International Journal of Nanoelectronics and Materials
Volume 16, No. 3, July 2023 [705-716]

A Review: Synthesis and Mechanism of Growth of the Carbon Nanotubes (CNTs) – Graphene Hybrid Material and its Application as Electrodes

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Received 9 September 2022, Revised 17 October 2022, Accepted 4 August 2023

ABSTRACT

The CNTs–graphene hybrids have many advantages and potential for use in a wide range of electronic applications as electrodes. The CNTs–graphene hybrid structure outperforms the structure of each material in terms of characteristics and performance. There are several methods to grow CNTs. This paper reviews the chemical vapor deposition (CVD) method used to synthesize CNTs–graphene hybrid material. This paper discusses the processes and growth parameters of the synthesis of the CNTs-graphene hybrid. This paper also discusses the growth mechanism and kinetics of CNTs. In addition, the potential and performance of CNTs–Graphene hybrid material as electrodes in batteries are also reviewed.

Keywords: Carbon Nanotubes, Graphene, CNTs–Graphene Hybrid, CVD method

1. INTRODUCTION

Carbon nanotubes (CNTs) are one-dimensional (1–D) carbon allotrope that forms cylindrical nanostructures. The CNTs have some graphene layers that are arranged on the CNTs' walls. CNTs have superior properties such as high tensile strength, good thermal conductivity, and large electric current carrying capacity. On the other hand, graphene is an allotrope of two-dimensional (2–D) carbon that can be an excellent support for catalysts. This is contributed by the highly tunable interaction between graphene and the catalysts. Not only that, graphene also can be a good catalyst itself due to the highly tunable graphene-substrate interaction. Behind its advantages, graphene has limitations that can reduce the device performance, because it tends to form irreversible aggregates due to strong van der Waals force interactions [1]. To minimize aggregation and eliminate agglomeration, CNTs are combined with graphene and produce a new CNTs–Graphene hybrid material which becomes three-dimensional (3-D). This hybrid material is formed by growing CNTs in the axial direction to graphene. This makes the material's properties better than CNTs and graphene in one state, such as increasing the overall electrical conductivity [2], wider surface area, an inner-tube design that makes a strong connection between CNTs and graphene layer, and better thermal stability [3], [4] due to the role of CNTs in reducing the electrical resistance in graphene.

The embodiment of soft sensors and transducers that depend on electronic components such as power supply and signal transmission needs to consider the mechanical flexibility of electronic

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materials and their electrical efficiency. Metal and Si thin films were commonly used electronic materials before, but due to their inflexibility, these materials were not suitable for producing the required sensor devices.

In recent decades, the development of flexible, stretchable electronic materials has become an important area of research. Due to their outstanding and flexible electronic and mechanical properties, CNTs and graphene have been the subject of much research devoted to their use as conductors or semiconductors in electronics, allowing for the latest advances in technical production processes. Due to its physical properties as a monolayer, graphene has been proposed as a stretchable electrode with high fracture strain resistance and low sheet resistance [5]. On the other hand, the high mobility and on–off ratio of CNTs make them ideal semiconductor materials for active channels in flexible electronics [6].

In addition, CNTs can also be a bridge between graphene sheets [7] and the CNTs arrays can be vertical or parallel to the graphene sheets. Vertical CNTs–Graphene hybrid has lower electrical resistance compared to the parallel CNTs–Graphene hybrids. Therefore, CNTs–Graphene hybrid materials have the potential to be applied in electronic applications, such as transparent conductors, hydrogen storage, electron field emitters, field effect transistors, sensors, and storage [8], electrodes and interconnects [9]. The position factor of CNTs and graphene in the CNTs–Graphene hybrids can affect the electrochemical phenomena of the catalyst–electrolyte interface and increase the performance of the electrochemical device, which can be carried out in random, horizontal, or vertical directions. Due to the covalent bond between CNTs and graphene in CNTs–Graphene hybrids, energy devices using this hybrid material have better performance because they can facilitate ion transport and accelerate charge transfer [10]. Recently, CNTs–graphene hybrids have been developed as flexible as well as stretchable electronic materials due to their 3D structural shape providing superior mechanical strength and percolation network forming efficiency, enabling significant improvements in electrical and mechanical properties [11]–[13].

Producing CNTs–Graphene hybrids for use in flexible and elastic electrodes is an exciting prospect. The resulting electrodes must be able to sustain conductivity under high strain conditions without experiencing significant alterations in electrical transport. These features allow for an optimum 3D–shaped combination of CNTs and graphene, which has led to the creation of flexible and stretchable electrodes based on CNTs–Graphene hybrids in a great deal of research [14]–[19]. CNTs and graphene can be placed on the surface of a polymer substrate to create a hybrid structure that can be used as an electrode. Nguyen et al. [16] report that flexible electrodes made from hybrid CNTs–graphene thin films are feasible to produce. On a graphene surface, CVD was used to synthesise thin CNTs networks. The CNTs–Graphene hybrid film created has a sheet resistance of just 420 Ω sq^{-1} compared to the graphene film's 2.15 kΩ sq^{-1}. The reduced contact resistance arising from the interactions between the graphene sheets and the CNTs network is responsible for the dramatic improvement in electrical conductivity. However, after 100 cycles of bending at an angle of 150°, the hybrid film's resistance on the polymer substrate only deviated by 7.2%, presumably because the CNTs lengthened without shattering.

This article focuses on the synthesis of CNTs on graphene or vice versa that led to the formation of CNTs–Graphene hybrid materials. This paper discusses the CNTs–Graphene hybrids from its synthesis using the chemical vapor deposition (CVD) method and the effect of carbon precursors and metal catalysts. The paper also discusses the growth mechanism of CNTs on graphene that involves all the related growth parameters and interactions. Finally, the recent potential applications of CNTs–Graphene hybrid material as electrodes are discussed.

2. SYNTHESIS OF CNTS–GRAPHENE HYBRID MATERIAL

CNTs grown from graphene tends to produce a uniform distribution of CNTs, because of that CNTs–Graphene is widely used, as well as the control of metal particle loading of the catalyst is simpler. The mechanical properties and distribution of CNTs–Graphene are determined by their area and orientation. CNTs–Graphene growth positions are categorized into random, horizontal, and vertical formations [8]. One of the CNTs growing formations that has the greatest electrical performance is Vertical CNTs–Graphene, because its arrangement makes CNTs grow perpendicularly away from graphene which can increase the surface area and volume of the material. This formation accelerates charge transport in hybrid materials [10].

The growth of CNTs cannot be separated from the role of synthesis and the catalyst employed. CVD is one of the most widely used processes because it is inexpensive, can be performed at low temperatures, and can produce the desired structure by reacting or decomposing precursors on the surface of the substrate. CVD requires carbon precursors and metal catalysts such as Fe, Co, or Ni for the growth of CNTs–graphene. These metal catalysts play a crucial role in CNTs development, facilitating and improving the reaction process.

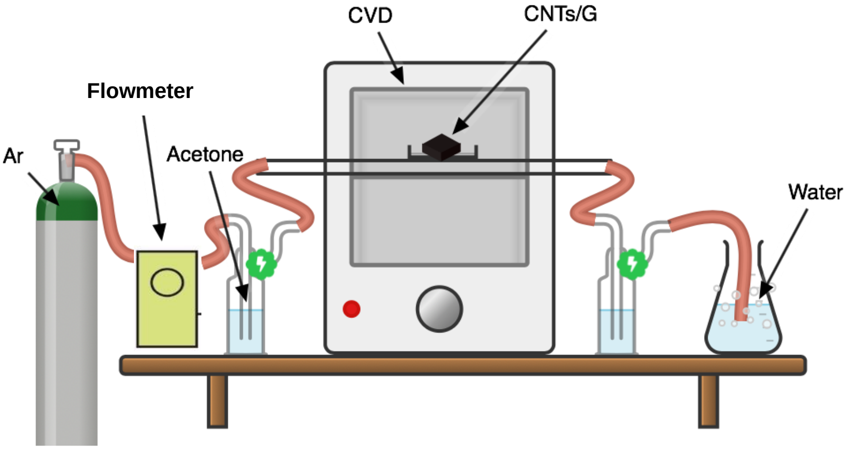

Figure 1. The schematic diagram of CVD technique.

Several techniques, including arc discharge, laser ablation, and CVD, can be used to grow CNTs on graphene or graphene on CNTs to synthesise the CNTs–graphene hybrid materials. Both arc discharge and laser ablation have difficulties that make them less desirable than alternative approaches. Carbon gas condensation during the reaction process with these approaches makes it less effective for developing well-distributed CNTs growth, and it is also extremely pricey. However, CVD is commonly used to create the thin film by depositing material on the substrate through the oxidation of volatile precursors [20], and it needs not only a carbon precursor but also metal catalysts like Fe, Co, or Ni to generate CNTs–Graphene hybrid materials by CVD. These metal catalysts play a crucial function in CNTs development, facilitating a straightforward and dependable response. By reacting or decomposing the precursor directly on the substrate surface, the CVD technique generates the required structure. There are fewer expenses involved in the procedure. The CVD approach has the advantage over other methods since it can be used to synthesise on a large scale and works at a low temperature.

As was previously noted, several catalysts can be used to synthesise CNTs–Graphene hybrid materials. Ni nanoparticles act as a catalyst for the formation of CNTs on graphene, removing unfavourable hydrogenation and decreasing graphene etching. This technique yields intact CNTs produced at 700°C in a reaction [21]. Depending on how much of the metal catalyst is exposed, CNTs can either cover the graphene surface uniformly or form clusters. CNTs can grow in a variety of random shapes and lengths. In horizontal CVD, CNTs grow perpendicular to the substrate surface, resulting in a longer final product. This occurs because the CNTs' gravity is diminished by the van der Waals interaction, resulting in the creation of horizontal CNTs on graphene [22]. Cleaning the substrate before CNT growth is essential for obtaining high–quality CNTs. This method was developed in an effort to lessen particle contamination of the substrate during CNT purification [23], [24].

In order to grow CNTs using the CVD approach, Falze Kibria et al. [25] used three different catalysts: Fe:Al_2O_3 (catalyst A), Ni:Al_2O_3 (catalyst B), and Fe:Ni:Al_2O_3 (catalyst C). The substrate sample was then reacted with the catalyst, which had been pre–mixed and calcined for 4 hours at 400°C. CNTs will be synthesised at 600°C in a flow of 10:100 sccm C_2H_2/H_2 gas after the catalyst has been activated at 900°C for 1 hour in a 100 sccm H_2 flow. CNTs' growth rate was investigated by performing a series of growth reactions at increasing times from 5 to 90 minutes long. SEM analysis showed that CNTs grown on catalysts A and B had average diameters of around 40 and 50 nm, respectively, while CNTs formed on that catalyst had an average diameter of about 20 nm. Compared to CNTs produced on catalysts A and B, CNTs grown on catalyst C had a greater density. CNTs grown using catalysts A and B, both single metal catalysts, averaged around 2 μm in length, while CNTs grown using catalyst C averaged about 4 μm in length.

Basheer et al. [26] include Fe as a catalyst in 5 mL of acetone before combining it with 2 g of bio-PAC. This procedure is based on work by Aljumaily et al. [27]. However, until all of the acetone evaporated, the mixture was sonicated at 60 °C for 99 min. Finally, after 24 hours at 105 °C the bio-PAC/Fe sample was dried. Inert gas (purified N_2, 200 mL/min) was then used to calcine the bio-PAC/Fe at 400 °C for 2 hours [27]. To grow the CNTs, we used a ceramic boat fitted with a CVD reaction tube and 300 mg of bio–PAC/Fe. At 550 °C and a flow rate of 160 mL/min, normal growth was achieved under an H_2 atmosphere. Then, carbon was obtained from C_2H_2 and combined with H_2 in a 1:4 ratio. For 47 min, we subjected the reaction to the heat of a reactor. The CVD reactor was cooled to room temperature using a purified N_2 flow rate of 200 mL/min once the reaction was complete, and a sample of the CNTs growth was then extracted.

Carbon nanofibers (CNFs) with a slightly greater diameter than the CNTs, which is >100 nm, can also grow alongside the CNTs in the CVD process [28]. Aligned CNFs were synthesised at the graphene on Ni thin film edge during the formation of CNTs in a study by Shamsuri et al. [29]. During the hydrogenation reaction, graphene can unintentionally etch, creating "scratch holes" through a metal catalyst. Holes are etched into the graphene sheet as a result of the motion of metal catalyst nanoparticles. If the reaction temperature in the CVD system is less than 700°C, these etched holes will not occur. Some surface oxidation was observed throughout development, as measured by XPS, likely as a result of the material's exposure to air following synthesis.

In order to create the CNTs–Graphene hybrid, Zhang et al. [30] used a layer of graphene produced at 1000°C using argon (Ar), hydrogen (H_2), and methane (CH_4) on Cu foil using the CVD method. The graphene transfer was facilitated by a polymer called poly(methyl) methacrylate (PMMA). To get graphene onto the Fe/Al_2O_3/SiO_2/Si substrates, first the PMMA layer has to be stripped away with acetone. In the end, CVD synthesis of CNTs arrays on the graphene surface was successful. According to prior research on the synthesis of the CNTs–Graphene hybrid material, partially exposed CNTs were created when single–walled CNTs (SWCNTs) were grown at 1080°C in Ar and H_2 gas. Graphene sheets supported by CNTs can be fortified by high temperatures and contact with Ar and H_2 gas [31].

Another study discovered that CVD allowed CNTs to grow vertically on top of and below the graphene layer. Depending on how far apart the graphene sheets are connected, the CNTs–

Graphene hybrid material can also function as inter–tube bridges. CNTs–Graphene hybrids can gain tensile strength through this creation [32]. Iron (II, III) oxide (Fe_3O_4) nanoparticles on graphene are often used as a metal catalyst for the vertical growth of CNTs in hybrid carbon materials [10]. The catalytic activity during the production of CNTs–Graphene hybrid materials can be affected by a number of factors. The creation of doped edges and the production of defects in carbon are two such factors. The electron density can alter, increasing the carbon's propensity for the transition into CNTs [10], depending on the form of the edge defects and the catalytic activity of the carbon. Interactions with oxygen involve interactions with nitrogen, and other experimental experiments have revealed that topological defects may play a role in these reactions [33]. The hybrid CNTs–Graphene material benefits from the existence of the topological defect, leading to enhanced catalytic activity.

3. THE GROWTH MECHANISM OF CNTS ON GRAPHENE

As was previously established, the production and expansion of CNTs are sensitive to variations in growth conditions and other factors. Carbon's surface diffusion along the outer wall of CNTs and carbon's contact with the catalyst are two contributing elements. The thermo-kinetic model of CNTs development accounts for the migration of carbon to the surface. CNTs can originate from a variety of materials, including metal-carbon nanoparticles, clusters of semi-fullerenes, and even graphene nanoparticles [34].

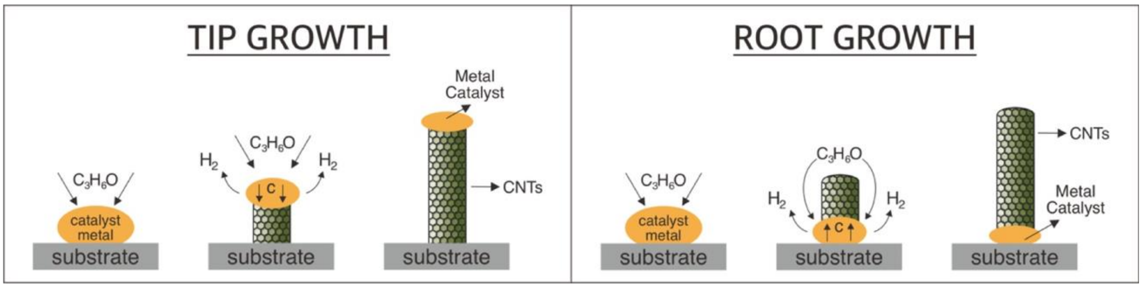

Figure 2. The illustration of mechanism CNTs growth: tip growth and root growth.

Both a "tip growth" [35] and a "root growth" [36] mechanism for CNTs are known to exist. Exposure to hydrocarbon gas that decomposes at high temperatures is necessary for tip growth after a thin metallic layer on a substrate has been applied to act as a catalyst. Hydrocarbons can be broken down by the metal catalyst. Later, the carbon enters the metal catalyst particle by diffusion and forms a precipitate. Over–coating then causes the catalyst to become inactive, stopping the formation of CNTs altogether. Separation of the metal catalyst particle and its movement to the growing CNTs' leading edge is another process for tip growth. Carbon is deposited into the graphite structure beneath the catalyst, which is forced upward by diffusion and osmotic pressure [37]. Tip growth incorporates carbon atoms into the open end of the tube, which speeds up the growth reaction; at this point, the metal catalyst prevents the end of the CNTs from closing, indicating only a modest connection between the substrate and the metal catalyst [38].

When CNTs expand upward from metal particles, this is known as base or root growth. When molten metal is cooled and solidified, carbon is liberated from the particle surface, and carbon deposition begins [37]. This is the first stage in the CNTs' root growth process. This vigorous root development exemplifies the powerful interplay between substrate and catalyst. A new theory regarding CVD, CNT growth has surfaced: open tip growth, with an initial sealing of the inner layer due to a decrease in carbon atom concentration. After this step, the CNTs' outer layer can be sealed. A sealed nanotube describes this idea. Previous research indicates that the tip growth mechanism predominates in CVD when CNTs are generated. It was hypothesised by Zhao et al. [38] that the CNTs' development ceased when both their inner and outer layers shut at the same time.

Growing CNTs in a CVD system calls for close monitoring of all relevant growth parameters. Desorption of gases from the inner wall of the reaction chamber, air leakage, and oxidation of contaminants in the gas all play major roles. It is important to have a high reaction temperature and a low pressure for the carbon precursor. The pace of the inert gas flow and the carbon precursor flow also play a role in CNT synthesis. Furthermore, a stable ratio of carbon precursors, H_2, and O_2 is necessary to maximise the CNTs' development rate [39]. The controlled growth of CNTs–Graphene hybrid materials requires a thorough understanding of the growth dynamics of CNTs on graphene substrates. Despite extensive study of CNTs characteristics and growth regulation, our knowledge of CNTs growth kinetics is limited due to ambiguous experimental observation. To learn more about the mechanism and kinetics of CNTs development, many theoretical growth model studies have been performed. CNTs growth velocities are shown to be proportional to the Burgers vector of the carbon atom dislocation and, secondarily, to the chiral angle, as discovered by Ding et al. [40]. Some experimental observation, are consistent with the results of theoretical investigations into the dislocation theory of the formation of CNTs [41]. However, other experimental works on CNTs development in CVD obtained conflicting results [42]. These works revealed no relationships between the CNTs' length, growth rate, or chirality.

The steady-state elongation rate of CNTs is dependent on the pressure of the gaseous carbon source and the temperature at which they are synthesised, as was discovered in a study by Zounmenou et al. [43]. It has been discovered that the developing edge of CNTs that should be in touch with the metal catalyst nanoparticles is smooth at low temperatures and has little driving force. However, in conditions similar to those seen on crystal surfaces–high temperature, strong driving force, or high pressure–CNTs develop a rough edge as they grow [43].

4. APPLICATION OF CNTS-GRAPHENE HYBRID MATERIAL

Electro–catalysis is just one of many possible environmental, technological, and energy uses for CNTs–Graphene hybrid materials because of their superior electrical and mechanical capabilities. In this study, we explore the possibilities of CNTs–Graphene hybrid material as electrodes in batteries, as well as its other possible uses. As a 3D carbon-based material structure, CNTs–Graphene hybrids have recently found usage in battery applications [44]–[46]. Carbon nanotubes (CNTs) can serve as a battery's electrolyte, membrane, or anode. CNTs–Graphene hybrids have significant challenges when used as anode materials in lithium-ion batteries. Previous research has shown that dye–synthesised solar cells and Li–ion batteries can both benefit from the use of vertically aligned CNTs (VACNTs) synthesised on graphene sheets as anodes. At a current density of 30 mAg^{-1} and after 40 charge-discharge cycles, it was found that the CNTs–Graphene hybrids have a steady discharge capacity of 290 $mAhg^{-1}$. The surface area of the optimised CNTs–Graphene can grow to 949.9 m^2/g. When separated from graphene, the hybrid catalyst grows in size (0.41 nm vs. 0.36 nm) and increases the amperage for Li–ions. At 303 $mAhg^{-1}$ [47], the charging capacity of the CNTs–Graphene hybrid is likewise respectable. The specific capacity of Li-ion batteries can be improved upon by further work on CNTs–Graphene hybrid electrodes to reach 700 $mAhg^{-1}$ [48].

When used as cathodes in lithium–sulphur (Li–S) batteries, CNTs–Graphene hybrid materials have been shown to work well, transfer electrons quickly, and let the right amount of electrolyte through. At 100 charge cycles, CNTs that were grown vertically had a capacity of 650 $mAhg^{-1}$ and a higher coulomb efficiency of 92% [49]. A CNTs–Graphene hybrid material has been used as a catalyst for Li–S batteries. The CNTs–Graphene hybrids' perpendicular and linked structure makes charge transfer at the anode faster. After 250 charges, the hybrids' capacity reaches 900 mAhg^{-1} with 100% Coulombic efficiency [50]. Sulphate serves as a cathode catalyst and a doping agent in CNTs–Graphene hybrids in Li–S batteries, with catalytic capacity decreasing to 1048 mAhg^{-1} after 1000 charge–discharge cycles (ca. 0.041%/cycle) [51]. Another study found that using CNTs–Graphene hybrids as the cathode material in a lithium-sulphur (Li–S) battery resulted in a high specific capacity of 1121 mAhg^{-1} with a declining capacity of 0.12% [52]. When comparing sulphur–doped CNTs–Graphene hybrids to undoped CNTs–Graphene hybrids, the researchers found that the attained conductivity level was high, by 324.7%. Capacity in Li–S batteries reached 877.4 mAhg^{-1} with a capacity drop of 0.08% each cycle when using sulphur-doped CNTs–Graphene hybrids as the cathode [53].

Heteroatom doping can be used to obtain the electrochemical–catalytic state of CNTs–Graphene hybrids by altering the charge density distribution in the modified carbon-based material. The CNTs–Graphene hybrid material has a power density of 253 mWcm^{-2} and a specific capacity of 801 mAhg^{-1} [54]. In a 500–cycle experiment, a CNTs–Graphene hybrid doped with nitrogen (N) and sulphur (S) as the cathode exhibited a low-capacity degradation rate of 0.08% per cycle and a Coulombic efficiency of 100% [50]. To boost conductivity and electrochemical performance, researchers have used ultrasonic synthesis and incorporation of S nanoparticles in CNTs–Graphene hybrids, finding a high specific capacity of 1067 mAhg^{-1} at a current density of 50 mAg^{-1} [53].

There has been a lot of work done in recent years to figure out how to use CNTs–Graphene hybrid material as electrodes in batteries. Other conventional metal electrode performance has been shown to be enhanced by the CNTs–Graphene hybrid material. Many other applications are either under way or projected to grow in the next few years based on the exceptional features of CNTs–Graphene hybrid materials.

5. CONCLUSION

This paper presents the synthesis of CNTs on graphene that results in a new hybrid material known as CNTs–Graphene Hybrids. Different methods exist for synthesising this CNTs-Graphene hybrid material; however, chemical vapour deposition (CVD) has emerged as the method of choice due to its dependability, low cost, and capacity to create CNTs on a large scale with good quality. Besides growth and reaction parameters like temperature, duration, heating rate, and gas flow rate, the catalyst and the precursor are the most critical factors in the production of CNTs-Graphene hybrids. Many electronic applications have found the CNTs-Graphene hybrid to be useful as electrodes.

ACKNOWLEDGEMENTS

The author would like to acknowledge the support from the Fundamental Research Grant Scheme (FRGS) under a grant number of FRGS/1/2020/STG07/UNIMAP/02/4 from the Ministry of Education Malaysia.

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