2D band of the graphene was shifted to higher frequency upon the p doping graphene with metal oxide [297]. Likewise, the G peak of graphene is shifted to higher frequency with p doing and shifted toward the lower wavenumber with n-doping [298]. It is also possible that by the deposition of TiO$_2$ nanoparticles onto graphene the defects were generated in the plane of graphene and these defects scatter the electrons to non-adiabatic state [299]. However,
Denys Naumenko et al is reported that the upshift in G and 2D peaks are due to the p doping \[^{300}\]. Similar observation was also reported by Jisook Lee et al \[^{253}\]. Consequently, the dynamic effect in decorated graphene with TiO\(_2\) nanoparticles was less dominant. In our case, the G and 2D bands of the graphene were shifted to higher wavenumbers upon the deposition of TiO\(_2\) nanoparticles. This indicates that upshift of G and 2D bands are due to p doping. Hence, the interaction TiO\(_2\) nanoparticle with graphene as an electron acceptor and the electrons are transferred from the graphene to the anatase TiO\(_2\) nanoparticles. This phenomenon is further explained in the section (6.5.3).

The level of the disorders and defects can be evaluated in graphitic materials by measuring the relative intensities of D and G band, higher intensity I\(_D\)/I\(_G\) ratio indicating higher disorders and defects in the graphene planes. Fig 6.7 depicts that the I\(_D\)/I\(_G\) ratio as a function of Ti/C sp\(^2\) atomic ratio obtained by increasing the RF power values. The I\(_D\)/I\(_G\) ratio increased with increasing the TiO\(_2\) concentrations onto graphene planes.

The I\(_D\)/I\(_G\) ratio was 1.64 for the undoped graphene and increased to 1.80, when the TiO\(_2\) nanoparticles were deposited at 80 W in a ratio of Ti/C sp\(^2\) =13.37 atomic ratio (%). This indicates that the structural defects increased with deposition of TiO\(_2\) onto graphene by increasing the RF power values.

In addition, the in-plane average crystallite size (La) were measured directly using the I\(_D\)/I\(_G\) ratio \[^{301}\],

\[
La(\text{nm}) = 2.4 \times 10^{-10} \lambda \left( \frac{I_D}{I_G} \right)^{-1} \ \\
\text{..........}(2)
\]

Where \(\lambda\) is the wavelength used for the analysis of the samples, (in our case is 633 nm). The calculated in-plane crystalline size of undecorated graphene and decorated graphene with TiO\(_2\) as a function of Ti/C (sp\(^3\)) is presented in Fig 6.7. The in-plane crystallites size of the graphene
were reduced from 23.1 to 21 nm when the TiO$_2$ were deposited onto graphene in the ratio of Ti/C (sp$^2$) = 13.37 at. %. These suggest that with the deposition of TiO$_2$ nanoparticles onto graphene at different RF power values, the sp$^2$ domains of the graphene were broken or may be shrinking with the interaction of TiO$_2$ nanoparticles. The reduction of the sp$^2$ domain size is further explained as follows, the hexagons of the sp$^2$ domain were distorted with deposition of the TiO$_2$ nanoparticles and the distortion increased with raising the amounts of the TiO$_2$ nanoparticles. Consequently due to the distortion of the sp$^2$ domain by the interaction of the sputtered atoms the sp2 domain was reduced.

![Graph showing variation of Raman peak intensity ratios of ID/IG and in plane crystallites size (La) plotted against the Ti/C.a (%)](image)

**Fig 6.7** Variation of Raman peak intensity ratios of ID/IG and in plane crystallites size (La) plotted against the Ti/C.a (%) 

### 6.4 influence of TiO$_2$ on the structural, chemical and electronic properties of graphene powder deposited by varying the deposition time.

In section 6.3, we described the interaction of the graphene with TiO$_2$ nanoparticles deposited by increasing RF power values. It was found that by the deposition of the TiO$_2$ nanoparticles onto
graphene induced the structural defects and the structural defects were enhanced in the sp\(^2\) domains with increasing the sputtered particles energies. In this section of thesis, we studied the influence of the TiO\(_2\) concentration on the structural and chemical properties of the graphene. TiO\(_2\) nanoparticles were deposited onto graphene by increasing the deposition time. For the structural characterization, the Raman and XRD analysis were used to investigate the types of defects. XPS analysis was used for the chemical analysis. Moreover the process parameters are presented in table 6.2.

Table 6.2 the process condition of decorated graphene with TiO\(_2\) nanoparticles

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6.4.1 XPS analysis undoped graphene and TiO\(_2\) doped graphene deposited with different times

The XPS analysis of the decorated graphene with TiO2 nanoparticles are depicted in Fig 6.8. The high resolution C 1s core level spectra of the undecorated graphene and decorated graphene with different times are displayed in Fig 6.8 (a). The C 1s core levels of the undecorated and decorated graphene with TiO\(_2\) were de-convoluted into three components by using the Gaussian shape line function after performing a Shirley background correction. The de-convoluted
components for the undecorated graphene are located at binding energy 284.45, 285.23 and 286.2 eV, which correspond to the C-C (sp²), C-H/C-C (sp³) and C-O bonds respectively. A small downshift was observed in the C 1s core level after the deposition of TiO₂ nanoparticles at 10 min. The shift in the C 1s core levels was further increased with increasing concentration of TiO₂ to graphene plane. The maximum downshift of 0.09 eV was observed with decoration of TiO₂ nanoparticles at 60 min of deposition. This observation suggests that with the interaction of graphene with TiO₂ nanoparticles the charge transfer occurring from graphene to TiO₂ due to the difference of work function. In this case the maximum down shift of 0.09 eV were detected with the deposition of the TiO₂ nanoparticles at 60 min in a ratio Ti/C sp² =5.26 atomic ratio (%) at 40 W RF power value compared to the downshift of 0.19 eV in C 1s level were observed upon the deposition of TiO₂ nanoparticles at 80 W in a ratio Ti/C (sp2) = 13.37 atomic ratio (%) at 40 min of deposition. The reasonable explanation for this is that by increasing RF power values (40 to 80 W) more sputtered particles were deposed onto graphene sheet energy compared to the deposition at constant RF power (40 W) value. This observation indicates that by increasing the amount of the TiO₂ nanoparticles onto graphene sheet, the interaction between the graphene and TiO₂ increased.
Chapter 6 Effect of TiO$_2$ concentration on the structural and electronic properties of graphene powder

Fig 6.8 (b) presents the XPS spectra of the Ti (2p) binding energy region for the decorated graphene with TiO$_2$ nanoparticle at different times of deposition. Two components centered at binding energies of 459.01 and 464.95 eV are attributed to the Ti (2p$_{3/2}$) and Ti (2p$_{1/2}$) respectively. The spin-orbital coupling of these photoelectrons was assigned to the chemical state Ti$^{4+}$. The separation between the spin-orbital couplings is 5.94 eV indicates that TiO$_2$ was formed on the graphene sheet $^{302, 303}$.

Fig 6.8 (a) XPS spectra from graphene powder and deposited TiO$_2$ nanoparticles at different times of deposition (a) C Shift in the C 1s core levels position and the shift of this position upon TiO$_2$ deposition. (b) Ti 2p core level spectra. [Process pressure = 6 Pa, Time=40 min, Frequency = 20 Hz RF power= 30 to 80 W]

A shift of 0.10 eV in the Ti 2p was observed with deposition of the TiO$_2$ nanoparticles at 60 min. The downshift of the Ti 2p is related to charge transfer between the TiO$_2$ and graphene due to the difference of work function. Due to the charge transfer from graphene to the TiO$_2$, the band of
the TiO2 bend toward the interface reduced the binding energy of the Ti core level and the result is shown schematically in Fig 6.14.

The O 1s XPS spectra for the decorated graphene with TiO2 nanoparticles at different times of deposition are presented in Fig 8.9 (a). The decorated graphene with TiO2 nanoparticles was deconvoluted into three components. The deconvoluted components centered at the binding energy positions of 530.59, 532.09 and 533.54 eV were consigned to Ti-O, C-OH, and C-O bonds respectively. The shifts in the OI component of O s binding energies were observed after the deposition of TiO2 onto graphene.

The downshift of the O 1s binding energies increased and reached 0.10 eV at 60 min of deposition of TiO2 nanoparticles onto graphene. The shift in the O 1s core level is due to the charge transfer between the TiO2 and graphene at the interface and reduced the binding energies
of the O core level. The band bending of the O 1s core level is further explained in the section 6.5.3

Additionally, OI/Ti ratio was evaluated for the decorated graphene with TiO\textsubscript{2} nanoparticles at different times of deposition and the results are illustrated in Fig 6.9 (b). It can be seen that the OI/Ti ratio is less than the ideal value of TiO\textsubscript{2} crystal, which suggest that the deposited TiO\textsubscript{2} nanoparticles onto graphene sheets are under stoichiometric Ti/C (sp\textsubscript{2}) atomic ratio were increased by stepping up the deposition times and reached in a ratio Ti/C sp\textsuperscript{2} =5.26 atomic ratio (%) at 60 min of deposition.

6.4.2 Raman analysis of undoped graphene and TiO\textsubscript{2} doped graphene deposited with different times

Fig 6.10 (a) present the Raman spectra of the undecorated graphene and decorated graphene at different times of deposition. Four characteristic bands (G, D, 2D, and D+G) were observed for the undoped graphene located at 1324, 1585.45, 2637 and 2875 cm\textsuperscript{-1} respectively. Additionally, the TiO\textsubscript{2} vibration modes were also observed with deposition of the TiO\textsubscript{2} nanoparticles onto graphene sheet. Four vibration modes for the decorated TiO\textsubscript{2} nanoparticles centered at 154, 394, 510 and 632 cm\textsuperscript{-1} respectively. No vibration modes of TiO\textsubscript{2} were detected at low deposition time, which indicates that low amount of TiO\textsubscript{2}, was deposited onto graphene sheets. By increasing the deposition time an intense peak at 151 cm\textsuperscript{-1} and three other small vibration modes were observed in the Raman spectra, which are attributed to the E\textsubscript{g}, B\textsubscript{1}\textsubscript{g}, or A\textsubscript{1}\textsubscript{g}, E\textsubscript{1}\textsubscript{g} modes of the anatase phase of TiO\textsubscript{2}, respectively [\textsuperscript{304}]. Moreover, a small shift in the G and 2D band by 3 and 2 cm\textsuperscript{-1} towards the high wavenumber were noticed at 10 min of deposition of TiO\textsubscript{2} nanoparticles onto graphene sheet as shown in Fig 6.10(a) (enlarged view). The shifts in the G and 2D bands increased with stepping up the deposition time. The shifts in G and 2D bands were further increased by 9.1 and
8.5 cm$^{-1}$, when the TiO$_2$ nanoparticles were deposited in a ratio Ti/C=5.26 atomic ratio (\%) at 60 min of deposition as shown in Fig 6.10 (b).

It is explained in the literature that, the shift in the G and 2D peaks discriminated the type of doping either p-doping or n-doping \cite{305}. Density functional theory revealed that the position of the 2D peak shifts toward the lower wavenumbers for the increasing electron concentration and shifts toward the higher wavenumber for increasing hole concentration \cite{306}.

![Fig 6.10](image)

In our case, with deposition of the TiO$_2$ nanoparticles onto graphene, the G and 2D peak were upshifted by 9.1 and 8.5 cm$^{-1}$ respectively. This upshifted of G and 2D indicates that graphene was p-doped with TiO$_2$ nanoparticles. This result is in good agreement with the XPS analysis.

The FWHM (G) of the undecorated graphene and decorated graphene with TiO$_2$ nanoparticles were evaluated using the Gaussian function line shape. The measured values of FWHM of G
peak as a function of Ti/C sp\textsuperscript{2} atomic ratio are shown in Fig 6.10 (b). The FWHM of G peak decreased from 78.5 cm\textsuperscript{-1} to 73.1 cm\textsuperscript{-1} by the deposition of TiO\textsubscript{2} at 60 min in a ratio Ti/C=5.26 atomic ratio. ( \% ). The reduction in the FWHM of the G peak is due to the doping. Pisani et al reported that, the Fermi level shifts from the Dirac point due to the doping in graphene and the excited charge carrier recombination probability were decreased. The reduction in the recombination of the excited charge also decreases the FWHM and sharpens the G peak [\textsuperscript{307}].

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig6_11.png}
\caption{Variation of G and D peak intensity ratio I_D/I_G and in plane crystallites size (La) plotted against the Ti/C atomic ratio(\%)}
\end{figure}

The I_D/I_G ratio was used to measure the defects and disorders induced in the structure of graphene by the interaction of TiO\textsubscript{2} nanoparticles. The measured I_D/I_G ratio of undecorated graphene and decorated graphene with TiO\textsubscript{2} nanoparticles as a function of Ti/C (sp\textsuperscript{2}) are illustrated in Fig 6.11
The \( I_D/I_G \) ratio increased from 1.66 and reached to 1.77 when the TiO\(_2\) nanoparticles were deposited onto graphene sheets in a ratio of Ti/C=5.26 at. %. This shows that the structural defects increased in graphene planes by increasing the TiO\(_2\) concentrations.

The in-plane crystalline sizes of the decorated graphene with TiO\(_2\) nanoparticles were calculated using equation [1]. The evaluated in-plane crystalline size as a function of Ti/C are presented in Fig 6.11. The in-plane crystallite size of graphene decreased from 23.1 to 21.49 nm with introduction of TiO\(_2\) to graphene plane in a ratio Ti/C=5.26 at. %.

The more reasonable explanation for the reduction of the in-plane crystallite size of graphene after the interaction sputtered particles and plasma species could be shrinking of the sp\(^2\) domain or may be the sp\(^2\) domain of graphene is broken with increasing the amount of TiO\(_2\) nanoparticles.

### 6.4.3 XRD analysis undoped graphene and TiO\(_2\) doped graphene at different times deposition

Fig 6.12 (a) presents the XRD pattern of the undecorated graphene and decorated graphene with TiO\(_2\) nanoparticles at different times of deposition. A broad and low-intensity peak of the (002) peak were observed at \( 2\theta = 25.11^\circ \) for the undoped graphene. For the decorated graphene with TiO\(_2\) nanoparticles, the (002) peak shifted gradually to higher \( 2\theta \) values by increasing the deposition time as shown in fig 6.12 (a) (enlarged view). The shift of the (002) toward the higher angles values suggests that the d–spacing between the sheet were decreased. The calculated d-spacing as a function of Ti/C (sp\(^2\)) are depicted in Fig 6.12 (b). The d-spacing values decreased from 3.54 to 3.49 nm with deposition of the TiO\(_2\) in a ratio Ti/C=5.26 at. %.
Chapter 6 Effect of TiO$_2$ concentration on the structural and electronic properties of graphene powder

![Graphene XRD patterns and Ti/C variation](image)

Fig 6.12 (a) XRD patterns of undoped and TiO$_2$ doped graphene at different times of depositions and (b) Variation of the 2$\theta$ angle position of the (002) peak C (002) position (degree) and d-spacing as function of Ti/C at.%

Additionally, with rising of the TiO$_2$ concentration onto graphene the FWHM of the 002 peak of the graphene is becoming wider. The evaluated values of the FWHM of the (002) peak as a function of Ti/C (sp$^2$) are presented in Fig 6.13. The FWHM of the 002 peak increased by raising the Ti/C (sp$^2$) atomic ratio (%). This suggests that the structural defects increased with rising of TiO$_2$ concentration. The crystalline thicknesses of undecorated graphene and decorated graphene with TiO$_2$ nanoparticles were calculated using the Scherer equation and the values are illustrated in Fig 6.13. The reduction of the crystalline thickness of the graphene after the deposition of TiO$_2$ nanoparticles indicates that the stacking orders of the graphene sheets were decreased. Our graphene flakes contain very few layers of graphene. The stacking orders of the layers are very poor due to widening of the (002) peak. When the TiO$_2$ nanoparticles were deposited onto the graphene sheets, the interlayer separation between the graphene sheets decreased. Therefore it influences the stacking order of the graphene sheets.
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6.5 The influence of TiO$_2$ nanoparticles on the structure and chemical properties of graphene powder via given different vibration frequencies

In the above two section (6.3, 6.4), the TiO$_2$ nanoparticles were deposited onto graphene at low powder vibration frequency (20 Hz). It was found from the TEM micrographs that, by deposition of TiO$_2$ nanoparticles with low powder vibration frequencies the sputtered particles were aggregated onto graphene sheets. The main objective of this work is to decorate the graphene sheets with well dispersed TiO$_2$ nanoparticles. TiO$_2$ nanoparticles were deposited onto graphene sheet with variations of the powder vibration frequencies discussed in this section. The influence of the interaction of TiO$_2$ nanoparticle with vibrating graphene powder was characterized by various techniques. In term of structural study the Raman and XRD were used and the chemical composition was studied by XPS technique. Moreover the process parameters are presented in table 6.3.

Table 6.3 the process condition of decorated graphene with TiO$_2$ nanoparticles
6.5.1 XPS analysis undoped graphene and TiO$_2$ doped graphene deposited at different powder vibration frequencies

Fig 6.15 presents the XPS spectra of the undecorated graphene and decorated graphene at different powder vibration frequencies. The high resolution C 1s XPS spectra of the undecorated graphene and decorated graphene with TiO$_2$ nanoparticles at different powder vibration frequencies are described in Fig 6.15 (a). The C 1s core level is considerably changed with the deposition of TiO$_2$ onto graphene powder at different powder vibration frequencies. Before the deposition the C 1s core level main peak C-C (sp$^2$) was located at 284.45 eV. But upon the deposition at 0 Hz vibration the C 1s core level was shifted to lower binding energy position to 284.40 eV. The downshift in the C 1s core level increased with variation of the powder vibration frequencies. The maximum downshift of 0.12 eV in the C 1s core level was observed at 100 Hz powder vibration frequencies. Recently several approaches were reported concerning about the doping of graphene. Generally, when graphene is contacted with high work function material like, TiO$_2$, MoO$_3$ and WO$_3$ charge is expected to transfer at the interface due to the work function differences. The charge transfer phenomenon at the interface between the graphene and metal oxide (hfO$_2$, MoO$_3$) has been explained by Jens Mayer et al\textsuperscript{100}. Simon Sanders et al is
also explained the same phenomenon. He described that shifts in the Fermi level of graphene from its Dirac point due to the charge transfer between the interface of metal oxide and graphene\(^{308}\). The downshift of the C 1s core level from its Dirac position is presented schematically in Fig 6.14. The downshift of the Fermi level from its Dirac point is due to the p doping and opposite for the n doped graphene. Upon the deposition of TiO\(_2\) nanoparticles onto graphene powder the C 1s core level shift toward the lower binding energy values and the downshift of the C 1s core level increased with rising of TiO\(_2\) concentration. The downshift of the C 1s core level of graphene after the deposition of TiO\(_2\) nanoparticles is indication of p-doping of graphene.

The high resolution XPS spectra of the Ti 2p for the decorated graphene with TiO\(_2\) nanoparticles at different powder vibration frequencies are presented in Fig 6.15 (b). For the decorated graphene with TiO2 nanoparticles two prominent peaks were observed, which are located at 459.08 eV and 464.93 eV respectively. The spin-orbit split of the photoelectron for the decorated graphene with TiO\(_2\) nanoparticles is represented to the Ti 2p\(_{3/2}\) and Ti 2p\(_{1/2}\) peaks. The separation between the Ti 2p\(_{3/2}\) and Ti 2p\(_{1/2}\) is 5.87 eV, which indicates that the presence of the normal state of Ti\(^{+4}\) and is consistent with reported data \(^{309}\). Addition to this shifts in the Ti 2p was observed toward the lower binding energies values. A downshift in the Ti 2p core levels were noted upon deposition of the TiO\(_2\) nanoparticles onto graphene sheets and the maximum downshift of 0.16 eV was obtained, when the TiO\(_2\) nanoparticles were deposited onto graphene at 100 Hz powder vibration frequencies. The downshift of the Ti 2p core level can be explained as follows, as described in the above text. When graphene contacted with TiO\(_2\) electrons are transferred from graphene to the TiO\(_2\) due to the large work function of the TiO\(_2\). This demonstrates that the electrons are lost in the graphene side produces positive space charge close
to the interface (space charge region) and the accumulation of the electrons in the TiO$_2$ induce negatively charged surface. This effectively generates an electric field between the graphene and TiO$_2$ at the interface.

![Diagram showing band alignment of graphene and TiO$_2$ nanoparticles](image)

**Fig 6.14 Band alignment of the graphene and TiO$_2$ nanoparticles**

The generated electric field in the space charge region of the contacted material leads to the distortion of the electronic band of graphene and TiO$_2$ close to the interface and the band bending occurred at the interface. As the work function of the TiO$_2$ (5.50 eV) is larger than graphene (4.33 eV), the electrons are transferred from the graphene to the TiO$_2$ nanoparticles and the bands of the TiO$_2$ bend downwardly towards the interface with the formation of an accumulation layer in the TiO$_2$. However when the graphene is contacted with low work function metal oxide, then the electrons is transferred from the metal oxide to graphene and the band of the metal oxide bends upwardly. A similar phenomenon has been reported recently by Yongqing Cai. et al [310].
Chapter 6 Effect of TiO$_2$ concentration on the structural and electronic properties of graphene powder

Fig 6.15 (a) XPS spectra of graphene powder and deposited TiO$_2$ nanoparticles at different powder vibration frequencies (a) Shift in the C 1s core levels position and the shift of this position upon TiO$_2$ deposition. (b) Ti 2p core level spectra [Process pressure = 6 Pa, Time=60 min, powder vibration frequency = [0 to 100 Hz] RF power= 40 W]

Fig 6.16 (a) shows the high-resolution XPS spectra of the O 1s core levels for the decorated graphene with TiO$_2$ nanoparticles at different powder vibration frequencies. Again the O 1s core level was de-convoluted into three components centered at the binding energy positions of 530.59, 532.09 and 533.54 eV were assigned to Ti-O, C=OH, and C-O bonds respectively. Chemical shifts in the O 1s core level were observed with increasing the powder vibration frequencies. The O 1s core levels were downshifted from 530.59 eV to 530.46 eV when the graphene flakes were decorated with TiO$_2$ nanoparticles at 100 Hz powder vibration frequencies. This indicates that by the increasing concentration of TiO$_2$ nanoparticles onto the graphene sheet through powder vibration frequencies, the chemical interaction between the TiO$_2$ nanoparticles...
and graphene increased and variation of the binding energies of the O 1s peak were observed. Due to the surface charge transfer from graphene to TiO₂ reduced the binding energies of the chemical components of the O 1s core level.

Moreover, the OI/Ti is important parameters to evaluate that the deposited TiO₂ nanoparticles are oxygen deficient or not. Measured OI/Ti ratios for the decorated graphene with TiO₂ nanoparticles at different powder vibration frequencies are shown in Fig 6.16 (b). The calculated value of the OI/Ti ratio indicates that, the deposited TiO₂ nanoparticles are under stoichiometric.

![Graph showing the variation of the Ti/C and OI/Ti atomic ratio as a function of different powder vibration frequencies.](image)

**Fig 6.16(a)** O 1s core peak of decorated graphene nanoparticles at different powder vibration frequencies

**Fig 6.16(b)** Variations of Ti/C and OI/Ti atomic ratio as a function of different powder vibration frequencies.

Fig 6.15 (a) demonstrates that by the variation of the powder vibration frequencies more TiO₂ nanoparticles were deposited onto graphene sheet compared to the without moving graphene powder. For the without moving graphene powder the obtained Ti/C = 3.86 at. % and reached to Ti/C = 9.46 at. % when the graphene powder vibrated at 100 Hz. It is explained already in
chapter 5, that by the variation of the powder vibration more sputtered particles are line of sight to the graphene flakes compared to the without moving graphene powder.

### 6.5.2 XRD analysis undoped graphene and TiO$_2$ doped graphene deposited at different powder vibration frequencies.

Fig 6.17 (a) depicts the XRD pattern of the undoped graphene and decorated graphene with TiO$_2$ nanoparticles at different powder vibration frequencies. The FWHM and position of the (002) of graphene were drastically changed by the deposition of TiO$_2$ nanoparticles at different powder vibration frequencies. Low intensity and broad peak of (002) peak suggest that graphene consists of very few layers of graphene (3 to 5 layers).

The (002) peak of the graphene shifted to higher 2θ values with deposition of TiO$_2$ nanoparticles at different powder vibration frequencies. This suggests that by interaction of graphene with TiO$_2$ nanoparticles the d-spacing of the graphene were reduced. The evaluated d-spacing as a function of the Ti/C (sp$^2$) obtained by the variation of the powder vibration are presented in Fig...
6.17 (b). The d-spacing decreased from 0.354 to 0.347 nm with obtained (Ti/C sp2= 9.45 at. %) onto graphene powder at 100 Hz powder vibration frequency. This demonstrates that the lattice of the graphene is contracted with the interaction of the TiO2 nanoparticles. Additionally, with variation of the TiO2 concentration onto graphene powder the FWHM of the graphene became wider. The FWHM of graphene and deposited TiO2 nanoparticles onto graphene powder at different powder vibration frequencies as a function of Ti/C (sp2) is displayed in Fig 6.18.

![Graph showing variation in FWHM and crystalline thickness](image)

**Fig 6.18 Variation in the FWHM of the (002) peak and crystallite thickness as function of Ti/C at.%**

This indicates the planes of the graphene were distorted with deposition of the TiO2 nanoparticles. The distortion increased with increasing the TiO2 concentration to the graphene plane. The crystalline thickness of the undecorated graphene and decorated graphene was calculated by Scherer equation and found that the crystalline thickness decreased from 1.7 to 1.5 nm with introduction of the TiO2 nanoparticles in a ratio Ti/C sp2 =9.45 at. % the results are
presented in Fig 6.17. The reduction of the crystalline thickness as a function of Ti/C suggests that with the interaction of the graphene with TiO$_2$ nanoparticles the stacking order is reduced or may be due to the shrinking of planes graphene with the interaction of TiO$_2$ nanoparticles.

6.5.3 Raman analysis undoped graphene and TiO$_2$ doped graphene deposited at different powder vibration frequencies

The Raman spectra of the undecorated graphene and decorated graphene at different powder vibration frequencies are illustrated in Fig 6.19 (a). Four characteristic bands of the graphene attributed to D, G 2D and D+G peaks were observed in all the Raman spectra. For the decorated graphene with TiO2 nanoparticles four addition bands were also observed in the Raman spectra. The main and strongest mode of the anatase phase centered at 151 cm$^{-1}$, which attributed to the stretching vibration mode of Ti-O bonds. The other three low intensity modes centered at positions 393 cm$^{-1}$, 513 cm$^{-1}$ and 632 cm$^{-1}$, which correspond to the $B_{1g}$, $A_{1g}$ and $E_{1g}$ modes.
By the deposition of TiO$_2$ nanoparticles onto graphene sheet at different powder vibration frequencies strongly affected the FWHM, position and intensities of graphene bands. The G and 2D position of graphene is shifted to higher wavenumbers by 4 and 3 cm$^{-1}$ with deposition of TiO$_2$ nanoparticles onto graphene powder without moving graphene powder (0 Hz). G and 2D bands were further shifted to higher wavenumbers by increasing the TiO$_2$ concentrations onto graphene with a variation of powder vibration frequencies. The maximum upshift in G and 2D are 10.65 cm$^{-1}$ and 9.12 cm$^{-1}$ observed when the TiO$_2$ nanoparticles were deposited in a ratio of Ti/C sp$^2$=9.45 at. % at 100 Hz powder vibration frequency and the results are presented in Fig 6.18 (a) (enlarged view). It is well established that doping of graphene changed the position of the G and 2D bands explained by Das et al [311]. Compressive strain and tensile strain has also changed the position of the graphene bands. Our XRD results show that by the deposition of the TiO$_2$ nanoparticle onto graphene sheet compressive strain is developed in the lattice of graphene. But in the case of compressive strain, the shift in the 2D band is greater than of shift in G band. Casiraghi et al. also reported that the shift in G and 2D bands toward higher frequencies is caused by the compressive strain, if the shift in the 2D band is larger than the shift in G band [312]. But in case of doping of graphene the shift in 2D band is not bigger than that of shift in the G bands. Addition to this, in case of doping the FWHM of the G peak also becomes narrower with the increasing the dopant concentration explained by Namphung Peimyoo et al [312]. In our case the G and 2D bands of the graphene were shifted to higher wavenumbers upon deposition of the TiO$_2$ nanoparticles and also the FWHM of the G peak became narrower as shown in Fig 6.19 (b), which suggests that the doping phenomena is dominated over the compressive strain. Therefore, the shift in the G and 2D toward the higher wavenumber is caused by p doping graphene with deposition of the TiO$_2$ nanoparticles. The degree of disorderness and defects
introduced in the structure of graphene with the deposition of TiO$_2$ nanoparticles were evaluated by using the $I_D/I_G$ ratio. It is shown in Fig 6.20 (a) that by the deposition of TiO$_2$ nanoparticles at different powder vibration frequencies the intensity of defects peak (D) enhanced. This indicates that the structural defects increased with increasing interaction of graphene with TiO$_2$ nanoparticles. The $I_D/I_G$ ratio for the decorated graphene with TiO2 nanoparticles as a function of Ti/C (sp2) are presented in Fig 6.19. The $I_D/I_G$ ratio increased from 1.66 and reached a value of 1.76 with deposition of TiO$_2$ nanoparticles at 100 Hz powder vibration frequency with a ratio of Ti/C sp2=9.45 at. %.

![Graph](image)

**Fig 6.20 Variation of G and D ratios $I_D/I_G$ and in plane crystallites size (La) plotted against the Ti/C at (%)**

Moreover, the in-plane crystal size La was measured for the undecorated graphene and decorated graphene at different powder vibration frequencies by using equation [1]. The in-plane crystallite size as a function of Ti/C (sp2) is shown in Fig 6.20. It shows that the in plane crystallite sizes decreased from the 23.1 nm to 21.6 nm, when the TiO$_2$ nanoparticles were introduced in a ratio of Ti/C sp2=9.45 at. %. The more probable reason of the reduction of crystallite size could be
sp² domain breaking or shrinking of the sp² domain size with deposition of the TiO₂ nanoparticles.

6.6 Concluding Remarks
In this chapter of thesis, the interaction of the graphene with TiO₂ nanoparticles were studied in detailed. Three deposition parameters were used to decorate the graphene powder with small and dispersed nanoparticles. The structural analysis of the decorated graphene with TiO₂ nanoparticles were investigated by XRD and Raman. The XPS analysis was used to study the chemical state and composition of the decorated graphene with TiO₂ nanoparticles. The particle nature of the deposited TiO₂ was confirmed by TEM examination. The following conclusions can be driven,

A. Structural analysis of the decorated graphene with TiO₂ nanoparticles (XRD)

- The lattice of graphene was distorted with decoration of the TiO₂ nanoparticles
- The spacing between the layers of graphene decreased by interaction of TiO₂ nanoparticles
- No diffraction peaks of TiO₂ were observed in the XRD patterns.
- The crystallite thickness of graphene flakes decreased with deposition of the TiO₂ nanoparticles
- The G and 2D bands of graphene were shifted to higher wavenumber with increasing TiO₂ concentration onto graphene sheet confirming the p doped graphene with TiO₂ nanoparticles.
- The structural defects and disorders increased by increasing the TiO₂ concentration to the plane graphene.
- The FWHM of G peak decreased linearly with increasing the doping concentrations in term of Ti/C sp² atomic ratio.
The in-plane crystallite size (La) of graphene decreased upon the deposition of TiO$_2$ nanoparticles

B. From the XPS analysis:

- The C 1s core level of the graphene were shifted to the lower binding energies values upon the deposition of the TiO$_2$ nanoparticles and downshift of the C 1s core level increased with rising of TiO$_2$ amount. The downshift of the C 1s core level indicates a charge transfer from graphene to TiO$_2$ nanoparticles due to the larger work function of TiO$_2$ relatively to that of graphene.
- Ti/C at. % ratio increased by increasing the powder vibration frequencies.
- Similar downshift in the Ti 2p and O 1s core level like C 1s core level were also observed upon raising the TiO$_2$ concentration.

The interaction of the graphene sheets with TiO$_2$ nanoparticles were presented in this chapter. The exploration of decorated graphene sheets with M and MO nanostructures applications will be presented in next chapter#7.
Chapter # 7

Exploration of decorated graphene with metal and metal oxide nanostructures

applications

7.1 Introduction

The main goal of this chapter is to study enhancement properties of the graphene with deposition of M and MO nanoparticles. It is already discussed that graphene have numerous properties and display some other novel properties, when the graphene surface is modified with M and MO nanostructures, such as with addition of the foreign atoms which is a promising approach to modify the electronic structures, catalytic activity and magnetic behavior. In this chapter, three different kinds of applications were studied for the decorated graphene sheets with TiO$_2$, Mg and Nb$_2$O$_5$ nanoparticles. The ferromagnetic behavior of the graphene and modified graphene with MO nanoparticles (Fe$_3$O$_4$, ZnFe$_2$O$_4$, CoFe$_2$O$_4$, and Co) already has been reported [313, 314]. The ferromagnetic behavior of graphene decorated with the Nb$_2$O$_5$ nanoparticles is not reported till now. The TiO$_2$ and graphene composite was extensively studied for the improvement of the photocatalytic activity. The photocatalytic activity of the decoration graphene with TiO$_2$ nanoparticles by RF sputtering technique is not reported in literature. The well dispersed Mg nanoparticles onto graphene shows good catalytic activity towards the hydrogen storage. It is reported that when the small Mg nanoparticles dispersed onto graphene sheet, the hydrogen storage capacity was enhanced at low temperature. Well dispersed Mg nanoparticles were deposited onto graphene sheets by RF sputtering. The hydrogen sorption test was carried out for the decorated graphene with Mg nanoparticles.
7.2 Magnetic properties of undecorated graphene and decorated graphene with Nb$_2$O$_5$ nanoparticles

The magnetic property was measured using vibrating sample magnetometer with PPMS (Dyna Cool) with collaboration of Department of Physics, Federal University of Rio Grande do Norte, Natal, RN, Brazil. The samples were analyzed by Prof M. A. Correa. The following deposition parameters were varied during the deposition. The graphene powders were decorated with Nb$_2$O$_5$ nanoparticles at different times of deposition (8 to 32 min). The Nb$_2$O$_5$ nanoparticles were deposited onto graphene surface without moving powder. The RF power and process pressure values were kept constant at 6 Pa and 40 W respectively. Moreover, with the decoration of Nb$_2$O$_5$ nanoparticles on the graphene sheet the defects were pronounced, which has been proved above from Raman and XRD studies. Now we have to proceed to study the magnetic properties of the undoped graphene and Nb$_2$O$_5$ decorated graphene. The ferromagnetic behavior was observed in our samples due to defect induced in graphene by the deposition of Nb$_2$O$_5$ nanoparticles. Fig 7.1 (a) illustrates the magnetic hysteresis (M-H ) loops of the undecorated graphene and decorated graphene with Nb$_2$O$_5$ nanoparticles, which suggest that graphene composite with Nb$_2$O$_5$ nanoparticles demonstrated the ferromagnetic property at low temperature range. The ferromagnetic behavior with hysteretic curves are displayed for the all the analyzed samples as a function of Nb/C (sp$^2$) atomic ratio (%) at high external magnetic field range for low temperature 5 K. The ferromagnetic behavior of the undoped graphene powder is probably due to the structural defects. This is confirmed from Raman spectroscopy which shows that ratio of I$_D$/I$_G$ is greater than 1$^{315}$. Pisani et al is also described that the graphene shows ferromagnetic behavior due to structural defects$^{232}$. It is well proved that structural defects play the main role in the ferromagnetism. It was observed that the saturation magnetization (Ms)
values at 5 K for the undoped graphene and 0.49, 0.62 and 0.75 at. % Nb doped graphene are 0.12, 0.38, 0.22 and 0.18 emu/g, respectively. For the undoped graphene flakes very low magnetic moment was observed. Similar results are also reported in the literature [316]. However, the ferromagnetic behavior of graphene increased from 0.12 emu/g to reach 0.38 emu/g, when a small amount of Nb$_2$O$_5$ nanoparticles were deposited onto graphene with a ratio Nb/C sp$^2$ = 0.67 at. %. On the other hand, the magnetic moment values decreased, when the Nb$_2$O$_5$ nanoparticles were deposited onto graphene in a ratio between Nb/C sp$^2$ between 1.05 and 1.31 at. (%). These phenomena can be explained by the fact that magnetic behaviors of the nanoparticles are strongly dependent on the shape, imperfection and size [317]. The magnetic property size dependence was described by two hitherto established phenomena.

![Fig 7. 1 (a, b) M-H curves for undoped graphene and with various Nb doping concentration measured at (a)) 5 K and (b) 300 K](image-url)
Firstly, the decorated nanoparticles on the surface of graphene can undergo coalescence to form 2D planer structure similar to a sheet when the particles size is very small, the size of nanoparticles would be in the range of 1 to 3 nm\[^{318}\]. In this context, the magnetic behavior and anisotropy was reported to originate from electronic delocalization and symmetry breaking. \[^{319}\]. Second, when graphene was decorated with large size nanoparticles and these particles made aggregation on the graphene sheet, the particles onto graphene sheet made 3D mass structure and in this case the magnetization values depend on the surface to volume ratio\[^{233}\]. In our case, from the TEM images it can be seen (Fig 4.7 in chapter # 4) that the size of deposited Nb2O5 nanoparticles onto graphene sheet is larger than that of described in first case and these nanoparticles is made 3D mass structure onto graphene sheet, then magnetic anisotropy generates perpendicular to the surface plane of particles. Consequently the behavior of our deposited Nb2O5 nanoparticles onto graphene sheet resembles the second type of behavior. The rapid increase in magnetic moment after deposition of Nb2O5 nanoparticles onto graphene in a ratio Nb/C sp\(^2\) = 0.67 at. %, can suggest that more nanoparticles linearly coupled with applied magnetic field increasing the magnetization behavior. However, the decoration of graphene with Nb2O5 nanoparticles in a high Nb/C sp\(^2\) ratio values between 1.05 and 1.31 at. (%), the random dipole coupling between nanoparticles was observed due to the agglomerated and concentrated nanoparticles. Even in well dispersed Nb2O5 nanoparticles in a ratio Nb/C sp\(^2\) = 1.31 at. % demagnetizations effects were observed from the coupling of the random dipole. To address this point, as reported in the literature, the hysteresis width for the non-interacting single domains only depends on the internal structure of the particles \[^{320}\]. This case is comparable to our deposited Nb2O5 nanoparticles onto graphene sheet. The isotropic interaction between Nb2O5 nanoparticles, such as in concentrated or agglomerated nanoparticles on the graphene surface,
cause a reduction in coercivity by decreasing the barrier for the magnetization reversal \[^{321}\]. Fig 7.1 (b) depicts the M-H curve as a function of the Nb\(_2\)O\(_{5-x}\) concentration at 300 K. The diamagnetism behavior was observed in long range of magnetic field for undecorated graphene and decorated graphene with different Nb\(_2\)O\(_{5-x}\) concentrations at 300 K. Again the undecorated graphene flakes illustrate the low diamagnetism behavior at high temperature with respect to the decorated graphene with Nb\(_2\)O\(_5\) nanoparticles. The high diamagnetism value was observed for the decorated graphene with Nb\(_2\)O\(_5\) nanoparticles in a ratio Nb/C sp\(^2\) = 0.67 at. %. It was observed that the saturation magnetization (Ms) values at 300 K for undecorated graphene and decorated graphene with Nb\(_2\)O\(_5\) nanoparticles in ratio of Nb/C sp\(^2\) = 0.67, 1.05 and 1.31 at. (%) were 0.03, 0.06, 0.05 and 0.04 emu/g respectively. The diamagnetic behavior of the decorated graphene with high Nb/C sp\(^2\) ratio decreased. The reduction of the diamagnetic behavior will be explained latter.

Furthermore magnetization measurements were carried out in magnetic field range -70 <KOe<+70 for temperature in the range 5≤T<300K irrespective of Nb concentrations shown in Fig. 7.2. The magnetic hysteresis (M-H) curve at a temperature range 5≤T<300K for undecorated graphene and decorated graphene with Nb/C sp\(^2\) atomic ratio in the range \{0.62 - 1.31\} indicates the two different regions of magnetism. The diamagnetism behavior was observed for the undecorated graphene and decorated graphene with Nb\(_2\)O\(_5\) nanoparticles at high temperature range, from 50 to 300 K, while for low temperature noticeable ferromagnetism appeared at temperature range between 5 and 10 K. We obtained a good convergence with our experimental data for the temperature approximately > 50 K which correspond to the region where the ferromagnetism behavior occurred. The diamagnetic contribution emerged for samples at temperature range 50 K < T < 300 K. It is clear, that at high temperature thermal disordering
counteracts the magnetic field. This phenomenon can be explained as follow, it is discussed in the above text that energy of magnetic particles is proportional to the particles size, volume and number of the magnetic molecules in a single magnetic domain under an external field. The thermal fluctuation reduces the total magnetic moment of the applied external field, when the energy of the magnetic particles becomes comparable to the thermal energy \[^{322}\].

![Graphene Magnetization Curves](image)

**Fig 7.2** Magnetization curves as a function of the applied temperature 5≤T<300K for each sample, for all Nb (%) concentration. (a) Magnetization curves for undoped graphene flakes (b) for doped graphene with 0.49 Nb (%) concentration. (c) For doped graphene with 0.62 Nb (%) concentrations. (d) For doped graphene with 0.75 Nb (%) concentrations.

Fig 7.3 depicts the maximum magnetization as a function of the temperature and the coercive field as a function of the Nb concentration. In the first case in Fig. 7.3 (a), a decrease of the magnetic moment with the increase of the temperature is noticed, irrespective of Nb
concentration. At the same time as already discussed, the high magnetic moment was observed for the decorated graphene with Nb$_2$O$_5$ nanoparticles with an atomic ratio Nb/C $sp^2 = 0.67$ in the temperature range between 5 and 10 K. On the other hand, the undoped graphene flakes show the lowest magnetic moment. The two distinctive behaviors regarding the coercive field were noticed in the range of temperature between $5 \leq T < 300$K. Considering low temperature values, high values of the coercive field was reached. This feature can be connected with the decrease in the diamagnetic response for this range of temperature. As a consequence, the ferromagnetic signal prevails and the coercive field increases. On the other side, at high temperature a competition between diamagnetic and ferromagnetic occurs to respond to the external magnetic field excitation leading to the decrease in the coercive field.

![Graph showing coercive field as a function of temperature and Nb concentration](image.jpg)

Fig 7.3 (a) Coercive field as a function of temperature for different Nb (%) concentrations. (b) Coercive field as a function of Nb concentration for different temperatures.
7.3 Photo catalytic activity of the TiO$_2$ and graphene composite.

The photocatalytic application of undecorated graphene and decorated graphene with TiO$_2$ nanoparticles were demonstrated in this section. The following process parameters [working pressure = 6 Pa, Time=40 min, Frequency = 20 Hz RF power= 80 W] were used to deposit the TiO$_2$ nanoparticles onto graphene powder. The photocatalytic activity study of the undecorated graphene and decorated graphene with TiO$_2$ nanoparticles with an atomic ratio (Ti/C sp$^2$= 13.37 at. %) was carried out by using the methylene red (MR) dye degradation as a model reaction under the UV and visible light. The absorbance peak of the MR decreased with increasing the reaction time under the ultraviolet and visible (Uv-vis) radiation as shown in Fig 7.4

![UV−vis spectra of decorated graphene with TiO$_2$ nanoparticles](image)

The decorated graphene with TiO$_2$ nanoparticles samples were analyzed by changing the C/C$_0$ with variation of the absorbance (A/A$_0$), where A$_0$ and C$_0$ is the initial absorbance and
concentration of MR respectively. Fig. 7.5 (b) presents the photo catalytic activity of the undecorated graphene and decorated graphene with TiO$_2$ nanoparticles. It was observed that the methylene red degraded slightly in the presence of the graphene powder. However, the degradation of MR was enhanced in the presence of graphene-TiO$_2$ catalyst. The dye was decomposed by about 30% of the initial dye upon the (Uv-vis) irradiation. From the TEM image shown in Fig (6.1) in chapter 6, the deposited TiO$_2$ nanoparticles onto graphene sheet were well
dispersed.

The enhancement of the photocatalytic activity of decorated graphene with TiO$_2$ nanoparticles can be explained as follows, it is reported that, three factors are important for the photocatalytic process, that is, the charge separation and transportation, absorption of light and the adsorption of the pollutant molecules and the scheme is presented in Fig 7.5 (b) [323]. Upon the irradiation of light onto the decorated graphene with TiO$_2$ nanoparticles, the valance band electrons of TiO$_2$ were excited to the conduction band and the photogenerated electron and hole could easily transfer to the nearby MB and theses photogenerated electrons and holes take part in the redox reaction. As a result the methylene blue decomposed, more methylene blue would transfer...
toward the interface from the solution, when the adsorption stability was broken and subsequently methylene red decomposed into CO₂ and H₂O through a series of redox reactions.

It is also reported that the formation of the charge transfer complex between the interface of the TiO₂ and graphene would be expected to facilitate the photocatalytic activity under the Uv-Vis light \(^{[324,325]}\). The interface charge transfer mechanism can facilitate excitation of electrons from graphene to conduction band of the TiO₂ upon the irradiation of the light; as a result the electron hole pairs were not recombined and well separated from each other, leading to enhance the photocatalytic activity through reduced pair recombination. Furthermore our XPS results demonstrate that, the deposited TiO₂ was under stoichiometric, which means that the deposited TiO₂ nanoparticles were oxygen deficient. It is well assumed that such oxygen vacancies in the TiO₂ nanoparticle can to enhance the photocatalytic activity of the TiO₂ and graphene composite. Because the oxygen vacancy in the TiO₂-x generate some localized state within the band gap of the TiO₂, which is ranging from 0.75 to 1.18 eV below the conduction band and leading the photoresponse to the light irradiation \(^{[326]}\).

### 7.4 Hydrogen sorption capacity of the decorated graphene with Mg nanoparticles

In this study, well dispersed Mg nanoparticles were deposited onto graphene sheets at 80 Hz powder vibration frequency. The other deposition parameters like \([\text{working pressure} = 6 \text{ Pa, deposition time}=40 \text{ min, RF power}= 40 \text{ W}]\) were kept constant. The deposited Mg nanoparticles onto graphene sheet were used for hydrogen storage application. In this composite, graphene serves as a supporting material for the decorated materials due to the high surface area. Hydrogen absorption and desorption characteristics of the decorated graphene with Mg nanoparticles were measured using a Sieverts PCT-Pro instrument at 2 bar and 8 bar pressure as shown in Fig 7.6. The hydrogen absorption and desorption were tested using two different
temperatures 330 °C and 360 °C. The hydrogen adsorption of the decorated graphene with Mg nanoparticles was reached a capacity of 3 wt. % within 80 min. Upon dehydrogenation 1.9 wt. % were released at same temperature within 100 min.

![Graph of hydrogenation and dehydrogenation of decorated graphene with Mg nanoparticle at 330° and 360°](image)

**Fig 7.6 Hydrogenation and dehydrogenation of the decorated graphene with Mg nanoparticle at 330° and 360°**

It was confirmed from the TEM micrographs that the deposited Mg nanoparticles were uniformly distributed onto graphene sheets, these Mg nanoparticles hydrogenated at 330 °C and 360°C and these particles saturated within 30 min, while these nanoparticles released the hydrogen and became dehydrogenated at the same temperatures. For the undecorated graphene the hydrogen absorption was measured at the 330° and a minimal value of (0.2 -0.5 %) of hydrogen was absorbed at 330 °C. The graphene is not absorbing the hydrogen at this temperature; this absorption could be due to some contaminations during the preparing sample for the absorption. This is the negligible contribution of the graphene in the Mg/graphene composites. It shows that only the decorated Mg nanoparticles absorbed the hydrogen. In our
case $H_2$ uptake capacity of Mg nanoparticle is high, because all the available Mg nanoparticles on the Mg nanoparticles absorbed the hydrogen to form MgH$_2$ onto graphene sheets. This point can be explained as follows, from the XPS analysis the calculated weight percentage of the Mg nanoparticles on the graphene surface was 45%. The total weight of the measured samples was 13 mg. The graphene surface contained only 4 to 5 mg of Mg nanoparticles. Due to the low amount of Mg nanoparticles onto graphene sheet the hydrogen absorption capacity was only 3% in graphene/Mg composite. The hydrogen absorption and desorption of the decorated Mg nanoparticles are presented in Fig 7.7. It was observed that the hydrogen absorption storage capacity for only the Mg nanoparticles was 6.6 wt. %. The similar results is also reported by Eunseon cho et al, they synthesized very small Mg nanoparticles onto graphene sheets and used the composite for the hydrogen absorption. They found that hydrogen storage capacity for Mg nanoparticles was 6.5 wt. % and 0.105 kg H$_2$ per liter in the total composite at 200 °C and 250 °C at 15 bars.

However, for the surface absorption of the hydrogen onto Mg surface to be accomplished fast kinetic required weak chemical bonding and low diffusion resistance. This is well established behavior between the high storage capacities and fast kinetics. To achieve this kind of fast kinetics’ large surface area of the Mg nanostructures sample would be prepared to support separation of gaseous hydrogen and also reduce the diffusion length resistance. Because the charge and discharge of the cycle one of the complex phenomenon, which involves molecular dissociation, diffusion, and chemical bonding. However, it is generally observed phenomenon that, hydrogenation process is controlled by molecular hydrogen dissociation at the Mg surface and hydrogen diffusion into the Mg bulk. Also it is well established that hydrogen molecules can be diffused onto the Mg nanoparticle and the hydrogen molecules must dissociated and form the
metal hydride. But, the molecular hydrogen is so stable and high energy is required to break the H-H bonding at normal temperature. However, with interaction of the molecular hydrogen by metal surface the metal surface weaken the H-H bonding and lowering the barrier of the effective dissociation. Consequently, at the surface of the Mg nanoparticles reflect the asset of the metal-H interaction. Addition to this the particle size of the deposited Mg nanoparticles was 8 - 12 nm. It has been reported that hydrogen up- taking capacity is strongly dependent on the size of Mg nanoparticles. Moreover, by optimization of the Mg nanoparticles size, contents and distribution is essential to improve the hydrogen absorption in graphene.

![Graph showing hydrogenation and dehydrogenation of the Mg nanoparticle at 330°](image)

**Fig 7.7 Hydrogenation and dehydrogenation of the Mg nanoparticle at 330°**

Moreover it should also be noted that the absorption and desorption temperature is still relatively high, which obstructs the practical applications of Mg-based hydrogen storage materials. Therefore, strategies to modify the thermodynamics of Mg-based materials to reduce absorption and desorption energy barrier are clearly to be important topics for further research.
7.5 Conclusions

In this chapter the application potential of the decorated graphene sheets with Nb$_2$O$_5$, TiO$_2$ and Mg nanoparticles was studied. It was found that with decoration of graphene with these metal and metal oxide nanostructures improve the properties of the composite. A ferromagnetic behavior was observed with decoration of graphene sheets with Nb$_2$O$_5$ nanoparticles. It was found that, the ferromagnetic property was enhanced with the deposition of the Nb$_2$O$_5$ nanoparticles. The photocatalytic activity was studied for the decorated graphene sheet with TiO$_2$ nanoparticles. It was observed that the decorated graphene sheets with TiO$_2$ nanoparticles showed reasonably catalytic activity. The hydrogen absorption and desorption was studied for the well dispersed Mg nanoparticles onto graphene sheets. It was found that the decorated Mg nanoparticles absorbed hydrogen. The hydrogen storage capacity for the decorated graphene with Mg nanoparticles was 3 wt. % in whole composite. However the hydrogen storage capacity of the decorated Mg nanoparticles only was 6.6 wt. %.
Concluding remarks and prospective

This thesis was dedicated to decorate graphene sheets with metal and metal oxide nanostructures by RF sputtering technique. Two main objectives were focused in this thesis. 1) To decorate graphene sheets uniformly with metal and metal oxide nanostructure without agglomeration. 2) To explore different kinds of application of decorated graphene sheets with metal and metal oxide nanostructures. In order to achieve the mentioned objectives, we designed and carried out the following research activities and driven the following conclusions.

In the first step, we presented the experimental study results about Nb_2O_5 deposition onto graphite nanoplatelets (GNPs) by the variation of the deposition process parameters. To optimize the deposition parameters, four deposition process parameters (RF power, process pressure, and powder vibration frequency and deposition time) were varied to deposit the Nb_2O_5 layers onto GNPs. The structural, chemical and electronic properties of the decorated GNPs with Nb_2O_5 layers were studied. It was found that with deposition of Nb_2O_5 layers onto GNPs, tensile strain was developed into the planes of the GNPs. The induced tensile strain in and between the planes of GNPs increased with raising the amount of the Nb_2O_5 concentration. The structural defects and disorderness were enhanced with deposition of Nb_2O_5 layers onto GNPs by increasing RF power and at low process pressure values. The structural defects, disorderness and tensile strain in the GNPs were confirmed by the X-ray diffraction and Raman spectroscopy analysis. TEM images shows that GNPs decorated with around 5 to10 nm uniform layer of Nb_2O_5 at 100 W on their surface were successfully fabricated. From the XPS analysis it was confirmed that, by increasing Nb_2O_5 layer thickness on the GNPs surface with rising RF power values binding energy downshift in C 1s peak suggests a p-type doping of GNPs due to charge transfer at the
Concluding Remarks and prospective

interface as a consequence of the higher work function difference between the Nb$_2$O$_5$ (4.70 eV) and GNPs (4.33 eV).

In the second step, the interface between the graphene sheets and Nb$_2$O$_5$ nanoparticles were studied. To achieve dispersion of Nb$_2$O$_5$ nanoparticles obtained onto graphene sheets three different process parameters were varied. The influence of the Nb$_2$O$_5$ concentration on the structural, chemical, morphological and magnetic properties of graphene was discussed. It was established that the structural defects were pronounced with increasing amounts of the Nb$_2$O$_5$ concentration. XPS measurement on graphene/Nb$_2$O$_5$ suggests p-type doping of graphene due to charge transfer at the interface as a consequence of the high work function of Nb$_2$O$_5$. The strong p-doping effect was also confirmed by Raman analysis where the positions of the G and 2D peaks of graphene gradually upshifted upon increasing the Nb$_2$O$_5$ concentration. The uniform distribution of decorated Nb$_2$O$_5$ nanoparticles onto graphene was confirmed from TEM analysis. The ferromagnetic behavior was observed for the undecorated graphene and decorated graphene with Nb$_2$O$_5$ nanoparticles. The ferromagnetic behavior of graphene was enhanced with decoration of the Nb$_2$O$_5$ nanoparticles.

In the third step, the effect of the Mg concentration on the structural, chemical and morphological properties of the graphene was described. Well dispersed Mg nanoparticles were decorated onto graphene sheets. The structural properties of the decorated graphene with Mg nanoparticles were studied by Raman and XRD techniques. It was found that from the XRD results, different sizes of the crystalline Mg nanoparticles were obtained onto graphene sheets with variation of the process parameters. The plane of graphene sheets were more distorted with increasing amount of Mg nanoparticles onto graphene sheets. Raman spectra indicated that G and 2D bands of the graphene were shifted to higher wavenumber with deposition of Mg.
nanoparticles. The upshifted in G and 2D bands increased with raising amounts of Mg nanoparticles onto graphene sheets, suggesting that graphene was p doped with interaction Mg nanoparticles. The in-plane crystallite size of the graphene was reduced with deposition of the Mg nanoparticles. The well dispersed and small size of Mg nanoparticles in the range of (8-12 nm) onto graphene sheets was decorated by using a high powder vibration frequency. No agglomeration of the sputtered particles was observed with high powder vibration frequency. This observation was confirmed by TEM micrographs. XPS analysis revealed that the decorated Mg nanoparticles onto graphene were oxidized due to exposure to the atmosphere. The well dispersed decorated Mg nanoparticles onto graphene sheets were studied for the hydrogen absorption and desorption at two different temperatures 330 °C and 360 °C at 2 and 8 bars pressure. The hydrogen up taking capacity for the decorated graphene sheets with Mg nanoparticles was 3 wt. % in whole composite. However, the up taking hydrogen storage capacity of the only Mg nanoparticles was 6.6 wt. %.

In the last step, the interaction of the graphene sheets with TiO₂ nanoparticles was studied. The comprehensive characterization techniques (XRD, Raman, XPS, TEM and photocatalytic activity) were used to study the interaction of the TiO₂ nanoparticles with graphene. The influence of the TiO₂ concentration on the structural, chemical, morphological and photocatalytic activity of the graphene sheets were discussed. The XRD results indicated that the lattice of the graphene sheets was distorted with increasing amount of the TiO₂ concentration. The particle nature of the deposited TiO₂ was confirmed by TEM examination and also the TEM analysis shows that TiO₂ nanoparticles were uniformly distributed onto graphene sheets. The Raman analysis showed that the G and 2D bands of graphene were shifted to higher wavenumber with increasing TiO₂ concentration onto graphene sheet confirming the p doped graphene with TiO₂.
nanoparticles. The FWHM of G peak decreased linearly with increasing the doping concentrations in terms of Ti/C sp$^2$ atomic ratio. The XPS analysis further confirmed the p doping of graphene upon the deposition of the TiO$_2$ nanoparticles. The binding energy downshift the C 1s core level of was observed after charge transfer from graphene to TiO$_2$ nanoparticles due to the larger work function of TiO$_2$ relatively to that of graphene. The well dispersed nanoparticles onto graphene were used for the photocatalytic application. It was observed that decorated graphene sheets with TiO$_2$ nanoparticles shows reasonably catalytic activity. This thesis provides results of a study of the interaction effects of the graphene sheets with Nb$_2$O$_5$, Mg and TiO$_2$ nanoparticles deposited by RF sputtering technique. The obtained results suggest new itineraries for the improvement of the properties of decorated graphene sheets with such materials. In this thesis, we discussed the structural, chemical and electronic properties of decorated graphene sheets with low quantity of Nb$_2$O$_5$ nanoparticles since the interfacial properties modification was the aim of the study. The deposition of thick nanoparticles would prevent such study by XPS analysis for example. However, from the point of view of specific applications using the photocatalytic activity or as gas sensing, decoration of graphene sheets with high quantity of Nb$_2$O$_5$ nanoparticles will be more useful. The range of the deposition parameters such as (RF power values, powder vibration frequencies) should be further extended to get very uniform decoration of the Nb$_2$O$_5$ nanoparticles onto graphene sheets. The decorated samples would be further tested to see the magnetic behavior of the uniform decorated graphene sheets.

It is discussed that the Magnesium is one of the ideal applicant for active hydrogen storage due to its high gravimetric hydrogen capabilities and affability. Moreover it was observed that the absorption and desorption of decorated graphene sheets with Mg nanoparticle are still relatively
Concluding Remarks and prospective

high temperature processes and of slow release/uptake kinetics, which limits the practical applications of Mg-based hydrogen storage materials. Therefore, strategies to modify the thermodynamics of Mg-based materials to reduce absorption and desorption energy barrier are clearly to be important topics for further research. For hydrogen absorption and desorption capacity evaluation, more samples of the decorated graphene sheets with Mg nanoparticles will be prepared. Specially to get the size of Mg nanoparticles within the range of 2 to 5 nm onto graphene sheets high RF power values would be applied to the Mg target with high powder vibration frequency. To increase the hydrogen up taking capacity and also increase the kinetics, a low quantity of the Nb$_2$O$_5$ or Ni or other transition metal will be decorated with Mg nanoparticles onto graphene sheets.

The detailed structure, chemical and electronic properties of the decorated graphene sheets with TiO$_2$ nanoparticle were presented. It was also noted that decorated graphene sheet with TiO$_2$ nanoparticles shows reasonable photocatalytic property. The deposition parameters will be varied to get uniform decoration of the graphene sheets with TiO$_2$ nanoparticles to improve the photocatalytic property. Furthermore it was observed that oxygen vacancies formation was clearly confirmed from the XPS analysis. Therefore, some other spectroscopic techniques (photoluminescence spectroscopy and X-ray absorption fine structure (XAFS) would be employed to study the interaction of the graphene sheets with TiO$_2$ nanoparticles.
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