Development of Graphene Oxide/Carbon Nanofiber Hybrid Structure

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Acceptance of Senior Honors Thesis

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Abstract

Graphene oxide (GO) and carbon nanofibers have unique individual properties that could be combined complimentarily to be utilized in a variety of fields. Combining these two materials together into self-standing structures would enable them to maximize their high surface area and electrically conductive properties into applications from lithium batteries to biosensors. This thesis aims to use a two-step process to develop a self-standing carbon nanofiber/GO structure. The first process is the electroless deposition process, and it is used to coat the GO with a metal catalyst. In the second step, a chemical vapor deposition technique is used to deposit carbon nanofibers (CNFs) on the surface of GOs. Results of this research included creating a self-supporting CNFs/GOs structure that demonstrated improved electrical conductivity. The technique is simple and can be employed to produce large area CNFs/GOs free-standing structure that can potentially be used as an electrode material and for other applications.

Development of Graphene Oxide/Carbon Nanofiber Hybrid Structure

Graphene by itself undergoes agglomeration or breakage which makes it ineffective during fabrication methods. To improve these weaknesses, carbon nanotubes (CNTs) or carbon nanofibers (CNFs) have been proposed to act as spacers between graphene sheets to enhance the overall material's surface area and electrical conductivity. Graphene oxide is a derivative of graphene that contains similar properties to graphene but is much easier to process. The goal in this research was to create a hierarchical system of vertically aligned CNFs/CNTs between the graphene oxide sheets to create a self-standing structure.

First, the electroless deposition process is used to coat the graphene oxide with a chosen metal that acts as a catalyst for carbon nanotubes/nanofibers growth on the substrate. Next, the chemical vapor deposition process grows the carbon nanotubes/nanofibers on the graphene oxide surface. The successful growth of vertically aligned CNTs on the graphene oxide surface will create hybrid material with a lower tendency towards instability as well as an increase in electrical conductivity properties. Particularly in this research, the objective was to grow vertical carbon nanotubes/nanofibers evenly on all surfaces of the graphene oxide substrate to develop a hierarchical, hybrid structure of graphene oxide sheets and carbon nanotubes/nanofibers. Fig. 1 depicts the desired vertically aligned CNTs between the graphene oxide sheets. The creation of free-standing layers of graphene and CNTs/CNFs will enable the material to be utilized as a biosensor in disease detection applications and as an electrode for lithium battery applications.
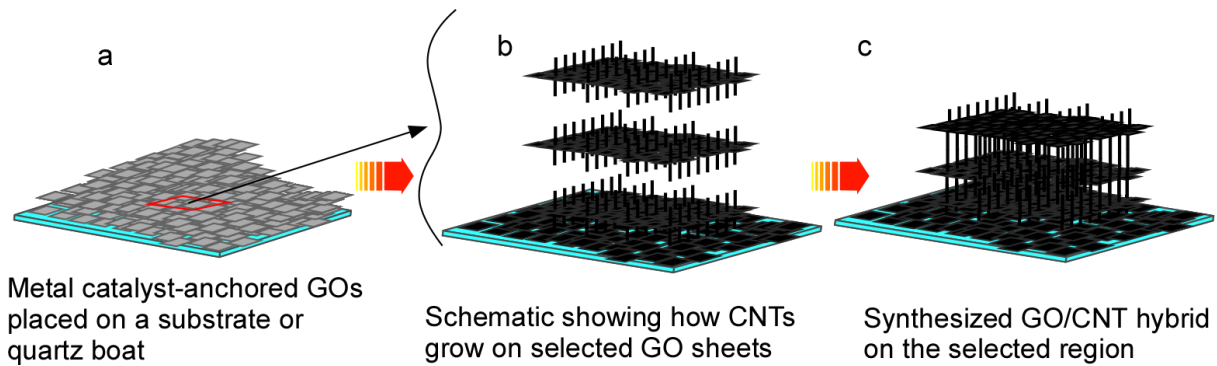
Fig. 1. Schematic representation of research objective. Permission use by Dr. Zegeye.

Literature Review

Electroless Deposition Overview

To coat graphene oxide with metal particles, the electroless deposition method is used. The method is convenient for lining materials with a metallic film and has been used by multiple researchers [1-4]. The electroless deposition method is purely defined by a chemical reaction and is advantageous as it does not require electrical current to initiate the deposition process [4]. Consequently, both metallic and non-metallic surfaces can be electroless deposited. The general chemical reaction of this method is to engage a reducing agent to stimulate the nickel or other metal to attach onto the substrate's surface. The substrate will have an overall negative charge from the reducing agent that will then be attracted to the metallic cations in the aqueous solution. The imbalance will cause the cations to bond to the surface of the negatively charged substrate. Once the bond forms, the metallic ions will change to their neutral form thus covering the entire surface evenly with the desired metal. Fig. 2 displays the chemical changes that occur during each step of the electroless deposition. The chemical reaction principles are the same for the graphene oxide substrate that was used in this research.
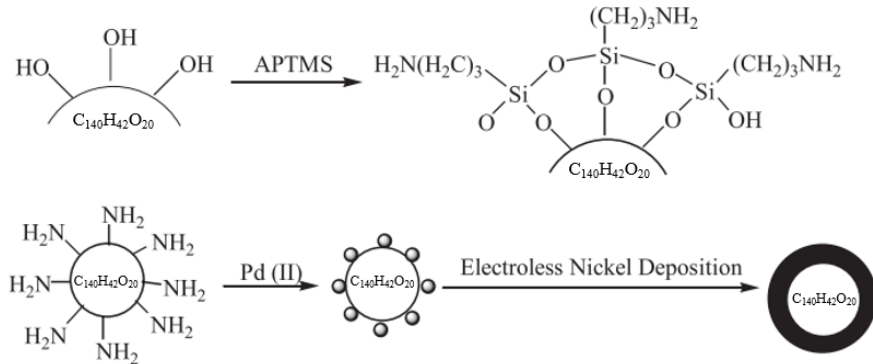
Fig. 2. Three step method involving the electroless deposition process. Adapted from [1].

There are four specific steps in the electroless deposition process. The first step is to clean all the impurities off the surface of the substrate that is to be coated. The main solution types that researchers used to clean the surface of the substrate are ethanol, distilled water, and aqueous ammonia [1-6]. After purification, the second step is to modify the surface of the substrate material using an amine group. Gao and other researchers used 3-aminopropyltrimethoxysilane (APTMs) in ethanol solution to modify the surface by using the amine functional group, and this process is called functionalization [1-4]. The reason for using the amine group is due to the fact that it is commonly known to be a strong electron doner [3]. However, modifying the substrate surface can involve other types of materials as well. Shukla reported using $SnCl_2$ as the solution for modifying the surface of the substrate concerning the electroless deposition of copper [4]. Furthermore, the solvent $SnCl_2$ was also used in a similar research that focused on depositing silver nanoparticles onto silica spheres [2]. After the functionalization of the substrate, the third step is to prepare and activate the surface with palladium. A different name for this step is creating active sites. It is important to have these catalytic sites for initiating electroless plating of metal onto non-metallic substances [3]. One

researcher used $PdCl_2$ in order to create these nucleation sites for the upcoming metallic bonding

process [4]. During the activation step, $PdCl_2$ needed to first be dissolved in HCl [7]. After the

addition of the palladium, the activated substrate can now begin the process of having the metal

bind to the surface of the substrate which is the final and fourth step in the electroless deposition

method. Sun et. al focused on fabricating nickel coated graphite particles using $NiSO_4$ solution at

room temperature for 0.5 h to adsorb nickel ions [8]. In the same manner, Ahmed used nickel

sulphate as the source for the metallic ions along with sodium hypophosphite as the reducing

agent in their research [9]. Once the substrate was covered with the desired metal, the material

was set out to dry. Gao set the material to dry at room temperature while Shukla dried it in a

vacuum oven at 110 °C for one hour [1, 4]. To verify whether the Ni or other metal coating is

present on the graphene oxide, an energy dispersive spectroscopy (EDS) and a scanning electron

microscopy (SEM) has been used [1, 10]. Consequently, the same tools will be utilized in the

characterization of the developed hybrid structure.

Chemical Vapor Deposition Method Overview

Carbon nanotubes must be grown on the surface of the graphene oxide substrate to create

the hybrid free-standing structure that is desired. One way to grow carbon nanotubes (CNTs) on

a substrate's surface is to use the chemical vapor deposition method. Yang discusses that thermal

chemical vapor deposition method is popular for its easy setup in laboratories, low cost,

successful use in long-term industry production [11]. A carbon nanotube is an allotrope of

carbon, present in sp^2-hybridized form [12]. These nanotubes can be single walled or

multiwalled [13]. Carbon nanotubes are mainly developed by the chemical vapor deposition

method. There are other methods for producing carbon nanotubes such as the arc discharge and

laser ablation methods, but the high degree of control, low set up cost, high production yield, and scalability of the CVD technique causes this particular method to become a standard mode of producing comparatively pure carbon nanotubes [12, 13]. The first step in growing carbon nanotubes using the CVD method is to deposit a metal on the substrate to act as a catalyst [12]. Various metals and metallic compounds have been used in the past as catalysts. Some of the transition metals used for this CVD method include Cobalt (Co), Iron (Fe), and Nickel (Ni) [14-16]. Concerning nickel, Palacio determined CNT-Ni is more homogeneous and stable than CNTs grown with other catalysts [17]. Additional research utilizing $Ni(NO_2)_3$ and $NiCl_2$ as a catalyst demonstrated that the metal nickel was an effective catalyst for the CVD method [15]. Contrarily, the metal cobalt could also be effectively used for inducing carbon growth through the CVD method. Lobiak et al. notes that during their comparison of nickel to cobalt in their catalyst cobalt (Co–Mo) produced slightly less defective CNTs as compared to the nickel catalyst samples [18]. Furthermore, Lee et al. concurs that their cobalt catalyst proved to have a better role in growing CNTs with thinner catalyst layer due to the faster growth rate of cobalt compared to nickel [16]. Due to diverging conclusions of which metal catalyst is more effective for carbon growth with the CVD method, both a comparison of the metal catalysts of nickel and cobalt will be used in this research.

The general process for the CVD method first involves the metal catalyst being applied as a thin film. The application of the thin film of metal will be performed through the electroless deposition method. This film ultimately nucleates into particles to form a seed layer where the formation is a key factor that determines the CNT's growth mechanism [16]. The chamber that the CVD process will take place in requires preparation steps such as increasing the temperature

of the chamber and introducing certain gases into the chamber. Before the gases containing the

carbon can be added, the substrate itself must first be heated in the chamber. The metal-covered

substrate within the vacuum chamber has its temperature increased between reaction temperature

of 550 °C and 1000 °C for carbon nanotubes [19]. Other research articles used various

temperature, time, and flow rate combinations when performing the CVD process. In one study,

the substrate of Ni-MgO was heated to 600 °C under Argon flow [20]. Another study that uses

Ni_4-Mo_{12}/MgO as the catalyst heated the substrate to 700 °C for 10 minutes and later increased

the temperature to 900 °C with the introduction of the C_2H_4 flow [18]. Research performed with

monometallic and bimetallic catalysts found that high yield carbon nanotubes were obtained at

700 °C [19]. While the temperature is increasing in the chamber, there are inert gases that are

placed into the chamber environment. Argon, hydrogen, and nitrogen have been used in a variety

of articles [12, 17, 18]. Concerning the carrier gas, Venkatesan used argon with the gas flow rate

of 100 ml min^{-1} [21]. Mohammad found that at a time of 60 min. and temperature of 700 °C, an

argon flow rate of 230 ml/min produced the maximum yield of CNT's [22]. Research dealing

with a graphene carbon nanotube hybrid grown on a copper foil reported pre-treatment of the

substrate at temperatures of 800 or 900 °C in the H_2 and Argon environment with 20% being H_2

at a gas flow rate of 100 sccm [23]. All the given temperatures are due to the conventional

thermal CVD method which involves coils. Temperatures do ultimately affect the nanotubes

developed. It was noted that the carbon nanotubes were curly in shape at 520 °C while at

temperature above 600°C, the nanotubes were straight [13]. The different values of temperature,

time, and flow rate combinations strongly influence the CNTs developed.

Once the substrate is uniformly heated in the vacuum chamber, the carbon source gas will be supplied to the chamber. In one article, the carbon source gas used for growing carbon nanotubes were hydrocarbons [12]. One such hydrocarbon used as a carbon source to grow CNTs is acetylene [12]. Ethylene (C_2H_4) as the carbon source was also used by research dealing with Ni–Mo and Co–Mo alloys creating CNTs while H_2 was used to purge the reactor at the end [16, 18]. Research entailing creating graphene–CNT hybrids involved ethanol vapor as the carbon source to be introduced into the tube by H_2 flow [23]. Further research into the CVD effects on multiwalled carbon nanotubes showed that the carbon precursor gas to be acetylene which was supplied to the reaction zone and was later replaced with argon until the furnace reaches room temperature again [21]. Another article using $NiSO_2$ found that hydrogen-free CO as the carbon source favors the growth of SWNTs with a narrow diameter distribution [20]. Concerning the precursor gas flow rates, Venkatesan discusses the fact that if the precursor gas flow rate was less than 100 ml min^{-1}, there was no tubular morphology in the samples whereas if the precursor gas flow rate was more than 180 ml min^{-1}, the highest number of tubular CNTs were found [21]. These conclusions were explained to be "due to insufficient diffusion of carbon atoms to the catalyst particles" when the flow rate is less than 180 ml min^{-1} [21]. Additionally, Lobiak diluted the carbon source gas of 100 ml/min C_2H_4 with 50 ml/min H_2 during the deposition of CNTs [18]. Dong discussed the ethanol vapor being introduced into the tube by H_2 flow of 40 sccm [23]. Concerning an effective carbon source flow rate, Mohammed noted that at a time of 60 min. and temperature of 700 °C, the optimum acetylene flow rate was 190 ml/min [22]. The main carbon sources that will be used with the thermal chemical vapor deposition method will be C_2H_4.

Benefits of Plasma Enhanced Chemical Vapor Deposition Method

Though the thermal chemical vapor deposition (TCVD) method is a commonly effective

process for coating and growing carbon nanotubes (CNTs) onto a substrate, there are a variety of

additional ways to perform the chemical vapor deposition process. According to Manawi et. al,

their article discusses that the CVD techniques employed for the production of CNTs include

hot-wire (HWCVD), hot-filament (HFCVD), microwave plasma-enhanced (MWCVD), etc. [13].

Any type of plasma involving chemical vapor deposition device is a subbranch of the general

chemical vapor deposition method.

Compared to the traditional thermal chemical vapor deposition (TCVD), the plasma

enhanced chemical vapor deposition (PECVD) method has a variety of benefits. According to

Yeh, the TCVD method requires multiple processing steps and relatively long times in both

substrate preparation and graphene growth [24]. Contrastingly, both time and temperature can be

shortened with the PECVD method. Because the conventional TCVD process requires high

temperatures of 1000°C, the plasma enhanced version of the chemical vapor deposition is more

beneficial because it involves a highly active environment producing graphene growth at a much

lower temperature and at a faster growth rate [11, 25]. High temperatures contain a variety of

dangers associated with them. According to Liu et. al, the issues with such high temperatures that

the traditional TCVD method requires is that there are safety concerns such as fire and explosion

hazards as well as the possibilities of catalyst agglomeration that decrease the catalyst

performance and lower the deposition rate [26]. Another difference between TCVD and PECVD

is seen when focusing on the chemical reactions taking place during the deposition. Sun et al,

points out that the thermal CVD involves neutral gas chemistry whereas plasma enhanced CVD

is a more complex process, which can manipulate the morphology and structure of vertical

graphene (VG) by altering the plasma source and adjusting a series of parameters [25].

Furthermore, PECVD has more potential than TCVD because it has a better control on

nanostructure ordering due to the presence of energetic electrons, excited molecules/atoms, free

radicals, photon, and other active species in the plasma region [25]. Therefore, the PECVD

method contains many benefits from decreasing the temperature and time necessities to

producing more controllable CNTs due to the more complex chemical process that it entails.

The carbon growth procedure involved with the PECVD method varies from the TCVD.

According to Shoukat and Khan, PECVD is a technique employed for the synthesis of nanotubes

by generating a glow discharge in the chamber [27]. This glow charge is the plasma that is

created due to the electrical current that is transmitted through the supplied gas which is typically

hydrogen. There are numerous sources that are used in the PECVD method to create the desired

plasma. According to Yeh, the sources are categorized by different power frequencies, which

include: direct current (DC) gas discharge sources; radio frequencies (RF) sources with

frequencies ranging from 1 to 500 MHz; microwave (MW) sources with frequencies ranging

from 0.5 to 10 GHz [24]. The plasma inducing devices work with a ground electrode, an

energized electrode, and a generator. With the particular gases flowing in between the two plates,

the gases implemented are ionized through a chemical reaction and are then deposited as a thin

film onto the substrate surface. Liu discusses how PECVD involves inelastic collisions between

electrons and gas molecules take place, resulting in the formation of reactive species [26]. Yang

continues to describe that the PECVD reactor generates electromagnetic fields which ionizes

hydrocarbon and other molecules and creates active radicals [11]. Due to the metal catalyst that

is on the substrate's surface and the temperature increase because of the plasma, the excited ions

will create nucleation sites and nano-islands to begin the foundation for growing carbon

nanotubes [11]. The desire in this research is that this PECVD method will effectively deposit

and grow vertically aligned CNTs uniformly from the nucleation sites.

There has been previous work performed to create vertically aligned CNTs through the

plasma enhanced CVD method. In Sun et al. research, they noted that the strongest electric field

was located at sharp tips, which can result in attracting carbon ions in the plasma for adsorption

and diffusion there, leading to an enhanced vertically oriented graphene (VG) growth mode and

increased denseness of the VG growth [25]. Their research showed that the electric field of the

PECVD device played a large role in the locations where more growth would occur. Another

observation that Sun detailed was that if remote plasma instead of local plasma is used in the

PECVD, the VG can hardly be grown [25]. When using a microwave plasma-enhanced chemical

vapor deposition (MPCVD), Liu et al notes that freestanding vertically oriented CNTs were

better grown by applying a negative bias voltage in MPCVD with a minimum absolute value of

150V as opposed to a positive bias [26]. Liu also points out that because of the shield placed

between the substrate and the plasma ball to prevent the etching of synthesized CNTs by direct

collision of the high energy particles in the plasma, the CNTs with the shield were vertically

aligned better than without the shield [26]. Another research involving vertical carbon nanowalls

(CNWs) noted that the novel process for deposition using a low-pressure plasma together with

high-voltage nanosecond pulses largely depended on the effect of the high-voltage nanosecond

pulses in terms of inhibition of wall growth, owing to enhanced adsorption of carbon atoms and

changes in the surface diffusion lengths [28]. In order to evaluate the benefits of using a different

carbon source gas and shorter deposition time, the PECVD method will also be implemented in this research.

<div align="center">**Materials and Methods**</div>

Electroless Deposition

The graphene oxide used for this research was a graphene oxide nanopowder. The average particle diameter was greater than 50 µm with the thickness being approximately 1-2 nm. Its purity was 98% while its oxygen content was between 30-50wt %. For the electroless deposition method, the same processes were performed for both metal catalysts of nickel and cobalt to be coated onto the cleaned graphene oxide. Three different deposition times were performed to compare which deposition time would be optimal for creating the metal catalyst islands. For preparing the surface of the substrate with nickel, 500.1 mg of graphene oxide was measured on a weighing dish. The graphene oxides were first repeatedly washed using ethyl alcohol.

For all mixing processes, a magnetic stirrer and hot plate were used. To separate the graphene oxide from the solution, a vacuum filtration system was used. To set up the filtration system, a Buchner funnel was set on top of a flask with a rubber stopper to create an effective seal. The flask with a side arm was then connected to a hose that attached to an aspirator. With the aspirator attached to the sink facet, turning on the water would create a vacuum within the flask that would pull the liquid within the funnel down into the flask. This filtering system set up was used with all filtering and cleaning processes during the electroless deposition process. The filter paper used with the funnel was 47 mm in diameter, and a fresh sheet of paper was used for each filtering process. After cleaning the graphene oxide twice with ethyl alcohol, 150 mL of

ethyl alcohol was separately measured into a squeeze bottle. That specific amount was used to

wash the filtered graphene oxide down into a beaker. With the cleaned graphene oxide in 150

mL of ethyl alcohol, 0.2 mL of 3-Aminopropyl triethoxysilane 98% (APTMS) was placed into

the beaker. This solution was mixed for 1.5 hours with a magnetic stirrer. This process would

adhere amine groups on the surface of graphene oxide and is called functionalization. While the

APTMS and graphene oxide solution was mixing, palladium chloride was prepared for the

activation step. To prepare the activation solution, 0.05 g of $PdCl_2$ was measured out in a

weighing dish. The $PdCl_2$ was placed in a beaker with 200 mL of ethyl alcohol and stirred for 25

minutes to dissolve as much of the $PdCl_2$ as possible into the solution. After the 25 minutes, the

solution was poured into a separate squeeze bottle to be used during the activation process later.

After the functionalization process, the graphene oxide particles were washed twice with ethyl

alcohol. Then, the $PdCl_2$ solution was used to pour the cleaned graphene oxide into a beaker. The

$PdCl_2$ with graphene oxide solution was stirred for 1 hour. Then, the activated graphene oxide

was first washed twice with ethanol and then with DI water. Once the graphene oxide was

filtered with DI water, the particles began to adhere to the surface walls.

     Four chemicals were combined to make the electroless deposition solution. Table I

displays the amounts of each chemical measured for the Ni solution while Table II displays the

chemical amounts for the Co solution. Additionally, 70 mL of DI water was measured out and

used to pour the filtered graphene oxide into a beaker. These four chemicals were then combined

with the graphene oxide in 70 mL of DI water. While this graphene oxide and Ni solution was

stirred, the pH was adjusted to 8.29 using ammonium hydroxide. The Co solution pH level was

increased to 8.3. The ammonium hydroxide was added drop by drop using a pipette. The solution

was continually stirred with the magnetic stirrer while a pH meter kept track of the pH level with

the added ammonium hydroxide. Then, the temperature of the mixture was increased to 70°C as

the solution was continually mixed. Once the solution reached 70°C, the mixture was stirred for

the three different deposition times of 5, 8, and 10 minutes. Fig. 3 displays the electroless

deposition process as the temperature was being increased. After the deposition time was

complete, the solution was filtered with DI water twice and then with ethyl alcohol twice.

TABLE I

THE FOUR CHEMICALS CONTAINED WITHIN THE NICKEL SOLUTION IN 70 ML OF DE-IONIZED WATER

Chemical Name	Mass of the Chemical Measured
$NiCl_2 * 6H_2O$	2.10 g
$NaH_2PO_2 * H_2O$	0.697 g
$Na_3C_6H_5O_7 * 2H_2O$	3.50 g
NH_4Cl	3.48 g

TABLE II

THE FOUR CHEMICALS CONTAINED WITHIN THE COBALT SOLUTION IN 70 ML OF DE-IONIZED

WATER

Chemical Name	Mass of the Chemical Measured
$Cl_2Co * 6H_2O$	2.10 g
$NaH_2PO_2 * H_2O$	0.697 g
$Na_3C_6H_5O_7 * 2H_2O$	3.50 g
NH_4Cl	3.48 g

Fig. 3. Electroless deposition with increasing temperature.

Formation of Thin Layer of GOs onto Silicon Substrate

Prior to growing the CNTs/CNFs on GOs, a thin uniform GO layer was formed on a

silicon wafer. For creating the thin uniform layer, the GOs were first suspended in ethanol

solution and poured onto a 3.7×2.4 in. rectangular tin box container. The containers were then

left in a fume hood to evaporate the ethanol. Rectangular containers were used to set the wafer

and the graphene oxide within an ethyl solution inside to dry. Initial GO masses of 0.3 g, 0.4 g,

and 0.5 g were dispersed in 10 mL of ethanol to determine the optimum thickness of the GO

formed on the silicon wafer. The final round of tests used 0.35g of GO in 10 mL of ethanol.

Chemical Vapor Depositions

For growing the carbon nanotubes on the graphene oxide, both the thermal and plasma

enhanced chemical vapor deposition were utilized. There were three rounds of PECVD testing

and one round of the TCVD experiments that were performed. The parameters varied in each

chemical vapor deposition method include the gas flow rates, deposition times, and temperature.

For the PECVD process, 100 sccm of Ar was flown during ramping the temperature to

800°C in 20 minutes. Once the temperature reached 800°C, the GOs were etched by flowing 80

sccm of H_2 for 3 minutes. The carbon deposition was performed by flowing 80 sccm H_2 and 20

sccm C_2H_2 for 30 minutes. The plasma was attempted to be turned on for the etching and carbon

deposition; however, difficulties with the PECVD system caused the plasma to not work

properly. After the deposition, the chamber was cooled to room temperature by flowing 100

sccm of Ar. Finally, the silicon wafers with graphene oxide were taken off the boat and stored in

containers to be characterized later.

For growing the CNFs on the graphene oxide, a thermal chemical vapor deposition

(TCVD) was utilized. For this method, the flow rates of the gases during temperature ramp were

280 standard cubic centimeters per minute (sccm) N_2 and 70 sccm Ar/H_2. During the actual

deposition, Ar/H_2 mixture was held and decreased to 35 sccm and 15 sccm C_2H_4 was introduced.

The time and temperature parameters of the TCVD process involved ramping the chamber from

room temperature to 800°C in 20 minutes. Once the chamber reached 800°C, the temperature

was set to remain constant for 60 minutes. After the 60 minutes had ended, the flow of C_2H_4 was

turned off while the N_2 flow of 280 sccm and the Ar/H_2 mixture flow of 70 sccm continued.

Once the chamber reached around 300°C, the top of the furnace was lifted to allow for a faster

cooling process. Once the temperature was 34°C, the ceramic boat was taking out of the glass

tube and set on the counter to cool a bit more. Finally, the silicon wafers with graphene oxide

containing Ni were taken off the boat and stored in a weighing dish to be characterized later. The

time for cooling was approximately two hours.

Characterization Methods

For characterizing the Ni-coated and Co-coated graphene oxide after the electroless

deposition was performed, a drop of the processed graphene oxide was placed on a tab with

graphite tape. An additional tab had a few particles of the plain graphene oxide applied to it to

see a comparison of the GO surface with and without the metal coating. The scanning electron

microscope (SEM) was utilized to take the images for visual, qualitative analysis of the

processed material. Additionally, the SEM was employed to perform an Energy Dispersive X-

Ray Spectroscopy (EDS) to analyze the chemical composition of the material.

Characterization of the GOs after the performed PECVD and TCVD method involved

placing portions of the nickel and cobalt samples on graphite tape that was attach to metal tabs.

Cleaned tweezers were utilized to deposit the graphene oxide onto the tape. These samples were

placed under the SEM to take images of the results of the PECVD and TCVD methods in order

to observe whether there was carbon growth on the GOs surface.

The electrical conductivity test involved first cutting small rectangular pieces of both the

metal coated GO that had carbon growth and the metal coated GO that did not have carbon

growth. The two pieces were placed on white sheets of paper. Silver paste was applied to the

ends of the rectangular samples of both the Ni and Co samples. Fig. 4 displays the setup of the
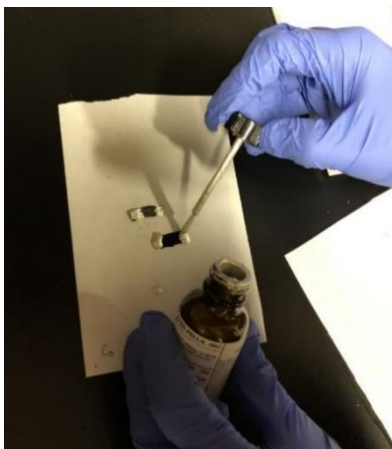
electrical conductivity test.

Fig. 4. Preparing the GO samples for the electrical conductivity test.

The graphene oxide samples that were taken from the TCVD system contained considerable carbon growth. A thin razor blade was used to separate the graphene oxide from the silicon wafer. Double sided tape was used to hold the silicon wafer in place while the razor was scraping off the graphene oxide strip. The strip of the sample was then lifted with a set of tweezers.

Results and Discussion

Electroless Deposition Results

The electroless deposition process with both metal catalysts was successful. An energy dispersive spectroscopy (EDS) scan was performed for both groups of particles to verify that the metal was deposited on the surface of the substrates. The EDS scan provided a map spectrum of the different elements that were present on the surface. A color spectrum of the various elements and the mass values of each element were also provided in the EDS scan. Fig. 5 displays the map spectrum EDS results of the nickel covered graphene oxide particles. Table III displays the specific atomic weight and percent weight of each element present for the nickel samples. Most of the particles were comprised of carbon and oxygen because graphene oxide is comprised of those two elements. As can be seen from the EDS analysis, there was nickel coated on the surface of the graphene oxide for all three deposition times of 5, 8, and 10 minutes.
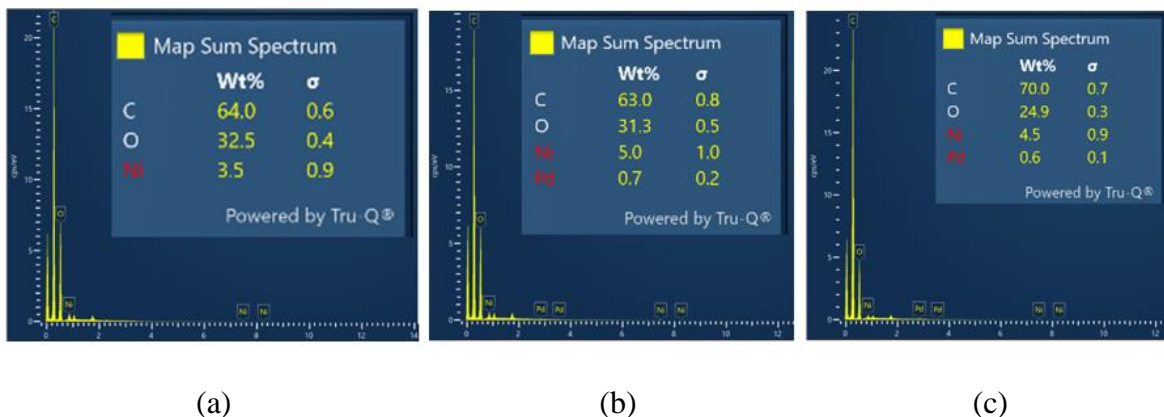
(a)   (b)   (c)

Fig. 5. Map spectrum of elements present. (a) For Ni 5 min. deposition. (b) For Ni 8 min. deposition. (c) For Ni 10 min. deposition.

TABLE III

WEIGHT PERCENTAGE VALUES FROM ENERGY DISPERSIVE SPECTROCOPY SCAN OF THE NICKEL

SAMPLES

Deposition Times	Element	Weight Percentage [%]
5 min	C	63.95
	O	32.51
	Ni	**3.54**
8 min	C	63.02
	O	31.28
	Ni	**5.05**
10 min	C	70.04
	O	24.87
	Ni	**4.45**

Similar results were obtained for the cobalt samples that can be seen in Fig. 6 and Table IV. The SEM EDS analysis for the cobalt samples displayed the chemical elements present in addition to their atomic and weight percentages. The main percentages of the samples were

carbon and oxygen due to graphene oxide being comprised of these two elements. Additionally,

a small percentage of cobalt was observed on the surface of the graphene oxide samples.

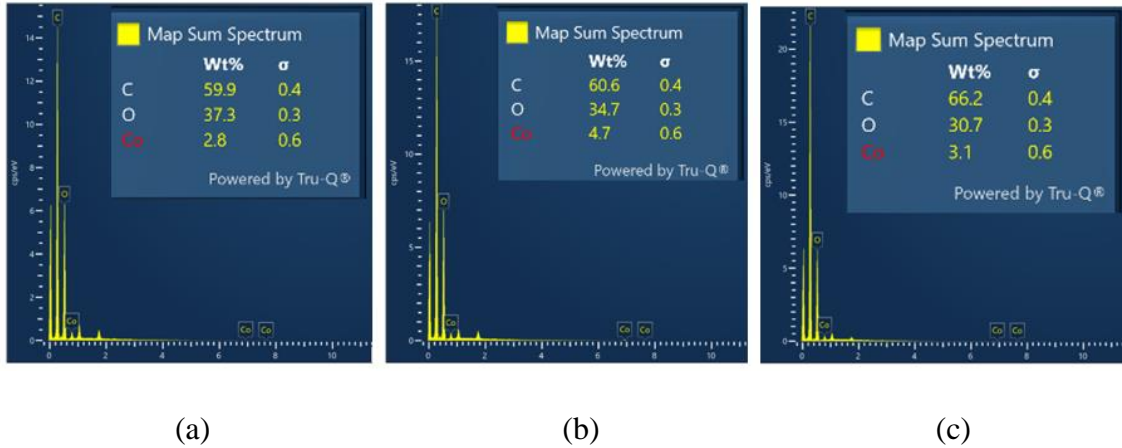(a)   (b)   (c)

Fig. 6. Map spectrum of elements present. (a) For Co 5 min. deposition. (b) For Co 8 min.

deposition. (c) For Co 10 min. deposition.

TABLE IV

WEIGHT PERCENTAGE VALUES FROM ENERGY DISPERSIVE SPECTROCOPY SCAN OF THE COBALT

SAMPLES

| Deposition Times	Element	Weight Percentage [%]
5 min	C	59.93
	O	37.27
	Co	**2.80**
8 min	C	60.59
	O	34.70
	Co	**4.71**
10 min	C	66.21
	O	30.70
	Co	**3.09**

GRAPHENE OXIDE/CARBON NANOFIBER HYBRID STRUCTURE

Once it was verified that the graphene oxide particles were coated in the two desired metals, an even layer of the metal coated GO was formed on the silicon wafers. The graphene oxide residue left behind on the silicon wafer evenly covered it.

Growth of Carbon Nanostructures Using Plasma Enhanced Chemical Vapor Deposition

The samples were observed under the SEM after both types of CVD methods were performed. Initially, multiple rounds of the PECVD method were performed in attempts to grow carbon nanotubes/nanofibers on the surface of the graphene oxide substrate. All the samples with different electroless deposition times were utilized in the PECVD process; however, difficulties with the plasma were one of the main causes for no carbon growth being observed under the SEM. Fig. 7 displays the lack of carbon growth on the graphene oxide surface for the first two experiments using the PECVD method.
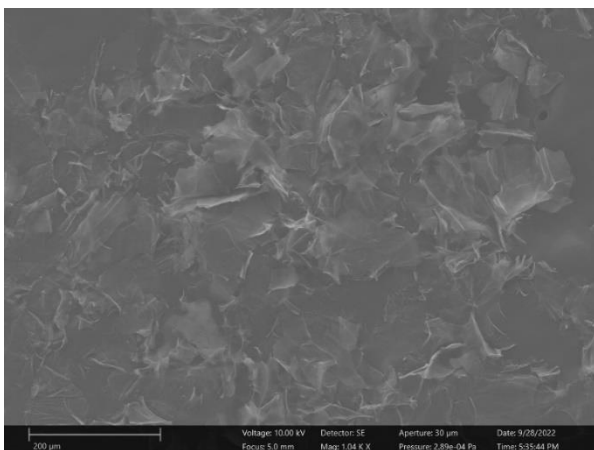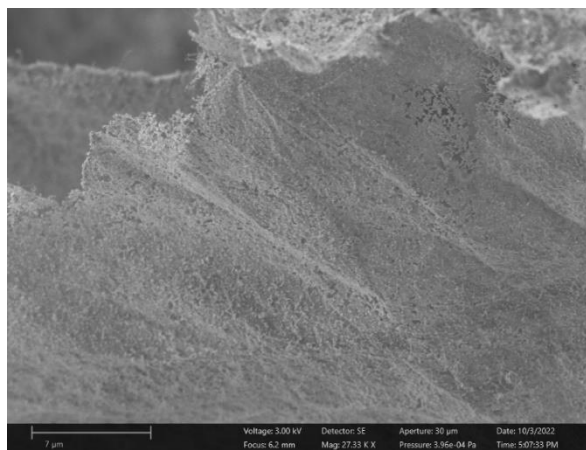


(a)   (b)

Fig. 7. Results of plasma enhanced chemical vapor deposition displaying no carbon growth. (a) First round with Ni 10 min. (b) Second round with Ni 10 min.

Although no growth was observed, Fig. 7(b) displayed deep etching on the surface of the graphene oxide. Due to the struggles associated with the plasma, the PECVD method was not successful in depositing any carbon growth onto either the Co or Ni samples. For the final round of CVD testing, all of the Co and Ni coated samples with different coating times were placed in the PECVD machine. Simultaneously, samples coated with Ni and Co for 8 minutes were run under the TCVD method. Even in the final round of PECVD, none of the samples displayed any carbon growth. Consequently, the PECVD method must be further adjusted before carbon growth can occur.

Growth of Carbon Nanostructures Using Thermal Chemical Vapor Deposition

The nanofiber growth on the GOs coated with Ni and Co 8 for min. was observed under the SEM. There was dense carbon nanofiber growth on both samples. Both top and bottom growth were seen under the SEM. Fig. 8 displays the carbon fiber growth that was observed.
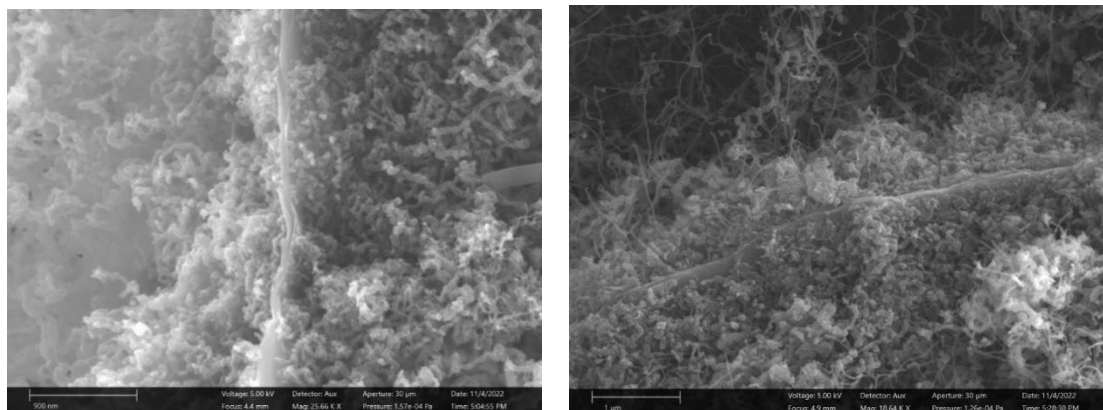
(a)   (b)

Fig. 8. Results of thermal chemical vapor deposition experiments with dense carbon growth from an edge view of the graphene sheets. (a) For Ni 8 min. (b) For Co 8 min.

There was clearly carbon growth on the top and bottom surfaces of the TCVD Ni and Co samples. The density of the filament was high across the substrate's surface. Additionally, interaction between individual graphene oxide sheets was observed as shown in Fig. 9.
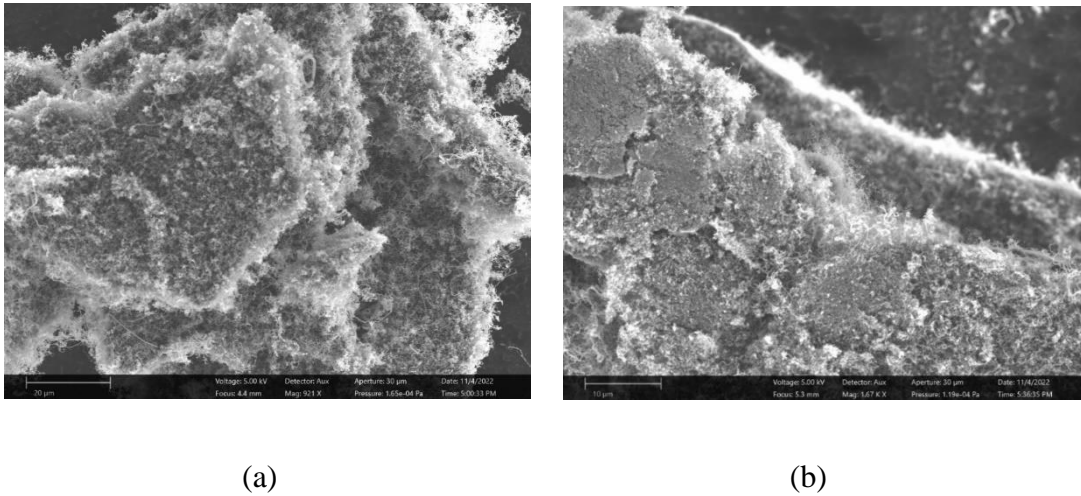

(a)   (b)

Fig. 9. Results of thermal chemical vapor deposition experiments with carbon growth affecting the GOs sheet interaction. (a) For Ni 8 min. (b) For Co 8 min.

There was much carbon interaction between the carbon fibers that were grown. The detailed interaction between the fibers of graphene sheets were not viewed under the SEM; however, the carbon growth interaction was strong enough to physically lift both the Ni and Co TCVD samples. Images of the GO samples being physically suspended with tweezers can be seen in Fig. 10.
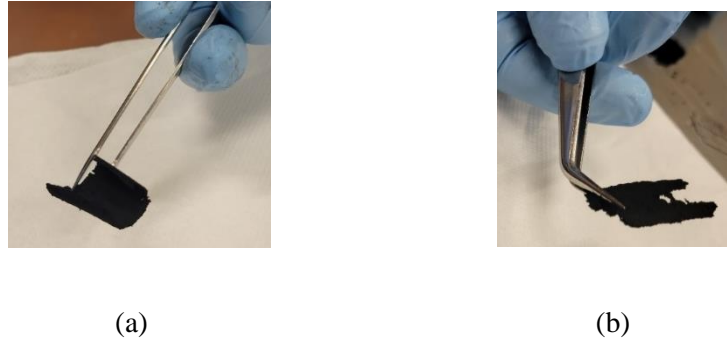
(a)   (b)

Fig. 10. Physically suspending the two thermal chemical vapor deposition samples with

tweezers. (a) For Ni sample. (b) For Co sample.

Electrical Conductivity Test Results

The carbon interaction between the graphene particles was strong enough to keep the GO

samples intact when lifted with the tweezers. Consequently, the self-supporting structure was

successfully created. With the success of developing the self-standing structure, an electrical

conductivity test was performed to determine the difference between the metal coated graphene

oxide with and without the carbon growth.

Once the silver paste had dried, the multimeter was utilized to take resistance readings.

Readings for the nickel sample were taken; however, the cobalt sample data was not determined

due to the cobalt fracturing and not transmitting the current for a reading. Table V displays the

nickel sample resistance difference between the graphene oxide with and without the carbon

growth. The resistance for the nickel demonstrated that the addition of carbon nanofibers to the

graphene oxide greatly decreased the electrical resistance of the system. Consequently, the

developed self-standing sample provided increased electrical conductivity properties. This

improved electrical conductivity was expected due to the addition of the carbon

nanofiber/nanotube material that is highly conductive. Due to graphene oxide alone having lower

electrically conductivity properties, the addition of carbon nanofiber structures enhances the

applications of this hybrid system making an electrical conductivity increase desirable.

TABLE V

ELECTRICAL CONDUCTIVITY RESULTS OF BOTH SAMPLES

Metal Sample:	Resistance without Carbon Growth	Resistance with Carbon Growth
Nickel	1.5 MΩ	13.3 Ω
Cobalt	No Result	No Result

Future Research and Conclusions

The research aimed to create a free-standing GO/carbon nanofiber structure by depositing

the nanofibers on the top and bottom surfaces of GOs through the chemical vapor deposition

method. No carbon growth was observed from any of the PECVD rounds. Amorphous, dense

carbon fiber growth from the TCVD was observed by the SEM. Verification that the top and

bottom surfaces produced a growth of the carbon filament structures for all the samples was

achieved. Furthermore, carbon interaction between the individual graphene sheets was visually

observed under the SEM and physically determined by suspending the GO samples of both Ni

and Co with tweezers. A free-standing structure was created using the TCVD method. Electrical

conductivity tests performed on the Ni sample showed that the carbon growth on the graphene

oxide greatly decreased the electrical resistance in the system. More improvements and

adjustments to the PECVD parameters along with the implementation of the plasma will be

performed in the future to develop more tube-like rather than fibrous-like carbon structures on

the GO surface. Additional characterization work could also be performed in the future to see the

surface area changes as well as the material properties of the developed hybrid structure.

Consequently, the research will be continued in the future to develop the free-standing graphene oxide and carbon nanotube lattice for material applications into disease detection and energy sources such as batteries.

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