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# REVIEW



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# Rapid production of carbon nanotubes: a review on advancement in growth control and morphology manipulations of flame synthesis

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Carbon nanotube synthesis using flame has enormous potential for large scale carbon nanotubes production. Carbon-rich and autothermal conditions within the flame environment allow for a rapid and continuous single-step carbon nanotube synthesis process, which is highly energy efficient and costeffective compared to the conventional carbon vapour deposition method. Despite its significant potential, controlling the synthesis of carbon nanotubes in flame remains a great challenge due to combustion physics that does not allow independent control of the flame temperature and gas phase composition. In the present review, systematic analysis of the optimization method of carbon nanotubes catalytic growth in flames using various combinations of flame configurations, catalytic materials, and fuel types is highlighted. Catalytic materials are added into the flame as aerosols or substrate-based, which has direct effects on the carbon nanotubes growth, yield and morphology. The effects of additional parameters such as residence time and inert gas dilution are also presented. The recent developments in the application of additives in flame synthesis to significantly enhance growth control and nanotube quality are highlighted. Furthermore, current progress on the advanced control mechanism over the flame synthesis process through application of electrical or magnetic force fields and novel nanotemplates is presented. These control mechanisms enable manipulation of the synthesized carbon nanotubes' physical characteristics, which is crucial for application in nano-mechanical and electrical instruments.

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## 1. Introduction

The discovery of a third carbon allotrope, buckminsterfullerene  $C_{60}$ , in 1985 by Kroto, Curl, Smalley, and co-workers<sup>1</sup> marked the beginning of an era of carbon nanostructured materials. With remarkable electrical, thermal, and mechanical properties, coupled with rapid development of nanoscience and nanotechnology, the last three decades has seen the emergence of carbon nanostructures in various applications for modern society.<sup>2</sup> The Nobel Prizes that were awarded to Curl, Kroto, and Smalley<sup>3</sup> for their work on Buckminsterfullerene, and to Geim and Novoselov<sup>4</sup> for extracting single layer carbon atoms known as graphene, are clear indications of the significant impact of carbon nanostructured materials on society.

Since the late 1990s, the global production of carbon nanotubes (CNTs) increases by nearly 60% every year<sup>5</sup> with the most substantial increase in the past decade.<sup>2</sup> The demand for CNTs



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is expected to soar in the next 10 years, with a projection of a total market value of USD 6.1 billion in 2023, increasing from just USD 1.13 billion in 2014.6 Rapid expansion of the market is driven by demand from the sectors which utilize CNTs in bulk, such as composites, electronics, and energy applications.<sup>6</sup> The market growth will be further strengthened by the transformation of the aviation sector where the application of carbon nanotubes reinforced polymer (CNRP) is predicted to replace conventional carbon fibre and carbon fibre reinforced plastic in the near future.<sup>7,8</sup> CNRP penetration in a highly-regulated aviation market signals the acceptance of CNTs as the latest generation of high performance materials. A comprehensive review of research related to CNTs' current and future application in the aerospace industries can be found in work by Gohardani et al.<sup>9</sup> Nevertheless, broader application of CNTs is currently hampered by the high production cost. Despite the continuously increasing production capacity, the current price of CNTs is still relatively expensive. Multi-walled nanotubes (MWNT) for bulk application, such as in polymers, paints, or epoxies, cost around USD 600 per kilogram, while high quality CNTs cost more than the nominal price of gold.<sup>10</sup>

As the CNTs market continues to expand, stiff competition between manufactures creates increasingly dynamic market conditions with the proprietary synthesis process playing a critical role. This is exemplified by the closure of the Bayer MaterialScience (now known as Covestro AG)<sup>11</sup> 260 metric tons per year CNT production plant in recent years.<sup>12</sup> Industry experts speculated that the decision was made based on Bayer's technical position in CNT synthesis technology. The CNT synthesis process on an industrial scale is a developing technology that is still frequently experiencing significant breakthroughs. Operating without industry-leading technology, the global giants, such as Bayer, are unable to react quickly enough to compete with smaller and much more flexible companies in this highly innovative market. OCSiAl is a CNT manufacturing company reported to produce up to 90% of the world's total single-walled nanotubes (SWNT) at 50 times cheaper than the closest competitor using a cutting-edge proprietary SWNT



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Electrical Engineering, University Teknologi Malaysia. Her research interests include networked control systems, optimal control and networked multi-agent systems. synthesis technology.<sup>13,14</sup> Regardless, the exponential growth of CNT market is still very attractive. Some major producers are increasing their production capacities<sup>15</sup> and several new major players are venturing into CNTs production, such as LG Chem Ltd., who opened a new CNT mass manufacturing plant with a capacity up to 400 tons in early 2017.<sup>16</sup>

Even though the important parameters related to CNT growth are well-established, a fundamental understanding of the role played by each parameter in regulating the overall growth process of CNTs remains unclear.5,17 Controlling CNT growth is extremely difficult due to the complex parameter space, where multiple parameters interact at different levels of the growth process.18 An inability to fully understand the role of each parameter in the CNT growth process has significantly limited the ability of CNTs manufacturers to produce CNTs with specific attributes. Various theories have been proposed to describe the growth process of CNTs.<sup>19</sup> However, these theories are generally developed to describe the growth process of certain CNT variants within the specific growth environment. In a technical interchange held in 2014 amongst the United States key players in CNT research, including NASA and several prominent universities, it was highlighted that the development of fundamental knowledge and technology related to growth control of CNT in bulk scale is one of the main technical challenges for the field.<sup>20</sup> Therefore, the CNT synthesis research field continues to attract immense interest from the scientific community and industrial players in an effort to further refine the fundamental understanding of CNT growth through various methods.

In general, there are three prominent types of CNT synthesis methods: plasma arc discharge, pulsed laser vaporization/laser ablation, and catalytic chemical vapor deposition (CCVD). Plasma arc discharge and pulsed laser vaporization/laser ablation produce CNTs in batches, and are limited to small scale production of high quality CNTs.<sup>21</sup> Using these techniques, the CNTs are synthesized at a very high temperature, around 4000 to 6000 K, producing high quality CNTs at a very high production cost.<sup>22</sup> These methods are still commonly used and continually developed by researchers due to their capability of synthesizing pristine CNTs for a niche market.<sup>17,21-23</sup> Das *et al.*<sup>21</sup> provide an in depth and comprehensive review on the current development of these CNT synthesis methods and shed light on its future in large scale production.

For most applications, CNTs produced by the aforementioned techniques are expensive and beyond the quality required to serve the purpose. Hence, most of the CNTs supplied to the world's market are produced using the CCVD method. The CCVD method is a continuous production process, producing relatively low quality CNTs at a reasonable price. The ability of CCVD to produce CNTs at low temperature and ambient pressure with high throughput makes it the best option for the majority of CNT manufacturers. Furthermore, the high degree of control in the CCVD technique allows for the rapid development of CNTs synthesis research to cope with the exponential rise of the market demand, in terms of volume and variations in CNT morphology.<sup>2,6</sup> Even though the main body of knowledge related to CNT synthesis is yet to be fully developed, the CCVD allows for high volume production of CNTs at a reasonable price.

Besides the CCVD method, flame synthesis is a less known CNT synthesis method that has been used to produce CNT commercially.24,25 Flame synthesis is also a continuous production process and technically simple to be scaled up for large volume production.26,27 The potential for CNTs to be synthesized in a flame environment was recognized early on by the discovery of tube-like structures in flame by Singer and Grumer in 1959.28 It did not take long for Saito et al.29 to make a breakthrough by being the first to identify CNTs within the sooty acetylene-air diffusion flame in the same year of Iijima's CNT rediscovery in 1991.<sup>30</sup> Fundamentally, the potential of the flame synthesis method for carbonaceous materials production at an industrial scale is well known, with current production of carbon black having a capacity of more than 6 million tons per year.<sup>27</sup> Nevertheless, currently there is only one company claiming to produce CNTs using the combustion process, Nano-C, Inc.25

In terms of CNT production, the development of the flame synthesis process is in its infancy when compared to CCVD. Due to market demand, continuous and rigorous development of the CCVD process has produced various versions of CCVD techniques that allow for precise control over the variety CNTs types, chirality, and morphologies produced. Nevertheless, the CNTs produced through this process are still relatively expensive for broad consumer applications. Efforts to further reduce the production costs are limited by the CCVD process efficiency. CCVD is not the most efficient process due to the utilization of an external heating mechanism and the relatively slow CNT growth. This is the gap that flame synthesis is envisaged to fill. Through development of the process in the last three decades, flame synthesis has been a candidate for an ideal CNTs synthesis process, showing a clear potential to significantly enhance the overall efficiency of the CNT synthesis process. Flame synthesis promises a quantum leap in energy efficiency as a result of the auto-thermal conditions and rapid synthesis process, which is theoretically reduces the time by an order of magnitude when compared to that of CCVD.<sup>26,27,31</sup> However, even though there is a clear potential for flame synthesis to be an alternative method to CCVD, significant further development of the process is required to enhance the control over the synthesized CNTs and flexibility of the process in order to produce diverse variants of CNTs.

In some applications, the use of flame to synthesise CNTs is proven to be beneficial towards the enhancement of the final product. The production of CNRP through CNTs direct grafting using an ethanol flame produces CNRP at higher quality and electrical conductivity compared to the conventional methods, such as spreading of CNT powder or dissolved CNTs, CNT array transfer, electrophoresis, or dipping and freeze drying methods.<sup>32–34</sup> The process is also fast, continuous, and suitable for a large surface area for industrial applications.<sup>35</sup> Additionally, the development of CNT synthesis in flames has led to the emergence of niche concepts such as "green" CNTs, where the CNTs are synthesized using recycled plastic waste.<sup>36–38</sup> Even though conversion of the plastic waste to hydrocarbon fuel is currently performed *via* an externally-heated furnace, a selfsustaining flame synthesis process where the waste heat from the flame synthesis process is harnessed for the pyrolysis of the raw plastics is expected in the near future.<sup>36</sup> Besides plastic waste, other waste materials such as sugarcane bagasse<sup>39</sup> and corn waste<sup>40</sup> have also been tested for suitability to be upcycled using a similar concept.

Development of a stable and well-controlled synthesis process within the highly complex flame environment has been proven to be the stumbling block for mainstream acceptance of the technology.<sup>27</sup> Compared to CCVD, the degree of complexity of the CNTs growth is significantly amplified in the flame environment because of the combustion process, which creates dynamic gas phase kinetics with a significant temperature gradient within the flame. Understanding the complex interaction between the fluid dynamics, scalar transport, and chemistry that determines the post-flame composition and temperature is crucial to predicting the region for CNT growth within the flame. However, currently there is a very limited amount of literature that focuses on the development of mathematical models that are capable of simulating concurrent processes of two highly complex mechanisms of combustion and CNT synthesis.24,41-43

A review on growth control in flame synthesis is deemed particularly important at a time when cheap CNTs, especially in the medium and low-quality categories, are highly demanded. Moreover, as the CNTs market is fast approaching maturity, major manufacturers will eventually have to turn to production process efficiency for profit growth. Significant cost reduction can only be achieved through a breakthrough in production process efficiency. It is envisaged that as reliable flame synthesis technology becomes accessible, opportunity for significant increase in production efficiency will compel the leading CNTs manufacturers to take advantage of the technology. Consequently, it will help to further reduce the CNT market price and economically allow for much broader CNT applications in consumer products.

Comprehensive review articles on CNT flame synthesis are scarce. The majority of the recent reviews only summarized the latest developments within the field, without providing analysis on the progress made in the detailed understanding of the CNT growth controlling parameters in flame.44,45,186 Thus, the present review intends to organize each regulating parameter of CNT inception and growth in the flame environment to be used as a comprehensive guide on the present topic. The following section is organized to highlight the current understanding of the effects of important parameters toward the structural features of the synthesized CNTs and challenges encountered to obtain a high degree of control in the synthesis process (Fig. 1). In addition, the advancement in understanding of the growth enhancer effect toward CNTs growth and morphology is also reviewed. Application of growth enhancer in flame synthesis has a clear potential in promoting production of high quality CNTs at a higher growth rate. In addition, improvement of the structural control mechanisms that were used to manipulate CNT morphology in flame synthesis is also presented. The structural control mechanism is crucial to the development of an adaptable, reliable, and highly controlled synthesis process to produce aligned CNTs for specialized applications. Wherever appropriate, important findings from CCVD studies that can be potentially applied to flame synthesis will be discussed.

# 2. The growth controlling parameters of carbon nanotubes in the flame environment

Most developed theories on the fundamental mechanism of CNT inception and growth in flame are adapted from the CCVD process. In general, there are three main steps toward CNT formation: carbon deposition by surface catalysis, carbon diffusion and transport, and carbon precipitation.<sup>17,19</sup> For CNT inception and growth to take place, there are three vital components that must be met: availability of suitable catalytic nanoparticles, adequate continuous supply of a gas-phase carbon source, and a conducive environment for hydrocarbon molecules dissociation and nanotubes formation.<sup>27</sup> Catalysts can be provided either as deposited nano-scale particles on a substrate or as a gas-phase in the flame. An environment with a suitable temperature and a gas-phase carbon source is created by the exothermic combustion process.

As mentioned earlier, CNT synthesis in flame offers an energy efficient and rapid growth process. However, some of the important parameters in the synthesis process, which can be independently regulated in the CCVD technique, are interrelated in flame. Hence, the independent parameters such as flame configuration, fuel and catalyst selection, residence time, and growth enhancer are reviewed separately in each individual subsection to provide a comprehensive and practical review on the effect of the specific parameters. On the other hand, the interrelated parameters such as gas phase composition, temperature, and inert diluent are reviewed within one subsection to create a constructive review on the effect of these parameters, without losing the understanding of the parallel effects that each parameter has on one another towards the overall process of CNT growth in flame.

#### 2.1 Flame configuration

Premixed flame,<sup>24,25,46-58</sup> co-flow diffusion flame,<sup>59-78</sup> inverse diffusion flame,<sup>79-85</sup> and counter diffusion flame<sup>76,86-101</sup> are the most common flame configurations that have been used to synthesize CNTs. There are also other types of flame variations that have been used, such as pyrolysis flame encircled by premixed flat flame<sup>102-109</sup> and multiple inverse diffusion flat flame.<sup>97,110</sup> Beside these, recently there has been research efforts exploring a unconventional premixed flame using an internal combustion engine to synthesize CNTs.<sup>111,112</sup>

Premixed flame is characterized by the complete mixing of fuel and oxidizer prior to the burning process. It is the preferred type of flame configuration for CNTs synthesis due to the ease of control of the flame stoichiometry *via* oxidizer-fuel equivalence ratio, which is vital in managing the species composition within the post-flame region.<sup>48</sup> Premixed flame is also suitable to be used with various types of fuel and has a high scalability



Fig. 1 Experimental parameters in CNTs synthesis in flame and the observed CNTs features in the flame synthesis process.

because it is not limited by diffusion rate.<sup>48</sup> These clear advantages motivated early pioneers in CNT flame synthesis to use a premixed flame configuration in their experiments. Moreover, the potential for premixed flame to be applied in large scale production of CNTs is already proven by the adaptation of this flame configuration by Nano-C, Inc.<sup>25</sup>

The three types of diffusion flame differ from one another by the configuration of the fuel and oxidizer supply. The co-flow diffusion flame is established on a burner with two annuli, fuel from the inner tube and the oxidizer stream from the outer tube. Conversely, for the inverse diffusion flame, the oxidizer steam is located in the inside tube and the fuel is delivered through the outer tube. In this configuration, the CNT growth region is located at the outside of the reacting zone. This is beneficial towards the CNT synthesis process as the synthesized CNT will not be exposed to the high temperature region of the flame front, hence minimizing CNT thermal defects.81 The counter-flow diffusion flame employs two converging nozzles with a fixed distance between each other. A nozzle issues the oxidizer that impinges on the fuel stream from the other nozzle and the flame stabilizes near the shear layer between the two streams. The 1-D flame geometry in the counter-flow configuration enables fundamental analysis on the response of the synthesis process towards temperature, catalytic substrate positioning, and gas phase composition. The simple geometry of the flame allows an accurate development of the flame model and can be operated at varying strain rates.88 Furthermore, this flame configuration minimizes the interaction between the flame and the substrate to allow the use of materials with relatively low melting temperatures, such as anodic aluminium oxide (AAO) nanotemplate.76

Pyrolysis flame was extensively used by Vander Wal and coworkers in a series of experimental works investigating the fundamental parameters of CNTs growth using a gas-phase catalyst.<sup>102-108</sup> A pyrolysis flame is established in a stainlesssteel tube surrounded by hot gas from the post combustion gas of the flat premixed flame. A mixture of hydrocarbon (carbon source), gas-phase catalyst, and inert gas is supplied in the tube where the pyrolysis process and CNT growth occurred. Pyrolysis flames are designed primarily for experimental work. It simplified the hydrocarbon pyrolysis process for better analysis of the CNT growth parameters.

#### 2.2 Fuel selection

Fuel selection is one of the earliest decisions needing to be made in designing an optimum environment for CNT synthesis in flame. Differing from the CCVD process, the fuel is not only crucial as carbon sources for the inception and growth of the CNTs, but also affects the overall flame temperature. Hence, while most hydrocarbons are found suitable as a carbon source for CNT synthesis in CCVD,113 there is a limited number of carbon sources that are suitable for flame synthesis. The suitable fuels for flame synthesis include methane, ethane, propane, butane, ethanol, ethylene, and acetylene. However, this list is not conclusive since in a recent experiment, nheptane was found to produce CNTs in a counter diffusion flame.<sup>101</sup> Theoretically, a fuel that exhibits minimal pyrolysis is preferred as it delay the formation of polycyclic aromatic hydrocarbon (PAH) and subsequently soot, which is detrimental toward CNT inception and growth.46,59 This point is observed by Diener et al.46 who conducted experiments on the role of medium and large hydrocarbons toward SWNT inception and growth in a premixed flame with an aerosol-type catalyst. It was observed that SWNT can be synthesized with ethylene and acetylene, but not with benzene. Incompatibility of benzene as a fuel for CNT synthesis in flame is further substantiated by Hall et al.<sup>56</sup> through experimental tests using ethyl benzene. In the experiment, fuel with a different chemical structure such as aliphatic (ethylene), aromatic (ethyl benzene), and oxygenated (ethyl alcohol) are compared for the tendency to synthesize CNTs. Hall et al. claimed that CNT inception and growth is inhibited in benzene flame due to early soot formation.<sup>56</sup> The aromatic rings readily present in benzene leads to rapid PAH formation and produce soot early in the flame reaction. Similar observations are made in recent experiments on CNT synthesis using an internal combustion engine. Only fuel mixed with alcohol that limits soot formation is able to produce CNTs.111,112 Tables 1-3 list the types of CNTs produced using several types of fuels with varied flame parameters. It is clear from the tables Table 1 CNT generated from different combinations of flame configuration, substrate-supported catalyst type, and fuel/oxidizer/diluent

	Catalyst	Substrate	Fuel/oxidizer	CNT structure	Ref.
Counter diffusion	Ni	Catalyst substrate	Ethanol/O <sub>2</sub> + N <sub>2</sub>	Varied MWNT morphology depends on O2 content	100
	Ni	Catalyst substrate	Ethylene/O <sub>2</sub> + N <sub>2</sub>	MWNT	94, 99 and
					114
	Ni	Catalyst substrate	Ethylene or methane/ $O_2 + N_2$	MWNT or CNO depends on O <sub>2</sub> content	98
	Ni	Catalyst substrate	Methane + ethylene/ $O_2$ + $N_2$	Curved and entangled MWNT	93
	Ni	Catalyst substrate	n-Heptane/O <sub>2</sub> + N <sub>2</sub>	MWNT and CNT depends on O <sub>2</sub> content	101
	Ni alloy	Stainless steel	Methane/air	Curved and entangled MWNT	76 and 92
	Ni alloy	Catalyst substrate	Methane/air	Entangled, small but uniform diameter MWNT	91
	Ni alloy	Catalyst substrate	Methane/air	Entangled, mostly large diameter MWNT	91
	Ni alloy	Catalyst substrate	Methane/air	Aligned MWNT, small diameter	91
	Ni alloy	Catalyst substrate	Methane + acetylene/ $O_2$ + $N_2$	MWNT, MWNT bundles, CNF	87, 89 and 90
Co-flow diffusion	Co	Stainless steel	Ethylene/air	Straight and uniform diameter MWNT	63
	Co and Ni	Molybdenum	Acetylene + $N_2/air$	MWNT	60
	Ni	Catalyst substrate	Ethanol/air	Disordered entangled MWNT	71
	Ni	Catalyst substrate	Ethylene/air	Vertically aligned MWNT	70
	Ni	Catalyst substrate	Ethylene + $N_2/air$	MWNT	77
	Ni	Stainless steel	Ethanol/air	MWNT	72 and 74
	Ni	Carbon fibre	Ethanol/air	MWNT (CNT direct grafting)	32-34
	Ni	Catalyst substrate	Methane/air	MWNT	78
	Ni	Catalyst substrate	Methane + ethylene + $N_2/air$	MWNT	115
	Ni, stainless steel, Ni alloy	Catalyst substrate	Ethanol/air	MWNT with CNF	69
	Ni alloy	Stainless steel	Methane/air	Entangled, curved, bundled of MWNT	62, 67 and 68
	Stainless steel	Catalyst substrate	Ethylene/air	Entangled and curved MWNT	63
	Stainless steel	Catalyst substrate	Ethylene/air	Entangled and curved MWNT	70
	Stainless steel	Catalyst substrate	Ethanol/air	MWNT	64 and 65
Inverse	Fe, Ni alloy	Catalyst substrate	Methane/air	Coiled and entangled MWNT	81
diffusion	Ni	Catalyst substrate	Ethylene + methane/ $O_2$ + $N_2$	MWNT, MWNT + CNO or CNO	85
	Ni	Stainless steel	Ethylene + $N_2/air$	MWNT and CNF	79 and 80
	Ni, Ni alloys	Catalyst substrate	Methane + $H_2/air$	MWNT and few layer graphene	110
Premixed	Со	Stainless steel	Ethane/air	MWNT	47 and 48
	Со	Stainless steel	Ethylene/air	MWNT	47, 48 and 53
	Со	Stainless steel	Acetylene/air	Mixture of MWNT and CNF	47 and 48
	Со	Stainless steel	Propane/air	MWNT	47 and 48
	Co alloy	Molybdenum	Acetylene/O <sub>2</sub>	Curved or straight MWNT	49
	Ni	Stainless steel	Ethyl alcohol or ethyl benzene or ethylene/air	Carbon nanomaterials, assumed to be MWNT	56
	Ni	Catalyst substrate	Ethylene/air/N <sub>2</sub>	MWNT	51, 54 and 55
	Ni	Stainless steel	Propane/air	Curved and entangled MWNT	57, 58 and 116
	Fe	Carbon fibre	Acetylene/O <sub>2</sub>	MWNT (CNT direct grafting)	35
	Stainless steel	Catalyst substrate	Ethylene/air	Curved and entangled MWNT and carbon nanomaterials	47 and 48

that the type of fuel plays a critical role in determining the produced CNTs morphology and yield.

Fuel type can significantly affect the yield and morphology of the synthesized CNT.<sup>103</sup> In a study using a pyrolysis flame, the combination of carbon monoxide (CO) and iron catalyst promotes SWNT formation with minimal presence of MWNT, whereas acetylene ( $C_2H_2$ ) with a similar catalyst produced an amorphous carbon with minimal presence of MWNT. The difference in the yield and morphology of the synthesized CNTs are a direct consequence of the unburnt C<sub>2</sub> hydrocarbon species such as acetylene, ethylene, ethane, and PAH presence in the flame.<sup>103</sup> As CO pyrolysis flame did not produce C<sub>2</sub> gas species and PAH, inception and growth of SWNT are initiated once the coagulated iron nanoparticles achieve a suitable size for SWNT formation.<sup>103</sup> Inadvertently, once the individual catalyst nanoparticles become SWNT growth sites, the catalyst nanoparticles will stop growing in size and inhibit the formation of MWNTs which require larger catalyst nanoparticles for nascent MWNTs

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Table 2	CNTs generated	using uncomm	on types of	f catalyst with	different flame	configurations	and fuel/	/oxidizer/diluen	t combinations
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Flame configuration	Catalyst	Fuel/oxidizer/diluent	Formation of carbon	Ref.
	Suturjet	r aci, chanler, anacht	Structure	
Counter diffusion	Co in AAO nanotemplate	Methane/air	Graphitized MWNT	76
Counter diffusion	AAO nanotemplate (no catalyst)	Methane + N <sub>2</sub> /air	Non-graphitized MWNT	92
Counter diffusion	No catalyst	Methane/O <sub>2</sub>	MWNT surrounded by soot	86
Co-flow diffusion	No catalyst	Methane + $H_2/air$	MWNT	75
Co-flow diffusion	Galvanized wire	Acetylene/air	Various carbon nanomaterials + MWNT and helical CNT	73
Co-flow diffusion	Galvanized wire	Methane/air	Mixture of MWNT, carbon filaments and nanorods	73
Co-flow diffusion	Galvanized wire	Propane/air	Bundled straight MWNT	73
Co-flow diffusion	Platinum	Ethylene/air	Minimal MWNT	70
Inverse diffusion	Spinel powders (CoAl <sub>2</sub> O <sub>4</sub> (Co), ZnFe <sub>2</sub> O <sub>4</sub> (Fe), NiAl <sub>2</sub> O <sub>4</sub> (Ni))	Methane + H <sub>2</sub> /air	Co and Ni based spinel powder produced MWNT only Fe based spinel powder produced both SWNT and MWNT	97
Premixed	CNT redeposited on SS plate	Ethylene + $N_2/air$	MWNT	55
Premixed	No catalyst	LPG/air	MWNT	117
Pyrolysis	Fe/Mo/Al <sub>2</sub> O <sub>3</sub>	CO/H <sub>2</sub> /He	MWNT	109

Table 3 CNTs generated using a gas-phase catalyst with different flame configurations and fuel/oxidizer/diluent combinations

Catalyst (catalyst delivery)	Flame configuration	Carbon source/oxidizer/ diluent	Formation of carbon structure	Ref.
Fe (powder evaporated by heating)	Pyrolysis	CO/H <sub>2</sub> /He	Mostly MWNT, with presence of SWNT	103
Ni (powder evaporated by heating)	Pyrolysis	Acetylene/H <sub>2</sub> /He	Mostly CNF, with presence of MWNT	103
Ni (powder evaporated by heating)	Pyrolysis	CO/H <sub>2</sub> /He	Mostly SWNT, with presence of MWNT	103
Ni or Fe (sublimed powder)	Premixed	Acetylene or ethylene/O <sub>2</sub>	SWNT with MWNT less than 5%	46
Co (inert gas bubbler through liquid reservoir)	Premixed	Acetylene or ethylene/O <sub>2</sub>	SWNT	46
Fe (inert gas bubbler through liquid reservoir)	Premixed	Acetylene/O <sub>2</sub> /Ar <sup>25,50</sup> Methane/O <sub>2</sub> /Ar <sup>24</sup>	SWNT	24, 25 and 50
Metallocene (not specified)	Diffusion	Acetylene or ethylene/air	SWNT – 10× yield using acetylene than ethylene	59
Fe + silicone or aluminum (inert gas bubbler through liquid reservoir)	Inverse diffusion	Ethylene/O <sub>2</sub> /N <sub>2</sub>	SWNT – 90% increase yield with additive	82-84
Co and Fe (sublimed)	Pyrolysis	Acetylene or ethylene or CO/ ( $H_2$ or methane)/(He or $N_2$ or $Ar$ )	SWNT – yield depends on fuel identity and presence of Ha	102
Ferrofluid, Fe nitrate, or Ni nitrate (nebulized solution)	Pyrolysis	Acetylene or CO/H <sub>2</sub> /Ar	SWNT with presence of MWNT	105
Fe (burning or ashless filter paper)	Pyrolysis	CO/H <sub>2</sub> /He	SWNT	107
Fe (sublimed)	Pyrolysis	CO or acetylene/H <sub>2</sub> /He	SWNT – CO yield more SWT than acetylene	108
Fe (nebulized solution)	Pyrolysis	Acetylene or ethylene or CO/ H <sub>2</sub> /He	SWNT yield depends on catalyst solvent	106
Fe + molybdenum (mixed in liquid fuel)	Premixed	Gas oil or dodecane + ethanol/air	MWNT	111 and 112

to be formed.<sup>103</sup> Whereas in  $C_2H_2$  pyrolysis flame, formation of a  $C_2$  gas species and PAHs in the pyrolysis flame creates inert graphitic deposits on top of catalyst nanoparticles that block

dissociative adsorption of carbon from occurring and impair the formation of nascent SWNT. Eventually, as the iron nanoparticles continue to coagulate and increase in size, some of the dissociative adsorption sites eventually open up to allow MWNT formation.<sup>103</sup> The analogous effect of  $C_2$  gas species and PAH are recorded when similar experiments are performed using a nickel catalyst instead of iron.<sup>103</sup> Other than that, Yuan *et al.*<sup>62,63</sup> observed that when a bulk catalyst metal is exposed in an identical flame with a different type of fuel, different types of oxides are produced. It was observed that the untreated nickel-chromium wire that was exposed to the methane diffusion flame produced nickel oxide nanoparticles with the presence of CNTs<sup>62</sup> whereas in an ethylene diffusion flame, the oxidation on the wire produced metal oxides together with amorphous carbon, indicating that the oxides produced in the ethylene flame are not suitable for the catalytic growth of CNTs.<sup>63</sup>

The combination of different fuels and catalysts also plays a role in CNT inception and growth in flame. For example, a methane flame produces CNTs on transition metals such as nickel<sup>76,81,92</sup> and iron,<sup>81</sup> or even without a catalyst,<sup>86</sup> but did not produce any CNTs using a cobalt catalyst.<sup>48</sup> Unfortunately, the actual reason behind the incompatibility of methane with cobalt catalyst to produce CNTs has not been further elaborated. Cobalt, however, is found to be a suitable catalyst for CNTs synthesis with various other types of fuel as shown in Tables 1–3. Interestingly, CNTs are successfully synthesized using a cobalt catalyst with methane as a carbon source in the CCVD process.<sup>19</sup>

Results from these experiments clearly established that the selection of fuel must be made based on careful overview of the hydrocarbon characteristics and other important parameters related to the CNT synthesis. In general, the selected fuel should have a low tendency to produce PAH and soot and have a preferable reaction with the selected catalyst towards CNT formation. While there are tendencies for certain types of CNT to be produced with certain combinations of fuel and catalyst, there is no conclusive correlation that can be made due to the limited literature available.

#### 2.3 Catalyst type and concentration

Transition metals are suitable to be used as catalysts in CNT synthesis due to their ability to catalytically decompose carbon molecules.<sup>118</sup> However, combination of additional characteristics of the transition metal such as melting temperature, carbon solubility, and carbon diffusion rate is the key determinant of its suitability as catalyst in the synthesis process.<sup>70,118</sup> The effectiveness of the selected metal catalyst is then a function of many other flame environment parameters such as temperature, gas-phase composition, and flame configuration. Thus, optimal selection of a catalyst is appropriate only for a set of experimental conditions, and may be ineffective in the others.

Similar to CNT synthesis using CCVD, transition metals that are used as catalysts in CNT flame synthesis can be in the form of pure metal<sup>24,97</sup> or metal oxides.<sup>50,76,84</sup> Depending on experiment conditions, CNTs growth are observed to have a preferential growth between pure metal and metal oxides, or it can grow on both pure metal and metal oxides in the same experiment setting. In an experiment of CNTs synthesis using a Fe based gas-phase catalyst in an acetylene premixed flame, Height et al.50 observed that metal oxides are the active catalyst for formation and growth of CNTs. However, when the experiment was replicated using a similar instrument by Wen et al.24 using a different fuel, methane, it was found that the pure metal is the active catalyst, even though metal oxides exist in the post flame region. In other experiments, both the pure metal and metal oxides are found to be catalytically active toward CNT formation and growth, with the former being found to produce more SWNT compared to the latter.84 Pure metal is less active toward CNT growth due to the lack of oxygen on the catalyst nanoparticles to enhance the breakup of C-H bonds.84 Another study suggested that a pure metal catalyst, such as Fe, has a higher surface carbon deposition rate compared to the internal diffusion rate, which results in the early oversaturation of catalyst particles that in turn caused a high rate of catalyst nanoparticles encapsulation,50 lowering its tendency to be an active CNT growth site. In contrast, the carbon deposition and the diffusion rate of the same metal oxides is balanced to provide conducive conditions for CNT formation and to allow the catalyst to be catalytically active for a longer period of time.84

Besides the preferential growth of CNT on pure metal or oxides, the composition of the metal catalyst also has significant effects on the CNT growth. In CCVD studies, the metal alloy catalyst is known to produce a higher CNT yield compared to pure metals. Physicochemical properties of binary and ternary alloy catalysts such as lower melting temperature and higher carbon solubility, compared to its pure metals counterparts, increase the catalyst reactivity toward CNT formation.<sup>118</sup> In flame synthesis, previous studies show similar trends of higher CNT yield in metal alloys compared to pure metals.<sup>110</sup> By comparing three types of Ni based alloys to a pure Ni catalyst in an inverse diffusion flame, it was found that the former yields a higher amount of CNTs with a broader temperature range of growth compared to the latter.<sup>110</sup> In another experiment, Xu et al. compared synthesis results of a binary (Ni/Cu) and ternary (Ni/Cr/Fe) alloy catalyst and found that the latter produces CNTs with a higher diameter uniformity and alignment.<sup>81</sup> A metal alloy surface is more susceptible to carbide induced breakup compared to pure metal as the grain boundaries are more inclined to carbon uptake and carbide formation due to weak bonds,110 which is an important characteristic for the catalyst. A detailed review on the formation of catalyst nanoparticles through surface induced breakup process is presented in the next subsection. Nevertheless, metal alloys are not always the best option if other types of metal are considered. Arana et al. reported that pure Ni yielded a higher volume of CNTs compared to that of stainless steel mesh with 74% Fe/18% Cr/ 8% Ni composition, which only produce CNF.<sup>70</sup> Even though this result is contradictory to earlier observations,<sup>110</sup> it reveals the significant roles played by the catalyst carbon solubility and diffusivity rate in determining the yield of the synthesized CNTs.<sup>70,118,119</sup> Carbon solubility of a pure metal is proportional to the temperature and inversely proportional to the particle diameter.118 Hence, a smaller Ni particle compared to Fe caused the former to have a higher carbon solubility compared to the latter. In turn, the former becomes supersaturated faster than the latter. Due to similar diffusivity rates of the two catalysts,

more carbon diffuses through Ni to produce a higher CNT yield compared to the Fe alloy. $^{70}$ 

Fundamentally, CNT synthesis in flame can be performed without the presence of a catalytic material. MWNT has been observed to be synthesized together with soot and other carbonaceous materials in the absence of a catalyst element in a premixed flame.<sup>120,121</sup> Uncatalyzed CNT synthesis in flame is not only found in a controlled environment, but can also be found in domestic propane/natural gas flame<sup>117,122</sup> and in an internal combustion engine exhaust.<sup>123</sup> Development of the uncatalyzed flame synthesis has been made using a counter diffusion configuration of the oxy-methane flame.<sup>86,88</sup> However, this method of producing MWNT has not been further pursued, presumably due to the low yield and lack of control over the characteristics of the produced CNTs.

Generally, the gas-phase and the substrate supported catalyst delivery system were observed to produce SWNTs and MWNTs respectively, though several studies show contradictory observations. SWNTs are synthesized alongside MWNTs using a substrate supported spinel powder (ZnFe<sub>2</sub>O<sub>4</sub>),<sup>97</sup> while in other experiments,46,103,105,111,112 MWNTs are synthesized using a gasphase catalyst. Gas-phase catalyst delivery provides finer catalyst nanoparticles compared to the substrate supported ones. Formation of SWNTs and MWNTs requires the catalyst nanoparticles to be within a certain range of sizes, with SWNT requiring much smaller sizes.97 Often, the gas-phase catalyst nanoparticles are small enough for SWNTs to form. Once inception and growth of SWNTs occurred on these catalyst nanoparticles, MWNT growth was inhibited.97 Whereas, the substrate supported catalyst nanoparticles commonly provides large catalyst nanoparticles that are unsuitable for SWNT formation, allowing the formation of MWNTs.<sup>124</sup> Nevertheless, the ability for substrate supported catalysts to synthesize SWNTs is well documented in the CCVD process through various wet catalyst preparation processes which produce finesized catalyst nanoparticles with a high catalyst density on the substrate.<sup>124,125</sup> The ability to organize the catalyst particles in the nanoscale allows researchers to formulate optimum spacing between SWNTs for highly efficient growth.<sup>126</sup> However, this catalyst preparation technique has yet to be applied in CNT synthesis in the flame environment.

To organize the large number of experiments reviewed in this section, the next two subsections will be separated into two main groups, MWNT synthesis using substrate supported catalysts, and SWNT synthesis using gas-phase catalysts.

**2.3.1** Synthesis control using substrate supported catalyst. Tables 1 and 2 list common and uncommon catalysts used for MWNT synthesis in flame, respectively. Based on Table 1, pure nickel and nickel-based alloys are proven to be very catalytically active in producing MWNTs and are often used in experiments. The nickel-based catalyst is found suitable in all flame configurations with different types of hydrocarbon fuels. Other common transition metals that have been used are cobalt, iron, and their alloy variants. These common metal catalysts have melting temperatures below ordinary flame temperature, high carbon solubility, and a high diffusion rate, which makes them catalytically active towards CNT formation in a flame

environment. A combination of these characteristics is crucial for metal catalysts in flame environments. Other transition metals are not suitable catalysts in flame synthesis, such as copper despite having a low melting temperature, because it has a low carbon solubility that limits the carbon diffusion and precipitation process.

The type of catalyst plays a significant role in determining the morphology of the synthesized CNTs.<sup>91</sup> Observation of the CNTs synthesized at the same location using different metalalloy catalyst probes in a methane counter-flow diffusion flame shows that each type of catalyst produced CNTs with distinct morphology as show in Fig. 2(a-c). A binary alloy probe with Ni/Cu and Ni/Cr content produced entangled CNTs that covered the catalyst probe with CNTs; on the former alloy these were relatively smaller and much more uniform diameter than the CNTs on the latter. Whereas the CNTs synthesized on a trinary alloy probe Ni/Cr/Fe are entangled with uniform diameter, but growing outwardly from the probe surface with a layer of catalysts at the top of the CNTs.<sup>91</sup> This is the result from the combination of numerous factors related to the catalyst properties such as carbon solubility, alloy elemental composition, and melting temperature.<sup>91</sup> In practice, due to the multiple parameters that play roles in determining the morphology of the synthesized CNTs, experimental testing is a crucial step to determine the suitability of the selected catalyst in any flame synthesis application.

Control over the deposited catalyst nanoparticles size on top of the supporting substrate has been pursued using several methods, such as: periodic reverse pulse plating,<sup>71</sup> catalysts in the form of spinel powder,97 and a controlled pre-oxidizing process using a strong acid.64,65,67-69,76,92 In periodic reverse pulse plating, the size of the catalyst nanoparticles is controlled by adjusting the output pulse frequency and duty cycle.<sup>71</sup> While in application of the catalyst in the form of a spinel powder, the atomic arrangement of the spinel powder allows for well-spaced nanoparticles with limited size to form when exposed at an appropriate temperature.97 Using a spinel powder, the formation of the SWNT and MWNT diameter can be controlled within a 20 nm range.97 The size variation is due the size distribution of the catalyst nanoparticles once reduced in a flame environment.97 In the method of controlled pre-oxidizing using a strong acid, the exposure time of the catalyst metal to the strong acid is the determining parameter that produces the desired size, density, and uniformity of the catalytic nanoparticles on the surface of the metal catalyst.76,92 Insufficient exposure and over



**Fig. 2** FESEM images of CNTs produced with different transition metal alloy compositions in a methane seeded acetylene counter diffusion flame. Metal alloy composition: (a) 45% Ni/55% Cu (b) 80% Ni/20% Cr (c) 60% Ni/16% Cr/24% Fe. Adapted from Xu *et al.*<sup>91</sup>

exposure in strong acid will lead to sparse and oversized catalyst particles, respectively.<sup>64,65</sup>

Other than the general practicality of using a substrate supported catalyst, substrate supported catalysts also allow for better observation of the fundamental mechanism of the CNT inception and growth in the flame environment. The minimization of agglomeration and coalescence of catalyst nanoparticles provides a clear path in understanding the effects of the catalyst and local flame characteristic on CNT growth. Catalyst particles are deposited on the substrate surface through various coating method such as physical vapour deposition (PVD),47,48,53 ultra-sonication,97 nano-sized catalyst powder coating,<sup>58</sup> pulsed controlled plating method,<sup>71</sup> and electro-deposition.49,63,66 These methods allow some degree of control over the nanoparticle size and uniformity. Often, the deposited catalyst creates a strong bond with the metal support, leading to CNT base growth formation.<sup>27</sup> Apart from the catalyst deposition method, catalytic nanoparticles can also be prepared on a bulk pure metal through grinding and polishing,71,110,127 metal pre-etching with strong acid<sup>64,65,67–69,76,92</sup> or surface/ carbide-induced breakup.27,110 The grinding and polishing technique and the pre-etching process create metal oxides or carbide nanoparticles on the metal surface. In the surface breakup method, the catalytic nanoparticles are produced when the substrate metal is exposed to a hydrocarbon-rich flame. Initially, a carbide layer will be formed on top of the exposed substrate metal catalyst due to sufficient dissolved carbon concentration from the carbon rich environment. The carbide layer then will induce localized stresses on the surface region due to lattice mismatches between the carbide phase and the underlying metal. Surface breakups will then occur along the grain boundaries and other surface faults, forming a wide range of catalytic particles in terms of shape and size.48,110

The catalyst nanoparticles formed through metal grinding and polishing or the surface breakup mechanism will lead to a tip growth mechanism where the catalytic nanoparticles are detached from the substrate surface and positioned at the tip of the growing CNT due to weak metal support bonding.48,128 Moreover, due to the heterogeneity of the formed catalyst nanoparticles, carbonaceous structures produced will also have a high degree of variation in terms of structure and size. In the surface breakup method, the synthesized CNTs are observed to have preferential growth on certain locations. Most of the CNTs will grow on surface-breakup-prone locations, such as on the mesh cross wire where mechanical stressing through the wire weaving process produced a strained and relatively brittle surface.48 Besides that, some of the formed defects and other surface asperities due to the surface breakup process will inadvertently act as various types of catalyst producing carbonaceous structures.48 Hence, CNTs produced using these types of supported catalysts are commonly known to have lower quality and purity.

Morphology comparison of the synthesized CNTs using a supported catalyst with the pre-deposited method and surface breakup catalyst nanoparticles were compared in an experiment using cobalt coated and uncoated stainless steel wire mesh.<sup>48</sup> The pre-deposited cobalt catalyst is dominant in directing CNT growth, producing highly uniform CNT with a high density through the base growth model as shown in the TEM image in Fig. 3(b). While on the bare stainless steel mesh, various types of carbonaceous structure in shape and size are produced, a clear indication of catalyst nanoparticles formation through the surface breakup mechanism (Fig. 3(a)). However, the observations of pre-deposited catalyst are only valid up to a certain flame equivalence ratio. Once the flame reaches a certain equivalence ratio threshold, the pre-deposited catalyst produced CNTs that exhibited similar characteristics of heterogeneity to that of those produced using bare stainless steel mesh.48 This is caused by an oversupply of CO in a highly rich flame, which led to coking and subsequent catalyst poisoning.48,129 Subsequently, it will induce formation of a carbide layer on top of the "poisoned" pre-deposited catalyst and initiate the surface breakup process. Eventually, a myriad of catalyst nanoparticles of varying shape and size will be formed on top of the surface and produce similar types of CNTs as on the bare stainless steel mesh.48 Therefore, control over the flame parameters such as the equivalence ratio (for the premixed flame) is crucial to manipulating the characteristics of the CNTs produced from the synthesis process.

Besides the common transition metals mentioned earlier, researchers have also tested several other materials such as platinum (Pt),<sup>70</sup> galvanized steel wire mesh,<sup>73</sup> transition metals in spinel powder forms,<sup>97</sup> purified carbon nanotubes,<sup>55</sup> and silicon based porous anodic aluminium oxide (AAO nanotemplate)<sup>66,76,92</sup> as listed in Table 2. In an experiment using pure Pt as a catalyst in an ethylene diffusion flame, it was observed that Pt is relatively inactive towards CNT growth in flame. This is due to its melting point at 2045 K, which is higher than the local flame temperature which inhibits initiation of the surface breakup process.<sup>70</sup> Pt has previously been recorded as being successfully used as a catalyst in CNT synthesis using the arc discharge method, which operates at a much higher temperature compared to that of the flame environment.130 While galvanized steel is used by others to synthesize CNTs in a diffusion flame using three different types of fuel, such as methane, propane, and acetylene.<sup>73</sup> Due to the zinc coating on



Fig. 3 TEM image of carbon nanotubes synthesized on (a) stainless steel wire mesh without a catalyst deposit (b) Co coated stainless steel wire mesh, in an identical flame (ethylene,  $\emptyset = 1.62$ ).<sup>48</sup> Reprinted with permission from *J. Phys. Chem. B*, 2002, **106**(51), 13122–13132. Copyright 2002 American Chemical Society.

the galvanized steel, the CNTs were successfully synthesized in flame using all three types of fuels with various shapes and sizes, as expected from catalyst nanoparticles formed through the surface breakup mechanism. Memon et al.97 introduced a method of creating transition metal catalytic particles on substrates using an ultra-sonicated spinel powder on top of the copper substrate, which was then exposed to a  $H_2$  flame for 10 minutes. The formed catalytic nanoparticles were evenly spaced with a uniform size. As a result, this is the only known CNT synthesis experiment using a supported catalyst method that was able to produce SWNTs.97 In another experiment, Woo et al.55 discovered that cleaned and purified CNTs harvested from flame synthesis can be used as a catalyst by depositing it on top of a stainless steel disc substrate. It was observed that the CNTs produced on top of the deposited CNT were much thicker, straighter, and contain less metal particles compared to the CNTs synthesized using Ni as the catalyst in the same flame environment. Among these uncommon catalysts, silicone based porous anodic aluminium oxide (AAO nanotemplate) is found to be most the efficient method of synthesizing vertically aligned, high quality, and well-controlled CNT properties.<sup>66,76,92</sup> Even though non-graphitized CNTs can grow on silicon based AAO nanotemplate without a catalyst, electrodeposited cobalt catalyst at the bottom of each nanotemplate enhances the production of CNT and produces well-graphitized CNT.66 More details regarding the nanotemplate utilization in flame synthesis are discussed in Section 3.2.

2.3.2 Synthesis control using a gas-phase catalyst. In brief, the process of CNT synthesis in flame using a gas-phase catalyst starts with a catalyst in the form of a solid (powder), liquid, or dissolved in solution. The catalyst vapour is created either through sublimation of the powder, an inert gas bubbler through the liquid, or nebulization and continuous supply into the flame through the fuel stream. A schematic interpretation of CNT inception and growth in flame using a gas-phase catalyst is illustrated by Height et al.<sup>50</sup> in Fig. 4. Once the catalyst vapour is introduced into the flame, the catalyst nanoparticles are formed through thermal-decomposition of the catalyst element. Nucleation of the catalyst nanoparticle starts as the catalyst vapour becomes supersaturated, and continues to increase in size through coagulation or agglomeration with other catalyst nanoparticles.<sup>131</sup> As the catalyst nanoparticles grow in size, hydrocarbon decomposition and deposition start to occur. Simultaneously, carbon diffusion and precipitation through the catalyst nanoparticles leads to the inception and growth of SWNTs once the catalyst nanoparticles reach a suitable size. The multiple-steps of the synthesis processes occur very fast, in a highly complex and transient flame environment.<sup>59</sup> The use of a gas-phase catalyst leads to the transformation of the bare catalytic particles from one end of the flame to the inception of CNT on the other within milliseconds, with the time scale being dictated by the buoyancy driven flow of the flame.<sup>105</sup> Thus, accurate determination of the growth rate, or even observation of SWNT growth through the flame posed significant challenges to the researchers.

Catalytic nanoparticles required for SWNT formation are produced through decomposition of organometallic materials.



**Fig. 4** Illustration of the multiple-step synthesis process of SWNTs using a gas-phase catalyst in a premixed flame. This illustration represents an experiment performed by Height *et al.* acetylene/oxygen/15 mol% Ar premixed flame with  $Fe(CO)_5$  vapour as the catalyst. The top part represents each process region. The luminous flame zone is represented by the grey band at around 5 mm height above the burner (HAB). Adapted from Height *et al.*<sup>50</sup>

Iron, nickel, and cobalt based metallocenes are the commonly used gas-phase catalysts in SWNT synthesis in flame, as shown in Table 3. These are similar metals that are commonly used in the substrate supported synthesis process. Even though the catalyst delivery method into the flame is different than the substrate-supported catalyst system, the growth mechanism of CNTs are similar between the two. Hence, the same physicochemical characteristics of these transition metals applies to both modes of catalyst delivery. Furthermore, decomposition of ferrocene, nickelocene, and cobaltocene at low temperatures below 700 K allows the formation of metallic particles within the flame environment prior to the onset of soot formation.<sup>102</sup> As shown in Table 3, only iron and cobalt consistently produce SWNT as a gas-phase catalyst. Nickle as gas-phase catalyst is found to produce mostly MWNT, with minimal SWNT formation in a CO based flame.<sup>103,108</sup>

Vander Wal observed that SWNT inception and growth within the flame environment using a gas phase catalyst is highly sensitive toward catalyst nanoparticles size. This phenomenon is described as size dependent reactivity,<sup>103</sup> which requires the nanoparticles to be within a certain range or size smaller than the ones for MWNT.<sup>103,107,132,133</sup> Interestingly, the size dependent reactivity is more prevalent in the flame environment compared to CCVD. The limited time scale or the incompatible gas composition are reported to be the reason why only SWNT is synthesized alongside inactive, large catalyst nanoparticles in gas-phase catalyst flame synthesis.<sup>107</sup> When a similar combination of carbon source and catalyst is used in

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a CCVD process, the catalyst is capable of producing SWNT, MWNT, or a combination of both depending on the sizes of the catalyst nanoparticles.<sup>107,134–136</sup> Even though SWNT is known to grow only on catalysts sized between 4 to 8 nm in CCVD,<sup>137,138</sup> the larger catalyst nanoparticles are active toward MWNT formation and growth, or other carbonaceous structures.<sup>127</sup>

Using the gas-phase catalyst method, CNTs yield can be controlled through the manipulation of the catalyst concentration, which is not possible through the substrate-supported catalyst system. Vander Wal and Hall<sup>108</sup> observed that there is an optimum concentration of gas-phase catalyst for each set of flame synthesis parameters. Excess catalyst concentration caused a high rate of catalyst nanoparticles encapsulation, producing a lower yield and short SWNTs.24,108 Decomposition of the metallocene as a catalyst in flame produces cyclopentadiene which is an intermediate species for the formation of PAH.<sup>108</sup> Therefore, an increase in metallocene concentration will magnify PAH formation and amplify its detrimental effect toward CNTs inception and growth. This is a significant problem, especially for metallocenes that have a relatively small molecule size such as nickelocene. Since metallocenes are not catalytically active until reaching a certain size, nickelocene requires five times more molecules compared to ferrocene to form a catalytically active nanoparticle.<sup>108</sup> Hence, application of a nickelocene gas-phase catalyst requires a far higher concentration compared to the other metallocenes which inadvertently magnifies the formation of PAH.<sup>108</sup> This may be one of the factor behind the minimal yield of SWNTs using a nickelocene gasphase catalyst in the flame environment. In addition, over concentrated catalyst nanoparticles also increase the chance for subsequent mass addition and size increment of the catalyst nanoparticles, even after inception and growth of SWNTs.<sup>108</sup> This condition can occur through condensation of carbon atoms or clustering on the exposed sites on top of the catalyst nanoparticles, or through mass addition from carbon atoms that have migrated along the walls of SWNTs to the catalyst nanoparticle.139 This is detrimental toward SWNT growth as once a SWNT is formed on the catalyst nanoparticle, the SWNT diameter is fixed and any changes on the diameter of the catalyst nanoparticle will subsequently deactivate SWNT growth.140 On the other hand, deficient catalyst concentration will only cause less SWNTs to be produced due to a reduced number of catalytically active nanoparticles available.108

Gas-phase catalyst nanoparticles can also experience sintering, coalescence, and solidification that eventually produce large, inactive catalysts toward SWNTs formation.<sup>131</sup> Molecular dynamic simulation reveals that intensive sintering process is predicted to occur on iron catalyst nanoparticles within the vicinity of highest temperatures in flame.<sup>131</sup> This may contribute to the formation of large, inactive iron nanoparticles that are commonly synthesized together with SWNT in flame synthesis.<sup>107</sup>

The majority of the literature available on SWNT synthesis in flame using a gas-phase catalyst focuses only on experimental observation and the fundamental understanding of the CNT synthesis process, such as feasibility of the proposed methodology, the yield, and morphology of the synthesized CNTs. Through these limited resources, it can be established that the catalyst selection has a limited role in determining the morphology of the synthesized SWNT, but has considerable influence over the SWNT yield and growth rate. However, it is obvious that the experimental works carried out by the researchers related to CNT synthesis in flame using a gas-phase catalyst are only scratching the surface of a very complex multidisciplinary problem. There are numerous aspects of the technique that are yet to be explored. Nevertheless, there is a significant momentum going forwards and future break-throughs in this technology will have significant impact as they will provide an incredibly efficient, high speed CNT synthesis production for highly demanded SWNTs.

#### 2.4 Catalyst residence time

Various effects of residence time toward synthesized CNTs vield and morphology have been reported previously, especially in the area of substrate supported catalyst flame synthesis. Different combinations of fuel, catalyst, and flame configuration induced different effects on the residence time towards the synthesized CNT. Yuan et al.<sup>62,67,68</sup> observed that in a methane diffusion flame with a Ni-Cr-Fe wire catalyst, the increase in residence time increases the MWNT yield but did not affect the synthesized CNTs morphology. However, when ethylene is used, the CNTs length increased with residence time during the first minute of exposure before it stopped and was followed by an increase in diameter.63 Further exposure eventually converted the synthesized CNT to a solid nanofiber.63 When similar fuel and catalyst (methane fuel, Ni-Cr-Fe catalyst) are used in an inverse diffusion flame, the increase of residence time produced longer CNTs, but did not affect the overall yield.<sup>81</sup> Other experiments observed the change in yield or morphology with the change in residence time. Studies by Pan and colleagues show an increase in yield of CNTs with the increase of residence time using an ethanol diffusion flame with a pretreated stainless steel mesh.<sup>64,65</sup> Similarly, in a recent experiment using a counter diffusion flame, CNT yield increase is observed with a longer exposure time from 30 to 90 seconds. However, a significant decrease in yield is observed at residence times longer than 90 seconds.<sup>101</sup> While in another experiment, both the diameter and length of the synthesized CNTs were observed to change with an increase in residence time using a diffusion flame with a galvanized steel as a supported catalyst.73 In experiments using a counter diffusion flame, the change of CNTs morphology was observed at varying strain rate.92,99 In the context of residence time, the increase in strain rate results in an increase in the carbon precursor flow rate while reducing the residence time of the precursors on the CNTs growth site.99,100 Despite varying observations on the effects of the residence time on the catalytic growth, the significant changes in the yield and the morphology suggested that residence time is one of the most important parameters that needs to be monitored during synthesis using a substratesupported catalyst.

The control over the residence time in SWNT synthesis using a gas-phase catalyst does not result in any significant effects as in MWNT synthesis using a supported substrate. This is due to the buoyancy accelerated convection and short residence time experienced by the aerosol-based catalyst in a flame environment.<sup>105</sup> Even though the adjustment of the HAB of the CNT collection point changes the residence time, the change in temperature shows more dominant effects. A previous study showed that as the residence time of the catalyst nanoparticles increases by a mere 0.06 second, the temperature difference that is experienced by the catalyst nanoparticles is about 1000 K.<sup>59</sup>

# 2.5 Gas phase composition and temperature distribution within the flame

Gas phase composition and temperature are two interrelated important parameters in flame CNT synthesis. The exothermic combustion process simultaneously creates the carbon bearing gas phase precursors and the thermal energy required for the CNT synthesis process to occur. CNTs synthesis process in flame have been recorded to occur within a wide range of temperatures from around 500 °C to 1300 °C. Therefore, most experimental works have been focused on creating an optimum gas phase composition, while the suitable temperature is obtained by probing the location with a suitable temperature in the vicinity of the flame. This subsection compiles together a review on the gas phase composition, temperature, and inert diluent effect over synthesized CNTs. Interrelation of these parameters must be acknowledged in the observation of the individual parameter effect towards the synthesized CNTs. An exception applies to pyrolysis flame, where the temperature can be controlled quite independently from the carbon precursor composition.102-109

Gas phase composition in flame is controlled through regulating the fuel and oxidizer ratio. Depending on the flame configuration, the equivalence ratio  $(\varphi)$ ,<sup>24,25,46–48,50–57</sup> stoichiometric mixture fraction  $(Z_{\rm st})$ , <sup>82–84</sup> fuel/oxidizer percentage75,86,88,93,99 or ratio63,67 has been used in the literature. Using different concentrations of fuel or oxidizer, rich flames are established to ensure a sustainable supply of carbon to promote CNT growth through incomplete combustion of the hydrocarbons.<sup>50</sup> In most cases, there is an optimum level of carbon concentration producing a maximum CNT yield. The effect of the gas phase composition in flame is reviewed in the next subsection. In addition, the utilization of inert gas has also been proven to be useful in producing an optimum flame for CNT synthesis by diluting the fuel or the oxidizer. Interestingly, inert gas thermal capacities also have a significant effect on synthesized CNTs by altering the temperature distribution within the flame.<sup>102</sup> A review of the effect of inert gas diluent toward synthesized CNTs is presented in subsection 2.5.3.

The temperature within the flame cannot be controlled independently. However, it can be manipulated by changing the sampling location within the flame, or through dilution/ increasing concentration of fuel, oxidizer, or inert diluent. Any changes in terms of fuel/oxidizer/diluent concentration fundamentally change the gas composition at the sampling position, which may obscure the actual correlation between the effects of temperature toward the synthesized CNT. Hence, most of the observations made regarding temperature effects in flame synthesis must be viewed as a combination of effects of temperature and gas phase composition in a certain location within a flame. These observations are reviewed in subsection 2.5.2.

2.5.1 Importance of CO and H<sub>2</sub>. The effects of gas composition of the flame on CNT yield was first studied by Vander Wal using a premixed flame with different fuels, after predicting the gas composition using an equilibrium calculation.<sup>47,48</sup> A clear correlation was observed between the concentration of CO and H<sub>2</sub> towards CNT yield leading to the conclusion that CO is the main carbon source for the CNTs growth process.47,48 Later, Gopinath and Gore<sup>53</sup> revisited the claims by Vander Wal by performing MWNT synthesis using a similar premixed flame setup. The authors argued that even though detailed chemistry calculations supported the correlation of the importance of CO as the main carbon source compared to the other  $C_2$  species, Vander Wal did not consider the overall measurement of the deposited carbonaceous materials in the process. The authors claim that there is a possibility that a higher concentration of CO only contributed towards the increased formation of amorphous carbon, while the carbon for the CNTs growth were supplied through the other C2 species. In the experiment, Gopinath and Gore used a detailed chemistry calculation based on a one dimensional premixed flame code with post flame heat loss to assess the assumption of the water-gas equilibrium used in Vander Wal experiments. There is a clear indication that points towards the C2 species playing a significant role in CNT growth. Approaching the maximum CNTs yield equivalence ratio, the unburnt C<sub>2</sub> hydrocarbon species and CH<sub>4</sub> mole fraction increases by up to 10 and 6 orders of magnitude respectively, relative to the hydrogen mole fraction which is qualitatively parallel to the increase in CNT yield. In the same instance, the increase in CO and H<sub>2</sub> concentrations are continuous and monotonic.53 Even though the results are inconclusive due to small amounts of CNTs generated in the experiment, they demand further evidence to be found on the actual mode of carbon delivery to CNTs in the flame environment. Interestingly, Gopinath and Gore also observed that the water-gas shift reaction is not at equilibrium in the range of equivalence ratio suitable for CNT growth, which contradicts the main assumption in Vander Wal's experiments.47,48 Nevertheless, in general, most literature agrees on the importance of CO and H<sub>2</sub> composition in post flame gas composition to the growth. More recent work by Wen et al.24 reiterates the importance of CO, C<sub>2</sub>H<sub>2</sub>, and CH<sub>4</sub> as a carbon source for CNTs, although CO is assumed to be more important as it has the highest concentration in the post flame gas composition.<sup>24</sup>

Within the flame environment, CO is likely to be the source of carbon through two mechanisms; the Boudouard reaction and the hydrogenation reaction<sup>141</sup> which are shown in eqn (1) and (2) respectively.

$$2\mathrm{CO}_{(\mathrm{g})} \leftrightarrow \mathrm{C}_{(\mathrm{s})} + \mathrm{CO}_{2(\mathrm{g})}, \Delta H = -171 \text{ kJ mol}^{-1} \tag{1}$$

$$CO + H_2 \leftrightarrow C_{(s)} + H_2O, \Delta H = -131 \text{ kJ mol}^{-1}$$
(2)

#### Review

Geurts and Sacco<sup>141</sup> reported that the Boudouard (disproportionation) and hydrogenation (reduction) reactions are the main reactions for carbon deposition and carbide formation on Fe and Co foils at a temperature around 900 K. Furthermore, Moisala *et al.*<sup>118</sup> stated that, based on the thermodynamic equilibrium at normal pressure, ideal temperature for CO disproportionation is around 800 to 1100 K, which is within the same range where most CNTs are synthesized in the flame environment.

In flame synthesis using a substrate supported catalyst, the presence of molecular hydrogen  $(H_2)$  is crucial in regulating the carbon supply rate onto catalyst nanoparticles. In the case of excessive carbon supply, H<sub>2</sub> competes for adsorption sites on the catalyst surface, slowing the CO adsorption and subsequently balancing the carbon supply.<sup>142-144</sup> A balanced carbon supply and solvation rate promote a longer catalyst life and aid the formation of uniform CNTs on the pre-deposited catalyst. In the elevated temperature environment in flames, H<sub>2</sub> co-adsorbs and readily dissociates on the catalyst surface.48 These hydrogen molecules then combined with elemental carbon and other hydrocarbon fragments to fulfil valences thereby weakening the intermolecular bond while strengthening the metal-carbon bond.<sup>48</sup> H<sub>2</sub> also helps to etch formation of amorphous carbon on the catalyst surface and possibly reduces surface carbide back to its element.48

However, if the  $H_2$  concentration on the surface of the catalyst is too high, the reverse effect of balancing the carbon diffusion and solvation will occur and  $H_2$  will flood the catalyst surface and inhibit CNT growth.<sup>142–144</sup> The high concentration of  $H_2$  also promotes formation of PAHs which is detrimental toward CNT inception and growth.<sup>60</sup> Whereas in the case of insufficient  $H_2$  concentration, a carbide layer is formed due to overloading of the carbon supply, consequently initiating the surface breakup process which leads to creation of heterogeneous CNTs with a combination of tip and base growth.

The effects of CO and H<sub>2</sub> concentration on synthesized MWNT morphology and yield in a premixed flame with a substrate supported catalyst was tested by Vander Wal, Hall, and Berger.47,48 The desired CO and H2 concentration were achieved using various types of fuel with different equivalence ratios. As H<sub>2</sub> concentration increases at a fixed CO concentration, the yield and the tube length increases while the diameter of CNT and the relative yield of other nanostructures decreases.47,48 When H<sub>2</sub> concentration further increases, the CNT diameter started to increase though the uniformity, yield, and quality remain unchanged.47,48 These results are consistent with the chemical and physical effects expected from H<sub>2</sub> as mentioned earlier.48 In SWNT synthesis using the gas-phase catalyst, Vander Wal et al.<sup>102</sup> observed the decrease of CNT yield with high H<sub>2</sub> concentration. This is caused by the catalyst dilution effect which may be more dominant in synthesis processes using the gas-phase catalyst.

At fixed  $H_2$  concentration, the low CO concentration in flame produces a wide variety of solid, contorted, and non-graphitic nanostructures, without CNTs (Fig. 5(a)).<sup>47,48</sup> As CO concentration increases to an optimum level, longer, thinner, and much more uniform MWNTs are produced in higher quantity



Fig. 5 SEM images of carbon nanotubes morphology as CO concentration increases (at nearly constant H<sub>2</sub> concentration) (a) ethane flame (CO mole fraction = 0.0699) (b) ethylene flame (CO mole fraction = 0.145).<sup>48</sup> Reprinted with permission from *J. Phys. Chem. B*, 2002, **106**(51), 13122–13132. Copyright 2002 American Chemical Society.

(Fig. 5(b)).<sup>47,48</sup> However, supply of CO above the optimum concentration results in production of nano-filaments that consisted of solid nanofibers and hollow CNTs with a low degree of graphitization (Fig. 5(c)). A combination of base and tip growth is observed due to the formation of catalytic nanoparticles by surface breakup.<sup>47,48</sup> In SWNT synthesis using a pyrolysis flame with a gas-phase catalyst, Vander Wal *et al.*<sup>102</sup> observed that SWNT length increases with the increase of CO concentration, while the yield is unaffected. As a general rule, CO concentration has to be kept below the soot formation limit.<sup>56</sup>

Vander Wal found that the equivalence ratio ( $\varphi$ ) has a significant impact on the morphology and yield of CNTs as it directly affects the post flame gas composition.48 Furthermore, there is a clear range of suitable  $\varphi$  according to the different types of fuels used in a premixed flame, for example ethane (1.52-1.62), ethylene (1.62), acetylene (1.52-1.83), and propane (similar observation as per ethane and ethylene).47,48 Similar observations were also made later by Height et al.50 using an acetylene/oxygen/argon premixed flame doped with ironpentacarbonyl as the gas-phase catalyst. Height et al. observed CNT growth at  $\varphi$  from 1.6 to 1.8, with an optimum yield of SWNT at a  $\varphi$  around 1.6 to 1.7. Formation of discrete particle and soot-like structures at a low and high limit of equivalence ratio was observed.<sup>50</sup> A similar effect of  $\varphi$  has also been observed in later works by Gopinath and Gore<sup>53</sup> and Hall et al.<sup>56</sup> using a premixed flame. In a recent experiment, Chong et al. managed to synthesize CNTs at  $\varphi$  up to 2.2 in a premixed flame, but noted that  $\varphi$  1.8 to 2.0 produced higher quality, well-graphitized CNTs.58 In another experiment, Unrau and co-workers utilized a stoichiometric mixture fraction  $Z_{\rm st}$  to observe the effect of gas composition on CNT growth in an inverse diffusion flame using a gas-phase catalyst.<sup>82-84</sup> By performing the experiment using three pre-set  $Z_{st}$  (0.69, 0.74, and 0.85), it was found that the optimum SWNT growth is at  $Z_{\rm st} = 0.74$  but SWNTs with a smaller diameter are synthesized with decreasing  $Z_{\rm st}$ .<sup>84</sup> Variations of fuel concentration around 1.2% has a significant impact on the diameter of the synthesized CNT.82 In a recent experiment, Hu et al. used a heptane diffusion flame in a stagnation-point liquid-pool system, and observed that CNTs are synthesized at a lower oxygen concentration near to flame extinction. While at a higher oxygen concentration, formation of soot leads to synthesis of carbon nano-onions only.101

2.5.2 Effect of temperature. Due to relatively limited literature available in flame synthesis, extensive research on the related topic in CCVD process is used as a basis to understand the temperature influence on CNTs yield and morphology.145,146 The effect of temperature can be clearly observed in the CCVD method as it allows for the temperature to be controlled independently of other parameters. Experimental results shows that temperature has a significant influence on CNT yield,  $I_{\rm D}/I_{\rm G}$  ratio (ratio of the intensity of D-Raman peak and G-Raman peak), CNT diameter, and overall CNTs morphology.145-147 In terms of CNT yield, it is common for a CCVD synthesis experiment to have an optimal temperature that produces the highest CNT vield. This optimal temperature however is valid only for the specific setting of the CCVD synthesis process. Any changes to other parameters, such as the type or the concentration of the carbon source or catalyst, will result in the process having a different optimal temperature.145-147 CCVD experimental results show a trend of decreasing  $I_{\rm D}/I_{\rm G}$  ratio values with increasing synthesis temperature. However, this trend will stop at a certain threshold temperature which is not correlated to the high limit of the optimal temperature range.145,146 The effect of temperature on diameter still remains an open question as both increasing and decreasing diameter of the synthesized CNTs is observed with the increase of temperature in various experiments.145,146 The competing effects of various parameters in CNT synthesis in CCVD obscure any discernible trend that can relate CNT diameter to the temperature.145,146 Selectivity of the synthesized CNT morphology can be observed at different synthesis temperatures in the CCVD process. Even though it is common for amorphous carbon or carbon nanocluster to be produced at lower or higher temperatures than the optimum temperature range, clear changes in the morphology of the synthesized carbon nanostructure can be observed in some experiments.145,146 In the CCVD process using Fe-Mo/MgO catalyst with ethanol as the carbon source, few MWNTs are produced starting at temperatures above 750 °C, carbon impurities are produced at 800 °C, a mix of MWNTs and SWNTs at 850 °C, and only SWNT are produced above 900 °C up to the tested temperature at 950 °C.148

In flame synthesis, Wen et al.24 suggested that temperature is one of the controlling parameters of SWNT yields by performing thermophoretic sampling at different HABs. In the experiment, the post flame gas composition is calculated to be constant and an increase in SWNT yield is observed as the temperature decreased at increasing HAB. Similar observations were also made by Height et al. as shown in Fig. 6.50 Even though the increase in HAB will increase the catalyst residence time in the flame, the increased duration is relatively insignificant compared to the change of temperature, as was discussed earlier at the end of subsection 2.4. The decrease of the  $I_{\rm D}/I_{\rm G}$ ratio at increasing synthesis temperature is expected, though there is no data from the literature to support the hypothesis. Similar to the CCVD process, there are several contradicting reports in the literature on the effect of temperature on the synthesized CNTs diameters in flame. Yuan et al.67 suggested that the higher synthesis temperature caused an increase in the



Fig. 6 TEM images of CNT morphology sampled at different HAB in an oxy-acetylene premixed flame ( $\varphi = 1.6$ ). Adapted from Height *et al.*<sup>50</sup>

CNT diameter. Initial observation of the average CNT diameter collected on the supported catalyst at different HAB indicated a significant increase in the CNT diameter as the temperature increased. As the flame is further diluted with inert gas to reduce the flame temperature, reduction in diameter of the synthesized CNT at a fixed sampling location is observed. However, these observations may indicate a combined effect of several parameters other than the temperature, since dilution affects the gas composition. On the contrary, Woo et al.54,55 suggested that temperature does not have any effect on the diameter of the synthesized CNTs in flame using a supported catalyst system. Using a double-faced wall stagnation flow, the produced MWNT has a different diameter when compared between CNTs from the top and bottom of the catalyst plate. Since the temperature of the plate is theoretically similar on both side of the plate, the difference in MWNT diameter suggests that the suitable temperature is only required to initiate CNT inception and growth, but does not have a significant effect on the diameter of the synthesized CNT. The temperature gradient across the plate surface is the actual parameter that effect the diameter of the CNTs.54,55

Other experiments observed an increase of CNT diameter with increasing HAB using a substrate supported catalyst methane counter diffusion flame, but relate the increase of CNT diameter observation to a combination of post flame gas composition and temperature,<sup>87</sup> not solely on temperature. Limited observation has been recorded on the effect of temperature on morphology of the synthesized CNT in the flame environment. Memon *et al.*<sup>110</sup> used H<sub>2</sub> seeded methane fuel in a multiple-inverse diffusion flame (m-IDF) and observed changes in the synthesized carbon nanostructure, from MWNT only at a temperature of around 500 °C, to a mixture of MWNT and few layer graphene (FLG) at temperatures between approximately 600-750 °C, and FLG only at temperatures above 800 °C on nickel and nickel alloy supported catalysts. In the following experiment using a similar m-IDF, Memon et al.97 observed that a mixture of MWNTs and SWNTs are synthesized on a spinel powder catalyst (ZnFe<sub>2</sub>O<sub>4</sub>). In another report, rather than changes of morphology from MWNT to SWNT or vice versa, Okuno et al.49 observed a change in the CNTs morphology as the catalyst substrate temperature changes. Samples from the oxyacetylene premixed flame show that the area where the substrate temperature is around 900 to 1100 °C produced curved MWNTs, while in the area with a higher temperature (above 1200 °C) straight MWNTs are produced. This observation was made on a sample from the same substrate and at the same HAB to reduce discrepancy regarding gas composition. Nevertheless, as the experiment uses a premixed flame configuration, the effects of temperature are still uncertain as the homogeneity of the gas composition in the radial direction from the centre of the flame is theoretically significant.

2.5.3 Effect of inert diluent. Yuan et al.63 utilized a diluent as a mechanism to control the temperature in an ethylene/air diffusion flame. By diluting the fuel with nitrogen ( $C_2H_4/N_2 =$ 0.25), the synthesized MWNTs on pre-oxidized stainless steel using a propane/air premixed flame were compared to MWNTs synthesized with an undiluted flame. It was found that nitrogen dilution helps to increase the formation of MWNTs with increased diameter uniformity, and reduces the formation of carbon fibers. A temperature reduction from 1547 to 1244 °C at low fuel concentration helped to reduce the pyrolysis rate of hydrocarbons. Which minimized the presence of pyrolytic carbon that produces carbon fibers and simultaneously promotes CNT growth.63 In addition, the uniformity of CNT diameter is caused by the reduction in the reaction rate when the flame temperature is reduced by addition of an inert gas.<sup>63</sup> In another experiment, using a methane/air counter diffusion flame with a nickel wire catalyst, addition of nitrogen is found to produce relatively straighter CNTs with a uniform diameter as shown in Fig. 7.92 Increasing the percentage of nitrogen mole fraction added to the flame means the diameter of the synthesized CNTs are uniformly larger. At the tested nitrogen concentration, a 21% nitrogen mole fraction produced CNTs



Fig. 7 Comparison between carbon nanotubes synthesized using a methane counter diffusion flame with a nickel wire catalyst. SEM images of CNTs synthesized in (a) undiluted CH<sub>4</sub>, (b) CH<sub>4</sub> + 21% N<sub>2</sub> (c) CH<sub>4</sub> + 33% N<sub>2</sub>. Adapted from Li *et al.*<sup>92</sup>

with a diameter around 60–70 nm, while at 33% mole, the diameter of the CNTs are much more uniform with a diameter around 100 nm. $^{92}$ 

In another experiment, Vander Wal et al.<sup>59</sup> use an acetylene and ethylene diffusion flame with a metallocene gas-phase catalyst to syntheses SWNTs in flame. They observed that SWNTs are only synthesized with the addition of an inert gas into the flame. Without the inert gas, the flame produced soot and the catalyst nanoparticles are found to be completely encapsulated within a carbonaceous matrix. Different types of inert gas like nitrogen and argon produce a similar outcome.<sup>59</sup> However, an excess concentration of inert gas reduces the CNT yield due to the decrease of the reactant concentration. A comparative study of the effect of argon and nitrogen diluents in a pyrolysis flame was performed by Vander Wal et al.<sup>102</sup> Interestingly, SWNT yield using argon is found to be lower compared to that of nitrogen at a similar inert gas concentration. This may have been caused by the difference in thermal capacities of the inert gas which caused the argon diluted flame to have a higher temperature around 100 °C.<sup>59</sup> Even though the observation of low yield at high temperature is not consistent with the temperature driven kinetics, the increase in temperature also promotes the formation of PAHs that limit the CNT growth sites.<sup>102</sup>

From these observations, diluents that are added into the flame environment clearly have a significant effect on the CNT yield and morphology. Unfortunately, with the limited literature available, no clear correlation can be made between the diluent type and concentration toward the morphology or yield of the synthesized CNTs. Nevertheless, these initial findings indicate possibilities for diluents to be used as another parameter that can be manipulated to better regulate the yield and morphology of CNTs synthesized through the flame environment in the future.

#### 2.6 Growth enhancer

2.6.1 Application in CCVD. Application of growth enhancer or additives in CNT synthesis to promote growth and increase yield has been practiced extensively in the CCVD process, specifically in CCVD processes using catalyst supported substrates. To the best of the authors knowledge, the use of water as an additive was first introduced by Hata et al. 149 in 2004 where the "super-growth" results in a ultra-high yield of dense and aligned CNT carpets, with lengths in the millimetre range.<sup>150,151</sup> The synthesized CNTs are usually vertically aligned, longer, much more uniform, and have a higher density and purity than synthesis processes without additives. More recent work reported the synthesized length up to a centimetre in range.152 In addition, these vertically aligned CNTs can be synthesized on top of one another creating very thick, multiple layers of vertically aligned CNT.<sup>153,154</sup> Many research groups have also successfully utilized a water-assisted CCVD process to introduce specific morphology into the synthesized CNTs, such as water or nitrogen doped CNTs,155,156 few-walled CNTs,154 and SWNT forests with CNTs diameters of less than 2 nm.125

Water as a weak oxidizer helps to promote CNTs growth by removing the amorphous carbon layer from the catalyst nanoparticles, thus increasing the active sites and the duration of catalytic activity.<sup>157,158</sup> Hata *et al.* provide physical proof of the amorphous removing capability of water vapour by introducing a black amorphous carbon-coated quartz tube into flowing water vapour at 750 °C and found that the tube was cleaned and transparent afterwards.<sup>149</sup> This observation agrees with the study by Yamada *et al.*<sup>159</sup> that found water could reactivate the poisoned catalyst by actively removing the amorphous carbon layer. In a computational study using density functional theory, a water-assisted CCVD synthesis process produced vertically aligned CNTs with high purity due to the removal of the amorphous carbon and unsaturated carbon atoms from the defective sites of the growing CNTs.<sup>155</sup>

Water vapour also helps to prolong the catalytic activity of the catalyst nanoparticles by delaying the catalyst Ostwald ripening or coarsening.<sup>150,158,160</sup> Ostwald ripening is a condition whereby through atomic interdiffusion, large particles with high strain energy grow at the expense of the small particles that shrink and eventually disappear as shown in Fig. 8(a). This findings is further substantiated in a study by Hasegawa and Noda<sup>158</sup> and Kim et al.<sup>160</sup> through different experimental tests. In further analysis, Amama et al.<sup>150</sup> suggested that the ability of water vapour to delay catalyst ripening is due to the hydroxyl stabilization process of the small catalyst clusters which restrict catalyst diffusion across the substrate as illustrated in Fig. 8(b).<sup>150</sup> Other than that, hydroxylation of the supporting substrate with a hydroxyl group in water vapour plays a significant role in inhibiting diffusion of small particles by forming complex catalysts, thus decreasing the ripening rate and prolonging the catalyst lifetime.161-164

Recent work shows that water not only delays the Ostwald ripening, but is also crucial in inhibiting the Smoluchowski ripening, a surface coarsening that occurs *via* islands of catalyst particles encountering one another and coalescing into a large island as shown in Fig. 9.<sup>165</sup> Water helps to prevent large particle



Fig. 8 Illustration of Ostwald ripening and hydroxyl stabilization process of Fe catalyst on a  $Al_2O_3$  substrate support (a) CCVD process without water vapour (b) CCVD process with addition of water vapour.<sup>150</sup> Adapted with permission from *Nano Lett.*, 2009, **9**(1), 44–49. Copyright 2008 American Chemical Society.

formation by oxidizing catalyst particles and increasing the interaction between the catalyst particles and the substrate.<sup>165</sup> The same study shows that by using ultra purified carbon sources with oxygen content below 1 ppb level, CNTs did not grow due to enlarged catalyst nanoparticles. The oxygen containing impurities, such as water in the carbon source are vital to inhibit catalyst migration. Hence removal of these impurities makes the problem of catalyst particle coarsening worse. These theories, however, are not conclusive. In 2011, Hasegawa and Noda reported that coarsening of the catalyst occurs even with the addition of water.<sup>166</sup> The authors however acknowledge this contradictory observation. They assumed that it may be caused by dissimilarity of the concentration of water and type of carbon sources used in the experiments, which may have induced a different kind of coarsening behaviour on the catalyst particles.<sup>166</sup> Nevertheless, the inconsistency of the experimental results is an indication that fundamental understanding, especially of the effect of water on catalysts in substrate supported CCVD is still far from complete.

Besides water vapour, there are many other types of substance that have been found suitable as CNT growth enhancers in the CCVD process as shown in Fig. 10.157 Additives such as carbon dioxide, acetone, tetrahydrofuran, ethanol, methyl benzoate, and benzaldehyde have all shown an enhancing effect toward CNT growth in CCVD. However, none has matched the enhancing performance of water vapour. Results from these extensive sets of experiments established a clear correlation between the oxygen content in the carbon source and the additive substance on the CNT yield and morphology. From Fig. 10, Futaba et al. concluded that for the additive to be an effective growth enhancer, the carbon source must be free from oxygen, while the additive substance must contain oxygen.157 Even though the most reported waterassisted syntheses in the literature fall within this general rule, exceptions to the rules have been discovered in recent works. An increase in the yield of SWNTs using a CCVD method was observed in an experiment that used ethanol as the carbon source167 and in another experiment where methane is used as the additive substance.<sup>168</sup> The presence of oxygen in ethanol as a carbon source and the absence of oxygen in methane used as an additive in the experiments are not aligned with the Futaba's rule. These recent discoveries prove that the rule is clearly not exhaustive, and indicate possibilities for other substances to be used as additives that may have not been explored.



**Fig. 9** Illustration of water vapour effect on catalyst particle mobility and CNTs growth.<sup>165</sup> Adapted with permission from *ACS Appl. Mater. Interfaces*, 2014, **6**(23), 21019–21025. Copyright 2014 American Chemical Society.



Fig. 10 Synthesized CNTs height compared using 27 combinations of carbon sources and growth enhancers/additives. Adapted from Futaba *et al.*<sup>157</sup>

2.6.2 Application in flame. The effect of different types of catalyst solvent toward the CNT yield and morphology in flame were first explored by Vander Wal.<sup>106</sup> Using a pyrolysis flame and CO as the fuel, three types of solvent are used in the preparation of the catalyst solution; ethanol, water, methanol, and its combinations. As the catalyst solution is nebulized into the flame, the solvent is entrained and carried into the flame as an additive. Using methanol as a solvent at different concentrations produced cleaner SWNTs, but no CNTs are produced when water is used as additive. Although pure ethanol is observed as being an optimum solvent, the CNT yield is not explicitly stated, though the reduced amorphous carbon deposit on the synthesized CNTs is denoted. The viability of ethanol as an additive is due to its pyrolysis products, which are ethylene and hydrogen. The adsorptive property of ethylene is then enhanced by the presence of CO promoting CNT growth.<sup>106</sup> In an earlier experiment, sulphur in the form of thiophene was employed as an additive in a pyrolysis flame with a nickel or iron gas-phase catalyst.<sup>103</sup> Sulphur has been proven to be an effective CNT growth promoter in CCVD through restructuring of the particle or steric blockage of a specific surface area.<sup>169,170</sup> Unfortunately, there are no observed changes in terms of CNT yield, growth rate, or morphology.<sup>103</sup> A detailed physical explanation is not provided, though the putative mechanism that plays a role in the CCVD process is not applicable in flame synthesis.

Unfortunately, all experiments related to additives in flame synthesis are performed using a gas-phase catalyst. None of the literature in flame synthesis reported success in replicating the effects of additives similar to substrate supported catalysts in the CCVD process. The role of the additive, especially water vapour in a flame environment using a gas-phase catalyst, is

fundamentally different than in the supported catalyst CCVD process. The gas-phase catalyst which allows the random movement of the catalyst clusters in the flame environment inhibit any substantial effect of water vapour as experienced by a relatively static substrate supported catalyst. Furthermore, the highly limited time scale of the gas-phase catalyst synthesis process further limits any observable water vapour effect. Additionally, Vander Wal's experiments on additives do not explicitly indicate any type of measurement used to quantify the amount of additive supplied into the flame.<sup>103,106</sup> In the CCVD water assisted CNT synthesis, water is only effective as a growth enhancer within a narrow range of concentration.<sup>152,171-173</sup> In Fig. 11, the series of FESEM images of synthesized CNTs using water-assisted CCVD clearly shows the presence of an optimum water concentration in water-assisted CNT synthesis.<sup>173</sup> By varying the water concentration in each experiment from 30 to 150 standard cubic centimetre per minute (sccm), the optimum water concentration is found to be at 50 sccm, where CNTs with the best alignment and with higher density are produced. Whereas, as the water concentration increased beyond 50 sccm, the synthesized CNTs become less aligned and dense. Ultimately, with a water concentration of 150 sccm, only a minimal amount CNTs were synthesized. Therefore, a lack of control over additive concentration may be counter-productive toward CNT growth. Other than that, the use of CO as the main carbonbearing species in one of the experiment is in direct contradiction with the Futaba's proposed rule on CNT "super-growth" synthesis which could affect the experimental outcome.157 Unfortunately, there is no literature published reporting an experiment with a water additive using a carbon bearing species with no oxygen content, such as ethylene or acetylene in flame. It will be an interesting observation to learn how the additive affects the CNT growth and morphology within a pyrolysis flame environment that adheres to Futaba's rule.157

There are additives that have been proven to be very effective as growth promoters in the flame environment. Employing the concept of utilizing a silicon or aluminium substrate to control carbon diffusion on the catalyst particle in substrate supported CCVD process, Unrau and Axelbaum<sup>83,84</sup> tested silicon and aluminium as additives in a oxy-ethylene inverse diffusion



Fig. 11 FESEM cross sectional image of SWNTs synthesized using water assisted CCVD with varied water vapour concentrations; (a) 0 sccm, (b) 30 sccm, (c) 50 sccm, (d) 100 sccm, (e) 150 sccm. Adapted from Hu *et al.*<sup>173</sup>

flame with an iron (sublimed ferrocene) gas-phase catalyst. In the experiment, a silicon or aluminium additive is added to the fuel stream prior to the flame using an inert gas bubbler to entrained silicon/aluminium particles from tetraethylorthosilicate or aluminium acetylacetonate liquid. At optimum additive concentration, nearly 90% of the catalyst produced longer SWNT with a higher diameter uniformity, compared to only 10% in synthesis without additive.83,84 Further analysis of the experiment reveals that the role played by the additives is different to the one played in substrate supported CCVD. As shown in Fig. 12 in the Car-Parrinello molecular dynamics simulations, silicon and aluminium additives in the gas-phase synthesis of SWNT reformed the iron nanoparticles to a substrate-supported like structure once combined with oxygen to from iron oxides. Fig. 12(a) and (b) shows that the homogeneous mixture of iron catalyst with silicon or aluminium additives are transformed into a substrate-supported like structure, with part of its surface being catalyst-rich while the other is catalyst-deficient with the presence of oxygen.<sup>31</sup> Referring to Fig. 12(c) and (d), as carbon atoms diffused into the Fe/O/Si cluster, the geometry optimization results suggest that a ring configuration of the carbon atoms is energetically favourable compared to being separated on the iron surface of the cluster.<sup>31</sup> This indicates that the dissociated carbons atoms on the catalyst-rich surface are preferentially bonded together, hence promoting early nucleation of SWNTs and consequently preventing the cluster from being encapsulated.31

There is an obvious lack of literature that explores the effects of additives on CNT growth in the flame environment. Substantial understanding of the additive effect on substrate



**Fig. 12** Illustrations of (a) Fe/Si cluster without an oxide layer, (b) simulation of cluster formation 5 ps at 1300 K environment with the presence of oxides, (c) addition of carbon atoms (grey spheres) into a Fe/O/Si cluster mix-up configuration, and (d) hexagonal configuration of carbon atoms. Colour coding: Si-yellow, Fe-purple, oxygenred.<sup>31</sup> Adapted with permission from *J. Phys. Chem. C*, 2010, **114**(23), 10430–10435. Copyright 2010 American Chemical Society.

supported catalysts in the CCVD process would provide useful guidance to exploring the possibilities of replicating the extraordinary effect of water vapour additives in flame synthesis. Although water failed to improve the growth in a pyrolysis flame,<sup>106</sup> water effects in conventional flame synthesis have not been studied. Pioneering work by Unrau and Axelbaum<sup>83,84</sup> in describing the additive distinct role in the gas phase catalyst environment paves the way for the utilization of various substances for the same purpose. In depth research on additives in flame synthesis is a worthy endeavour to propel CNT synthesis in flames into the main stream of CNT production technology.

# 3. Carbon nanotube growth manipulation in the flame environment

Besides the critical parameters of CNT growth that have been reviewed in previous chapters, there are also other techniques that have been designed specifically to manipulate CNTs morphology within the flame environment. This section will review the recent techniques reported in the literature to highlight their potential for future applications.

#### 3.1 Electric and magnetic field bias

Electrical field application over CNT growth was first introduced in CCVD<sup>174-177</sup> and plasma synthesis.<sup>178-180</sup> The electrical field method was proven to be a practical technique for controlling CNTs alignment and morphology. It was first applied in flame CNT synthesis by Merchan-Merchan et al.89 who employed the method in the counter diffusion flame. In the experiment, the synthesis of CNTs on a nickel catalytic probe is performed in two modes; Floating Potential Mode (FPM) when the electrical field is generated between the nickel catalyst probe and the edges of fuel and oxidizer nozzle, and Grounding Probe Mode (GPM) that represents a synthesis without electrical field generation. Comparing CNTs synthesized using FPM and that of GPM, Merchan-Merchan observed several clear benefits of using FPM that include increased growth rate, uniformity of CNTs diameter, alignment, and wide flame region suitable for CNT synthesis. CNTs produced with the assistance of electrical field also benefit from a significant reduction in contaminant and soot.89

Fig. 13 illustrates the theorized effects of electrical field toward vertical alignment of CNT.<sup>27</sup> As the electrical field *E* is introduced during the growth of CNT, the polarization effect generates an electrical charge *q* at the end of each the tube resulting in an alignment force  $F_{\rm TF} = qE \sin \theta$ , where  $\theta$  is the angle between the tube axis and the electrostatic force acting on the growing tube. The axial component force  $F_{\rm AF} = qE \cos \theta$ stretches the tube and reduces thermal vibration that is experienced by the growing CNTs. Merchan-Merchan *et al.* studied the electrical field effect on synthesized CNTs over a range of applied voltages.<sup>90</sup> It was observed that different ranges of applied voltage produced CNTs with different characteristic as shown in Fig. 14. At a minimum voltage of 0.3 V to 1 V, the synthesized CNT has a high purity, and is a well-aligned CNT,



Fig. 13 Illustration of forces acting on the carbon nanotubes in the presence of an electrical field. Adapted from Merchan-Merchan *et al.*<sup>27</sup>

the arrays thickness increases with the increase of voltage applied. As the voltage increases from 1 to 3 V, saturation of the CNT array thickness is observed. As the voltage increases further towards 12 V, a new CNT growth mechanism is observed. Some of the CNTs grow along the trunk of existing CNTs from the sprout of new catalytic particles. Above this voltage limit and up to the maximum voltage tested, 25 V, structurally modified Y-branching, T-branching, and multibranching CNTs are synthesized. The branching phenomena is due to the sprouting catalytic particle in a tip-growth mode. Since the maximum electrical field occurred at the tip of the CNT, ion bombardment at this location causes the catalytic nanoparticles to sprout. The sprouted catalytic particle then forms new catalytic site on the CNT with an opening from the edged graphite, producing the branching effects.<sup>90</sup>



Fig. 14 Morphology evolution of the synthesized carbon nanotubes when the growth process is introduced to a range of voltages. Adapted from Merchan-Merchan *et al.*<sup>27</sup>

Xu et al.<sup>81</sup> further explored the application of electrical field by applying a voltage bias on an inverse diffusion flame fuelled with methane with two types of catalytic probes. A similar positive outcome was observed, as per the earlier experiment by Merchan-Merchan<sup>89</sup> on the synthesized CNTs, such as aligned tip-growth, increased growth rate, and increased purity. Voltage bias applied to the system helps to produce pure CNTs by electrophoretically removing soot particles and their precursors, while optimizing carbon supply through a chemical effect initiated by transposing and re-distributing ionic species by the action of the electric fields.<sup>81</sup> Interestingly, Xu et al. found that both positive and negative voltages produce a similar effect, with the former having a relatively better outcome compared to the latter as shown in Fig. 15. However, further explanations related to this condition are not provided. The use of the catalytic probe in the floating potential mode results in -24 mV which also produces a similar positive outcome as shown in Fig. 15(b).

A later study reported on the synthesis of the aligned CNTs using an ethanol diffusion flame on a dried nickel catalyst on top of a stainless steel plate with electrical field bias generated using a DC power supply.72 The CNTs growth mechanism is also by a tip-growth mode as per the earlier experiments. Similar improvement are observed on the tip-growth CNTs such as alignment, diameter uniformity, and crystallinity of graphite sheets.<sup>72</sup> Simulation of the macroscopic electric field indicates that electrostatic forces acting upon the catalyst particles at the tip are far greater than the CNTs tube throughout the CNT growth process, promoting formation of aligned CNTs as shown in Fig. 16(c). This result further enhanced the understanding of the actual driving force in the formation of vertically aligned CNTs in an electrical field proposed earlier by Merchan-Merchan et al.<sup>89</sup> It also reveals the limitations of the method, in that it is only affective for tip-growth CNTs.

In a more recent experiment, the application of an electrical field on a pyrolysis flame has been employed.<sup>109</sup> The pyrolysis flame consists of a main pyrolysis chamber with temperature



Fig. 15 SEM images of CNT morphology with application of various voltage bias (sampling performed at same location within flame). Adapted from Xu *et al.*<sup>81</sup>



**Fig. 16** HRTEM images of CNTs synthesized in an ethanol flame (a) without a magnetic field, (b) with a magnetic field, (c) and (d) are electrostatic forces (generated using a DC power supply 25 V) and magnetic forces acting upon the catalyst particles and CNT tube throughout the CNT's growth process respectively.<sup>72,74</sup> Reprinted with permission from *J. Phys. Chem. C*, 2008, **112**(35), 13470–13474. Copyright 2008 American Chemical Society.

controlled by regulating two  $C_2H_2/air$  burner heating two sides of the chamber. The pyrolysis flame is established using a mixture of CO and H<sub>2</sub>. The voltage bias is created between a stainless steel probe coated with Fe/Mo/Al<sub>2</sub>O<sub>3</sub> and the main pyrolysis chamber. The synthesized tip-growth CNTs in the presence of the electrical field shows similar trends of CNT synthesis like in other studies. Furthermore, an increase in the catalyst lifetime is observed with the increase of the voltage applied.<sup>109</sup> Interestingly, the range of voltage applied in this experiment, which was 30 to 60 V, is an order of magnitude higher than compared to the previous studies.<sup>72,81,89,90</sup> However, the author did not indicate any branching phenomena, which is found in the Merchan-Merchan *et al.* experiment at a much low voltage.<sup>90</sup>

In other experiments, rather than the electric field, the magnetic field is generated using a permanent magnet located at the top of the flame.74 Using a similar ethanol flame setup as in previous work by Bao and Pan,72 a neodymium-iron-boron (Nd-Fe-B) permanent magnet with a surface magnetic flux of 380 mT is used. An aluminium plate is placed in between the magnet and the flame as a barrier to prevent the magnet block from being heated above the Curie point, where the magnetic property will diminish. A Ddip and dried coating technique as used in the previous experiment<sup>72</sup> and the pulse electrodeposition technique are used to coat the copper plate substrate with the nickel based catalyst. The magnetic force produces a similar effect of an increase in alignment of the CNTs graphitic layers as per the electrostatic force in the flame, shown in Fig. 16(a) and (b). However, the dip and dried catalyst coating process produced tip growth CNTs while the electrodeposited catalyst produced base growth CNTs, both with a similar yield and morphology. This outcome is contradictory to the earlier assumption that the CNTs vertical alignment is

driven by the electrostatic force that acts upon the catalyst particles at the tip of the growing CNTs.74 Simulation of a magnetic field acting on growing CNTs reveals an equal but opposing magnetic force acting upon the CNTs tip and its tube, as shown in Fig. 16(d).<sup>74</sup> The magnetic forces that acts on the CNT tubes are perpendicular to the substrate, while the same force is in the opposite direction for the catalyst particles at the tip of the CNTs.<sup>74</sup> Even though the magnetic force acting upon the catalyst particle is nearly constant throughout the growth period, the force can be neglected since Ni lost its ferromagnetism properties in the CNT growth process which occurred far beyond the nickel Curie point of 358 °C.74 Hence, the magnetic force that acts upon the CNT tube is the main driving force in promoting the formation of vertical CNTs.74 Therefore, compared to CNT synthesis in the electromagnetic field, the utilization of a permanent magnet is better for allowing enhanced stability, repeatability, and controllability of the synthesis regardless of the growth mode.

#### 3.2 Novel nanotemplate (AAO thin film)

CNT synthesis using a novel AAO film is an effective technique to grow CNTs with a well-controlled geometry. This thin film has highly ordered nano-sized pore arrays called nanopores or nanotemplates which confine CNT growth, thus duplicating the size of the pores and creating uniform, well organized CNTs. Conveniently, the size of the pores on the AAO nanotemplate can be adjusted by varying the voltage during the anodization process. The main disadvantage of the method is that the fabrication of the AAO nanotemplate is multi-step and time consuming. Yang *et al.*<sup>181</sup> reported that typical fabrication can take up to 10 hours, while others<sup>182</sup> reported up to 24 hours for the fabrication process. In CCVD, the application of an AAO nanotemplate has been applied extensively.

The first successful application of an AAO nanotemplate in a flame environment was reported<sup>61,183</sup> using a silicon wafer as a substrate. The application of a silicon based substrate is important as the Si melting point is higher than the flame environment, allowing for extended exposure to the flame without damaging the nanotemplate. Using a similar approach as a previous study in CCVD,<sup>184</sup> a Co catalyst particle was electrodeposited at the bottom of the pores on the AAO thin film, as shown in Fig. 17(b). With an ethylene/air co-flow diffusion flame, the template was introduced into the flame perpendicular to the gas flow, and the CNT growth process only took around 5 minutes. As expected, the synthesized CNTs replicated the geometry set earlier on the AAO nanotemplate. The growth ceases once the CNT reaches the top layer of the nanotemplate, conveniently creating CNTs with uniform length.<sup>61,183</sup> Due to the higher temperature of the flame environment compared to that of CCVD, the CNTs synthesized in flames are well graphitized compared to that of CCVD on the aluminium sheet substrate.66 In a later experiment, Hu et al.66 tested CNT synthesis using a similar AAO nanotemplate, but without Co as catalyst. The CNT was successfully synthesized, but the tube walls were not well graphitized compared with the ones with the Co catalyst and the CNTs do not have as strong a hold to the silicone



Fig. 17 Cross-sectional SEM images show a clear image of (a) AAO nanotemplate without Co catalyst, (b) AAO nanotemplate with electrodeposited Co catalyst at the bottom of each pore. Adapted from Hu et al.<sup>61</sup>

substrate.<sup>66</sup> Later, others<sup>76,92</sup> employed a AAO nanotemplate in different flame configurations, such as co-flow and counter diffusion flame using a 1D sandwich-structured Si-substrate with a AAO template and 2D AAO nanotemplate, as shown in Fig. 18(a) and (d). By determining the best location within the flame using a Ni-alloy wire, the 1D and 2D nanotemplate was then introduced to the flame to produce well-aligned and

uniform CNTs replicating the dimension of the nanotemplate. It was observed that application of the 1D nanotemplate was suitable in a counter diffusion flame to minimize the interaction between the flame and the nanotemplate, whereas the 2D nanotemplate was suitable for a co-flow diffusion flame to produce CNT arrays as shown in Fig. 18(c). Aligned 1D CNTs array can be synthesized using a 1D nanotemplate as shown in Fig. 18(f).<sup>76,92</sup>

With a relatively simple control in the production stage of the AAO nanotemplate, a specific configuration of the CNT diameter and length can be produced.<sup>66</sup> The successful synthesis of a CNT with a horizontally aligned 1D nanotemplate, led towards the expansion of knowledge on the process of direct growth of CNTs onto a silicon integrated circuit for the fabrication of nanoscale electronic devices.<sup>92,185</sup> Nevertheless, the extra cost to produce an AAO nanotemplate and the purification process to harvest the synthesized CNT limit its application to certain users or producers.

# 3.3 Stagnation wall, rotating flame, and acoustic excitation techniques

A stagnation wall method was first proposed by Nakazawa *et al.* to synthesis MWNTs.<sup>51</sup> An ethylene/air premixed flame impinging a jet on a stagnation ceramic disk which consists of a deposited nickel catalyst, creating a stagnation wall with a trumpet shape flame on top of the disk as shown in Fig. 19. Through this mechanism, the unburned reactant gas is exposed directly to the catalyst while the surrounding flame provides a suitable temperature for CNT inception and growth. The stagnation wall flame also prevents over exposure of the growth CNT towards the elevated temperature of flame and highly



**Fig. 18** (a) Illustration of 2D AAO nanotemplate; (b) SEM image of synthesized CNTs in 2D AAO nanotemplate pores; (c) SEM image of the exposed CNTs after the AAO template (sample in (b)) is dissolved; (d) illustration of 1D AAO horizontal nanotemplate; (e) SEM images of 1D AAO horizontal nanotemplate; (f) SEM image of parallel CNTs synthesized using 1D AAO nanotemplate. Adapted from Li *et al.*<sup>76,92</sup>

oxidizing environment. Nakazawa *et al.* suggested that a donutshaped CNT growth region observed on the catalyst disk indicates that the suitable temperature and concentration of reactant gases is achieved within the region.<sup>51</sup> A strong interaction between the flame and the outer region of the wall results in a high temperature region, while the temperature reduces toward the centre of the wall creating a region with a suitable temperature for CNT inception and growth. Since the stagnation wall is located downstream of the flame front, the gas composition within this region is highly effected by the diffusion with respect to the flame front and by the thermal decomposition.

Variation of the stagnation wall technique was later proposed by Woo et al. using a double-faced wall stagnation flow (DSWF) burner where a flame impinged on a vertically placed catalyst coated stagnation wall from top and bottom.54 This experiment also observed the effect of the flame stretch rate through varying the flame jet velocity V, where the global stretch rate is defined as K = V/s with s representing the distance between the flame tube exit to the stagnation wall.<sup>54</sup> To counterbalance the buoyancy effect acting on the flames, the upper and lower flames are set at different stretch rates, where the upper flame has around a 2.3 times higher stretch rate than the bottom flame. The DSWF burner increases the area of the growth region and produces CNTs with relatively higher uniformity compared to that of a single stagnation wall flow (SWSF) burner. The residence time for CNT synthesis using DSWF also shortened to 3 minutes compared to that of SWSF.



Fig. 19 (a) Illustration of single wall stagnation flow burner configuration, (b) image of trumpet-shaped flame on the stagnation wall. Adapted from Nakazawa *et al.*<sup>51</sup>

In more recent literature, the work on DWSF burner was further extended by the addition of another dimension of a controlled parameter, that is the combination of flame stretch rate and equivalence ratio ( $\varphi$ ).<sup>55</sup> Using a similar setup as in the previous experiments, the CNT synthesis limit was first identified to be at  $\varphi$  of 1.5 to 1.8 and the flame stretch rate of 236 to 1648 s<sup>-1</sup> with the upper flame stretch rate always set at 2.3 times higher than that of the lower flame, to account for the buoyancy effect. At each different combination of  $\varphi$  and *K* within the identified limit, a different rate CNT yield and morphology is observed. However, at  $\varphi = 1.7$ , the flame stretch rate is found to be the most extended, thus allowing for optimization of the stretch rate to control the CNT yield and morphology. Most of the reported benefits are on the increment of yield with a minimal effect on morphology.

Other than the stagnation wall method, recent studies proposed the use of a counter diffusion flame with a rotating flame nozzle to create a spinning flame.94,99,114 Rotating the flow effect of the mixing level of the fuel and oxidizer significantly altered the flame temperature distribution. It was observed that the rotating nozzle creates some level of control over CNT yield and morphology through the control over the rotational speed of the nozzles. In addition, research was also conducted into the utilization of acoustic modulation to enhance CNT synthesis using different types of fuel and fuel combinations.77,78,115 Significant enhancement of CNT growth can be observed near to the acoustically resonant frequency of the fuel used. At this frequency, the acoustic excitation helps to improve the flow mixing and produce better conditions for CNT growth. Both the rotating flame and acoustic modulation methods served as alternative ways to control the fuel/oxidizer mixture to affect the gas phase concentration in the flame.

### 4. Conclusion

It is evident from this review that CNT synthesis in flame is a highly complex process with a combination of intricate CNT growth mechanisms and complex flame environments. Nevertheless, it has been the subject of intense investigation by researchers due to its significant potential as a CNT mass production process. As the CNT market continues to expand, economical, rapid, and energy efficient processes for CNT synthesis in flames are becoming much more relevant. A fundamental understanding of the effect of flame geometry, temperature and gas phase composition, catalytic materials type and concentration, mode of catalyst delivery, and residence time toward yield and morphology of the synthesized CNTs has been extensively reviewed. A breakthrough in flame synthesis control requires a detailed understanding of the effects of flame

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and catalyst parameters on the growth, therefore systematic fundamental study and modelling remains an open field of research. Morphology and purity control of the synthesized CNTs are further enhanced through the application of advanced controlling mechanisms, such as electrical or magnetic field forces and nanotemplates. Electrical and magnetic forces increase CNT purity and vertical alignment, while nanotemplates enable CNT orientation, alignment, length, diameter, and control of the internal structure. Initial investigations on the application of additives in flames show significant potential for the method to be further developed to increase the yield for production of high quality CNTs.

# Conflicts of interest

There are no conflicts to declare.

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