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# Synthesis and characterization of graphene and carbon nanotubes: A review on the past and recent developments



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# ABSTRACT

Carbon nanotubes (CNTs) and graphene have built broad interest in most areas of science and engineering because of their extraordinary physical, mechanical, thermal and optical properties. Graphene is a two-dimensional one-atom-thick planar sheet of sp<sup>2</sup>-bonded carbon atoms while CNTs are a cylindrical nanostructure which composed entirely of sp<sup>2</sup>-bonded carbon atoms as well. This review presents and discusses the past and current advancement of synthesis and characterization of graphene and CNTs. The review also concludes with a brief summary and an outlook on the challenges and future prospects in the growth of graphene and CNTs.

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# 1. Introduction

Graphene is the thinnest material with one-atom-thick planar sheet of sp<sup>2</sup>-bonded carbon atoms densely packed in a honeycomb crystal lattice [1]. It is the basic structure of graphite, carbon nanotubes (CNTs), and fullerenes [2,3]. The sp<sup>2</sup> bonds and its electron configuration are the main reasons why graphene possess extraordinary properties such as double surface area than that of single-walled carbon nanotubes (SWCNTs), ultra-high mechanical strength, a tunable electronic band gap, excellent thermal conductivity, room-temperature Hall effect, and ultra-high elasticity [4].

CNT is one of the most investigated materials before the invention of graphene since it was discovered by Iijima [5]. Its unique physical, chemical, mechanical and thermal properties due to the nano size, cylindrical structure, and high aspect ratio of length to diameter have attracted very much attention from scientists around the world. SWCNT is made of a single graphene sheet wrapped around to form a cylinder [6]. A multi-walled carbon nanotube (MWCNT) consists of concentrically nested cylinders with an interlayer spacing of 3.4 Å and a diameter typically on the order of 10–20 nm [6].

Both graphene and CNTs are excellent material for electrochemistry application [7–10]. However, graphene has two advantages compared to CNTs: (1) graphene contains higher purities than CNTs [11]. It is because CNTs contain metallic impurities which affects the electrochemistry of CNTs. (2) cost production is lower than CNTs because graphene can be synthesized from cheaper graphite [6]. This review article focus on the brief history and recent advancement synthesis of graphene and various characterization methods related to its 2D structure. This article also presents the past and recent synthesis and characterization techniques of CNTs.

### 2. Synthesis of carbon nanotubes (CNTs) and graphene

CNTs were much earlier synthesized in 1991 compared to graphene. Both nano materials can be produced by using the same technique such as chemical vapor deposition (CVD). Several methods to produce CNTs include arc discharge, laser ablation and CVD while graphene can be synthesized by mechanical exfoliation, chemical reduction of graphene oxide, CVD, plasma enhanced CVD and thermal decomposition on SiC and other substrates. All methods above will be discussed in detail.

# 2.1. Synthesis of CNTs

#### 2.1.1. Arc-discharge

Arc-discharge was first used by lijima [5] to synthesize CNTs. The experimental setup and conditions are same with those applied for production of fullerenes. This technique involves placing two graphite electrodes close to each other's about 1 mm in an atmosphere of inert gas like helium at a pressure of 500 Torr [12]. An arc occurs between the electrodes when a voltage of 20–25 V with a current of 50–120 A is applied. The temperature is very high in the chamber and evaporates carbon from the electrodes. This arc-evaporated material then re-condenses on the cathode, and the subsequent deposit contains CNTs. SWCNTs were

produced by doing the electrode with metals such as Ni, Fe, Co, Gd and Y [13]. The disadvantage of this technique is carbon impurities and encapsulated nanoparticles are usually produced beside CNTs [12]. Short CNTs are tending to be produced as well. However, the advantage is both of SWCNTs and MWCNTs are easily to be synthesized and moderate cost production is needed.

It also has been demonstrated that the production of MWCNTs can be achieved by conducting an electric arc-discharge under the surface of liquid nitrogen in an open vessel [14] without evacuation of reactor. The nitrogen gas was released from the evaporation of liquid nitrogen resulting from the heat input from the discharge itself. The existence of nitrogen gas was to clear all oxygen for the fast reaction. This method was quite attractive due to the simplicity of experimental set up and the possibility of simple approach to the reaction chamber during the operation. In another words, liquid nitrogen gives a suitable environment to grow MWCNTs. However, the arc-discharge has caused too much evaporation and allows very low thermal exchange between the produced carbon material and its surroundings. As a result, most of the synthesized MWCNTs show low quality structure.

In addition, the synthesis of MWCNTs and polyaromatic carbon shells by arc-discharge in deionized water has also been reported [15–18]. Liquid water besides providing a better suitable environment as compared to liquid nitrogen, it also gives good thermal conditions necessary to achieve good quality MWCNTs. It is because no major effect is observed during the reaction between the water and hot carbon. Moreover, the produced amorphous carbon is probably easily removed by thermal oxidation to get high purity of MWCNTs.

In order to achieve large-scale production of CNTs using arcdischarge, several methods have been reported. Shi et al. [19,20] demonstrated that SWCNTs with high yield (10 g per day) were synthesized under very high helium pressure of 500 or 700 torr. This confirms the finding by Saito et al. [21] that the vapor pressure of the catalyst metal is an important factor to grow SWCNTs. The high helium pressure is an advantage for the co-evaporation of metal and carbon to reduce the vapor pressure of the catalyst metal. By increasing the discharge current, the production rate of collected soot can be increased but the purity of SWCNTs was decreased as reported by He et al. [22]. During the reaction in reactor, part of the catalyst were attracted to the cathode by the force of electric field, and the other part, which is play the main role in synthesizing SWCNTs, was evaporated with carbon atoms into the atmosphere. As electric current increased, more catalysts were attracted to the cathode, and less catalyst was emitted into the chamber atmosphere to catalyze the production of SWCNTs. Therefore, the synthesis of amorphous carbon particles from the evaporated carbon and carbon clusters was induced at higher currents, but it also decreased the amount of SWCNTs produced in the soot. Besides, Ando et al. [23] also reported that the large-scale production of SWCNTs can be achieved by increasing the discharge current using the plasma jet assisted DC arc-discharge. The highest amount of the nanotubes was  $1.24 \text{ g min}^{-1}$  when current was 100 A and the best purity of the SWCNTs was about 50% when current was 70 A.

Recently, large-scale synthesis of few-walled CNTs (FWCNTs) was demonstrated through employing low-pressure flowing air as buffer gas during DC arc discharge, in which iron was used as a

catalyst and sulfur used as a promoter [24]. They found out that the production of FWCNTs was influenced by the air pressure. When the air pressure was lower than 3 kPa or greater than 15 kPa, low yield of FWCNTs was achieved. The FWCNTs can be synthesized effectively only under air pressure between 6 and 12 kPa. They explained that the movement of heat and carbon vapors was very slow under low pressure than 3 kPa, leading to low synthesis of FWCNTs. However, the as-synthesized FWCNTs and carbon vapors were oxidized too fast during arc discharge with air pressure larger than 15 kPa and decreased the amount of FWCNTs. Therefore, a suitable balance between gas pressure and oxidization provides excellent reaction condition for high yield of FWCNTs.

# 2.1.2. Laser ablation

Laser ablation operates at same conditions to arc discharge. Both methods involve the condensation of carbon formed from the vaporization of graphite. When target doped with metals such as Ni, Co and Pt, SWCNTs are formed. In this technique, the graphite target is placed in a quartz tube surrounded by a furnace heated at 800–1500 °C. A 500 Torr of argon gas is passed through the tube to carry the soot formed to a water-cooled Cu collector. It has been claimed by Thess et al. [25] that high yields with more than 70–90% conversion of the graphite to CNTs are achieved with this technique. The disadvantage is the cost production is very high due to high power and expensive of laser is required. Moreover, the produced CNTs are in carbonaceous soot, where impurities such as metal catalysts and amorphous carbon are exist as by-products as well. Thus, complicated purification treatments are required which always damage and dope the final CNTs.

A "CVD-like" process to grow SWCNTs, which deposited nanoparticles catalyst on SiO<sub>2</sub>/Si substrates using pulse laser deposition (PLD) and exposed them to the carbon vapor produced by the KrF-laser ablation of a pure graphite target, was reported by Aïssa et al. [26]. They demonstrated that the size of nanoparticles catalyst can be controlled between 1.5-2.7 nm by correctly adjusting the number of laser pulses to synthesize individual SWCNTs in the range of  $\sim$ 1 nm. This "CVD-like" process was shown an advantage in removing unwanted amorphous carbon partially by thermal oxidation during the laser ablation. Laser vaporization of graphite that contains B<sub>4</sub>C in Ar ambient gas was shown to synthesize MWCNTs effectively [27]. Different with conventional laser ablation method, a continuous wave (cw) Nd:YAG laser was used to vaporize graphite containing a metal to release hot species of carbon atoms into an inert gas atmosphere. Vapor-liquid-solid growth mechanism plays the main role in synthesizing MWCNTs which were found strongly depend on the boron content and Ar gas pressure. It is because higher boron content resulted in larger molten BC particles which act as seed at high temperature to grow MWCNTs that have up to 80 graphene walls. In addition, the laservaporized carbon and boron species were at temperature of 5000 °C and had low expansion velocities of 102–103 cm s<sup>-1</sup> due to the high-pressure Ar gas confining their expansion.

A new method to synthesize CNTs using laser ablation method targeting a solid carbon in liquid was demonstrated [28]. Carbon nanocages with various shapes were also synthesized in the experiment. The growth mechanism was different with the precipitation mechanism previously explained in literature because no metal catalyst was mixed with the carbon target [29]. The mechanism of a bubble blowing formation was proposed in which the carbon nanocages and CNTs were synthesized by blowing when the inner pressure was high enough created from laser power density (LPD). When LPD was increased, the mobility of carbon atoms and carbon gas pressure were increased as well to form longer inner hollow and the higher quality structure of carbon nanocages and CNTs was formed. Besides, Giuseppe et al. [30] also demonstrated the synthesis of carbon nanowalls in liquid

such as water, acetonitrile, methanol and cyclohexane. However, electric field-assisted laser ablation was used and it has been found that the electric fields responsible to carry the negatively charged particles to the anode where the carbon nanowalls were started to grow.

Schauerman et al. [31] investigated the influence of catalyst particle size on the synthesis of SWCNTs using pulsed laser vaporization. Nanometal catalyst particles and micronmetal catalyst particles were used to synthesize SWCNTs and the purity, yield and purification efficiency of produced SWCNTs were compared. They found out that the nanometal catalyst particles performed better than micrometal catalyst particles by increasing the yield and offers single thermal oxidation to remove carbonaceous impurities to achieve higher purity of SWCNTs. It is because nanometal catalyst particles are more active than micrometal catalyst particles to synthesize SWCNTs.

The synthesis of freestanding carbon nanosheets (CNSs) was conducted through laser ablation of poly(phenylcarbyne) (PPC) using a pulsed Nd:YAG laser [32]. Various types of carbon nanostructures of different phases including amorphous carbon, ultrathin amorphous CNSs and thick carbon films were synthesized from the polymer-to-carbon transition. The formation mechanism of CNSs is involved three steps including ablation, carbonization and landing. The graphitization and carbonization of CNSs were improved significantly when the laser influence increased. The photothermal process and the high temperature have found plays main roles in the polymer-to-carbon into graphitic sp<sup>2</sup> carbon [33,34].

# 2.1.3. CVD

The last technique is CVD, metal catalysts are used to crackdown the molecules of carbon sources to synthesize CNTs [35,37,38]. A supported catalyst is heated in a furnace to 600-1000 °C together with hydrocarbon gas for a period of time [37]. The carbon sample is then allowed to cool down in an inert gas environment to avoid etching away the CNTs by reaction with oxygen. MWCNTs are mainly formed at lower temperatures (300-800 °C), whereas SWCNTs require higher temperatures (600-1000 °C). Many types of carbon sources such as methane, benzene, camphor, ethanol, ethane, alcohol, carbon monoxide, hexane, cyclohexane, naphthalene, anthracene and others have been used to produce CNTs [36]. For the synthesis of SWCNTs, carbon monoxide and methane have been found to be effective [37]. The most popular metals used to produce CNTs are iron, nickel, cobalt and molybdenum [37]. However, the combination of two metals is active to form CNTs, particularly mixtures of molybdenum with other metals. The most common metals such as silica, alumina and magnesium oxide are used as supports [38]. The advantage of this technique is the production of CNTs can be scaled up and controlled better over the growth of CNTs due to the greater scope for controlling reaction conditions, such as designing catalysts [38,39]. However, the disadvantage is mixture of SWCNTs and MWCNTs are produced together during the CVD.

Very recently, metal-free catalysts such as diamond, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, ZrO<sub>2</sub> and graphite have been used for production of CNTs [40–49]. Besides, Qiu et al. [50] also demonstrated the synthesis of MWCNTs without any metal catalyst which can be produced by one-step annealing of polyacrylonitrile microspheres (PANMSs) at a relatively low temperature (1000 °C). This method can produce MWCNTs in large-scale quantity because PANMSs can be prepared in large scale quantity at low cost production. Varshney et al. [51] reported the synthesis of CNTs on free-standing diamond (FSD) films by using a novel approach of hot filament CVD. This novel approach is an interesting and scalable technique of producing CNT-populated FSD film that can be easily separated from the

parent substrate. Thus, it can prevent the damage effect of metal particles resides on CNT-based electronic devices. Na<sub>2</sub>CO<sub>3</sub> were used as catalyst for the selective production of carbon nanofibers (CNFs) and CNTs because Na<sub>2</sub>CO<sub>3</sub> is water-soluble and it can be washed away using water only to get the high purity and large amount of CNFs and CNTs [52]. In other words, Na<sub>2</sub>CO<sub>3</sub> catalyst is simple for use, inexpensive and ecosystem-friendly. Another method to synthesize metal-free CNTs is to etch Si/SiO<sub>2</sub> wafers with 48-50% hydrofluoric acid as demonstrated by Tan et al. [53]. The wafer etched at 1 min after CVD at 900 °C for 1 h showed a low I<sub>D</sub>/I<sub>G</sub> from Raman analysis which indicates that high graphitization of CNTs were synthesized. The reason for producing CNTs is the formation of islands of SiO<sub>2</sub> nanoparticles after hydrofluoric acid dissolves parts of the SiO<sub>2</sub> layer which is hydrophilic, while the aqueous solution shrinks onto the bottom of the hydrophobic Si layer. The SiO<sub>2</sub> nanoparticles are the catalyst play the main role to activate the growth of CNTs.

It is well known that Fe, Co, Ni, and their alloy are the most popular catalysts used to synthesize CNTs in CVD except Cu because it has low catalytic activity due to its nearly zero carbon solubility [54]. A simple and effective approach was developed by Yang et al. [54] to synthesize bamboo-like MWCNTs using unmodified Cu catalyst supported on Al matrix under a low temperature (600 °C). Another type of CNTs called helical or coiled CNTs can be produced by catalytic chemical vapor deposition (CCVD) using the decomposition of hydrocarbon on transition metal containing supported catalysts [55]. They can also be synthesized by reducing ethyl ether with metallic zinc [56] and obtained as by-products in microwave plasma-enhanced CVD [57] or by CCVD pyrolysis of a vapor mixture of Fe(CO)<sub>5</sub> and pyridine or toluene [58]. Fixed bed reactors are normally used for the production of coiled CNTs [55,59,60], but fluidized bed was used to synthesize coiled CNTs successfully as well [61]. A triple helix CNT was found in the CNTs samples produced using marine manganese nodule, a naturally mineral [62]. At low temperature of 450 °C, high amount of helical CNTs, worm-like CNTs and nanocoils

can be produced using Fe deposited on a ceramic plate [63]. Csató et al. [64] also demonstrated the production of coiled CNTs by CCVD from acetylene on supported catalyst. Recently, several types of hydrocarbons have been chosen as carbon source to synthesize CNTs. Scrap tyre rubber was used as carbon source by Yang et al. [65] to prepare CNTs successfully using CVD which provided an alternative idea for reuse waste rubber for CNT production. Li et al. [66] used heavy oil residue as carbon source to grow SWCNTs because it cheaper and suitable industrial carbon source for production of SWCNTs with high quality. Besides hydrocarbon, bamboo charcoals can be a new material for synthesis of CNTs. Zhu et al. [67] demonstrated the use of bamboo charcoals to synthesize MWCNTs using CVD in the presence of ethanol vapor. They observed that the tips of MWCNTs produced at 1200-1400 °C consists mainly of calcium silicate which acted as catalyst for the nucleation of MWCNTs. Fig. 1 shows the MWCNTs produced from bamboo charcoals. So far, several materials have been used as support for active metals, for example zeolites [68,69] SiO<sub>2</sub> [70,71], Al<sub>2</sub>O<sub>3</sub> [72], CaCO<sub>3</sub> [73] and MgO [74]. However, the use of clay as support to the synthesis of CNTs can be found in [75,76]. Clay minerals have some advantages such as very fine of clay particles, possess ion exchange properties and inexpensive. So far, several phyllosilicates such as montmorillonite [77], wollastonite [78], mica [79], diopside [80], vermiculite [81], kaolinite, nontronite and sepiolite [82] have been used for synthesis of CNTs. CNTs produced on clay minerals may likely to be used as a component of composite materials.

# 2.2. Synthesis of graphene

#### 2.2.1. Mechanical exfoliation

Mechanical exfoliation of small mesas of fresh graphite, is the first technique employed to prepare graphene. This was successfully done by Novoselov et al. in 2004 to prepare graphene from monocrystalline graphitic films [83,84]. However, the yield is too low which is not suitable for the large-scale production of



Fig. 1. SEM images of CNTs formed on bamboo charcoals pyrolyzed at (a) 1200, (b) 1300, and (c) 1400 °C. Insets are their respective magnified images. (Reproduced with permission from [67].)

graphene for biosensor application. On the other hand, although huge quantity of graphene oxide (GO) monolayer could be produced by chemical oxidation of graphite and followed by exfoliation, significant structural defects on the GO were shown by Raman spectra [85,86]. Fig. 2 shows the high intensity of D-band for reduced GO indicating the presence of substantial amount of defects. Consequently, the electronic properties of graphene were disrupted and modified to semiconductive.

Moreover, as shown by XPS studies, neither chemical reduction nor thermal annealing is possible to rebuild original structure and restore original electronic properties of graphene [87]. Thus, in order to preserve graphene structure and electronic properties, physical exfoliation method is favorable. Blake et al. [88] and Hernandez et al. [89] have shown that graphite could be exfoliated by using surface energy of N-methyl-pyrrolidone and graphene to produce defectfree monolayer graphene in N-methyl-pyrrolidone. However, the high cost and high boiling point of solvent have become the disadvantage of the solvent. Lotya and coworkers have demonstrated that graphene could be exfoliated in water by using a surfactant (sodium dodecylbenzene sulfonate, SDBS). The advantage of this surfactant is graphene monolayers could be stabilized against aggregation [90]. Similarly, sodium cholate could be used as surfactant to exfoliate graphite and at the same time to separate the monolayer graphene and graphite which have different buoyant density using density gradient ultracentrifugation [91].

# 2.2.2. Chemical reduction of GO

Graphene can be produced from reduction of GO as well by using chemical reduction such as hydrazine,  $NaBH_4$  [92] and



**Fig. 2.** The Raman spectra for graphite (top) GO (middle) reduced GO (bottom). (Reproduced with permission from [86].)

hydroquinone [93] on vigorous stirring at 80–100 °C. The structure and conductance of GO could be restored at low temperatures under hydrazine reduction. However, strong defect were formed on graphene as shown in Raman spectra. In order to reduce the amount of defect and oxygenic group formed on graphene, solvothermal technique was developed by Dai and co-workers to reduce the GO in more effective manner [94]. Solvothermal reduction was completed in N,N-dimethylformamide (DMF) at 180 °C using hydrazine monohydrate as the reducing agent. The reduced graphene sheets showed an average Raman D/G intensity ratio lower than that of the as-made graphene by solvothermal reduction of graphene sheet, which suggested that the solvothermal reduction actually increased the average size of the crystalline graphene domains. In addition, it also increased the conductivity of reduced graphene sheet close to that of pristine graphite. It is because large amount of oxygen functional groups were removed by hydrazine at high temperature, which was proved by the insolubility of the reduced graphene sheet due to low oxygen functional group. Hydrazine [85,95] and sodium borohydride (NaBH<sub>4</sub>) [96,97] have been well known as strong chemical reducing agents but it also caused the reduced GO film become rigid while NaBH<sub>4</sub> reduction caused the reduced GO film become fragile. This problem can be solved through the reduction of GO films using hydrohalic acid to preserve their integrity and flexibility as demonstrated by Pei et al. [98].

The above chemical reduction methods showed some disadvantages such as produced toxic waste and harmful to the environment. First hydrazine vapors are highly poisonous. Second, thermal reduction is involved heat-released multi-step removal processes of H<sub>2</sub>O molecules, COOH (carboxyl group), OH (hydroxyl group), and >O (epoxy group) which gives highly impact to environmental and economic when scale-up for production. Thus, environment-friendly and highly effective reducing agents are needed to substitute the conventional methods to reduce GO [99]. Lately, environment-friendly chemical reducing agents, such as vitamin C [100-102], aluminum powder [103], reducing sugar [104] and amino acid [105] have been used to synthesize reduced GO. Wang et al. [106] showed that GO can be reduced by making use of the reducing capability and the aromatic rings of tea polyphenol that exists in green tea solution. The characterizations of the reduced graphene sheets confirmed the efficient removal of the oxygen-containing groups in GO. Their approach demonstrates that several advantages for large-scale production of reduced graphene sheets such as environmentally friendly reduction process, low cost and simple reduction procedure, no hazardous waste was produced, both of the reduction of GO and surface functionalization of graphene sheets were carried out simultaneously which guarantee the good dispersion in different solvents and the biocompatible tea polyphenol make the soluble tea polyphenol reduced graphene a widely used material in biosensor. The dispersion of graphene oxide in organic solvents (ethylene glycol, N,N-dimethylformamide, N-methyl-2-pyrrolidone, tetrahydrofuran) was studied by Paredes et al. [107] in which graphene oxide was exfoliated almost completely into single-layer sheets. Therefore, it is demonstrates that the graphene oxide can be dispersed but not dissolved due the graphene is relatively chemically inert in any solvents that we mentioned above.

Tanizawa et al. [108] developed a hybrid method for the production of reduced graphene sheets using microorganism extracted from a riverside. This procedure facilitates the production of  $\sim$ 100 µm sized high quality of reduced graphene sheets as indicated by Raman spectra. The main advantage of this method is no reducing agent was used to reduce GO to graphene sheets. Besides, Gurunathan et al. [109] demonstrated an environment friendly, cost effective, simple method and green methods to reduce GO using Escherichia coli biomass. The biomass of E. coli



Fig. 3. Scanning electron microscopy (SEM) images of GO (A) and reduced GO (B). (Reproduced with permission from [109].)

reduces exfoliated GO to graphene at 37 °C in an aqueous medium without the addition toxic substances as a reducing agent. The GO are hexagonal shape and layered, however, the reduced GO material consists of individual sheets closely associated with each other (Fig. 3). The reduced graphene sheets are dispersible in water which would open up the application in biosensor.

The combination of  $NaBH_4$  and metal nanoparticles is another alternative to reduce GO sheets in environmentally friendly manner. The metal nanoparticles can greatly accelerate the reduction of GO sheets at room temperature. Co [110,111], Au [112], Cu, Fe and Ni [111] have been identified as the active catalysts and NaBH<sub>4</sub> as reducing agent. Compare to other conventional methods, this method facilitates the scale-up production of graphene sheets at low cost and the metal nanoparticles can be reused for many times as the catalyst.

### 2.2.3. Chemical vapor deposition (CVD)

CVD growth has been reported as the most popular method for large-scale production of mono- or few-layer graphene films. The main difference between CNTs and graphene synthesized by similar method CVD would be the catalyst only which is used to decompose the carbon source into atom carbon. Catalyst nanoparticles are prepared and used to synthesize CNTs, however, foil is used to synthesize graphene. It is because the shape of CNTs is formed according to the spherical shape of catalyst nanoparticles whereas a sheet of graphene is synthesized based on the shape of one piece of foil. There are several reports on the formation of monolayer graphite were found in early investigation of CVD on metal single crystals [113-115]. However, the first successful production of few layer graphene films using CVD was reported by Somani et al. using the Ni as foils and camphor as carbon source [116]. Fig. 4 shows the planer few layer graphene structures which is consist of 35 numbers of graphitic layers. Since then, several new approaches of synthesis of graphene and some unsolved issues related to controlling the number of layers have been reported. Many researchers have been motivated to synthesize graphene with different layers on several types of metal substrates [85,117-123]. After CVD, metal substrate is etched to detach the graphene layers so that it can be transferred to a new substrate without going through complicated mechanical exfoliation or chemical reduction. It was reported that the growth mechanism of graphene is similar to the initial step of graphene cap formation during the growth of CNTs. Thus, metal such as Co and Ni with mediate-high carbon solubility (>0.1 at%) have been used to facilitates the

diffusion of carbon into the metal thin film at high temperature and followed by precipitation of carbon out from the metal thin film to metal surface when cooling [119,124]. By taking Ni as substrate for an example, the carbon are dissolve into the Ni substrate first, then followed by a precipitation of carbon to the substrate surface when Ni is cooled. During the CVD, Ni substrate is placed in a tubular furnace at reaction temperature below 1000 °C and a vacuum of 10–3 Pa with a diluted hydrocarbon gas. The thickness and quality of graphene layers can be controlled by optimizing the reaction parameters such as cooling rate, concentration of carbon precursor, reaction time and reaction temperature. Besides, the type of carbon precursor also affects the formation of graphene.

# 2.2.4. Plasma enhanced chemical vapor deposition (PECVD)

Graphene can be synthesized at a lower reaction temperature by using PECVD compared to CVD to reduce cost production. First



**Fig. 4.** High resolution of central planer few layer graphene film edges. (Reproduced with permission from [116].)

high amount of graphite was obtained after using a dc discharge PECVD in a fabrication of "nanostructured graphite-like graphite". The first production of mono- and few layer of graphene on several types of substrates by radio frequency PECVD was reported which used a gas mixture of  $CH_4$  and  $H_2$  at 900 W and in the reaction temperature of 680 °C [124–126]. Since then, many reports related to the understanding growth mechanism of graphene and optimizations of experimental parameters to control the number of layer of graphene have been found [127–129]. Zhu et al. [129] produced graphene sheet from 30 s to 8 min and demonstrated that during the first few minutes of growth, graphene layers grow parallel to the substrate surface until a sufficient level of force develops at the grain boundaries to curl the leading edge of the top layers upward (Fig. 5). There are two advantages of PECVD compared to CVD: less than 5 min deposition time and a lower



**Fig. 5.** (a) SEM image of carbon nanosheets directly grown on the curved surface of a Ni TEM grid. (b) SEM of an enlarged nanosheets edge with a thickness less than 1 nm. (c) High resolution transmission electron microscopy (HR-TEM) as indicated by the two parallel fringes. (Reproduced with permission from [129].)

growth temperature of 650 °C can be done. It is because plasmaenhanced CVD having additional high-density reactive gas atoms and radicals which facilitates low-temperature and rapid synthesis of carbon nanostructures [129–131]. Recently, graphene was produced as low as 700 °C on Fe<sub>2</sub>O<sub>3</sub>/Si substrate using inductively coupled plasma CVD [132]. It is because the presence of catalytic Fe element from Fe<sub>2</sub>O<sub>3</sub> which enhances the decomposition of carbon source and growth of graphene sheets.

# 2.2.5. Thermal decomposition on SiC and other substrates

Graphite can be produced on SiC surface by annealing SiC surface using ultra-high vacuum (UHV) which is a most used method by semiconductor industry because graphite are synthesized on SiC substrates and could be used immediately [133–136]. During the heating of SiC substrate under UHV, silicon atoms sublimate from substrate. With the removal of silicon atoms, the arrangement of carbon atoms will takes place to form graphene layers. The annealing time and temperature could influence the number of graphene layer. Few layers of graphene could be produced at 1200 °C in few minutes annealing of the SiC surface [137]. More recently, at higher temperature than 400 °C (above UHV temperature), vapor phase annealing has been used to produce improved thickness homogeneity few layer of graphene on SiC substrate [138,139]. There are several challenges are still remain for the application of graphene on SiC substrate such as controlling the number of graphene layers for large scale production, controlling the growth patterns on different SiC polar face such as Si-face or C-face and so on. Graphene sheets were found to grow at different pattern on the C-face surface and Si-face surface where unusual rotational graphene stacking were observed clearly in multilayers graphene grown on the C-face surface only. Consequently, the electronic and physical properties of graphene are affected.

Such grow of trend leads to the effect of decoupling between different layers of graphene and cause each of layers behaves as a single-layer [140]. However, the unusual grow pattern was not observed on SiC face, thus the electronic properties of multi-layers graphene are not affected [134]. Further study should be carried out to understand more on the graphene growth mechanism. The last problem to solve is to understand the interaction between the graphene and substrates and the electronic properties of the interlayer between produced graphene and substrate [136]. For example, (0001) faces of ruthenium (Ru) crystals were annealed under UHV to synthesize multilayers graphene where the first layer paired strongly to the Ru substrate, while the second layer was not interacting with Ru substrate and possessed same electronic properties with free-standing graphene [141,142]. There are other types of metal substrates such as Pt, Co, Ni and Ir have been used to synthesize graphene layers [143].

# 2.2.6. Other methods

CNTs can be unzipped to form graphene by using a chemical reaction into pieces [144–148]. Besides using chemical reaction, polymer (PMMA) has been used to coat the CNTs and unzip them by using plasma processing in order to establish a process which is compatible with silicon technology [147]. Recently, Mohammadi et al. [149] demonstrated the synthesis of vertical CNTs on silicon substrates and they were unzipped using a sequential passivation and hydrogenation subsequences in a reactive ion etching unit. Hydrogen plasma is believed to be responsible to unzip CNTs and the passivation step is needed to preserve the burst wall of CNTs.

Graphene sheets can be mechanically produced by rubbing MWCNT bulk sample on micro-blades of glass [150]. This process offers a novel, convenient and effective method to produce graphene sheets. In addition, this method allows graphene sheet can be produced easily on any substrates by rubbing. In the past

few years, nanomaterials such as metal oxide nanoparticles and nanochalcogenides can be synthesized using sonochemical method [151,152]. The mechanism of sonochemical method is relies on the acoustic cavitation phenomenon which happens at very high temperature about 5000 K, pressure about 20 MPa and extremely high cooling rate about 1010 K s<sup>-1</sup> [153–156]. With those reaction conditions, the reduction of GO was demonstrated by Krishnamoorthy et al. [157] and high quality of graphene sheets were obtained.

The existing reduction method of chemical exfoliation is used for large-scale production of graphene sheet. However, the graphene sheet could be attached by some functional groups such as hydroxyl and carboxyl and wall defects, which degrades the physical and chemical properties. Moreover, after thermal or chemical treatment, the functional groups could be partially removed and cause the degradation of conductivity of graphene sheets. Zhang et al. [158] reported an easy and effective method to reduce GO using hot pressing under vacuum at 500, 1000, and 1500 °C for 5 min with 0, 5, 10, 20, 30, 40 MPa uniaxial pressures, respectively. They found out that very less of amount oxygen was observed from the XPS and no D peak was appeared in the Raman spectrum. The graphene sheets synthesized showed significant higher electron mobility (1000 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) than other reduction of GO.

Recently, a new method called photo-irradiating related process has been used for GO reduction. The methods are UVinduced photocatalytic reduction [159,160], photo-thermal reduction using a pulsed Xenon flash [161], selective reduction by direct laser writing [162] and laser converted graphene from GO [163]. The main advantage of photo-irradiating process is no chemicals and high temperatures have been used. Pulsed laser irradiation was demonstrated by Huang et al. [164] to reduce GO with removal most of the oxygen functional groups (Fig. 6). The reduced GO produced by this method showed a good electrical conductivity. Pulsed laser irradiation is simple, fast, consumes very less energy and environmentally friendly compared to conventional chemical and thermal reduction methods. Besides, another technique is called femtosecond laser which used for the reduction of GO in aqueous solution without any reducing agents [165]. The femtosecond laser has shorter laser pulse duration than the electron cooling time and transfers minimum heat into the target materials [166]. There are several researchers used different techniques such as continuous wave diode laser [162], pulsed laser excitation [167] and picosecond pulsed laser



**Fig. 6.** Illustration of the experimental setup of pulsed laser reduction system. The inset is optical images of GO solution (15 mL, 0.1 mg mL<sup>-1</sup>) before (a) and after (b) after pulsed laser irradiation. (Reproduced with permission from [164].)

irradiation [168] to reduce GO. These methods appeared to be a promising procedure for large-scale synthesis of graphene and open a new method to produce graphene composites for wide range of applications.

# 3. Characterization of carbon nanotubes and single-layer graphene

The characterizations of CNTs such as Raman spectroscopy, TEM, SEM, thermogravimetric analysis (TGA), X-ray diffraction (XRD) are reviewed. For single-layer graphene, all past and latest characterizations techniques such as ultraviolet–visible (UV–Vis) spectroscopy, XRD, TEM, atomic force microscopy (AFM) and Raman spectroscopy have also been reviewed in detail.

# 3.1. Characterization of CNTs

# 3.1.1. Raman spectroscopy

This technique provides some information of CNTs such as the presence of SWCNTs and the degree of graphitization of sample. Raman spectroscopy is a quick and non-destructive technique to analyze carbon sample. RBM are the peaks found at low wave number,  $<350 \text{ cm}^{-1}$  [169]. These modes created by the symmetrical expansion and contraction of the tubes around the tubes axis by the carbon atoms moving radially, and they are unique to CNTs. The presence of SWCNTs in the sample is confirmed by the appearance of RBM peaks. However, RBM peaks are not appeared in the Raman spectra of MWCNTs due to the very low intensity of RBM peaks. The low intensity is because of the peaks are broadened by the interactions between the carbon layers [169]. The frequency of a RBM is inversely proportional to the diameter of the tube. It has been found empirically that the diameter of tube  $(d_t)$  can related to the frequency  $(\omega)$  of the RBM by [169,170]

$$d_t (\text{nm}) = \frac{248}{\omega_{\text{RBM}} (\text{cm}^{-1})}$$

~ . .

The most intense peak in the spectra of CNTs is the G band that can be found around 1590  $\text{cm}^{-1}$  [170]. The G band is a feature of all sp<sup>2</sup> bonded carbon materials [169]. While the G band is associated with high order in sp<sup>2</sup> bonded carbon materials, the D band is related with disorder [171]. The D band is different from the RBM and the G band because it is a defect-mediated mode [169,171]. The D band appears around  $1350 \text{ cm}^{-1}$  and is similar with the Raman band found in the spectrum of diamond [14]. Therefore the D band has been attributed to  $\operatorname{sp}^3$  bonding defects in the nanotubes. A common way to measure the quality of a CNT samples is the ratio of the intensity of the D band to the G band,  $I_D/$  $I_G$  [172,173]. Pure, defect free SWCNTs have low  $I_D/I_G$  ratio. In other words, carbon atoms are sp<sup>2</sup> bonded with few defects. Large quantities of impurities or defects in the nanotubes in the sample were indicated by a high I<sub>D</sub>/I<sub>G</sub> ratio. A typical Raman spectrum is shown as below Fig. 7 [174].

#### 3.1.2. Thermogravimetric analysis (TGA)

TGA is an analytical technique used to determine thermal stability of a material and its fraction of volatile components by monitoring the change in weight that occurs as a specimen is heated [175]. The measurement is normally conducted in air or in an inert atmosphere, such as Helium or Argon, and the weight is recorded as a function of increasing temperature. Sometimes, the measurement is performed in a lean oxygen atmosphere ((1 to 5)%  $O_2$  in  $N_2$  or He) to slow down oxidation [176]. In the case of CNTs, the weight change in an air atmosphere is typically a superposition of the weight loss due to oxidation of carbon into gaseous carbon dioxide and the weight gain due to oxidation of residual metal



**Fig. 7.** (a) Raman spectrum for SWCNTs samples and (b) low frequency region of the Raman spectrum. (Reproduced with permission from [174].)

catalyst into solid oxides [177–179]. TGA can be used to determine the percentage yield of the carbon deposit. Liu et al. [179] demonstrated that weight loss due to the oxidation of carbon occurred at temperature range of 400–680 °C. The carbon content of the catalyst was calculated as  $100 \times (m1 - m2)/m1$ , where m1 and m2 are the weights of the sample before and after the carbon oxidation, respectively. The calculated carbon content was 19%. The content of amorphous carbon was approximately 0.19%, a very low value as shown by the small bump appearing at 325 °C (Fig. 8). The sample contained 0.25% moisture.



Fig. 8. Thermal analysis of carbon samples. (Reproduced with permission from [179].)



Fig. 9. A SEM image showing vertical aligned CNTs. (Reproduced with permission from [182].)



**Fig. 10.** High-magnified TEM images of CNTs grown on unreduced catalyst. (Reproduced with permission from [184].)



**Fig. 11.** XRD patterns of Co-La-O catalyst before reaction (a) and after CNT synthesis at different temperatures for 5 min at (b) 615 °C, (c) 645 °C, (d) 675 °C and (e) 705 °C. ( $\blacktriangle$ ) LaCoO<sub>3</sub>; ( $\bigtriangleup$ ) Co<sub>3</sub>O<sub>4</sub>; ( $\bigcirc$ ) C; ( $\blacktriangledown$ ) La<sub>2</sub>O<sub>3</sub>; ( $\bigcirc$ ) Co. (Reproduced with permission from [164].)



**Fig. 12.** UV-visible spectra of GO/unfractionated heparin (UFH) and graphene/UFH solution in water. (Reproduced with permission from [187].)

# 3.1.3. SEM

SEM is a characterization tool to examine the topography, morphology, composition and crystallographic information of materials [180,181]. Electron beam is used to scan samples in a SEM. When the electron beam is moved across the surface of the



Fig. 13. XRD patterns of pristine graphite, GO and graphene. (Reproduced with permission from [189].)

sample, the charge will be accumulated on it that would affect the imaging if the sample is not conducting. Fig. 9 shows an example of SEM image [182].



**Fig. 14.** Height (a),(c) and corresponding phase (b),(d) tapping-mode AFM images of unreduced (a),(b) and chemically reduced (c),(d) GO nanosheets deposited from aqueous dispersions onto freshly cleaved highly oriented pyrolytic graphite (HOPG). The images were recorded in the attractive regime of tip sample interaction. Superimposed onto each image is a line profile taken along the marked red line. (Reproduced with permission from [191].)



**Fig. 15.** (a) HRTEM image for single-layer graphene. (b) HRTEM image for bilayer graphene. (c) Electron diffraction pattern of graphene sheet in (a). (d), (e) Electron diffraction patterns taken from the positions of the black (d) and white (e) spots, respectively of the graphene sheet shown in (b) using the same label in (c). (Reproduced with permission from [89].)

# 3.1.4. TEM

In TEM, a beam of electrons is transmitted through the sample and an image is formed onto a phosphor screen so that the image can be seen which is different with SEM [183]. As the electron pass through the sample, internal structure of CNTs can be observed to differentiate between SWCNT and MWCNT. The diameter of CNTs can be measured from the TEM images. Energy dispersive X-ray (EDX) spectra can be also collected to provide information about the element exists in the samples. An example of TEM image is shown in Fig. 10 [184].

# 3.1.5. X-ray diffraction (XRD)

When X-rays interact with a crystalline substance (phase), a diffraction pattern is created. The XRD pattern of a pure substance can be described as a fingerprint of the substance because the same substance always gives the same pattern. In a mixture of substances, each gives its pattern independently of the others. The graphite peak could be observed at 26.1° due to the formation of CNTs. As can be seen in Fig. 11, the intensity of graphite peak becomes stronger with the increase of reaction temperature [185]. It is because the amount and quality of CNTs were increased at higher reaction temperatures. Therefore, this method is ideally suited for characterization and identification of polycrystalline phases.

# 3.2. Characterization of single-layer graphene

#### 3.2.1. UV-visible spectroscopy

The pristine graphene and single-layer graphene oxide (GO) shows absorption at 262 nm and 230 nm respectively in the UV-visible spectrum. This is due to the  $\pi$ - $\pi$ \* transitions of aromatic C-C bonds. Fig. 12 shows that the graphene have less transparency than GO which is attributed to the recovery of sp<sup>2</sup> carbons to restore electronic conjugation in reduced graphene

after reduction [186,187]. Moreover, the transmittance of monolayer graphene is 97.1% at a wavelength of 550 nm which is higher than stacked graphene as reported by Sun et al. [188]. With the increased of graphene layer, the transmittance of graphene decreased from 94.3% of bilayer graphene to 83% of six-layer graphene at the same wavelength [188]. Thus, the number of graphene layer can be determined using UV-visible spectroscopy.

#### 3.2.2. XRD

XRD can be one of the tools but not perfect for the determination of single-layer graphene. Pristine graphite shows a basal reflection (0 0 2) peak at  $2\theta = 26.6^{\circ}$  in the XRD pattern. After pristine graphite was oxidized, the (0 0 2) peak shift to a lower angle at  $2\theta = 13.9^{\circ}$  which is due to the existence of oxygen functionalized group and water molecules in between the layer of graphite. After GO was thermal exfoliated completely, there was no apparent diffraction peak detected which means the GO structure was removed and graphene nanosheets were formed (Fig. 13) [189].

#### 3.2.3. AFM

Single-layer graphene can be determined successfully using AFM. The thickness of single-layer graphene is in a range 0.34–1.2 nm [92,189,190]. However, this technique has troublesome to scan bulk graphene because of large area. In addition, AFM imaging provides topography images only, which unable to distinguish number of layer for GO. However, a pristine graphene and GO can be distinguished based on the different thickness using AFM imaging. This can be explained by the interaction forces between the AFM tip and the functional group. Paredes et al. [191] demonstrated the chemically reduced and unreduced GO nanosheets can be distinguished using attractive regime of tapping-mode AFM. They observed that the thickness of chemically reduced GO was 0.6 nm while thickness for unreduced GO

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**Fig. 16.** The Raman spectra of monolayer, bilayer, tri-layer, and four-layer graphene on quartz (a) and SiO<sub>2</sub> (300 nm)/Si substrate (b). The enlarged 2D-band regions with the curve fit are shown in panels (c) and (d). (Reproduced with permission from [200].)

was 1.0 nm. These differences are attributed to the hydrophilicity arising from distinct oxygen functional group on the unreduced GO as shown in Fig. 14. Besides thickness and imaging characterization, different AFM modes can be used to study the mechanical [192], frictional, electrical, magnetic and elastic properties of graphene nanosheets.

#### 3.2.4. TEM

The thickness of graphene can be determined accurately by TEM analysis as reported by Hernandez et al. by observing a large number of TEM images to generate a series of thickness statistics [89]. Single-layer graphene can be observed as transparent sheets by TEM analysis. When graphene sheets were fold back, crosssectional can be viewed and the number of layers can be measured using HRTEM at several locations [119]. Monolayer and bilayer folded graphene can be observed as one and two dark lines, respectively when the folded graphene sheet are placed parallel to the electron beam [193]. A more accurate identification way of number of graphene layer can be determined by nanoarea electron diffraction patterns by changing incidence angles between the electron beam and the graphene sheet [89,194]. Fig. 15 shows the HRTEM images of single and bilayer graphene and their corresponding electron diffraction patterns. Hernandez et al. explained that the main difference between single and bilayers of graphene is the {2110} spots seem to be brighter to the {1 1 0 0} spots as shown in bilayers graphene electron diffraction pattern in Fig. 15 (e).

#### 3.2.5. *Raman spectroscopy*

Carbon allotropes possess their identity at D, G, and 2D peaks around 1350, 1580 and 2700 cm<sup>-1</sup> respectively under Raman spectroscopy investigation. Therefore, the quality and number of graphene layers can be investigated using Raman spectroscopy. Graphene produced using chemical reduction showed a higher amount of defects on the graphene structure compared to the graphene prepared by CVD and other synthesis method which exhibited very less defects [83,89,119,188,195-197]. The G-band corresponds to the tangential stretching  $(E_{2g})$  mode of highly oriented pyrolytic graphite (HOPG), while the D-band originates from disorder in the sp<sup>2</sup>-hybridized carbon atoms, characteristic for lattice distortions in the curved graphene sheets and/or tube ends whereas the 2D band is at almost double the frequency of the D band and originates from second order Raman scattering process [198–200]. Fig. 16 shows the comparison of Raman spectra between monolayer, bilayers, three layers and four layers graphene on quartz and SiO<sub>2</sub>/Si substrate [200]. For graphene, there is no D band appears in the Raman spectra which confirms no defects is detected. The most important band that needs to study is the shape and intensity of 2D band of graphene and graphite. A single sharp peak can be observed for 2D band of monolayer graphene whereas two peaks appear in graphite for this band [201]. In addition, monolayer graphene shows lower intensity of G band compared to bi-, tri or multi-layer graphene. In other words, the number of graphene layers increases proportionally with an increase in G band intensity as shown in Fig. 16 [200]. In Fig. 16, it can be observed that bilayer graphene possess a much wider and up-shifted 2D band compared to monolayer graphene. Ferrari et al. have demonstrated successfully that Raman spectroscopy can clearly differentiate between a single layer, bilayer, and several layers (<5 layers) [201]. Therefore, many researchers have used Raman spectroscopy as a non-destructive tool to investigate quality and number of graphene layers.

The ratio of peak intensities  $I_D/I_G$  can be used to investigate the level of disorder in graphene [202–205]. When the disorder in graphene increases,  $I_D/I_G$  shows two different regimes: low defect density and high defect density. In low defect density regime,  $I_D/I_G$ will increase when higher defect density occurs and creates more elastic scattering. However,  $I_D/I_G$  will start to decrease when defect density increases which attributed to more amorphous carbon structure in high defect density regime [206]. These two regimes are called as nanocrystalline graphite and mainly sp<sup>2</sup> amorphous carbon phases, respectively [206–210]. An empirical equation called as the Tuinstra-Koenign [205] was proposed to calculate the crystalline domain size,  $L_D$  for low defect density regime,

$$\frac{I_D}{I_G} = \frac{C_\lambda}{L_D}$$

where  $C\lambda = (2.4 \times 10^{-10} \text{ nm}^{-3}) \times \lambda^4$  [210]. In the high-defectdensity regime, the relation between  $I_D/I_G$  and  $L_D$  can be written as below equation [197,200,211]:

$$\frac{I_D}{I_G} = D(\lambda) \times L_D^2$$

where the constant  $D(\lambda)$  is obtained by imposing continuity between the two regimes.

# 4. Conclusion

In this review, the past and recent developments in the synthesis and characterization of graphene and CNTs have been studied. Though the 1st synthesis of CNTs was started in 1991, the production is still continued with some new methods in catalyst preparation such as metal-free catalyst and new carbon sources such as tyre, heavy oil residue and bamboo charcoals have been reported. It is important to emphasize that the techniques of synthesis still have some room to be more efficient and cost effective. In spite of the enormous advances that have been made in the synthesis, the explanation of growth mechanism of CNTs is still remaining a fair amount of controversy. The reason is there are several possible methods to synthesize CNTs and the fact that there is no single universal CNT growth mechanism. The development of synthesis routes for the large-scale mass production of CNTs is highly desirable due to their excellent electronic and mechanical properties which make their application are almost endless. From biosensor, hydrogen storage, battery, nano electronic devices and composites materials, CNTs could revolutionize the science and engineering of the world.

The invention of graphene sheets has attracted much more researchers' attention because of their very large 2-D electrical conductivity, large surface area, low cost production and do not contain metallic impurities as CNTs do. The number of publications for synthesis of CNTs decreases while the number of publications for synthesis of graphene increases dramatically according to ISI Web of Knowledge<sup>SM</sup>. Graphene has been proven is a biocompati-

ble nanomaterial [55] while the presence of metallic impurities within CNTs causes the toxicological effects [56]. In other words, graphene is a non-toxic material for wide application in biosensor. Graphene can be produced from graphite, which is much cheaper than the cost of CNT production from carbon sources such as methane. Moreover, graphene can give larger surface area than SWCNTs for better electroactive and higher density site for immobilization and hybridization of biomolecules. The mass production of multi-layer graphene is easy; however, for singlelayer graphene is a great challenge that, if can be solved, could bring huge benefit to all mankind.

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