Methods for synthesis of carbon nanotubes - Review

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ABSTRACT: Carbon nanotubes have different properties such as high strength and high Young's modulus, thermal and electrical conductivity, chemical reactivity and other unique physical, mechanical and chemical properties. With attention to these properties; they could have various applications in industrial, medicine and agriculture. Carbon nanotubes synthesis by variety methods and each of the mechanisms have precise features that can have specified properties of carbon nanotubes. Arc discharge, laser ablation and chemical vapor deposition are most common methods and Mechano-thermal, electrolysis and flame are others ways for synthesis carbon nanotubes. In this paper, synthesis of carbon nanotubes with common methods and other different methods were compared and discussed.

Keywords: ARC Discharge; Carbon nanotubes; CVD; Electrolysis; Flame Synthesis; Laser Ablation; Mechano Thermal; Synthesis methods of carbon nanotubes

INTRODUCTION

Carbon nanotubes are fourth allotrope of carbon that observed by Iijima in 1991 (Khosravian and Rafii-Tabar, 2007, Iijima, 1991); however first discover of cnt attributed to Radushkevich et al., (Radushkevich and Lukyanovich, 1952). Their formation by torsion hexagonal graphene sheets with sp² bonds and create tubal structure with specified diameter (Sgobba and Guldi, 2009). By structural formation, Carbon nanotubes categorization to zigzag, armchair or chiral; also end of them like hemisphere fullerene can be open or closed (Khosravian and Rafii-Tabar, 2007, Smalley, et al., 2003, Guldi and Martin, 2010, Varshney, 2014). High surface ratio, very small diameter, symmetric structure, charge absorbing and transfer, conductive and semi conductive type, strong π and σ bonds and 1 TP young modulus are important reasons of unique physical and chemical properties (Meyyappan, 2004). Due to the specific properties of CNT (Carbon Nanotube); could be predicting different application of carbon nanotubes; such as; separation, biological and chemical purification for air and water filtration, collar cells (Kumar, et al., 2016), agriculture (Mukherjee, et al., 2016), pharmaceutical and medicine application (Ji, et al., 2010, He, et al., 2013), textile industrials, saving energies and gasses, coatings, sensors, transis-tors, computer memories and field emission displays (Meyyappan, 2004, Guldi and Martin, 2010). By pay-
ing attention to the band gap of CNT; these nanostructures are ideal for optical devices with 300-3000nm wave length. Other application of carbon nanotubes are biosensors (Varshney, 2014), to build artificial arm (Aliev, et al., 2009) and as reinforcement phase in composite materials (Mansoor and Shahid, 2016).

SYNTHESIS METHODS OF CARBON NANOTUBES

First synthesis of CNT was done accidentally by arc discharge (Iijima, 1991) and now synthesis methods of carbon nanotubes are different and various. Generally, produce type can specified properties of CNT (Guldi and Martín, 2010); precursor (which can be solid, liquid, or gas), heat source, time, temperature, atmosphere of reactions and commonly; mechanism, determinate traits of CNT. Most common methods for synthesis of carbon nanotube are arc discharge, laser ablation and chemical vapour deposition (Guldi and Martín, 2010); precursor (which can be solid, liquid, or gas), heat source, time, temperature, atmosphere of reactions and commonly; mechanism, determinate traits of CNT. Most common methods for synthesis of carbon nanotube are arc discharge, laser ablation and chemical vapour deposition (Guldi and Martín, 2010); precursor (which can be solid, liquid, or gas), heat source, time, temperature, atmosphere of reactions and commonly; mechanism, determinate traits of CNT. Most common methods for synthesis of carbon nanotube are arc discharge, laser ablation and chemical vapour deposition (Guldi and Martín, 2010). Relation (1) shows formation lithium carbide (Terrones, 2003).

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2\text{Li}^+ + 2e^- + 2\text{C}_{(\text{graphite})} \rightarrow \text{Li}_2\text{C}_2
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By forming lithium carbide (Li₂C₂), synthesis of CNT can be started in liquid phase. Generally; diameter of CNT in this method was 2-10 nm and length of them is 0.5 micrometer or more was reported and amorphous carbon, carbon nanofibers, nanographites and encapsulate CNT are byproducts of this method (Chen, et al., 1998). Obtained CNT usually are multi walled, but also in some researches, produced single walled CNT (Ren, et al., 2012). Different salts, applied for producing CNT such as NaCl, LiCl, KCl, and LiBr (Guo, et al., 1995a). Current density, electrolysis regimes, time, molten salt and temperature are the controller parameters of reaction (Rafique and Iqbal, 2011, Chen, et al., 1998, Guo, et al., 1995b). By optimizing condition of process, the reaction yields up to 20-40% increase for producing multi walled carbon nanotubes (Terrones, 2003). Electrolysis can be done in low temperature, they don't need to advanced equipment, possibility to controlling process of synthesize, have high quality, having low energy consumption and also they are not suitable for mass production (Szabó, et al., 2010, Rafique and Iqbal, 2011).

CVD

CVD method known as simple way with gas precursor that containing carbon such as CO₂ or C₂H₂, C₂H₄ and...
other hydrocarbons (Gului and Martin, 2010, Söylev, 2011, Kumar and Ando, 2010) and temperature of CVD changing amount 350-1000°C (Meyyappan, 2004, Gului and Martin, 2010). Different parameters influence on growth; such as: time and temperature of reaction, diameter of catalyst, rate and type of reactant gas (Öncel and Yürüm, 2006). Classification methods of CVD, based on energy source and categorization in various types; for example when heat source is thermal resistance, flame or infrared lamps, this CVD called thermal CVD (Meyyappan, 2004) and also mechanism and catalyst of process effective in nominated of CVD. Common methods for synthesis CNT are: plasma enhanced PE-CVD (Plasma Enhanced Chemical Vapor Deposition) (Boskovic, et al., 2002, Meyyappan, et al., 2003, Hu, et al., 2009, Hoffmann, et al., 2003), aerosol CVD AA-CVD (Aerosol-Assisted Chemical Vapor Deposition) (Queipo, et al., 2006, Byeon, et al., 2010, Abdullayeva, et al., 2015), with aerogel (Zheng, et al., 2002), with alcohol catalyst assisted AC-CVD (Alcohol Catalytic Chemical Vapor Deposition) (Murakami, et al., 2003, Ayala, et al., 2008), with laser LCVD (Laser Chemical Vapor Deposition) (Gului and Martin, 2010, van de Burgt, 2014, Bäuerle, 1996), water assisted WA-CVD (Water Assisted Chemical Vapor Deposition) (Patole, et al., 2008, Dupuis, 2005), hot filament HF-CVD (Hot Filament Chemical Vapor Deposition) (Sahoo, et al., 2014, Chaisitsak, et al., 2004, Jung, et al., 2004), oxygen assisted (Zhang, et al., 2005, Chen, et al., 2015), with plasma radio frequency RF-PE-CVD (Radio Frequency Plasma Enhanced Chemical Vapor Deposition) (Yabe, et al., 2004, Wen, et al., 2007), with plasma microwave MPE-CVD (Microwave Plasma Enhanced Chemical Vapor Deposition) (Chen, et al., 2005, Choi, et al., 2000) and catalytic CVD or CCVD (Catalytic Chemical Vapor Deposition) (Cantoro, et al., 2006, Biris, et al., 2006, Awadallah, et al., 2012). Fig. 2 shows variety of methods CVD for synthesis carbon nanotubes. Using plasma leading to increase velocity of reactions and Main properties of plasma enhanced is lower temperature than other methods, whilst minimum temperature of normal CVD 500°C reported (Meyyappan, 2004), synthesis temperature of carbon nanotubes and carbon nanofibers by plasma assisted even 120°C reported (Boskovic, et al., 2002, Hofmann, et al., 2003) and also this type with comparison other low temperature methods, have better vertically growth (Meyyappan, 2004). In CVD with aerosol, aerosol using as catalyst which catalyst particles distribution on substrate and help to synthesize CNT on substrate (Queipo, et al., 2006) Many researchers reported this method synthesizing high quality single and multiwall carbon nanotubes (Queipo, et al., 2006, Byeon, et al., 2010, Abdullayeva, et al., 2015). In aerogel type, sediments deposit on aerogel. Efficiency of Aerogel CVD is high (200% weight percentage for single-wall). The key point for high efficiency is high surface area of aerogel and so increase performance of alumina catalyst (Su, et al., 2000). In alcohol CVD, alcohols use as carbon source (Maruyama, et al., 2004, Murakami, et al., 2003) which Fe and Co catalyst put on zeolite and evaporated alcohol (often methanol and ethanol), splashing over catalyst particles. Temperature of process is rather low (about 550°C) that lower than other common CVD methods. Diameter of carbon nanotubes about 1 nm and efficiency of process is 40% (Maruyama, et al., 2004, Murakami, et al., 2003, Maruyama, et al., 2002). Due to the high purity, low production costs and high efficiency, this method can be used for mass production of carbon nanotubes. In L-CVD: focusing a laser beam on a small portion of the substrate, prevents damage of substrate. We have more control over synthesis parameters and on the other hand does not need to warm up all the substrate (van de Burgt, 2014, Rahmanian and Zandi, 2012). In water assisted CVD, the amount of water entering the process can be controlled and with precise control of amount of water can be achieved over 7 mm length of CNT (Futaba, et al., 2005, Futaba, et al., 2006, Chakrabarti, et al., 2006). In oxygen assisted-CVD, with a certain proportion adding oxygen to other gases, single walled CNT with high efficiency could be synthesized. In fact; by adding oxygen to hydrogen, can have more control over the process and stop destruction sp² bonds that led to the steady alignment growth of single-walled nanotubes (Zhang, et al., 2005). Added oxygen also leads to the loss of amorphous carbon and other carbon impurities and remove the destructive precursor role during the growth (Chen, et al., 2015, Wen, et al., 2007) and on the other hand, increasing the purity and efficiency;
however, this method for some catalysts like separate iron nanoparticles due to carbothermal reaction, is not suitable (Byon, et al., 2007).

**Mechano Thermal**

Mechano thermal containing two main steps; first producing amorphous carbon and subsequently, annealing them in vacuum furnace (Byon, et al., 2007, Manafi, et al., 2011, Chen, et al., 2003). Carbon amorphisation have done by high energy ball milling. Milling time for synthesis amorphous carbon up to 180 h that change for different condition: difference in type of atmosphere (Argon or air), cup speed (300 rpm or more), ball to powder ratio, numbers of balls and purity of powders. With increasing milling time, crystallite size decreasing and finally forming amorphous structure (Chen, et al., 2003). With attention to long time of milling, very small amount of metal powders due to Friction between the cup and balls, enter the graphite powder and possibility help to nucleation and growth of CNT in thermal step. Produced amorphous carbon was put in vacuum furnace. Temperature of furnace 1400°C for a few hours connects atoms of amorphous carbons together and forming carbon nanotubes. Structure of produced carbon nanotubes is usually springy multi walled nanotubes. Properties of Mechano thermal includes: simple process, suitable for mass production, low cost, and don’t need to special equipment, but the time of process is too long and mechanism of process is not continuous and includes two steps (Manafi, et al., 2011, Chen, et al., 2003, Bai, et al., 2002)

**Laser Ablation**

In Laser ablation/vaporization, by strike pulsed laser or continuous wave laser on graphite target; nucleation and growth of carbon nanotubes to be started (Rafique and Iqbal, 2011, Terrones, 2003). First formation a hot evaporation and subsequently quickly cooled. During cooling of the samples, small molecules and carbon atoms quickly condense and form larger clusters and synthesized carbon nanotubes by van der Waals forces stay together. For producing multi wall carbon nanotubes use pure graphite rods and for single wall use composite block of graphite (Vander Wal, et al., 2002, Vander Wal, et al., 2004). For producing single walled, Graphite composited with metal catalyst, such as Fe, Ni and Co and He-H₂, and Ar use as ambient gas.

In pulsed laser, needs more intensity laser’s light than continuous laser. Nd:YAG and CO₂ are most common lasers used for laser ablation (Rafique and Iqbal, 2011). Diameters of CNT which produced by this method 4-30 nm and length of them is about 1 micrometer. Byproducts and impurities are amorphous carbon, catalyst particles, fullerene etc. Catalyzers also help to growth of carbon nanotubes. Most of catalyst were used in laser ablation are: Co, Cu, Nb, Ni, Pt, Co/ Ni, Co/Pt, Co/Cu, Ni/Pt. quality of production related to target composition (Maser, et al., 2001), power of laser beam and laser properties (Rafique and Iqbal, 2011, Braidy, et al., 2002a), catalyst type (Braidy, et al., 2002, Nishide, et al., 2003), type of ambient gas (Nishide, et al., 2003), temperature of reactions (Bandow, et al., 1998) and distance between substrate and target (Rafique and Iqbal, 2011). Produced carbon nanotubes by this method have high purity, high yield and most produced single wall CNT; but not suitable for mass production and also need expensive and especial equipment (Söylev, 2011).

**Flame Synthesis**

In this method, CNT synthesizing by direct combustion of carbon source in presence of an oxidizing gas (Terrones, 2003). Generally; flame synthesis contain of three steps: First; producing carbon source by hydrolysis of hydrocarbon. Second; diffusion of carbon's
atoms to metallic catalyst and third; nucleation carbon nanotubes on surface of catalyst and it's gradual growth. Oxidation gas can be oxygen or nitrogen and carbon feedstock are acetylene, methane, ethanol and ethylene. Type of flame created, have essential role on quality of produced carbon nanotubes and determinate amount of amorphous carbon in final producing. For optimizing condition, must be controlled temperature, composition of fuel gas and catalyst of reactions (Height, et al., 2004, Height, et al., 2003). This way is economic, suitable for mass production and most synthesizing single walled CNT, but rate of growth is relatively low (Lee, et al., 2002, Wu, et al., 2016).

**Arc Discharge**

Arc discharge known as one of oldest method for producing carbon nanotubes (Iijima, 1991). Two high-purity graphite rods used as anode and cathode and by applied direct current (in some cases pulsed current), a stable arc is created. Due to the power of created arc, carbon separated from anode and condensed on cathode to forming of soot (Terrones, 2003). Arc discharge done in various environment such as: liquid environment (liquid nitrogen, toluene, not ionized water), gas environment (Ar, Ar-H, He) or in plasma rotating arc discharge. Plasma rotating arc discharge is an economic method for large-scale synthesis of carbon nanotubes (Smeulders, et al., 2005). Centrifugal force which created by rotation, accelerating the evaporation of anode and also cause uniform and stable dispersion of arc and so increases volume and temperature of discharge plasma. Most carbon nanotubes that synthesised by arc method are multi walled but by penetration graphite rods and filling them with graphite's powder and metal catalyst; can be achieve to single wall carbon nanotubes. Pressure of Steam chamber and flow rate; are two key parameters for controlling the process. In arc discharge; speed of process is high and synthesis condition is controllable, but both of quality of productions and efficiency of process is low (Söylev, 2011).

**CONCLUSIONS**

Among of the main methods for synthesising carbon nanotubes, chemical vapour deposition due to simplicity, controllable mechanism, high ability for synthesizing aligned CNT, variety modified types for producing different kind of CNT, high efficiency close to 100% and suitable for mass producing; is the most attractive way for synthesis of carbon nanotubes. Flame synthesis have high potential for producing economical large scale of CNT that have a simple mechanism; but increasing impurities is a big problem in this mechanism. Laser ablation and Arc discharge are common method for synthesis CNT that both of them are not suitable for mass production, besides that; quality of yields in arc discharge is low. The problem of mass production also exists for electrolysis, and this method used in laboratory scale. In mechano thermal despite simplicity and large scale of production, not continuous (consist of two steps) and process is very slow.

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