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Systematic review of catalyst nanoparticles synthesized by solution process: towards efficient carbon nanotube growth

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Abstract Nano-field research has been expanded rapidly since those tiny materials such as carbon nanotubes (CNTs), cobalt catalyst and iron catalyst can give huge impact to the application products with their extraordinary properties. The scientific discovery of these materials can be defined as a magic key to solve the raw materials shortage and unlock the limitation performance of the devices. CNTs have been found to be one of the new nanomaterials that can improve different kind of devices' performance. CNT can be grown on the substrates with the presence of active metal catalysts. Since small metal catalyst particles (diameter <10 nm) are crucial in growing CNTs, the deposition method of metal catalyst on the substrates has been studied. The optional processes using solutions to produce catalyst nanoparticles will be discussed in this review. Sol–gel process along with spin coating is the most suitable deposition method with low cost of production and the easiness to control particle size deposited on the substrates.

Keywords Carbon nanotube · Metal catalyst · Nanoparticles · Sol–gel process · Spin coating

1 Introduction

Nowadays, people are talking about nanotechnology in all fields of studies such as sciences, engineering, medicine,

etc. Nanotechnology is all about producing, manipulating small objects and building from objects that are extremely small which is less than 100 nm. There are several advantages in economic and technology by making things smaller such as the cost of production will be reduced by a mass production when the materials or things getting smaller. The quantity of materials used for the production also can be cut-off due to the extraordinary properties of the nanomaterials themselves. Thus, the shortage of nature's sources could be solved accordingly.

1.1 What is CNT?

Carbon nanotube (CNT) is just tiny structures in nano-scales in which the diameter is about 10,000 times smaller than human hair but they have huge impact on science and technology. They have been rapidly known by the people in the world ever since Sumio Iijima had been published his research in 1991 [1] and exposed the unique structural and properties of CNTs to the world. His invention often cited in most of the published paper on the topic of carbon nanotubes. However, he was not the first person who discovered these allotropes of carbon because CNTs had been observed prior to his invention by many researchers since 1952 until 1989 [2–18]. Basically, carbon nanotubes are formed from a repeated chemical element of carbon (C) in which bonded by covalent bonding. Covalent bonding is a strong chemical bond that involves in sharing electron pairs between atoms. The most well-known allotropes of carbon are 2D-graphite, 3D-diamond, and amorphous carbon. Graphite has been widely used as the cores of pencils after lead because lead has poisonous issue back then. Diamond is the hardest nature material known because it is arranged in diamond lattice. The highest hardness own by this structure leads to the restructured as synthetic diamond to

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be used in industrial application like cutting and polishing tools. Another form of carbon is OD-fullerene that has been discovered by Kroto [19]. Hence, based on that finding, nanotubes can be classified as one of the fullerene's family member.

CNTs can be classified based on the helicity and the direction of CNT growth. There are two famous types of carbon nanotubes related to helicities found in the research field such as single-walled CNT (SWCNT) and multi-walled CNT (MWCNT) [20]. SWCNT structure is like wrapping a 2D-graphene sheet into a seamless cylindrical structure or by elongating a Bulkyball or C_{60} to be a tubular structure [21–23]. There are three ways of graphene sheet is wrapped which are zigzag, armchair and chiral. Different ways of wrapping will promote different properties in which can be used in various application. Meanwhile, MWCNT structure is quite similar to the SWCNT but the different is only that it consists of multiple rolled layers of graphene. However, SWCNT has been a spot interest because of its physical properties. CNTs can be grown entangle or align. Aligned CNT in which can be used to improve the device performance is divided into two patterns; vertically and horizontally [24–26]. These two patterns can be tailored by controlling several parameters especially during the catalyst preparation and CNT growth process in which will be discussed further in the next section.

1.2 CNT growth

CNT growth is the most important process in order to produce high quality of CNT. In order to grow the CNT, there are three main materials needed to achieve the goal which are catalyst, substrate, and carbon sources. Those 'ingredient' is like the concept of planting a tree. Without the seed, soil, water and sunlight, tree cannot be grown. It is the same goes to CNT growth. Without the main materials, the CNT cannot be grown out of nowhere. In addition, the CNT growth process selection is also crucial. There are several processes that have been used by the researchers up to this century in which will be elaborated later. Moreover, along with the catalyst preparation and CNT growth stages, there are also several parameters that are needed to take into account.

1.2.1 Catalysts selection

Catalyst selection is one of the most important things towards a good result of CNT production. With proper selection of materials and good control of particle size of catalyst, the desired type, quality and characteristics of CNT can be achieved. Transition metals are the most effective catalyst to grow CNT on substrate especially iron

(Fe), cobalt (Co) and nickel (Ni) [27]. These metals have high solubility of carbon at high temperature and high diffusion rate in which very helpful during the CNT growth process. Moreover, the melting point for those catalyst candidates is suitable to grow CNT since the growing temperature is in range of 700–900 °C [28]. They also have stronger adhesion with the CNT produced at the end of the process and potential in forming high curvature of CNT. Back then, the CNT growths were carried out with different single metal catalysts (Fe, Co and Ni). Iron catalyst has potential to produce higher CNT deposit on the selected substrate due to high catalytic effect in hydrocarbon decomposition own by this metal but the CNTs were poorly graphitized [29]. Meanwhile, cobalt has the opposite effect on CNT growth found on iron catalyst. Thus, by combining these two metals means that the individual advantages are combined, hence it will improve the quality of CNTs. It was proved by Nakayama's group that binary catalyst was able to grow CNTs and the study was successful at low temperatures [30]. In short, by combining more metal catalysts for CNT growth will give an interesting result but of course it will be more complicated.

Besides those metals, other metals in the same group such as Pt, Ag, Cu, and Pd are also potential in CNT growth [31–35]. Apart from transition metals, other metals which are known as new catalyst for CNT like Al, Mg, Sn, Cr, Mo and Mn are also very useful for CNT growth especially to grow horizontally-aligned SWCNT [24]. In order to produce aligned CNT, catalyst support is needed to be employed. The examples of catalyst supports that are commonly used are Al, Al–O, Al_2O_3 , and SiO_2 [36–41]. All the catalyst particles; main catalysts and catalysts support, are in nano-scaled, hence they need careful handling to make sure that they are attached well to the substrates. So, the route to synthesize catalyst nanoparticles is very crucial to determine the attachment ability of the catalyst to the substrate as well as to drive the quality of CNTs produced. There are many ways to synthesis nanoparticles like wet chemical, mechanical, form-in-place and gas-phase processes. All these four methods will be discussed further in the following sections.

1.2.2 Substrates selection

A good selection of catalyst should come with a good selection of substrate for CNT growth. There are many available substrates for CNT growth such as Si, SiO_2 , SUS 310 S and many more. The most common substrates that have been used in the CNT studies are graphite [10, 11], quartz [42, 43], magnesium oxide [44–46], alumino-silicate; zeolite [47, 48], alumina [49, 50], silicon [51, 52], silicon carbide [53, 54] and silica [55, 56]. Furthermore, every substrate has its own special catalyst-substrate

interaction with the selected catalyst in the direction of enhancing the growing process of CNTs. This interaction is related to the chemical bonding formation between these two things. A good chemical bonding of catalyst-substrate will help to avoid the detachment of catalyst particles from the substrate especially during the CNT growth process. Thus, it will lead to produce good quality of CNTs in straight direction.

In addition, good handling of substrate during the experiment is a must because substrate is a very sensitive product especially substrate with Si base like silicon and silicon oxide wafers. Si based substrates are quite brittle and easily breakup when dropped. Besides, the uniformity of catalyst thin film formed on the substrates during the deposition process could be affected by the uniformity of substrates' surface. When there are scratches on the substrate, the uniform catalyst thin film is difficult to be achieved. Other factor that will lead to the failure of catalyst deposition process is the existence of impurities on the surface of substrates. Thus, cleaning process is needed before the catalyst deposition process. There are several methods for substrate cleaning. Substrates can be cleaned by piranha solution. This solution is a mixture of 1/1 (v/v) sulphuric acid and hydrogen peroxide. After 15 min of treatment by that solution, then substrates are rinsed with de-ionised water before the spin coater is used to dry them at speed of 8,000 rpm for 30 s [57]. Furthermore, substrates also can be cleaned with acetone by sonication process for 5 min. Then, just like the first method of cleaning, the substrates are washed with de-ionized water. Lastly, dry them with nitrogen gas [58]. The third suggestion of cleaning substrate is by acetone ultrasonic cleaning, followed by ultraviolet ozone cleaner treatment [59]. The last method is rinsed the substrates with acetone, subsequently treated by ethanol through sonication process for 10 min [60, 61]. Proper cleaning will contribute to good

result of CNTs. Thus, proper selection of substrates cleaning method is very important.

1.2.3 CNT growth methods

CNT growth is the climax part of CNT growth process. There are three growth methods to produce CNTs such as arc discharge, laser ablation and chemical vapor deposition. Other methods like pyrolysis, flame and liquid hydrocarbon synthesis also have been employed in this field but the scope is just up to laboratory level. These methods have their own contribution towards CNT growth. The differences of these methods are given in Table 1.

Early of the CNTs discovery, arc discharge method has been used for the CNT growth purpose. It is a method where a direct-current arc voltage is applied across two graphite electrodes (<1 mm apart) immersed in an inert gas such as He and Ar [63]. MWCNTs and SWCNTs can be produced through this method by the employment of pure graphite rods as cathode. MWCNTs will be deposited on the cathode by the deposition of fullerenes (as soot) inside the chamber. In 1992, the first CNT was obtained from this method; MWCNT. The dimension of the MWCNT was in micrometer length and the diameter was about 5–30 nm [64]. SWCNTs can be generated only with the existence of metal catalyst in graphite anode along with a pure graphite cathode. The first SWCNT was produced in 1993 [65]. However, defects have been detected on the produced CNTs. Thus, it was the start point where researchers have found laser ablation to improve the quality of the CNTs. Both methods have some similarities in terms of the processing principle; the evaporation of carbon solids generates carbon atoms condensation. The difference is just on the source of heat needed to produce high temperatures, as the laser ablation used laser source and arc discharge used electric arc source. These sources lead to the high cost of

Table 1 Comparison of the available CNT growth methods [62]

Method	Arc discharge	Laser ablation	Chemical vapor deposition
Description	Vaporization of carbon in the presence of catalyst under reduced atmosphere of inert gas; formation of CNTs on electrodes during quenching	Vaporization of carbon target by laser; formation of CNTs on substrate during quenching	Formation of CNTs by decomposition of hydrocarbons on catalyst nanoparticles
Processing parameters	Temp: >3,000 °C Pressure: 50–7,600 Torr (under vacuum)	Temp: >3,000 °C Pressure: 200–750 Torr (under vacuum)	Temp: <1,200 °C Pressure: 760–7,600 Torr
Advantages	High quality of CNTs; MWCNT and SWCNT	High quality of CNTs; SWCNT	Flexibility of substrates; variety forms of CNTs can be grown; mass production is possible
Disadvantages	Limited types of substrates; mass production is difficult; expensive	Limited types of substrates; mass production is difficult; expensive	Quality of CNTs varied from each laboratory

CNTs production and the mass production is quite difficult due to the ineffective cost for commercial purpose.

Then, the CNT technology has shifted to catalytic vapor deposition (CVD) method. This method is the solution for the cost problem of arc discharge and laser ablation methods. This is because the processing temperature needed for CNT growth is low which is in range of 600–1,200 °C and the energy source to transfer energy to gaseous carbon molecule is plasma or a resistively heated coil in ambient pressure [27, 65, 66]. CVD is a method of decomposition of hydrocarbon gases; methane, ethanol, carbon monoxide, acetylene, ethylene, etc., with the present of metal catalysts to grow CNTs in a tubular reactor [67]. There are five types of CVD available in this research world such as alcohol catalytic CVD (ACCVD), water-assisted CVD (WACVD), floating catalyst CVD (FCCVD), thermal CVD (TCVD) and plasma-enhanced CVD (PECVD) [21]. By controlling the processing parameter; temperature, pressure, gas flow rate, carbon feedstock, deposition time, reactor geometry and catalyst, the desired CNT structures can be tailored [28, 68–70]. The function of catalyst to synthesize CNTs throughout the process is to enhance the nucleation of CNTs by reducing the activation energy, E_a , from carbon feedstock into reactive atomic carbon. The reactive carbon is then diffused towards the substrate to generate the CNTs by heating and coating with the transition metal catalyst like Fe, Co and Ni. In addition, the diameter of CNTs can be varied by varying the particle size of metal catalysts. Small diameter of CNTs will increase the device performance. Thus, to produce CNTs with small diameter (<10 nm), it is very important to select the suitable process to synthesize catalysts nanoparticles. There are four routes to synthesize nanoparticles; wet chemical, mechanical, form-in-place and gas phase processes, in which will be discussed in the next section.

1.3 Four routes to synthesize nanoparticles

There are two different approaches to nanofabrication which are top-down and bottom-up [71]. Top-down approach is about breaking materials into basic blocks or structure. This kind of approach is time consuming, thus it is not suitable for large scale production since it is difficult to control the process and to get the narrow distribution of nanoparticles size. Lithography which is placed in form-in-place process is one of the examples for this approach. It can cause the crystallographic damage to the pattern itself. Other than that, mechanical process is also placed under the same approach meanwhile gas-phase process is classified under bottom-up approach. Bottom-up approach is a process of combining simple atomic level components to be a complex system. The simple components can be atom-by-atom, molecule-by-molecule or cluster-by-cluster. The desired products can be

achieved by this approach with some modification on the processing parameters such as temperatures, concentration and etc. The most interesting part is that it is an inexpensive process. Wet chemical process is a unique approach because it can be classified in both approaches and this process will be elaborated in details through the upcoming section.

1.3.1 Wet chemical processes

Wet chemical process is a process that involved in the reaction of two or more chemical solutions under certain conditions and processing parameters [72]. It is the best method for production of nanoparticles especially to prepare catalyst nanoparticles for CNT growth because the homogeneity of the nanoparticles can be achieved from the molecular level design of the materials. Homogeneity of the solution is crucial due to achieve a good distribution and good uniformity of the deposited nanoparticles on substrates. Chemical processes also allow control of particles size and size distribution, morphology and agglomerate size through single manipulation of the parameter [73]. Those parameters are important to determine nucleation, growth and coalescence of the nanoparticles themselves. Moreover, growth rate also another point that is needed to take into account because it will give huge effects on particle size, particle size distribution, amount of crystallinity, crystal structure and degree of dispersion [73]. The growth rate can be controlled by controlling four factors; (1) concentration of reagents, (2) processing temperatures, (3) pH and (4) the order in which the reagents are added to the solution [73].

Furthermore, wet chemical process has three main types which are colloidal chemistry, hydrothermal and sol–gel methods. The additional types to this process are combustion and organized membranes method. Each method has their own suitable precursors, solvents and other materials such as surfactants in which will be discussed in details later. The advantages of this method compared to others are it is a simple technique, cheap; less instrumentation, and low temperature (<350 °C) synthesis [73]. It is also able to produce large scale of production in variety of sizes and shapes. A wide variety of inorganic, organic and metallic nanoparticles can be fabricated through the wet chemical methods. Other than that, during the synthesis, it is possible for doping of foreign atoms (ions) into the process. Since it is able to convert the liquid form into dry powder or thin film easily especially sol–gel method, thus it has been suggested as the most suitable method to prepare metal catalysts for CNT growth.

1.3.2 Mechanical processes

Mechanical process is one of the simplest top-down nanomanufacturing techniques. This process consists of

two types of methods which are mechanical milling or attrition and mechanical alloying. Mechanical milling can be divided into two types; mechanical milling process and mechanochemical process. In mechanical milling process, the only happen is physical change of powder; single element or complex compound, in which the particles size is reduced. For example, the synthesis of CeO₂ nanopowder uses a tungsten carbide ball-milling medium with toluene as a process control agent at 300 rpm for 10 h [74, 75]. Meanwhile, for the mechanochemical process, the chemical reaction is happened. For example, by mixing ultrafine Si nanoparticles with graphite ball-mill, silica powders can be synthesized [76].

Mechanical milling process is a famous process to produce materials with nanocrystalline grain size. It is also the most productive method of producing large quantities of nanocrystalline powders from different materials such as metals, alloys, intermetallics, ceramics and composites. The objectives of this method are to reduce and change the particle size and shape, accordingly. Besides, for the mechanical alloying, it is aimed for mixing or blending of different materials to be a new phase and to synthesize nanocomposites. The minimum grain size obtainable by milling has been attributed to a balance between the defect/dislocation structure introduced by the plastic deformation of milling and its recovery by thermal processes [77]. In order to avoid the contamination during the process, hydrogen or argon atmosphere has been preferred. Other than that, processing control agent; stearic acid and toluene, also can be considered.

1.3.3 Form-in-place

Form-in-place process is a process that mainly aimed on the production of nanostructure layers and coatings. There are four examples of form-in-place process such as lithography, physical and chemical deposition and spray coating. Lithography method is usually employed in the microfabrication of integrated circuit (IC). It is more about patterning the microcircuit and most of the time this process contributes to wastage. Moreover, this method is quite expensive. For the physical and chemical deposition, they are usually seen to be used in CNT growth. Physical vapor deposition (PVD) is a neat method in which the uniform thickness of catalyst thin films and catalyst nanoparticles with the desired particle size can be obtained. However, this method also is quite expensive because it involves in high-temperature vacuum evaporation with subsequent condensation, or plasma sputter bombardment [78]. Thus, this method is not a cost effective method for the large scale of production. PVD consists of five variants which are cathodic arc, electron beam vapor, evaporative, pulsed laser and sputter depositions. All these methods have the

similarity to deposit thin film onto substrates except the source and procedures for the deposition. PVD coatings are usually harder and have high corrosive resistant as well as good impact strength. Since the process needs high temperature to be conducted, thus it is important to have a cooling water system to evacuate large heat loads.

Furthermore, chemical vapor deposition (CVD) has similarity with PVD which is based on deposition of vapor to deposit the thin films onto the substrates. However, the operating cost for this method much lower than PVD. This is due to the low processing temperature needed for the deposition process and the equipment is much simpler than the PVD one. It is also can produce high purity of products as good as PVD. Thus, this method is often to be used in most of the semiconductor industry. Besides, as stated in the previous section, CVD is one of the methods to produce CNT. For the CNT deposition, the carbon source is being used meanwhile for other deposition materials, other kinds of sources are employed according to the purposes. All of the stated methods classified under form-in-place process can be used to fabricate nanoparticles by scraping the deposits from the collector.

1.3.4 Gas-phase processes

Gas-phase process is a process that involved in precursors in gas form. Generally the processing temperature can reach up to several thousand Kelvin. High temperature is needed to generate nanoparticles from the vapor sources. The example of gas-phase process is flame pyrolysis or synthesis. Flame synthesis is a process that has been widely used in industry to produce carbon black and ceramic particles. It is a process of formation of molecular nuclei from either condensation or chemical reaction and subsequent growth by coalescence in high temperature region during the process. The generation of nanoparticles from the flame reactors is either from vapor or sprayed liquid precursors. Usually, the temperature of the flame can reach up to 2,500 K which is where the precursor gas phase will be decomposed [79]. Electro-explosion, laser ablation, high temperature evaporation and plasma synthesis are also included in the gas-phase processes [80].

2 Types of wet chemical routes

In order to synthesis particles from a solution, there are two important stages involved which are nucleation and growth stages. By governing these two stages, the particle size, size distribution and morphology of the particles can be controlled well. The nucleation stage can be indicated when the precipitation is begins by numerous small crystalline initially formed. However, these small particles are

not in a thermodynamically stable state. They are in the state of 'lonely'. Thus, they tend to make 'friend' with their 'neighbors'. Then they started to agglomerate (growth stage). Agglomeration is a process that is needed to be avoided since it will affect the particles size and size distribution of the products. Hence, single nucleation event is necessary to prevent additional nucleation during the subsequent growth so that highly uniform nanocrystals can be formed.

Since agglomeration is occurred when the nucleation and growth stages is happened at the same time, thus, it is possible to separate these two stages so that agglomeration can be avoided. LaMer and his friends has utilized a process called homogeneous nucleation to overcome this problem; LaMer concept [81]. In the homogeneous nucleation processes, nuclei appear in a homogeneous solution without any seed for heterogeneous nucleation. There exists a high energy barrier to nucleation because the system spontaneously changes from homogeneous phase to heterogeneous phase (liquid + nanocrystals). The LaMer diagram in Fig. 1 will show clearly how this energy barrier works to separate nucleation and growth stages.

The LaMer plot can be divided into three phases:

A. Initiation phase:

- i. The concentration of 'monomer' (the smallest subunit of the bulk crystal) increases continuously with time.
- ii. The precipitation does not occur in phase I even under supersaturated conditions because the energy barrier for spontaneous homogenous nucleation is very high.

B. Nucleation phase:

- i. Nucleation occurs—the degree of supersaturation is high enough to overcome the energy barrier, thus resulting in the formation of stable nuclei.

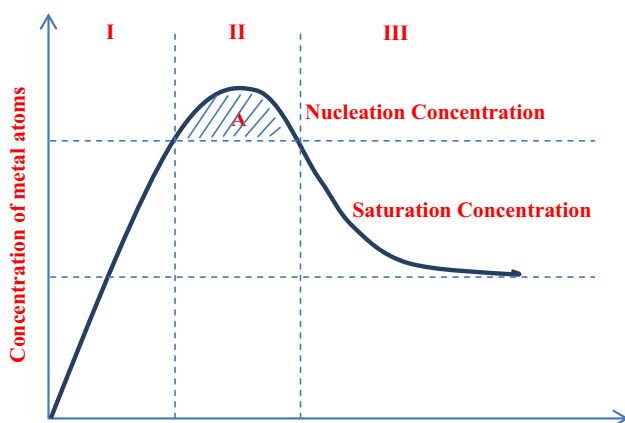


Fig. 1 The LaMer diagram illustrating variation of the monomer concentration with time during the growth process to obtain monodisperse of nanocrystals

- ii. Since the rate of monomer consumption resulting from the nucleation and growth processes exceeds the rate of monomer supply, the monomer concentration decreases until it reaches the level at which the net nucleation is zero.
- iii. The 'A' label in the figure is indicated the nucleation period.

C. Growth phase:

- i. Below this level, the system enters the growth stage.
- ii. The nucleation is effectively stopped and the particles keep growing as long as the solution is supersaturated.

2.1 Metal and intermetallic

Metal can be defined as a solid material (an element, compound, or alloy) that is hard, definite shape, shiny, and has good electrical and thermal conductivity. Metals are generally malleable, fusible and ductile. In the periodic table, 91 materials are metals. Meanwhile, intermetallic is a compound as solid phase consisting of two or more metallic elements, with optionally one or more nonmetallic elements has different structure form its constituents. The general method in synthesis of metal colloidal dispersions in order to obtained metal nanoparticles is reduction of metal complexes in dilute solutions [82]. By combining a low concentration of solute and polymeric monolayer (stabilizer) adhered onto the growth surfaces, the formation of metallic nanoparticles can be achieved. There are three main 'ingredients' for this type of chemical route; (1) precursors, (2) reduction reagents and (3) other chemicals (polymeric stabilizer or surfactants) (Table 2; [83]).

Metal and intermetallic nanoparticles can be obtained by two methods; (1) aqueous method and (2) non-aqueous method. Both methods have quite similar chemical synthesis set-up except the solvent. Glass reactor chamber is usually used for the chemical reactions.

2.1.1 Aqueous method

Aqueous method is a method that used water as the solvent. As known, water is a good solvent for polar or ionic compounds and has been widely used as solvent system for most of the chemical solution reaction. This is due to the high permittivity of the water. Elemental metal nanoparticles for catalytic and biomedical application such as Au, Ag, Pt and Pd nanoparticles may be prepared by adding liquid reducing agents to aqueous solutions of respective salts in the presence of a stabilizer. For example, CdS nanoparticles has been synthesised by rapid mixing of

Table 2 Summary of precursors, reduction reagents and polymer stabilizers [83]

Precursors	Reduction reagents	Polymer stabilizers
Metal anode: Pd, Ni, Co	Hydrogen (H ₂)	Polymer stabilizers
Palladium chloride (PdCl ₂)	Sodium citrate (Na ₃ C ₆ H ₅ O ₇)	Poly(vinylpyrrolidone), PVP
Hydrogen hexachloroplatinate IV (H ₂ PtCl ₆)	Hydroxylamine hydrochloride (NH ₄ OH + HCl)	Polyvinylalcohol, PVA
Potassium tetrachloroplatinate II (K ₂ PtCl ₄)	Citric acid (C ₆ H ₈ O ₇)	Polyethyleneimine
Silver nitrate (AgNO ₃)	Carbon monoxide (CO)	Sodium polyphosphate
Silver tetraoxylchlorate (AgClO ₄)	Phosphorus in ether (P)	Sodium polyacrylate
Chloroauric acid (HAuCl ₄)	Methanol (CH ₃ OH)	Tetraalkylammoniumhalogenides

Na₂S and Cd(NO₃)₂•4H₂O flow streams within a silicon/glass micromixer based on the principle of flow lamination [84]. The stabilizer and reduction reagent used for this reaction were sodium polyphosphate and Na₂S, accordingly.

The selection of reduction reagents for the process is crucial and it may affect the nucleation rate and particle growth which in turn influences the particle size and size distribution of the nanoparticles. Strong reduction reagents may lead to fast reaction rate and produce small particles. Meanwhile, for the selection of weak reduction reagents may induce a slow reaction rate and thus favors larger particles. In addition, slow reaction will tend to give two kinds of results which are wider and narrower size distribution of particles. For the wider size distribution, it leads to a continuous formation of new nuclei while for the narrower one; it will lead to diffusion-limited growth. Based on the comparison of average sizes of Au nanoparticles in Table 3, the reduction ability of citric acid is higher than sodium citrate. Since citric acid is a strong reduction reagent, thus the obtained particle size of Au nanoparticles is smaller than sodium citrate with the SEM result of 12.5 nm compared to 17.6 nm.

The suitable selection of polymer stabilizer or surfactant also should be made. It is employed to the reaction to form a monolayer on the surface of the nanoparticles. The addition of the stabilizer may help to prevent agglomeration of nanoparticles. Particle with smaller size has higher surface area and more reactive compared to the large one. Thus agglomeration is usually happened to these nanoparticles. Hence, stabilizer is really needed. However, the presence of such polymer stabilizers during the formation of nanoparticle can have various influences on the growth process of nanoparticles. Interaction between the surface of a solid particle and polymer stabilizer may vary significantly depending on the surface chemistry of the solid, polymer, solvent and temperature. A strong adsorption of polymer stabilizers would occupy the growth sites and thus reduce the growth rate of nanoparticles while a full coverage of polymer stabilizer would hinder the diffusion of growth species from the surrounding solution to the surface of growing particle.

2.1.2 Non-aqueous method

Non-aqueous method or can be called polyol method is a method that needs no water as the solvent. Polyol is a short form for polyalcohol (e.g. ethylene glycol (EG), diethyleneglycol or 1,2 propanediol). The polyol will act as both reduction reagent and solvent. This non-aqueous may minimize the agglomeration and surface oxidation problems. It is an ideal method for the preparation of larger nanoparticles with well-defined shapes (i.e. cubic, rod, etc.) and controlled particle sizes (various shapes). Elemental metal (Cu, Ni, Co, Pt, Co–Ni) and oxide particles can be obtained by this method. Since the employment of non-aqueous solvent only can minimize the agglomeration and oxidation problems, thus suitable stabilizer is needed for the reaction. Generally, PVP (Poly(vinylpyrrolidone) is used as the capping or stabilizing reagent owing to its excellent adsorption abilities [85]. In a typical polyol synthesis, the reduction of a metal salt was carried out by liquid polyol or diol in the presence of a stabilizing agent.

The polyol method is basically conducted by adding precursor compound (oxides, nitrates and acetates) into a mixture of stabilizer dissolved in polyalcohol. Then, the mixture is heated (<200 °C) in a certain duration of time. For example, to obtain zinc oxide nanoparticles, a mixture of zinc(II) acetate with its polyalcohol and stabilizer was heated at 170 °C for 30 min with constant stirring. When the white suspension was obtained, then it was left overnight and centrifuged at 8,000 rpm for 20 min to separate the particles from the suspension [86]. The particles obtained should be rinsed with ethanol several times to remove the organic compounds and the stabilizer leftover. Then, Ar atmosphere is needed to dry the particles.

The advantage of polyol method compared to aqueous method is that this method results in the synthesis of metal nanoparticles protected by surface-adsorbed glycol, thus minimizing the problem of oxidation. Other than that, the use of non-aqueous solvent may help in reducing the problem of hydrolysis of fine metal particles that often occurs in the aqueous case. The products from this method have been widely used in several application such as the

use of Ag nanoparticles in washing machine. It is called 'Silver Wash'. Microscopic bits of electrolyzed silver (about 400 billion silver particulates) are dispersed and dissolved into the wash water, where they infiltrate fabrics on an almost molecular level. The silver nanoparticles kill 99.9 % of bacteria and fungi, says the manufacturer. Another example is in fresh box containers in which naturally kill bacteria and limit mold growth without toxins.

2.2 Hydrothermal

Hydrothermal is an important method for the synthesis and processing of advanced ceramics (structural and functional), catalysts, composites, alloys, intermetallic and nanomaterials from high temperatures aqueous solution at high vapor pressures. It is a non-conventional method to obtain nanocrystalline inorganic materials. Various inorganic materials can be prepared at temperatures substantially below those required traditional solid-state reactions. Moreover, the products obtained from hydrothermal method do not need post-annealing treatment and most of the time they are in crystalline structure. Thus, this may cut-off the cost of production.

As known, wet chemical route is involved in chemical reaction and hydrothermal also is not excluded from this reaction. The chemical reaction of hydrothermal is occurred in water system at above ambient temperatures (>100 °C) with pressure during the heating more than 1 atmosphere. The maximum limits of the process may reach up to 1,000 °C and 500 MPa pressure [87]. Since the required processing temperature and pressure is quite high, thus an autoclave is needed to withstand the processing condition for a long time. The autoclave also can provide a sealed or closed system. Hydrothermal process has a special type of chemical transport reaction because it depends

on liquid-phase transport of reactant for nucleus formation of the desired final products. The presence of water at elevated temperatures may help a lot for the precursor material transformation. Water is a common solvent in which will display different characteristics at different temperatures. For this case of process, the water can be an intermediate for the transformation of heat, pressure and precursor of the materials. The added chemicals compound also can be dissolved easily at the particular temperature. For certain cases, water also serve as the precipitating agent.

Hydrothermal method has five main parameters; (1) initial pH of the medium, (2) duration of synthesis, (3) temperatures of synthesis, (4) pressure of the system, and (5) concentration of reactants and additives. Those parameters may determine the processing space and thus influence reaction and crystallization kinetics. This process is occurred rapidly so that all precursors' reaction will be finished within several hours in order to avoid a significant growth of the product particles. Moreover, high pressure is required to increase the solubility in the aqueous medium so that continuous crystal growth can be obtained. Thus, it leads to the non-ideal and non-equilibrium state to the reaction. By that, the solvent is always at its near-critical, critical or supercritical state. All these conditions may help for obtaining an effective reaction and hence produce a good result of particles formation.

A wide range of chemical compositions can be used to produce nanoparticles especially to produce ceramic nanoparticles. Most of the materials synthesized by this method are materials that cannot be obtained using classical synthesis at high pressure. The most common oxide materials are ZrO₂, TiO₂, SiO₂, ZnO, Fe₂O₃, Al₂O₃, CeO₂, SnO₂, Sb₂O₅, Co₃O₄, HfO₂, etc. The examples of complex oxides are BaTiO₃, SrTiO₃, PZT, PbTiO₃, KNbO₃, KTaO₃, LiNbO₃, tungstates, vanadates, molybdates, zeolites, etc. [88]. Since the process needs simple equipment and low energy, thus this may leads to cost effective process. Even the autoclave is quite expensive, but with large scale of production, the cost effective still can be obtained. However, it is agreed that it is impossible to observe the reaction process (black box).

2.3 Sol-gel

Sol-gel or chemical solution deposition is one of the wet chemical routes. Recently, this process has been widely used in the fields of materials science and ceramic engineering. Sol can be defined as a colloidal suspension of solid or macromolecular particles (1–1,000 nm in size) in a liquid. It has an unfixed shape in which the particles in the solid phase can move freely. Besides, gel is a porous 3-dimensionally interconnected solid network surrounding

Table 3 Comparison of average sizes of Au nanoparticles synthesized using various reduction reagents, all in nanometer [83]

Reduction reagents	SEM
Sodium citrate	17.6 ± 0.6
Hydrogen peroxide	15.7 ± 1.1
	19.7 ± 2.6
Hydroxylamine hydrochloride	22.8 ± 4.2
Citric acid	12.5 ± 0.6
Carbon monoxide	5.0 ± 0.5
	7.5 ± 0.4
	12.2 ± 0.5
Phosphorus	8.1 ± 0.5
	15.5 ± 1.7
	25.6 ± 2.6
	35.8 ± 9.7

by a continuous liquid medium (phase). It has a fixed shape. The particles in the solid phase are fixed in accordance with certain network structure and the movement is limited.

There are five steps in sol–gel process; (1) solution preparation, (2) sol stage (3) gel stage, (4) deposition technique and (5) heat treatment. In this process, there are two main ingredients should be presented which are precursors and solvents. The suitable precursors and solvents for the desired product should be determined properly. The typical precursors for this process is from metal alkoxides and metal chlorides. However, metal alkoxides are much more favored because they readily undergo hydrolysis. The general chemical formula for metal alkoxides is $[M(OR)_n]$, where R is an alkyl group, inorganic or organic salts. Metal alkoxides require low processing temperature for fabrication of nanomaterial with required phase selection with correct stoichiometric ratio.

At the stage of preparing the precursor solution, the solid precursor will be dissolved in an organic solvent miscible with water or the reagent. Once the homogeneous solution is obtained, the solution will be converted to sol by the treatment with a suitable reagent. Hydrolysis reaction is occurred at this stage. It is a reaction in which metal alkoxide ($M-OR$) react with water to form metal hydroxide ($M-OH$). Normally, it takes several minutes to complete the reaction but it still depends on the types of metal precursors employed for this process. At the sol stage, the sol can be used to be transformed into thin films, powders, fibers and patterns. Thin films can be produced from sol by spin-coating, dip-coating, flow-coating and electro-deposition. While for the powder, it can be formed by spray-drying technique. Furthermore, fibers can be formed by electro-spinning, blow spinning, pulling-down and pulling-up techniques. For the patterns, many techniques can be used to fabricate the patterns such as UV patterning, electron-beam lithography, X-ray direct writing techniques and etc.

By allowing the sol to change into gel through polycondensation, dense product, powders, monoliths, other forms can be produced. Condensation is a reaction which occurs when two metals hydroxides ($M-OH + HO-M$) combine to give a metal oxide species ($M-O-M$). The reaction forms one molecule of water. It is a process to induce the formation of small solids particles or cluster in a liquid (1–1,000 nm). Then, when the gel has been shaped to the finally desired shapes, the semi-products are going to heat treatment process in which to create a strong bonding between the particles and remove the solvent left in between particles.

2.4 Combustion

Besides hydrothermal method, combustion method also an important technique for the synthesis and processing of advanced ceramics, catalysts, composites, alloys,

intermetallic and nanomaterial. Combustion synthesis in solid-state chemistry is also known as metathesis reactions or self-propagating high-temperature synthesis (SHS) [89]. Generally, the high temperature is achieved not by placing the samples in a furnace but rather by using the heat generated by the exothermic chemical reaction itself. Combustion synthesis or combustion method can be characterized by fast-heating rates, high temperatures and short reaction times. Those indicators are quite similar to the hydrothermal except pressure used in hydrothermal method. There are two methods of combustion; (1) solid state combustion and (2) solution combustion.

Solution and solid state combustion has slightly different in terms of the initial form of precursors only. Solution state combustion is combustion of a mixture of solvent and precursor in a chamber. Generally, the mixture is brought to boils until it ignites. Once the self-sustaining and rather fast combustion reaction occurs, a dry, crystalline and fine oxide powder will be produced. The common metal precursor used is metal nitrate due to its high oxidization ability. The source to ignite the combustion process is organic fuel (glycine, urea, carbonylhydrazide or citric acid); reducing agents). A strong exothermic reaction is occurred during the process in which leads to the formation of nanopowder at substantially lower temperature than otherwise required. Usually, the flames produced from the combustion can reach temperatures that exceed 1,500 °C due to the large amount of gases formed at initial [90].

Frequently, nitrates are chosen as metal precursors. This is because the NO_3^- groups are oxidizing agents. This group also has high solubility in water, thus allows a sufficiently high solution concentration. Furthermore, organic compound has been favored as fuel for combustion. It is due to the high availability of the sources in the market and cheap. The most convenient fuel is urea. The organic fuel is the source of C and H which in combustion the CO_2 and H_2O will be formed for heat releasing. They are also formed complexes with metal ions facilitating homogeneous mixing of the cations in solution.

2.5 Nanoparticles via organized membranes

As mentioned in the previous section, surfactants or polymeric surfactants are used to stabilize the colloidal particles by controlling the interface force. Utilization of self-assembled membranes such as micelle or microemulsion can be an alternative approach to synthesis stabilized and size controlled nanoscale particles. Microemulsion is a thermodynamically stable dispersion of two immiscible liquids with the assistance of an emulsifier or surfactant. It is formed from many unimers. The unimer has amphiphathic property in which the head is hydrophobic; like water, while the tail is hydrophilic; dislike water (Fig. 2).

Basically, there are three types of micelles; (1) normal micelle, (2) reverse micelle and (3) bilayer lamella (Table 4). The hydrophobic hydrocarbon chains of normal micelle are towards the interior of the micelle and leaving the hydrophilic groups in contact with aqueous medium. While for the reversed micelle, it is formed in non-aqueous medium in which the hydrophilic groups faced towards the interior of micelle. Normally, most of the precursors used are easily dissolved in water medium compared to oil medium. Thus, reversed micelle has been used widely rather than normal micelle. Surfactants as self-assembled structures can act as reactor chambers to synthesis nanoparticles by controlling particle nucleation, growth, size and shape of the particles (in a confine space). In this synthesis, the reaction is done only inside the micelle in which the available reactant is in the desired amount. When the reactants are completely consumed, the process will be automatically terminated.

As shown in Fig. 2, the amphipathic or surfactant structure consists of two parts; (1) head: hydrophilic and (2) tail: hydrophobic. They are usually self-assemble at air/aqueous solution or hydrocarbon/aqueous solution interface when the surfactants are dissolved into a solvent (water or oil). Then the hydrophilic part is turned towards the aqueous solution. Micelle will be formed when the concentration of the surfactants or block polymers exceeds a critical level. The surfactant will reside at the interface separating hydrocarbon and aqueous solution. These interactions allow the molecules to self-assemble into membrane structure with minimum energy configuration. The micelle or microemulsion can be formed in two ways; (1) direct and (2) reverse. Direct reaction is happened when oil is dispersed in water, (o/w) colloidal system while the reverse reaction is vice versa. Direct reaction is a cost effective process and environmental friendly but limited precursor can react in oil core. However, reverse reaction has been intensively studied because various metal salts and organometallic compound can stay in aqueous solution through hydrolysis.

In order to prepare the nanoparticles, two microemulsions are prepared separately by mixing each precursor

Fig. 2 Schematic diagram of amphipathic structure

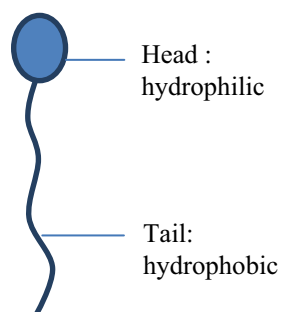





Table 4 Types of micelles [91]

Types	Structures	Sizes
Spherical/normal micelle		3–6 nm
Reverse micelle		3–6 nm
Bilayer lamella		30–60 nm in diameter

with surfactant, oil and water until the systems become homogeneous (transparent liquid). Then both microemulsions are mixed together. During vigorous stirring, the micelles or reverse micelles collide with each other as a result of Brownian motion, which lead to the formation of transient dimers with oily or aqueous channel between two micelles or reverse micelles. The channels provide exchange opportunities of precursors in different microemulsions in which the exchange process determines the particle growth rate. After the breakup of dimers, the micelles or reverse micelles containing both precursors become independent nanoreactors in which the chemical reactions take place rapidly, thus leading to the nucleation of nanoparticles when reactants supersaturate the nanoreactors. The particles are either filtered or centrifuged and then washed with acetone and water to remove any residual oil and surfactant molecules adsorbed on the surface of nanoparticles. Subsequently, the powders are calcined to form the final product.

3 Flow of sol–gel (thin films formation)

3.1 Types of functional solutions

Thin film can be deposited on the selected substrates through sol–gel process [92]. As mentioned in Sect. 2.3, thin films can be produced by spin-coating, dip-coating and etc. These techniques require catalyst solution to achieve the desired deposition products. Alcoholic solution containing metal salts is the most common catalyst solution [25, 93, 94]. Alcohol is one type of solvent that can dilute the metal salts well (i.e. methanol, ethanol). It is also has high volatility in which very helpful in the formation of thin film during the deposition process. Among the available metal catalyst solution, metal nitrate and metal acetate

Table 5 Summary of metal nitrates and metal acetates for CNT growth

Functional solution	Metals	Type of CNT	Ref
Nitrates (NO_3^-)	Fe	SWNTs	[95, 96]
Nitrates (NO_3^-)	Co	SWNTs	[97, 98]
Nitrates (NO_3^-)	Ni	MWNTs	[99, 100]
Acetates ($\text{C}_2\text{H}_3\text{O}_2^-$)	Fe	MWNTs	[101]
Acetates ($\text{C}_2\text{H}_3\text{O}_2^-$)	Co	Aligned-SWNTs	[102–105]
Acetates ($\text{C}_2\text{H}_3\text{O}_2^-$)	Ni	MWNTs	[106]

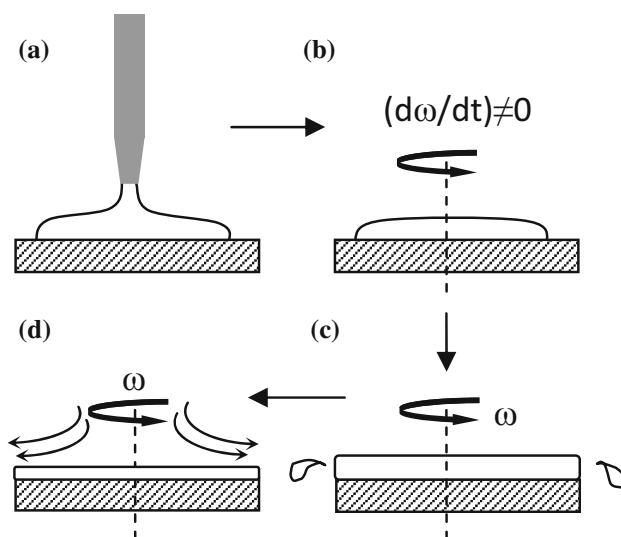
have been favored as the catalyst precursors due to their high solubility in alcohol (Table 5).

3.2 Thin film preparation

3.2.1 Spin coating

Spin coating has been widely used in microelectronics industry to produce photoresists; the thickness typically in micron range. This process is one of the famous processes for thin film deposition such as electrodeposition [107], spray pyrolysis [108], chemical bath deposition and dip coating technique [59]. However, the thin film production in nano range which is less than 100 nm is still remained largely unexplored. Thin films (<100 nm) is favored for catalyst thin films for the purpose of CNT growth. It is expected that if that thickness of film is achieved, the particles will be formed in the size of several nano-meter. It is also expected that the CNT grown on the particles will have the same or less diameter as the catalyst particles. Since spin coating has a potential to control the thickness of thin films by controlling the spin speed, spin duration and angular acceleration, thus, this method has been started to be explored [109, 110].

The principle of spin coating method is basically the solution precursor (metal precursors dissolved into solvent) is deposited on the cleaned substrate. According to a group of researchers, the substrate is rapidly accelerated according to the desired spinning rate [111]. During the spinning process, due to the centrifugal force, the deposited solution flows radially and it cause the excess is executed of the edge of substrate. This phenomenon will cause the deposited solution to form thin film when the equilibrium thickness is obtained due to solvent evaporation [111, 112]. The mathematical modeling also can be used to explain the principle of spin coating process and modify the controlled parameter in order to obtain the desired thickness of thin films. However, it is not covered in this area of discussion. The spin coating process is basically consists of four steps, as illustrated in Fig. 3.

**Fig. 3** Four steps of spin coating process

- Solution dropping:** The catalyst precursor dissolved in solvent is dropped on the center of the cleaned substrate, initially at rest.
- Spin-up:** The centrifugal force allows the deposited solution to flow radially on the substrates.
- Spin-off:** The excess solution at the edge of the substrate is ejected in drops and leads to thin the film layer. The execution of the excess solution is decreasing throughout this step because as the thickness of the layer is decreased, the viscosity of the solution will be increased due to the high flow resistance.
- Evaporation:** It occurs along the spinning process to remove the solvent and thinning the film especially during the spin-off step till the end.

By depositing a colloidal solution (a mixture of PEG-400-ethanol-iron nitrate) dissolved in 50 % ethanol on a 15 mm² of silicon wafer (1,000 Å thermal oxide layer) with the spinning condition of 8,000 rpm spin speed, 30 s spin duration and 300 rpm/s angular acceleration, a group of researchers was able to obtain a uniform size distribution of iron particles with the average particle size of 5.08 nm [57, 95]. They were also able to confirm the SWCNT growth on the thin film from the obtained intensity ratio of the G- to D-band (I_G/I_D) of Raman spectrum with the average ratio of over 10. Meanwhile, when the spin speed used was 5,000 rpm, the size of cobalt catalyst particles obtained was 14 nm [113]. It shows that the selection of spin speed will affect the size of particles formation. It is also found that the spin duration of 30 s has been used frequently in this area of research [57, 95, 114]. Hence, proper selection of the parameter is very crucial to determine the size of catalyst particles.

3.2.2 Dip coating

Dip coating is an ideal technique for the translation symmetric substrates. The process is simply placed the substrate in the solution and by controlling the velocity (usually constant), the film is uniformly covered the immersed surface during the withdrawn substrate from the solution. This film is left drying for some minutes to allow the sol–gel transition to take place. The available withdraw velocities are from 1 up to 50 cm min⁻¹. The film thickness increases with increasing withdrawal rate and for a given withdrawal speed the film thickness increases with an increase in oxide content. The thickness coating by this process is usually in range of 50–500 nm. The thickness can be calculated by the Landau–Levich equation [115]. The steps involved in dip coating process are illustrated in Fig. 4.

$$h = \frac{(\eta * v)^{2/3}}{\gamma_{LV}^{1/6}(\rho * g)^{1/2}} \quad (1)$$

h = coating thickness; v = viscosity; γ_{LV} = liquid–vapour surface tension; ρ = density; g = gravity.

The uniformity of the thin film produced by this process can be controlled. However, the process is quite slow compared to spin coating process. A film layer with the thickness of 96 nm has been obtained from the deposition of solution (cobalt acetate tetrahydrate and ethanol) by dip coating with speed of 4 cm/min [58]. In other paper, the same drawing speed has been used and the coated substrate has been successfully grown the SWCNTs with the diameter range of 0.8–1.4 nm [59].

3.3 Heat treatment

Heat treatment is the final step for catalyst particles formation. It is a heating and cooling process in which will

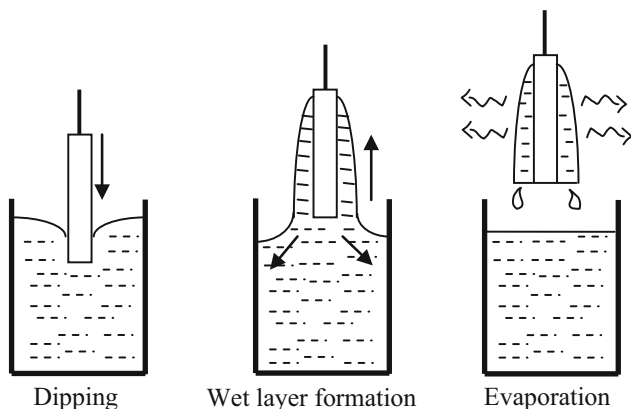


Fig. 4 Stages of the dip coating process

turn the thin film form into particles form. There are several parameters that will affect the size of catalyst particles. Since the small particle size is very important towards CNT growth, thus every factor that will affect the value is taken into concern. For the analysis purpose of the uniformity of catalyst distribution along the substrate surface, it is helpful to compare the roughness value with the average film thickness. If the roughness is considerably smaller than the thickness, the catalyst film is likely to be continuous. The quality of the thin films by sol–gel spin coating process and crystallization was influenced by heating temperature [116]. Magnetic elements, such as iron, have a strong tendency to combine at high temperatures because of their magnetic properties and their high specific surface energy [117]. The particles that were close to each other coalesced, forming larger particles with an elliptical shape [57].

The stability and the uniformity of the cluster play an important role in formation of CNTs and also their properties. Cluster combines at high temperature of reduction or oxidation and reaction when salt are treated to obtain the metal catalyst [118]. With the suitable temperature, the large agglomeration of iron salt can be prevented. The diameter of CNTs could be controlled directly by the size of the catalytic nanoparticles [119]. During the particles formation, the surface cracks opened up and expanded to a larger size, meanwhile, the widths of cracks increased with increased temperature. Then, after heat treatment, the surfaces of the splats became rougher with formation of new tiny particles. The roughness of particles increased with increased temperature. Cracks widening might be related to the volume change associated with the transformation of amorphous to crystalline, changing a loose packed amorphous structure to a close packed crystalline structure [120]. The illustration of heat treatment process is shown in Fig. 5.

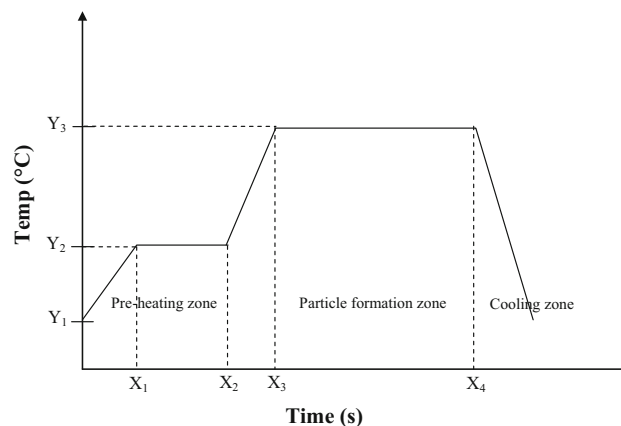


Fig. 5 Schematic diagram of heat treatment process

Table 6 Summary of analysis on cobalt and iron catalyst

Methods	Description	Findings	Ref
XRD	Using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$)	The average particle sizes of Co ₃ O ₄ thin film were calculated using the full width at half maximum (FWHM) of (311) peak from the Scherrer's method: $D = C\lambda/\beta \cos \theta$ β : full width at half maximum D: crystallite size, λ : wave-length C: correction factor = 0.90	[103]
	The phase purity of the samples is examined using Cu-K α radiation, 40 mA and 45 kV	XRD of SWNTs is characterized by a small relative intensity of the peak located at 2θ equal 26.097°	[58]
SEM	Model: JSM-6380 High resolution SEM operated at 20 kV in KSU Model: JEOL-JSM-6360, Japan, operated at 20 kV	The resolution of the used SEM is not high enough to show the detailed features of the surfaces The surface morphology for all films was nearly the same with slight increase in grain size The film surface looks smooth and composed of very fine elongated particles smaller than 80 nm in length connected by two–three spherical grains of about 40–45 nm in diameters Overgrowth of clusters is clearly seen	[58] [103]
FESEM	The study was performed using a Gemini LEO 1525 instrument operating at 15 kV FESEM (ZEISS SUPRA 40)	FESEM images of the CNTs grown on the wafer with five different absolute ethanol to PEG ratios and only diluted ethanol after 30 min of methane CVD Dense CNT arrays were grown when colloidal solutions with 0, 25 and 50 % ethanol were applied CNTs found were larger in diameter and carbon nanocapsules were visible when colloidal solutions	[119]
		High aspect ratio nanostructures are observed on the two catalyst film surfaces	[121]
TEM	TEM investigation was carried out using a JEOL 2010F operated at 200 kV and equipped with a Gatan imaging filter (GIF) system 20 kV Tecnai-G2 F-20 model of FEI. Device resolution from 0.14 to 0.18 nm maximum thermal current is greater than 100 nA There is 0.5 nA or larger current in 1 nm probe. The energy distribution is around 0.7 eV	Single-walled CNT was not found in the sample Too large catalyst particle to form single-walled CNTs Three kinds of multi-walled carbon morphologies were observed: Lengths from about 0.1 μm to a few microns, Tipped with catalyst particles partially exposed to environment CNT diameter is nearly 10 nm The appearance is darker in the picture. The CNTs have diameters between 1.5–5 nm and also are transparent	[122] [96]
AFM	Scan size: 0.5, 1.0 and 2.0 μm . Root mean square (rms) and peak-to-valley roughness values MPF3D Asylum Research with a cantilever (Arrow TM NC, Nanoworld) operated in the tapping mode. Scan rate: 1 Hz Scan domains were varied from 2×2 to $1 \times 1 \mu\text{m}$, while maintaining the resolution at 512×512	The oxide surface roughness was measured to be quite small, not exceeding 0.1–0.2 nm To evaluate the surface roughness RMS value increases from 0.14 nm at 600 °C to 0.69 nm at 800 °C, indicating the presence of more nanoclusters on surface after reduction at higher temperatures	[123] [124]

3.4 Characterization method

There are many characterization methods can be employed to analyze the properties and morphology of the particles obtained. Surface morphology can be studied by scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). Besides, the particle size can be measured either by the obtained morphology or X-ray diffraction (XRD). Commonly, the important information that is needed to measure and study is the particle size, particle distribution, uniformity and thickness of the thin film. Table 6 summarized the analysis for cobalt and iron catalysts.

4 Summary

The optional processes to produce nanoparticles have been viewed. The available processes are wet chemical, mechanical, form-in-place and gas-phase. Out of those available processes, wet chemical process is the most suitable process to deposit the selected metal catalysts on the selected substrates for CNT growth purpose. Since the thickness of the deposited catalyst thin film is the matter of concern, thus spin coating is the most suitable method to achieve the desired thickness of thin films. The thickness of thin films is inversed to the spin speed, spin acceleration and duration of spin. The particles are formed during the heat treatment process. Hence, the pre-heating and heating temperature must be taken into account. The particle size and shape will be affected by the employed temperature. Since it is a cost effective process, perhaps the spin coating method can be used widely to deposit metal catalysts for CNT growth purpose. In conclusion, solution process is a good alternative technique for metal catalyst thin film deposition and particles formation towards CNT growth due to low cost of production, simple equipment, low energy consumption and can be conducted in ambient temperature.

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