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# Microwave irradiation synthesis of carbon nanotubes: Advances, purification techniques, and scalability prospects

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ABSTRACT

Carbon nanotubes (CNTs) has been a subject of extensive research and development due to their exceptional properties. This article provides an overview of CNT production techniques, focusing on conventional methods such as arc discharge and chemical vapor deposition (CVD), as well as the emerging alternative, microwave (MW) irradiation technique. The MW irradiation technique offers a promising alternative with potential advantages in terms of energy efficiency and economical aspect. The article also discusses various purification techniques, mainly categorised into chemical and physical purification, underlining their advantages and challenges. Scalability of these production methods are also extensively discussed to explore the potential for scaling up MW irradiation technique, suggesting new alternative for achieving cost-effective and high-quality CNT production on an industrial scale. This review aims to provide insights into the current state of CNT production advancement and identify future opportunity for research and development in this field.

## 1. INTRODUCTION

Discovered by Iijima in 1991, carbon nanotube (CNT) is a carbon allotrope derived from graphite sheets, featuring a hexagonal lattice structure of carbon atoms with $sp^2$-hybridised arrangement, as in Fig. 1, that forms either single-walled (SWCNT) or multi-walled (MWCNT) nanotubes (Polizu et al., 2006; Rathinavel et al., 2021). SWCNTs typically measure 1-2 nm in diameter, while MWCNTs can reach up to 100 nm (Liu et al., 2011; Mubarak et al., 2011; Rathinavel et al., 2021). Both are represented in Fig. 2.

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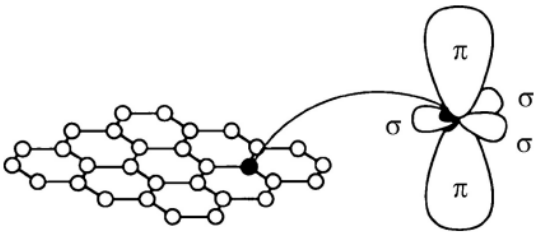


Fig. 1. The carbon atomic in $sp^2$-hybridised arrangement

Source: Jorio et al. (2011)

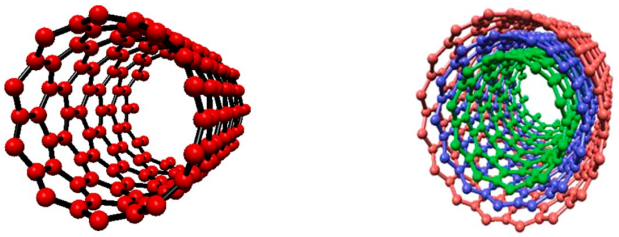

Fig. 2. (left) 3D representation of SWCNT; (right) 3D representation of MWCNT

Source: Rathinavel et al. (2021)

CNTs exhibit exceptional mechanical, electrical, thermal, and optical properties, making them highly valuable in various fields such as materials science, electronics, and nanotechnology. Their unique structure and properties have gained attention in research and technological advancement since their discovery. Currently, arc discharge and chemical vapor deposition (CVD) is the most applied methods in producing CNTs at large scale (Baghel et al., 2022). Many literatures have studied the growth of CNTs using these techniques as reviewed by Rathinavel et al. (2021) and Arora & Sharma (2014). However, more synthesis methods are being explored to find more economical routes to produce CNTs on large scale and one of the promising ones is the microwave (MW) irradiation technique. This method utilises the ability of carbon to absorb and convert microwave energy into thermal energy and act as heating material (Kure et al., 2017). Despite its significant potential, there is still a lack of comprehensive review on this method, especially on the aspect of large-scale production. Hence, this study will review the synthesis of CNT using MW irradiation technique compared with other established conventional routes followed by the most effective purification methods and the scalability of the technique.

## 2. SYNTHESIS OF CARBON NANOTUBES

The synthesis of CNTs has become a popular area of research as various methods have been developed and studied for large scale production to satisfy the growing industrial demands. Different methods such as arc discharge, CVD and MW irradiation offer their own advantages and challenges in terms of operating condition, cost, scalability, and quality of the produced CNTs.

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### 2.1 Arc discharge method

The arc discharge method stands as the pioneering technique for the synthesis of CNTs. The first discovery of carbon nanotubes by Iijima was made using the arc discharge method. He observed the carbon soot produced by the arc discharge between two graphite electrodes and found that the soot contained multi-walled carbon nanotubes (MWCNTs), which were composed of concentric graphene tubes with a helical atomic arrangement as shown in Fig. 3 (Iijima, 1991). Since that discovery, this method has been extensively studied, understanding its mechanisms, optimisation of parameters, as-produced CNT's structural characteristics, and potential industrial applications. In this method, a high-current electric arc is generated between two graphite electrodes within a controlled environment. These electrodes are aligned parallel to each other, usually with a small gap between them. The carbon in the anode vaporises or sublimes and the carbonaceous compounds deposit within the chamber, whether on electrodes or at the wall, yielding soot containing CNTs. This method is able to produce both SWCNTs and MWCNTs by varying the catalyst usage (Ando & Zhao, 2006). The yield and quality of CNTs produced by this method are heavily influenced by parameters such as type of environment, type of catalyst, and electrode geometry (Arora & Sharma, 2014).

The setup involves a chamber housing two types of electrodes which are anode (usually graphite), filled with a powdered carbon precursor and catalyst usually iron or nickel as base (Zhou et al., 2024; Arora & Sharma, 2014), and a cathode that is usually pure graphite. The environment inside the chamber can be varied whether to fill with gas such as nitrogen, argon, helium, air and hydrogen (Sakhapov et al., 2022; Arora & Sharma, 2014) or submerged in a liquid such as deionised water and saline solutions (Hernandez-Tabares et al., 2024; Yousef et al., 2013). The electrodes come into contact upon activating the power supply, that can be direct current (DC), alternating current (AC) or pulsed DC, to initiate an arc with stable and non-fluctuating arcs are crucial for high-quality product synthesis (Singh et al., 2024; Saucedo-Jimenez et al., 2023; Arora & Sharma, 2014). The generated arc current reaches temperatures above 1700 °C (Sakhapov et al., 2022) causing the carbon precursor inside the anode to sublime into carbon vapours (Rathinavel et al., 2021). These vapours then combine in the gas phase and move toward the cathode or wall chamber, cooling and condensate as they travel due to the temperature gradient. After several minutes of arc application, normally about 20 to 100 minutes (Rathinavel et al., 2021), the discharge ends, and a deposit forms on the chamber walls, comprising CNTs and soot. This deposit undergoes further purification to remove impurities like amorphous carbon, fullerene and metallic substances from catalyst (Arora & Sharma, 2014). The simple schematic representation of common set-up for arc discharge method is shown in Fig. 4.

Fig. 3. One of the electron micrograph images of the microtubule structure obtained in the first report of CNT discovery comprising of five graphitic walls with a diameter of 6.7 nm

Source: Iijima (1991)

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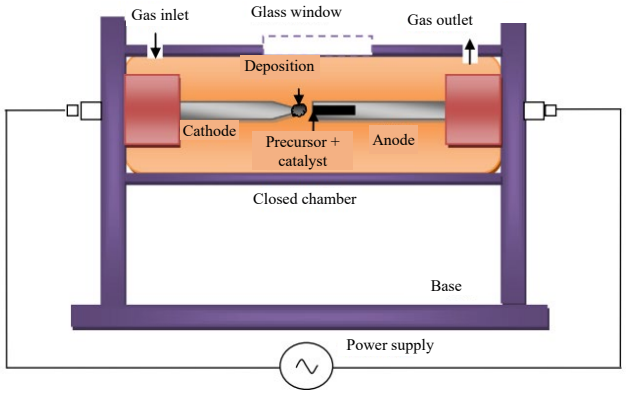


Fig. 4. Schematic diagram of an arc discharge setup

Source: Arora & Sharma (2014)

Sumio Iijima has sparked the interest of many researchers to further evaluate and improve this method. A year after that, Ebbesen & Ajayan (1992) discovered the method to produce CNT in considerably high quantities using a variant of fullerene synthesis using arc-discharge using graphite electrodes under helium gas condition. They varied several parameters such as inert gas, type of current (AC and DC), voltage and electrode size to find the optimal conditions. Later they found the highest yield achieved at pressure of 500 torr with electric supply of 100 A at 18 V DC under helium gas using pure graphite anode (6 mm OD) and cathode (9 mm OD). Jong Lee et al. (2002) later found the new large-scale MWCNTs synthesis method using plasma rotating arc discharge that promotes homogeneity of electric field distribution. The experiment was done at 500 torr of pressure under helium gas atmosphere with 80–120 A electrical current at 20–30 V using pure graphite electrodes with optimum rotating speed of 10,000 rpm to obtain 80% yield of MWCNTs after purification that was done by heating in atmosphere at 700 °C. Roch et al. (2007) has reported the production of high quality SWCNTs based on pulse arc-discharge technique resulting from 100 A of current and 50 V of voltage with the utilization of Ni-Co combination as catalyst and argon as the inert atmosphere. Table 1 summarises production of both SWCNTs and MWCNTs via arc discharge method from various researchers based on the product specification and operating conditions.

The arc discharge method, while it is well-known in the synthesis of CNTs, presents several disadvantages that demand consideration in the broader context of nanomaterial production. One significant drawback involves the need for high-energy source, normally more than 50 A and can reach up to 100 A, to produce electrical arc and sublime the carbon precursor. This condition contributes to increased operational costs and can make the method less energy-efficient if the electricity used in the process is derived from non-renewable sources. In addition, this method also requires high growth temperature in order to sublime the carbon and synthesise CNTs with good crystallinity. To promote CNTs with that structure plus good conductivity and mechanical strength, the growth temperature can reach up to 2000 K (Liu et al., 2019). This condition poses safety challenges during handling the equipment and contribute to wear and tear on the equipment during the process. Furthermore, this method commonly demands the use of inert gas as the atmosphere inside the chamber. The inert gas is used to remove free oxygen and avoid the reaction with carbonaceous species produced to end up as carbon dioxide especially at the high temperature condition (Liu et al., 2019). Inert gases can be more expensive than ambient air, contributing to the overall cost of the synthesis process. Besides that, the batch nature of this technique limits its efficiency for large-scale production, hindering its viability for widespread commercial use. These disadvantages underscore the need for continued research and development on alternative synthesis routes to overcome these inherent limitations for practical and efficient CNT production.

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Table 1. Review of CNT synthesis using the arc-discharge technique

| CNT Type | Diameter (nm) | Cathode/ Anode | Inert Gas | Voltage/ Current | Remarks | Ref. |
|---|---|---|---|---|---|---|
| MWCNT | 5–20 | Graphite/Graphite | Argon | - | The first discovery of CNTs. | (Iijima, 1991) |
| SWCNT | ~ 1.4 | Graphite/ Graphite–Ni–Y | Helium | 30 V 100 A (DC) | Several grams of CNTs in high crystalline bundle are produced. | (Journet et al., 1997) |
| SWCNT | 1.3–1.8 | Graphite/ Graphite–NiO–$Y_2O_3$ | Helium | 90–120 A (DC) | 45–50% yield of as-prepared SWCNTs soot with 45– 60 at% purity. | (Lv et al., 2005) |
| SWCNT | 1.06–1.66 | Graphite/ Graphite–Ni–Co | Argon | 50 V 100 A (DC) | 60 wt% SWCNT from 40 wt% SWCNT in soot after acidic purification treatment using short arc pulses. | (Roch et al., 2007) |
| MWCNT | ~ 10 | Graphite/Graphite | Hydrogen-helium | 60 A (DC) | 900 mg of as-prepared soot with 97 at% purity after purification treatment using H2O2 mixture of sulphuric acid and nitric acid, centrifugation and filtration. | (Suzuki et al., 2006) |
| SWCNT | 10–30 (bundles) | Graphite/ Graphite–Fe–W | Hydrogen–argon | 80 A (DC) | 35% yield of purified SWCNTs from as-prepared after two-step purification process of heat and acidic treatment. | (Fang et al., 2013) |
| MWCNT | 5–13 | Graphite/Graphite | Deionised water | 238 V 75 A (AC) | A yield of 0.6 g/h of as-prepared MWCNT soot with 60% purity while submerged in liquid and using AC power supply. | (Yousef et al., 2013) |
| DWCNT | 1.52–2.33 | Graphite/Graphite–Ni–Fe–Co–S | Hydrogen | 150 A (DC) | Pulsed electric arc discharge with spinning anode was utilised to yield DWCNT with 32% purity. | (Saucedo-Jimenez et al., 2023) |
| MWCNT | 12 | Graphite/Graphite–Fe | Nitrogen | - (DC) | Able to produce defect free MWCNT compared to the conventional method when using iron catalyst under 60 kPa nitrogen atmosphere. | (Zhou et al., 2024) |

Source: Authors' illustration and compilation

## 2.2 Chemical vapor deposition (CVD) method

Chemical vapor deposition (CVD) has become the most widely used technique for synthesizing CNT due to its great versatility and control over nanotube characteristics compared to other methods. In context of CNT, CVD method is defined as the deposition of carbon compound on heated surface resulted from thermal dehydrogenation reaction of carbon-rich gases with the presence of metal catalyst such as iron, nickel or cobalt (Mubarak et al., 2014). CVD has plenty of history starting from the mid-twentieth century, where it emerged as a viable technique for synthesizing carbon microfibers utilizing thermal decomposition processes facilitated by metal catalysts (Kumar & Ando, 2014). In 1952, Radushkevich and Lukyanovich pioneered the production of tubular carbon filaments with diameters ranging from 50 to 100 nm (Radushkevich & Lukyanovich, 1952). This breakthrough involved the thermal decomposition of carbon monoxide in the presence of iron catalysts at 600 °C, depositing carbon monoxide onto the iron surface. Subsequent advancements by Davis et al. in 1953 explored deeper into characterizing carbon nanofibers synthesised through the reaction of CO and $Fe_2O_4$ at 450 °C within blast furnace brickworks (Davis et al., 1953). They found that the catalyst for this reaction, which could be either iron or iron carbide, formed as a speck on the surface of iron oxide and initiated the growth of carbon threads. A groundbreaking moment emerged in 1996 by Li et al. (1996) where the CVD method was established in producing CNT catalysed

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by iron nanoparticles embedded in mesoporous silica. Their work brought CVD methodologies into a new era of synthesis of CNTs.

Fig. 5 shows the schematic diagram of CVD setup. The CVD process begins with purging the reaction chamber to remove unwanted gases. Carbon-rich gases like hydrocarbon gases (precursors) are then introduced and heated as they approach the deposition surface. Upon acquiring sufficient energy, these gases react or decompose to form a solid carbon phase (C), which deposits onto the substrate. With the help of catalysts, the decomposing temperature can be reduced. Meanwhile, an exhaust system removes volatile by-products like hydrogen to maintain a clean environment. Without a substrate, the carbon solidifies on the chamber walls. CVD is a controlled method enabling precise carbon deposition through gas reactions or decomposition and that is the reason why this method stands tall compared to others. It normally takes about 5 to 60 minutes of synthesis time (Rathinavel et al., 2021). Catalyst precursors in CVD may exist in various forms (solid, liquid, or gas) and can be positioned inside the reactor or introduced externally.

CVD methods consist of diverse variations dependent on several critical parameters, allowing their categorization into distinct types. All of these variations based on pressure, reactor type, carbon source and heating method were discussed by Sengupta (2018). However, the three most popular techniques based on CVD are HiPCo®, CoMoCAT®, hot filament CVD and plasma-enhanced CVD. The HiPco® method, a shortform for High Pressure Carbon Monoxide method, is unique in which the catalyst is supplied in gas phase into the reaction chamber together with the carbon precursor and inert gas (Rafique & Iqbal, 2011). This method, discovered at Rice University, utilises carbon monoxide (CO) with preheated temperature of 1000 °C and metallocene as catalyst under high pressure (up to 30 atm) to promote fast decomposition of CO molecules into C atoms to form SWNCTs (Nikolaev et al., 1999). While CoMoCAT® was discovered by Resasco et al. (2002) in which they reported a high-selectivity production of SWCNTs via CVD using cobalt and molybdenum (Co–Mo) combination as catalyst support under high pressure (1 to 10 atm) with CO as the carbon source under helium atmosphere at more than 700 °C. Dikonimos et al. (2004) have reported the production of CNTs using hot filament CVD technique with the presence of nickel catalyst on a substrate made of silicon and nickel film with $SiO_2$ coating in between. The reaction took place within a mixture of hydrogen gas and methane that acted as carbon precursor with the hot filament was produced using 1.5 kW of DC current to obtain temperature of 1800 °C. Moreover, plasma-enhanced CVD has been reported by Choi et al. (2000) where CNTs were produced using a mixture of methane gas (carbon precursor) and hydrogen gas (inert gas) at temperature range of 520–700 °C enhanced by microwave plasma. Table 2 highlights the various variety of CVD techniques commonly used in industry.

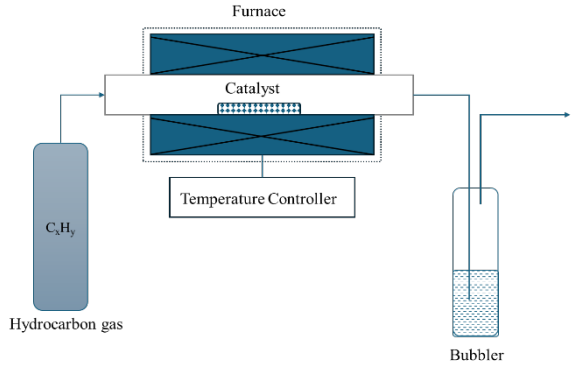


Fig. 5. Schematic diagram of CVD setup

Source: Reproduce from Kumar & Ando (2014)

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Table 2. Review of CNT synthesis using the various CVD techniques

| CNT Type | Diameter (nm) | Carbon Source | Catalyst/ Substrate | Inert Gas | Temperature /Pressure | Remark | Ref. |
|---|---|---|---|---|---|---|---|
| SWCNT | 0.7 | CO | Iron penta-carbonyl | - | 1200 °C 10.133 bar | HiPCo® method. 44% yield of as-prepared CNTs at production rate of 1.24 mg/h. | (Nikolaev et al., 1999) |
| SWCNT | - | CO | Co–Mo | $N_2$ | 700–950 °C 1–10 bar | CoMoCAT® method. Yield 0.25g CNT/g catalyst with selectivity higher than 80% after purification treatment with NaOH, HCl and air oxidation. | (Resasco et al., 2002) |
| MWCNT | 10–35 | $CH_4$ | SiO layer between Si and Ni | $H_2$ | 600 °C 0.005 bar | Hot filament method. Good production of high purity CNTs. | (Dikonimos et al., 2004) |
| MWCNT | 10–50 | $CH_4$ | Ni-coated/ Si | $H_2$ | >600 °C 0.013 bar | Microwave plasma-enhanced CVD method. At higher temperature, the CNTs obtained with higher density and length. | (Choi et al., 2000) |
| MWCNT | 31–36 | $C_2H_2$ | Ferrocene | Ar | 850 °C | Gas source CVD. Yields a batch of CNT with 95% purity | (Mubarak et al., 2011) |
| MWCNT | 30 | $C_2H_2$ | Co | $H_2$, $NH_3$ | 825 °C 0.026 bar | Plasma-enhanced CVD using microwave. The CNT growth rate of 100 nm/s. | (Bower & Zhou, 2000) |
| SWCNT | - | $C_2H_4$ | Fe–$Al_2O_3$ /Si | Ar, $H_2$, steam | 820 °C 1.013 bar | Water-assisted method. The "super growth" method demonstrated remarkable nanotube growth rates, reaching millimetre-thick forests within 10 minutes. | (Noda et al., 2007) |
| MWCNT | ~10–100 | $CH_4$ | Iron nanoparticles/ Corning® | $H_2$ | ~300 °C 0.060 bar | Microwave plasma-enhanced CVD method. Produced diameter controlled CNTs at low temperature. | (Das & Roy, 2020) |
| MWCNT | <10 | $CH_4$ | Ferrocene and thiophene | Ar, $H_2$, steam | < 400 °C | The floating catalyst CVD method. The production rate of as-produced CNT was 1.29 mg/min. | (Park et al., 2020) |
| MWCNT | 14–75 | Toluene | Ferrocene/Quartz | Ar, $H_2$ | 800 °C 1.013 bar | The aerosol-assisted CVD method with the presence of $H_2$ gas. Produced a forest of vertically aligned with a density of $5\times10^9$ CNTs/cm$^2$ and growth rate of 20 µm/min. | (Charon et al., 2021) |

Source: Authors' illustration and compilation

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However, like any manufacturing process, CVD has its drawbacks that can impact the efficiency and scalability of CNT production. One of the primary drawbacks of CVD is the requirement for high operating temperature which typically involves heating the catalyst substrate to temperatures ranging from 700 to 900 °C (Rafique & Iqbal, 2011). Such elevated temperatures not only demand significant energy input but also pose challenges in terms of material compatibility. Moreover, the usage of explosive gases like acetylene, carbon monoxide and hydrogen in the CVD growth of CNTs introduces significant explosion risks. This poses serious safety concerns throughout the CNT growth process due to the inherent combustible nature of these gases, combined with high temperatures involved in the CVD method, creating a hazardous environment. In addition, another challenge with CVD techniques is the use of non-selective heating that leads to the difficulty in controlling the temperature precisely for targeted areas (Liu et al., 2019). This lack of selectivity in heating can bring variations in the growth conditions, affecting the uniformity and quality of the produced CNTs. These drawbacks highlight the importance of ongoing research and innovation to explore alternative synthesis pathways that can address these inherent limitations, paving the way for more practical and efficient CNT production.

### 2.3 Microwave irradiation method

Among various synthesis methods of CNT that have been discovered, one of the promising ones is the microwave (MW) irradiation technique. This method utilises the ability of carbon to absorb and convert microwave energy into thermal energy and act as heating material (Kure et al., 2017). Ferrocene is commonly used as the catalyst due to its ability to act as carbon source and provide iron nanoparticles at the same time after being decomposed by heating substance such as graphite. The rapid localised heating on the heating material induces the decomposition of carbon source and the catalyst (iron nanoparticles) helps in the rearrangement of the carbon atoms into CNTs (Vivas-Castro et al., 2011). This method is pioneered by Hong et al. (2002) where they reported the production of well-graphitised MWCNTs using direct microwave irradiation on cobalt-loaded carbon black with acetylene gas as catalyst. Subsequent discovery was made by Kharissova (2004) that has reported the use of ferrocene as a solid carbon source and catalyst using microwave oven in synthesizing vertically aligned MWCNTs within 30 minutes. Many studies have been made since the discovery of this innovative method that suggest MW irradiation technique possesses high potential in manufacturing CNTs since this method can resolve all the problems mentioned regarding the conventional methods (Baghel et al., 2022; Druzhinina et al., 2009; Liu et al., 2019).

The synthesis setup for this method typically consists of a domestic or laboratory microwave where CNT growth will take place as shown in Fig. 6. A carbon precursor, usually ferrocene that acts as both carbon source and catalyst, is placed within the vial or quartz tube together with microwave absorber such as graphite before being applied with microwave irradiation. Microwaves used normally set the power ranging from 800 W to 1000 W (Algadri et al., 2017; Nie et al., 2013; Vivas-Castro et al., 2011). The carbon-containing material like graphite within the chamber absorbs the microwave energy, before being converted into thermal energy. Unlike conventional methods (arc discharge and CVD) that rely on external heating sources, the microwave method induces internal heating directly within the precursor material. This internal heating leads to the rapid and localised elevation of temperature, creating conditions suitable for the growth of carbon nanotubes (Liu et al., 2019). The elevated temperature triggers the chemical reactions necessary for the nucleation and growth of CNTs after decomposition of ferrocene. Carbon atoms or carbon-containing molecules are deposited onto catalyst particles, initiating the formation of nanotube structures. Most of the time, MWCNTs are produced rather than SWCNTs. One of the notable advantages of the microwave method is its ability to achieve high growth rates in a short period. This rapid growth is attributed to the efficient and localised heating generated by microwave radiation. After the desired growth duration, the CNTs are typically collected from the reaction chamber for further processing and analysis.

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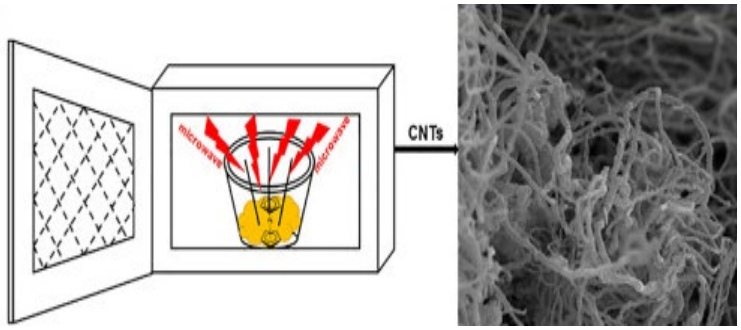


Fig. 6. Diagram of setup for microwave irradiation technique

Source: (Liu et al., 2019)

Zhan et al. (2017) studied ultrafast growth of well-graphitised sheets of the as-grown MWCNTs using microwave irradiation technique. They carried out the process using ferrocene as carbon source and catalyst with various metal wires i.e. copper, molybdenum, iron, steel as heating material placed inside quartz crucibles in domestic microwave of 800 W within 20 s to 40 s of reaction time under normal atmospheric conditions to various dimension of nanotubes with diameter ranging from 10–160 nm. The Thermogravimetric analysis (TGA) result showed that the as-produced MWCNTs consists of 70% CNTs, 10% amorphous carbon and the rest were metal particles. The quality of the CNTs produced was proven based on the intensity ratio of the D-band compared to the G-band ($I_D/I_G$) studied using Raman spectrometer where D-band represents the defects of CNT while G-band reflects the graphitic structures of CNT. They found that CNTs produced using this method achieved a ratio of 0.49 which suggests that the products are high quality and crystallinity. Algadri et al. (2017) also reported the production of MWCNTs in domestic microwave with 800 W of power using graphite/ferrocene mixture with various ratio whereas graphite acted as heating material in 30 seconds under ambient conditions. The as-prepared CNTs using graphite/ferrocene mixture ratio of 70:30 was found to have the best quality with an average diameter of 44–79 nm with low $I_D/I_G$ ratio of 0.62 with absorbance of almost 2.5 a.u. using UV–vis absorption spectra at wavelength of 250–260 nm, indicating the highest yield. Asnawi et al. (2018) utilised dried waste rice husk powder to produce CNTs by mixing with ferrocene and treated with microwave irradiation at 600 W and 2.45 GHz frequency inside the household microwave oven. The quartz tube was used as the container for the mixture and the pressure inside the tube was set to be at $1.3 \times 10°$ mbar. Reaction time of 38 minutes was employed with the rice husk acted as the main carbon precursor originated from cellulose and lignin cells to synthesise CNTs with $I_D/I_G$ ratio of 1.013, lower than previous reports. However, the as-produced CNTs contained high purity of CNTs which was 85 wt% with 10% of amorphous carbon and the rest were iron particles based on the TGA result showing that this method successfully produced high yield of CNTs. Table 3 summarises the recent development of CNT production using microwave technique.

The microwave irradiation technique for carbon nanotube (CNT) synthesis offers several advantages, making it stands out compared to other conventional methods. Firstly, one of the notable advantages lies in the rapid growth of CNT achieved through microwave irradiation. Unlike traditional methods that may take extended periods, the microwave technique enables the synthesis of CNTs within a remarkably short duration, often within a matter of seconds (Algadri et al., 2017; Nie et al., 2013; Zhan et al., 2017). Another significant advantage is the ability of this technique to operate under the ambient conditions. The process can be conducted at room temperature and atmospheric pressure, eliminating the need for high temperature furnaces or specialised environments (Nie et al., 2013; Zhan et al., 2017). Furthermore, the elimination of the need for explosive carbon sources is one of its advantages. Unlike some conventional methods that rely on explosive gas for carbon source, the microwave technique operates under ambient conditions and utilises

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solid carbon source (Liu et al., 2019). Although this technique presents several advantages for CNT synthesis, it is essential to acknowledge the drawback associated with this method. One notable concern is the encapsulation of iron particles within the CNT structure during the growth process. However, this issue can be overcome by going through the purification treatment that will be detailed in the next section. After all, this method stands as a promising and accessible approach in the advancement of CNT production.

Table 3. Review of CNT synthesis using the microwave irradiation technique

| CNT Type | Diameter (nm) | Carbon Source/ Catalyst | Heating material | Microwave Type/ Power | Pressure (torr) | Remarks | Ref. |
|---|---|---|---|---|---|---|---|
| MWCNT | 20 | Ferrocene | Carbon fibre | Domestic 1000 W | 760 | Placed inside vial. Almost all of the ferrocene was converted to CNTs with the highest yield for CNTs was 40%. $I_D/I_G$ ratio of 1.1. CNTs are encapsulated with iron particles. 20 seconds of synthesis time. | (Nie et al., 2013) |
| MWCNT | 40–60 | Graphite/Iron acetate | Graphite | Domestic 1000 W | $10^{-4}$ | Placed inside quartz ampoule. CNTs are encapsulated or attached with iron at the tip-end. 3 minutes of synthesis time. | (Vivas-Castro et al., 2011) |
| MWCNT | 30–40 | Ferrocene | Copper wire | Domestic 800 W | 760 | 70 wt% purity of treated CNTs. Placed inside quartz crucibles. $I_D/I_G$ ratio of 0.49. Purification treatment with removing the metal with tweezers and with acid. 20 to 40 seconds of synthesis time. | (Zhan et al., 2017) |
| MWCNT | 44–79 | Ferrocene | Graphite | Domestic 800 W | 760 | Placed inside porcelain boat. $I_D/I_G$ ratio of 0.62. CNTs are encapsulated with iron particles. 30 seconds of synthesis time. | (Algadri et al., 2017) |
| MWCNT & SWCNT | - | Dried rice husk/ Ferrocene | Drief rice husk | 600 W | 1 | Placed inside quartz tube. $I_D/I_G$ ratio of 1.013. Long synthesis time (38 minutes). 85 wt% purity of as-produced CNTs. | (Asnawi et al., 2018) |
| MWCNT | 22–48 | Biochar/ Ferrocene | Biochar | CEM Discover microwave reactor. 200 W | 880 | Placed inside glass vial. Superior CNTs quality produced using wheat straw and hazelnut hull pyrolysed at 600 °C. $I_D/I_G$ ratio of 0.8 and 0.71 for both. Synthesised CNTs have encapsulated iron particles along their entire length. 5 minutes of synthesis time. | (Hidalgo et al., 2023) |

Source: Authors' illustration and compilation

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## 2.4 Comparative analysis

The synthesis of CNT involves various methods, each with its own advantages and drawbacks. CVD and arc-discharge are the most common conventional methods used in this industry. However, due to their disadvantages that limit the evolution of CNT production, the search for new conventional methods is on-going with microwave irradiation technique emerging as a new potential candidate. Based on the previous discussion, a comparative analysis of these methods is presented based on several critical parameters including synthesis time, operational conditions and scalability as shown in Table 4.

Table 4. Comparative analysis of carbon nanotube synthesis methods

| Parameter | Arc Discharge | CVD | Microwave Irradiation |
|---|---|---|---|
| Synthesis time | Within several minutes to hours | Within several minutes to hours | Within several seconds to minutes |
| Operating condition | High-energy usage, high temperature, inert gases | High temperature, explosive gases | Ambient temperature, ambient or inert gas atmosphere |
| Impurities | Fullerene, amorphous carbons, catalyst (for MWCNTs) | Amorphous carbons, catalyst | Amorphous carbons, catalyst |
| Catalyst encapsulation | Susceptible to encapsulation (for MWCNTs) | Susceptible to encapsulation | Susceptible to encapsulation |
| Scalability | Batch process, limited scalability | Batch or continuous, high scalability | High scalability |

Source: Authors' illustration and compilation

Synthesis time of CNT formation is one of the key factors in large-scale production. Arc-discharge method and CVD typically require longer duration for CNT growth ranging from several minutes to hours (Rathinavel et al., 2021; Arora & Sharma, 2014). Comparatively, MW irradiation technique offers significantly faster growth rates with the ability to produce CNTs within seconds (Algadri et al., 2017; Zhan et al., 2017). The rapid growth achieved by this technique makes it particularly appealing for large-scale applications that require fast and efficient CNT synthesis. Moreover, the operating conditions during CNT synthesis is also crucial especially in highlighting the practicality and safety of that method. Both arc-discharge and CVD methods demands high-energy usage due to the requirement of high-current electricity (for arc discharge) and high growth temperature. Arc discharge method commonly demand the electricity with the current exceeding 50 A and reaching up to 100 A coupled with long operation time, contributing to increased operational costs and energy inefficiency (Arora & Sharma, 2014). While CVD requires high operating temperatures, typically between 700 and 900 °C, which still demand significant energy input (Rafique & Iqbal, 2011). High growth temperatures pose safety challenges and contribute to equipment wear and tear.

In addition, safety concerns are heightened in both methods due to the use of explosive gases and high temperatures, creating a hazardous environment (Liu et al., 2019). CVD methods involve explosive gases like acetylene, carbon monoxide, and hydrogen, posing significant safety concerns. In contrast, MW irradiation technique can be conducted under relatively milder conditions, eliminating the need for high-temperature furnaces and explosive gases, simplifying the operational setup and reducing costs (Liu et al., 2019). Furthermore, the encapsulation of catalyst nanoparticles within the CNT structures that compromise the quality and purity of the products also emerges as one of the challenges in producing CNT. MW irradiation technique, while offering rapid growth, is susceptible to this issue (Liu et al., 2019; Zhan et al., 2017). Catalyst particles, such as iron, can become encapsulated along the length of the CNTs during the growth process. On the other hand, the arc discharge and CVD methods also face challenges related to catalyst encapsulation (Suzuki et al., 2006; Vivas-Castro et al., 2011). However, purification treatments are typically employed to overcome this issue and will be explained in the next subchapter.

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Lastly, efficiency and scalability are among the fundamental criteria in evaluating the synthesis method. The arc discharge method, being batch-oriented, poses challenges for scalability while limiting its efficiency for industrial production. CVD method has already been used as the synthesis method for large-scale production of CNT (Rathinavel et al., 2021). However, the non-selective heating may lead to variations in growth conditions, affecting uniformity and significant amount of heat are wasted (Liu et al., 2019). MW irradiation technique, with its rapid growth rates and simplicity in synthesis, holds potential for efficient and scalable CNT production. As long as the reaction mixture can be replaced automatically after being exposed by microwave, the production can be conducted in continuous mode.

It can be concluded that MW irradiation technique for CNT synthesis can be used for large-scale production with the right method in handling the reactant and product mixture. The next issue is the impurities present in the as-produced CNT such as amorphous carbon and iron nanoparticles from catalyst.

## 3. PURIFICATION OF CARBON NANOTUBES

Generally, the synthesis of CNTs using various methods including MW irradiation technique produces variety of impurities in the form of amorphous carbon, particles from catalyst (typically iron and cobalt) within or outside the tube and graphitic nanoparticles (Ribeiro et al., 2021). Fullerene is also produced using arc-discharge method but in the case of microwave technique, it is unlikely to be found within the produced carbon soot (Baghel et al., 2022). The presence of impurities affects the quality of the CNTs produced by altering the physical properties. It will also consequently affect the market value due to the low purity. The need for purification treatment is crucial to remove the impurities, improve the quality, enhance the physical properties and obtain high selling price. The study and evaluation on various purification methods focus on the treatment for MWCNTs since MW irradiation technique only produces MWCNTs although most of the techniques can be applied for SWCNTs purification.

### 3.1 Purification methods

Tones of work have been published regarding the purification treatment of CNTs where it can be generally classified into chemical and physical treatment processes. In chemical treatment, the oxidation process is utilised to remove the carbonaceous impurities and catalyst particles using gas or liquid phase oxidizing agents while for the physical treatment, the methods employed are based on physical separation such as ultrasonication, filtration, centrifugation and high temperature vacuum annealing (Hou et al., 2008; Jahanshahi & Kiadehi, 2013). The chemical purification treatment is governed by the oxidative method which is known for its simplicity and effectiveness on impurities, especially amorphous carbon and graphitic nanoparticles. The method takes advantage of higher oxidative activity of those carbonaceous compounds compared to CNT (Hou et al., 2008). This method can be further classified into gas phase and liquid phase oxidation depending on the oxidizing agent. Gas phase oxidation involves the heat treatment with $O_2$, air, a mixture of Ar and $O_2$ (wet air), and $CO_2$. The mechanism of impurities removal using oxidation can be described based on the oxidation of carbonaceous compound and metal particles inside CNTs. Meanwhile in liquid phase oxidation, acid treatment using mineral acids like nitric acid, $HNO_3$, alkali treatment like sodium hydroxide (NaOH) and refluxing in oxidants like hydrogen peroxide, $H_2O_2$ are utilised are used to simultaneously dissolve carbonaceous compound and metal particles encapsulated inside the tube (Rathinavel et al., 2021).

*a) Gas phase oxidation*

Gas-phase oxidation selectively oxidise amorphous carbon including other carbon impurities from the surface of CNTs and metal catalyst encapsulated inside the CNTs, leaving behind structurally improved nanotubes (Park et al., 2006). The oxidation of carbonaceous compounds due to the reactivity of the structure with pentagon and heptagon carbon ring are higher than the highly ordered wall of CNTs

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(Rathinavel et al., 2021). Meanwhile the metal catalysts require the oxidants to breach the tubes before being oxidised in order to crack open carbon coatings after the increase in volume of metal oxides (Park et al., 2006). Dry air, wet air (Ar-$O_2$ mixture), $CO_2$, $Cl_2$, and $H_2$ are commonly selected as gas phase oxidants. It is usually followed by liquid phase oxidation treatment to dissolve the residual carbonaceous compound and oxidised metal particles (Ismail et al., 2008; Park et al., 2006). During the oxidation, the carbonaceous compound such as amorphous carbon is oxidised by $O_2$ to carbon dioxide ($CO_2$) while $CO_2$ also can oxidise the carbon into carbon monoxide (CO) as shown in Eq. (1) and (2) below.

$$C + O_2 \rightarrow CO_2 \quad (1)$$

$$CO_2 + C \rightarrow CO \quad (2)$$

The oxidation process is normally conducted and controlled below the oxidation temperature of the as-produced CNTs that varies depending on the presence of metal oxide (Asnawi et al., 2018). It is reported that the annealing process starts at 480 °C due to the common decomposition temperature of amorphous carbon is at 480–500 °C (Ismail et al., 2008). To obtain a more accurate oxidation temperature for specific as-grown CNTs mixture, TGA can be utilised. Amorphous carbon decomposes at lower temperature than CNTs. Zhan et al. (2017) observed the decomposition of amorphous carbon occurred around 400 °C equivalent to 10% weight loss while CNTs decomposed at temperature between 500 and 600 °C as shown in Fig. 7. Meanwhile, Asnawi et al. (2018) reported the weight loss of amorphous carbon took place at 343 °C before the CNTs were decomposed up until 490 °C based on the TGA result done on as-synthesised CNTs as shown in Fig. 8.

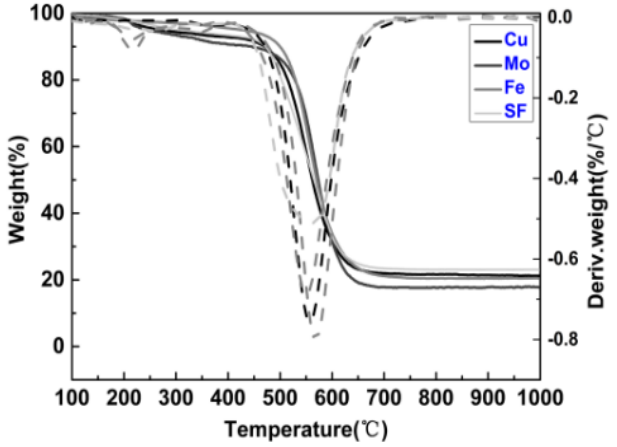


Fig. 7. Thermogravimetric analysis of MWCNTs derived from various metals mixed with ferrocene

Source: Zhan et al. (2017)

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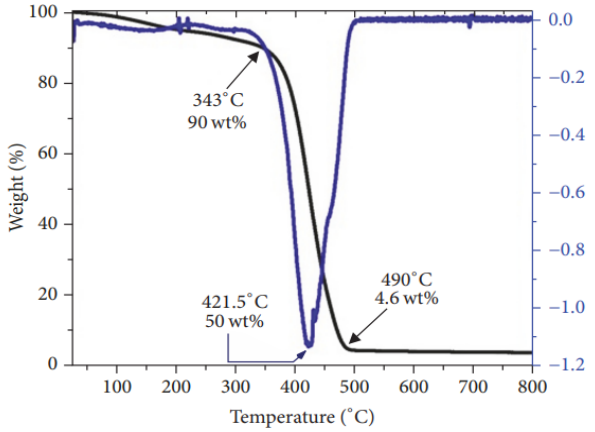


Fig. 8. Thermogravimetric analysis of synthesised CNTs using dried rice husk and ferrocene

Source: Asnawi et al. (2018)

The earliest report using this method is by Ebbesen & Ajayan (1992), the as-produced MWCNTs using arc-discharge method was oxidised in air at 750 °C for 30 minutes, however, only 1–2 wt% of sample left after the heat treatment due to the uneven exposure of CNTs to air. To have a better air exposure on CNTs, Park et al. (2001) have proposed the use of rotating quartz tube and annealed as-produced MWCNTs using arc-discharge method at 760 °C under ambient air for 40 minutes in which 40% yield obtained with higher purity as suggested by the increment of the ratio of the intensity between G-line peak and D-line peak from Raman scattering measurements. Meanwhile for metal-containing CNTs, Chng et al. (2013) used $Cl_2$ gas oxidation at high temperature (1000 °C) for 10 minutes to vaporise the metallic particles within the CNTs and obtained higher purity MWCNTs based on X-ray fluorescence analysis and cyclic voltammograms. The problem with gas phase oxidation is limited works have been found on single-step oxidation for purification of MWCNTs since most of the optimised treatment require more than one method due to inability to remove the carbonaceous impurities and metal particles simultaneously.

*b) Liquid phase oxidation*

To overcome the problem with gas phase oxidation, liquid phase oxidation is introduced whereas both carbonaceous compounds (i.e. amorphous carbon) and metal particles from catalyst can be removed at the same time. For this treatment, the two types of most common liquid oxidizing agents are acids (i.e. $HNO_3$, HCl and $H_2SO_4$) and oxidants ($KMnO_4$ and $H_2O_2$). The crucial parameters involved in this treatment is the oxidation time and temperature. The right conditions (duration, concentration, and temperature) that effectively remove impurities are required to avoid excessive damage to the CNT structure due to the destruction of CNTs structure and the expulsion of metal particles from the tubes (Park et al., 2006). Meanwhile in insufficient conditions, the removal of the impurities might be incomplete (Hou et al., 2008).

For the oxidation using acid treatment (also known as refluxing), concentrated mineral acid such as $HNO_3$ is commonly utilised, due to mild oxidation condition and inexpensive, to oxidise and dissolve metal particles and carbonaceous impurities (Hu et al., 2004). The reaction represents the oxidation of carbonaceous compounds as given in Eq. (3). Mirershadi et al. (2009) reported the purification MWCNTs using boiling 5 M nitric acid for 3 hours that improved the purity to 93% due to the removal of amorphous carbon and defective structures. In spite of that, the immersion also introduced destructive effects on the MWCNTs. Reyhani et al. (2008) compared the effectiveness of different acid treatments (HCl, $HNO_3$, $H_2SO_4$, and HF) by immersing in 3 M of the acid solutions for 24 hours at room temperature. Later they

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found that treatment using $H_2SO_4$ was able to remove the amorphous carbon (0.1 wt%) with 87% yield based on TGA results.

$$C + 4HNO_3 \rightarrow CO_2 + 2H_2O + 4NO \quad (3)$$

Next is oxidation using liquid phase oxidants such as $H_2O_2$ and $KMnO_4$. The surface of the carbon compounds are oxidised by metal cations inside the agents due to their high oxidation ability (Park et al., 2006). The oxidation of carbonaceous compounds using $H_2O_2$ and $KMnO_4$ are as shown in Eq. (4) and (5). The key parameters that contribute to the efficiency of this treatment are the redox potential of the overall system and the structure of CNTs. Hernadi et al. (2001) studied this treatment method and found that $H_2O_2$ was preferable compared to $KMnO_4$. Although both were capable of removing amorphous carbon, but they found that the oxidation using the latter required extra step to remove the $MnO_2$ from the products. Azodpour & Baniadam (2019) improved the method by applying microwave-assisted purification using a mixture of 0.113 M $KMnO_4$ and various concentration of $H_2SO_4$ as the oxidizing agents at 75 °C using 700 W microwave oven to obtain 96% wt% purity of MWCNTs after successful removal of amorphous carbon and iron particles. They also compared the effectiveness of different oxidizing agents (ammonium persulfate and $H_2O_2$) replacing $KMnO_4$ where the result showed that $KMnO_4$ was superior.

$$C + 2H_2O_2 \rightarrow CO_2 + 2H_2O \quad (4)$$

$$3C + 4KMnO_4 + 4H^+ \rightarrow 4MnO_2 + 3CO_2 + 4K^+ + 2H_2O \quad (5)$$

Chemical purification tends to destroy the tube due to oxidation and introduce functional groups at the wall of CNTs when acid treatment is utilised (Chen et al., 2016). Physical purification method can be used as an alternative. This purification involves techniques that rely on physical mechanisms to separate and purify nanotubes from impurities. Unlike chemical methods, physical methods aim to achieve purification without introducing chemical alterations to the structure of CNTs. These methods are often considered milder, preserving the important properties of the nanotubes to a greater extent. Various physical purification techniques are employed to isolate, segregate, and refine CNTs based on their physical properties such as ultrasonication, filtration, chromatography and high temperature annealing.

*c) Ultrasonication*

Ultrasonication is an effective technique used for the dispersion and separation of CNTs. This method involves the application of high-frequency sound waves, generating cavitation bubbles in a liquid medium. The collapse of these bubbles produces hotspots with extreme local heating and pressure leading to the dispersion of CNTs that breaks down the large CNT aggregates while the small aggregates are separated (Kharissova et al., 2013; Yang et al., 2013). Ultra-sonication involves the application of high energy to the CNTs in the commonly used solvents such as water, ethanol, DMF, aqueous Arabic gum etc. Chen et al., 2016; Desforges et al., 2014; Reyhani et al., 2008; Suri & Coleman, 2011). The high energy input facilitates the dispersion of CNTs in the liquid medium. The molecules present in the solvent are capable of interacting with CNTs during ultrasonication, leading to the solubilization of the nanotubes (Ismail et al., 2008). This interaction is essential for the effective dispersion of CNTs and preventing their re-agglomeration. Simultaneously with the ultrasonication treatment, the isolation of CNTs increases. This method is usually utilised prior to chemical purification (Hou et al., 2008). Chen et al. (2005) found that the ultrasonic treatment helped the raw sample to be more dispersed and improved the effectiveness of acid treatment. Lu et al. (1996) explained that ultrasonication can have both positive and negative effects on the CNT structure. Defects such as bending and buckling may occur at high concentrations. The outer layer of graphite may be stripped, leading to thinning of the nanotubes. However, the inner tubes can act as a protective layer, absorbing some of the damage.

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*d) Filtration*

Filtration is a separation technique that isolates nanotubes based on their sizes, in terms of both length and diameter. This method employs membranes featuring narrow pores, acting as selective barriers during the filtration process (Ismail et al., 2008). The choice of membranes with diverse pore sizes facilitates fractionation, allowing for the isolation of CNTs with specific dimensions. The filter holes only let the CNTs with large impurity particles pass through the membrane while the smaller size get filtered out (Hou et al., 2008). One of the most used membrane types is polytetrafluoroethylene (PTFE) that have been used as separation step prior to chemical treatment (Azodpour & Baniadam, 2019; C. Chen et al., 2005; Ribeiro et al., 2021). The pore size of those membranes ranges from 0.1 μm up to 10 μm. This method stands as a valuable means of selectively isolating CNTs based on their size characteristics, contributing significantly to the purification processes in nanomaterial research.

*e) Centrifugation*

Centrifugation is a separation technique that utilises the effect of gravity on particles with different weights in suspension. Based on this idea, this technique is able to separate the carbonaceous impurities from CNTs due to the different stabilities of dispersions in aqueous media formed based on different surface charges after acid treatment (Hou et al., 2008). To remove amorphous carbon only, low speed centrifugation is effective while to remove other carbonaceous compounds also, high speed centrifugation is required to suspend the CNTs in the medium. Yu et al. (2006) obtained CNTs with almost no carbonaceous impurities and only ~1–2 wt% of residual metal content left by using high-speed centrifugation at 20000 G after nitric acid treatment.

*f) High temperature vacuum annealing*

Annealing is a type of heat treatment that usually supplied at very high temperature. The treatment can occur in both under air and vacuum condition but the latter is more favorable since it can avoid oxidation of CNTs and also lower the evaporation temperature of metal particles (Huang et al., 2003). It takes advantage of different physical properties between CNTs with carbonaceous impurities and metal particles (Hou et al., 2008). Graphite are stable at event 3000 °C while metal catalysts evaporate at lower temperature than that (Hou et al., 2008). Hence, once vacuum annealing is applied at suitable temperature, the CNTs can be extremely purified. The most interesting part about this treatment is not only impurities are removed, the structure and crystalline layers are also improved (Boudard et al., 2015; Chen et al., 2007; Khanbolouki & Tehrani, 2020). The treatment increases the mechanical, thermal and electronic properties of CNTs. However, there is no evidence that this treatment can remove high amount of carbonaceous compounds, hence, pretreatment is required for this purpose such as gas phase oxidation.

Andrews et al. (2001) utilised high temperature vacuum annealing at 1600 °C to 3000 °C to purify MWCNTs obtained from low temperature CVD by removing iron particles encapsulated within nanotubes and microstructural defects. The method was able to remove almost all iron particles whereas only < 0.1 wt% left. Huang et al. (2003) also reported purification of MWCNTs using the same method at temperature between 1500 to 2150 °C under vacuum pressure between $10^{-3}$ and 10 Pa with varying time to obtain ultrahigh purity of MWCNTs and compared with acid treatment result. The treatment at 2000 °C within 30 minutes successfully removed the iron catalyst with only 0.1 wt% left to obtain 99.9 wt% of MWCNTs. Meanwhile, Guo et al. (2023) performed the annealing at 2000–2800 °C under Ar atmosphere for about 3–4 hours. As a result, the iron and aluminium content in MWCNTs were reduced to below 100 ppm from 81700 and 29800 ppm, respectively, while the structural order of MWCNTs was proven to improve the $I_D/I_G$ ratios from Raman spectroscopy.

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### 3.2 Comparison of purification methods

As-produced CNTs in various methods especially metal catalyst-based processes require purification to remove various impurities, such as carbonaceous impurities and metal catalyst particles, which are typically introduced during synthesis. As discussed in the previous section, several common methods are available which are gas phase oxidation, liquid phase oxidation, ultrasonication, filtration, centrifugation, and high-temperature vacuum annealing. This section elaborates on their respective advantages and disadvantages since different purification methods offer unique benefits and challenges as highlighted in Table 5.

Table 5. Comparison between various purification methods of CNT

| Method | Advantage | Disadvantage |
|---|---|---|
| Gas Phase Oxidation | Simple method<br>No sidewall defects | Unable to remove encapsulated metal particles<br>Might open the tube-end |
| Liquid Phase Oxidation | Remove carbonaceous impurities and encapsulated metal particles simultaneously | Destroys the CNTs (by cutting and opening the tube-end)<br>Introduces oxygenated functional groups<br>Difficult to obtain ultrahigh purity of CNTs |
| Ultrasonication | Disperse CNT bundles into individual nanotubes | Only removes carbonaceous impurities that loosely-bound with CNTs<br>Require acid treatment afterwards<br>Unable to remove encapsulated metal particles |
| Filtration | Based on physicochemical interactions of carbonaceous compounds only<br>No damage on CNTs | Unable to remove encapsulated metal particles<br>Time-consuming |
| Centrifugation | Based on the influence of gravity on carbonaceous compounds only | Require acid pretreatment to introduce functional groups |
| High Temperature Vacuum Annealing | Almost complete removal of metal particles<br>Improve the defects and structure of CNTs | Require vacuum and high temperature condition |

Source: Authors' compilation

One of the chemical purification methods, gas phase oxidation is a straightforward method known for its simplicity in procedure. One significant advantage of this technique is it can sustain the structure of CNTs since no defects are introduced to their sidewalls (Ismail et al., 2008). However, gas phase oxidation comes with limitations, one of them is, it is ineffective at removing metal particles encapsulated within the CNTs, a critical drawback for applications demanding high purity CNTs (Hou et al., 2008). Moreover, this method may result in the opening of the tube ends.

Another chemical purification method is liquid phase oxidation, on the other hand, is highly effective at simultaneously removing both carbonaceous impurities and encapsulated metal particles in CNTs (Ribeiro et al., 2021). This dual function capability makes the treatment very efficient. However, the process can be quite harsh, often leading to the destruction of CNTs by cutting and opening their tube ends (Hou et al., 2008). Additionally, the method introduces oxygenated functional groups onto the CNTs and high removal of metal particles encapsulated inside CNTs is still difficult to achieve (Ribeiro et al., 2021).

Ultrasonication is good for dispersing CNT bundles into individual nanotubes, thereby increasing the surface area available for subsequent purification steps (Kharissova et al., 2013). Despite this benefit, ultrasonication primarily removes only loosely-bound carbonaceous impurities and often requires an additional acid treatment to remove encapsulated metal particles and achieve higher purification efficiency (Hou et al., 2008).

Filtration, which purifies CNTs based on the physicochemical interactions of carbonaceous compounds, does so without damaging the CNTs, thus preserving their structural integrity. This method is especially beneficial when maintaining the original properties of CNTs is crucial. However, filtration is

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unable to remove encapsulated metal particles, and the process is time-consuming, which makes it less suitable for large-scale purification efforts (Hou et al., 2008).

Centrifugations utilise the effect of gravity to separate carbonaceous compounds from CNTs, providing a non-destructive route for purification. However, this method requires acid pretreatment to introduce functional groups that facilitate the separation process (Yu et al., 2006). Centrifugation cannot be used as a standalone method to remove encapsulated metal particles and achieve high purity.

High-temperature vacuum annealing stands out for its ability to achieve near-complete removal of metal particles from CNTs (Andrews et al., 2001; Huang et al., 2003). This method also improves the structural defects of CNTs, enhancing their overall properties. However, it demands a vacuum environment and high temperatures, which can be energy-intensive and require safety considerations. Besides that, there is no evidence this method can remove amorphous carbon.

In conclusion, each purification method for CNTs presents unique strengths and weaknesses, as simplified in Table 5. Usually, the methods are combined into multistep purification to obtain higher efficiency.

### 3.3 Evaluation of purification treatment protocol

Developing a purification treatment protocol for CNTs usually involves both chemical and physical separation known as a multi-step procedure. This procedure requires careful selection and execution of the purification methods to remove impurities and enhance the quality of the CNT samples. The multi-step procedure is found to be more effective compared to a single-step method as it can remove more impurities present in the CNTs. Different treatment methods are applied for SWCNT and MWCNT. According to Duesberg et al. (1999), oxidative methods produced lower yield on MWCNT while the SWNCT is more susceptible to the surface functionalization on the structure. CNTs produced using microwave irradiation technique are mostly MWCNT-type (Liu et al., 2019). Hence, the review of the purification treatment only focuses on those protocols on MWCNTs that have potential to produce high purity of MWCNTs.

Chen et al. (2005) has studied the purification treatment on MWCNTs assisted by microwave heating. Approximately 0.6 g of as-prepared MWCNTs with an initial diameter ranging from 40 to 60 nm began to undergo the treatment with the dispersion in 25 ml of deionised water through ultrasonic agitation for one hour before dried and reduced into 0.2 g. The samples then received microwave-assisted purification with 5 M $HNO_3$ from a temperature ramp-up from room temperature to 210 °C over 30 minutes before an isothermal treatment at 210 °C for 90 minutes. Following microwave purification, the resulting suspension was digested and filtrated using a 0.1 μm PTFE membrane in deionised water. The filtered material is then rinsed with alcohol and subjected to vacuum drying for 8 hours. This protocol was able to produce MWCNTs with 99.9 wt% purity without damaging the structure of the wall.

Huang et al. (2003) successfully obtained 99.9% purity of MWCNTs synthesised using catalytic CVD by using high temperature (1500 to 2150 °C) vacuum annealing under pressure of $10^{-3}$ to 10 Pa within an electrical resistance graphite oven (HZS-30) for varying time (2 to 8 hours). The optimum condition for annealing was found to be at 2150 °C for about 30 minutes where the content of metal particles (mostly iron and aluminum) within MWCNTs dropped from 14 wt% to 0.1 wt% to obtain 99.9 wt% purity of MWCNTs. Nevertheless, the as-produced MWCNTs were already low number of carbonaceous impurities (< 5 wt%) based on TGA results, hence, they did not prove that this method can remove the carbonaceous impurities.

Das et al. (2014) reported the wet chemical treatment method on 95 wt% of MWCNTs using HCl and $H_2O_2$. 0.5 g of MWCNTs initially were dispersed in a solution comprising 25 mL of a mixture containing 70% HCl (36 wt%) and 30% $H_2O_2$ (30 wt%). The resulting mixture was sonicated at a temperature of 50 °C for a duration of 5 hours, employing a frequency of 40 kHz. They managed to achieve 98.78 wt% purity of MWCNTs where in terms of purification yield, 100% of the elemental components were removed.

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Chen et al. (2016) studied the effect of purification treatment on MWCNTs using heat treatment method. 10 g of MWCNTs were applied with 500 °C of heat treatment using a thermostat oven for 6 hours with heating rate of 10 K/min under air atmosphere, resulting in 97 wt% of MWCNT. Table 6 summarises the various purification methods. Combination of various methods is able to produce high purity of CNTs by removing the carbonaceous compounds and metal catalyst.

Table 6. Review of different CNT purification treatment protocol

| Preparation | Diameter (nm) | Purification Protocol | Purity |
|---|---|---|---|
| MWCNTs prepared by thermal chemical vapor deposition (TCVD) | 40–60 | Ultrasonication in deionised water for 1 hour<br>Microwave-assisted chemical treatment using 5 M $HNO_3$ for a total of 120 minutes<br>Filtration using a 0.1 μm PTFE membrane | 99.9% |
| MWCNTs prepared by catalytic chemical vapor deposition (CCVD) | 3–25 | Vacuum heating in an electrical resistance graphite oven model HZS-30 under temperature of 2150 °C and pressure of $10^{-3}$ to 10 Pa.<br>The treatment was done for 30 minutes | From ~85% to 99.9% |
| CNT fibres composed of MWCNTs prepared by floating catalyst chemical vapour deposition (FCCVD) | 10–20 | Winded around graphite rod and placed inside vacuum chamber below $10^{-3}$ Pa<br>The treatment was done for 30 minutes | From ~90% to > 99% |
| MWCNTs prepared by catalytic chemical vapor deposition (CCVD) | 7–17 | Mixed chemical treatment using 70% HCl (36 wt%) and 30% $H_2O_2$ (30 wt%)<br>Ultrasonication for 5 hours at 70 kHz at 50 °C | From 95% to 98.78% |
| MWCNTs prepared by catalytic pyrolysis of hydrocarbon | 5–30 | Heat treatment at 500 °C for 6 hours in thermostat oven. | 97% |
| MWCNTs prepared by catalytic pyrolysis of hydrocarbon | 5–30 | Heat treatment at 500 °C for 6 hours in thermostat oven. | 97% |

Source: Authors' compilation

## 4. SCALABILITY PROSPECTS

A process is scalable when it can be replicated on a larger scale production while maintaining a significant efficiency. The scalability can be viewed from several perspectives which are technical feasibility, economic viability, energy requirement, yield consistency etc. (Piccinno et al., 2016). A certain process must have the ability to control and regulate the process conditions like temperature and pressure to ensure the control on product quality can be achieved. Energy usage in a process also plays an important role in determining the scalability since the cost related with energy significantly influences the overall production cost (Towler & Sinnott, 2013; Turton, 2012). Both aspects closely related with the economic viability of the process. Most of the time, a trade-off between the technical feasibility and energy requirement with total production cost is required by conducting a thorough analysis on these factors.

In context of process for production of CNT, arc discharge method is not quite scalable due to the difficulty to maintain consistent arc condition at larger scale plus high energy requirement to produce the electric arc. Meanwhile for CVD, it is more common to be conducted in continuous mode as reported in the literature (Mubarak et al., 2014). This process is more scalable since the reaction can adapt variety of process conditions with good control and the reactor design is not too complicated (Mubarak et al., 2014). The energy requirement is considerably lower than that of arc discharge (Rathinavel et al., 2021). However it is significantly high and long reaction time (Liu et al., 2019). Hence, MW irradiation technique comes into consideration as the promising alternative for these conventional methods due to its relatively lower energy requirement and quick reaction. However, its scalability is not yet evaluated.

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Techno-economic assessment (TEA) is commonly utilised as a mean to analyse the economic viability of certain process with respect to the process design and modelling (Barahmand & Eikeland, 2022). Typically, TEA begins with conducting a market study to gather data, then designing the process flow equipped with mass and energy balance followed by a detailed cost estimation and economic evaluation (Haeldermans et al., 2020). Several economic performance indicators usually used are net present value (NPV), payback period (PBP), minimum selling price (MSP) and more (Chai et al., 2022). Lastly, the process involves executing a sensitivity analysis (Barahmand & Eikeland, 2022). Sensitivity analysis provide a means to evaluate the impact of various factors on economic metrics, offering valuable insights for refining and optimizing manufacturing processes (Cesar et al., 2023; Patel et al., 2012).

Limited work has been done on CNTs production in the literature and none for MW irradiation technique. Saravanan et al. (2010) have done the assessment on the production of MWCNTs by open air discharge method by performing both the experimental aspects of the research. The process was carried out using metal arc welding machine followed by multi-step purification obtaining yield more than 60%. Based on the economic assessment, the production cost was found to be USD 3 per milligram. More recently, Rahatwan et al. (2020) carried out the TEA on pilot scale CNTs production using CVD method from liquefied petroleum gas (LPG). The process was done at more than 900 °C in fluidised bed reactor (FBR) followed by multi-step purification. The selling price obtained was USD 0.37 per gram of CNTs with 200 to 250 kilograms per year capacity targeting the Southeast Asia market. The economic evaluation was found to be 18.88% on IRR, NPV more than USD 77 thousand and a payback period of less than 5 years. Table 7 reviews include the existing studies of TEA on nanoparticles productions and microwave-based processes to draw parallels and contrasts between different sectors to discover shared challenges or solutions that might be applicable or adaptable to CNT production using MW irradiation technique. TEA evaluation is required to assess the scalability of this technique. The MW irradiation technique can be conducted by placing the catalysed graphitic carbon under microwave irradiation as shown in Fig. 9. Roughly, a catalyst is needed to induce the formation of the CNT on the surface of the graphite.

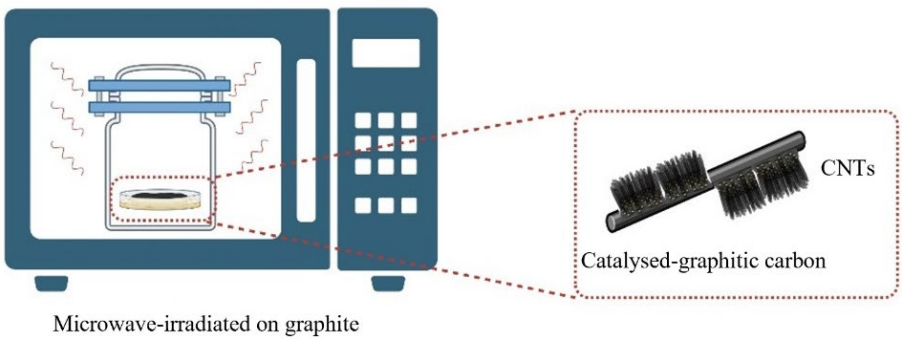


Fig. 9. Growth of CNTs under microwave irradiated condition

Source: Authors' illustration

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Table 7. Review of Techno-Economic Assessment (TEA) on related production process

| Authors | Scope | Market Analysis | Technical Analysis | Cost Analysis | Economic Indicators | Sensitivity Analysis |
|---|---|---|---|---|---|---|
| (Saravanan et al., 2010) | CNTs | - | Synthesis of MWNTs using arc discharge method. Lab-based process design. | Considers utility cost only. | - | - |
| (Rahatwan et al., 2020) | CNTs | Based on supply and demand analysis. | Pilot scale CNTs production using CVD method from liquefied petroleum gas (LPG) in fluidised bed reactor. Simulation-based process design. | CAPEX and OPEX are determined. | Minimum selling price, IRR, NPV and PBP. | Product and raw material price, labour salary and the total bare module cost. |
| (Haeldermans et al., 2020) | Microwave | Based on market volume. | Biochar production from different residue streams using conventional and microwave pyrolysis. Lab-based process design. | CAPEX and OPEX are determined. Equipment cost acquired from confidential quotations and literatures. | Minimum selling price, NPV and discounted PBP. | Product and raw material price. |
| (Neha et al., 2022) | Microwave | - | Co-pyrolysis of food waste and low-density polyethylene (LDPE) using microwave to produce bio-oil, biochar and pyrolysis gas. Scaled-up lab-based process design. | Equipment cost, CAPEX and OPEX are determined based on scale-up ratio. | IRR and BEP. | - |
| (Ragadhita et al., 2019) | Nanomaterial | - | The synthesis of titanium dioxide using the liquid-phase synthesis method based on the use of titanyl nitrate and glycine. Scaled-up lab-based process design. | CAPEX and OPEX are included. Equipment cost acquired from online market. | Gross profit margin, IRR, discounted PBP, cumulative NPV, BEP and probability index. | Raw materials, utilities, labour, selling price and tax value. |
| (Nurdiana et al., 2022) | Nanomaterial, microwave | - | The synthesis of zinc sulphide from zinc nitrate hexahydrate and thioacetamide via microwave irradiation technique. Scaled-up lab-based process design. | CAPEX and OPEX are included. Equipment cost acquired from online market. | Gross profit margin, IRR, discounted PBP, cumulative NPV, BEP and probability index. 264 working days | Raw materials, utilities, labour, selling price and tax value. |

Source: Authors' compilation

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## 5. CONCLUSION

Over the years, significant advancements have been made in the synthesis methods of carbon nanotubes (CNTs) to improve their yield, quality, and scalability. This review assesses conventional synthesis techniques like arc discharge and chemical vapor deposition (CVD) alongside emerging methods, particularly microwave (MW) irradiation. Arc discharge, though historically vital as the first CNT synthesis method, is limited by high energy costs and batch-mode operation, hindering its scalability for industrial use. Conversely, CVD has become the most versatile and widely used technique due to its ability to control CNT properties and support large-scale, cost-effective production. The MW irradiation technique presents a promising alternative, leveraging carbon materials' capacity to absorb and convert microwave energy into thermal energy, thus facilitating CNT synthesis more efficiently and cost-effectively. However, further technological advancements and comprehensive studies are necessary to optimise MW irradiation for large-scale production. Purifying CNTs is also essential, with methods like gas and liquid phase oxidation, ultrasonication, filtration, and vacuum annealing offering unique benefits that, when combined, can improve CNT purity. Scalability remains a key challenge, where CVD leads due to its continuous production process, precise parameter control, and high yield of quality CNTs, whereas the arc discharge method lags due to its batch limitations. Meanwhile, MW irradiation shows potential for large-scale production, warranting further economic and technical evaluation. In summary, although traditional methods such as arc discharge and CVD are well-established, emerging techniques like MW irradiation signal a promising future for CNT synthesis. Continued research in synthesis and purification will be critical to addressing current challenges and enhancing CNTs' potential for diverse industrial applications.

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## CONFLICT OF INTEREST STATEMENT

The authors agree that this research was conducted in the absence of any self-benefits, commercial or financial conflicts and declare the absence of conflicting interests with the funders.

## AUTHORS' CONTRIBUTIONS

**Muhamad Nor Iqmal Hafizi Kamaruddin**: Conceptualisation, methodology, formal analysis, investigation and writing-original draft; **Siti Shawalliah Idris**: Conceptualisation, supervision, writing-review and editing; **Noor Fitrah Abu Bakar**: Writing-review and editing; **Atikah Kadri:** Writing- review and editing.

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