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Review of Single Step Techniques for Production of ACNT's

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Abstract-

The perpendicular orientation of carbon nanotubes to a substrate are vertically aligned carbon nanotubes (VACNT), and parallel to the substrate are horizontally aligned CNT's. Their proper and dense alignment along with outstanding physical and chemical properties enables ACNT to be used to may various fields. The most common single step methods to produced aligned carbon nanotubes (ACNT's) are Thermal pyrolysis and flame synthesis, and both are relatively simple. This review explore different methods used for ACNT growth, the process parameter determine the morphology ACNT and the application of structured ACNT's.

1. Introduction:

Aligned carbon nanotubes (ACNTs) were first reported by Thess et al., who were able to bundle 70% of the volume of nanotubes into crystalline ropes in 1996. In the same year, the Chinese Academy of Science reported that a 50 lm-thick film of highly aligned nanotubes had successfully been grown by chemical vapor deposition (CVD).

Vertically aligned CNTs (Fig. 1) are quasi-dimensional carbon cylinders that align perpendicular to a substrate. Vertically aligned with high aspect ratios, and uniform tube length made it easy spinning into macroscopic fibers. The ACNT arrays are typically grown from a catalyst that is pinned to a substrate, which produces long, high-purity nanotubes with sidewalls that are free of catalysts. Because of these properties, arrays of ACNT are widely used in nanoelectronics or in composite materials as reinforcing agents. Large arrays of ACNTs with a high degree of uniformity in terms of tip radius and height provide excellent field emission properties. Furthermore, vertically aligned CNTs also exhibit a high capability to produce high current densities under low operating voltages. ACNTs have a very large surface area and a high thermal conductivity, both of which facilitate rapid heat transfer to the surrounding, making those important materials in the construction of solar cells. ACNTs have also been used in hydrogen storage, as the interior and interstitial surfaces of open-ended CNTs have a strong binding energy for adsorbing hydrogen gas molecules compared with planar carbon surfaces [01].

Aligned multi-walled carbon nanotubes (MWCNTs) were found to possess a higher adsorption rate of hydrogen than nonaligned CNTs because of the large inter-nanotube space in between the parallel nanotubes. The subnanometre pores of ACNTs are suitable for separation of gases and other small molecules, such as hydrogen and water. The subnanometre pores of ACNTs are suitable for separation of gases and other small molecules, such as hydrogen and water.

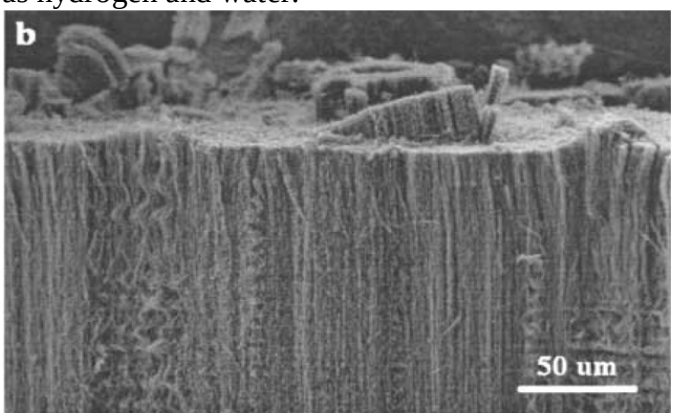


Fig. 1 – A scanning electron microscopy (SEM) image showing ACNTs [01].

These super-aligned CNTs were successfully spun into continuous yarns with excellent mechanical and electrical properties, which can be further developed

to a touch panel, liquid crystal display and transparent loudspeaker. The property study shows that the yarns possessed mechanical strength greater than 460 MPa. Instead of yarns, a transparent CNTs sheet also can be drawn in parallel from ACNTS arrays and can be employed to make organic light emitting diode. Since the first ACNT array was reported in 1996, numerous papers describing the growth of ACNTs have been published. Over more than a decade, various modifications have been made and new techniques have been discovered that make it possible to grow high-quality ACNTs with scalable production.

2. Single-Step Methods

2.1. Thermal Pyrolysis Method:

Thermal pyrolysis is also known as metal–organic CVD or FCCVD. It is one of the most popular methods for synthesizing dense and aligned forms of CNTs. FC-CVD involves the pyrolysis of organ-metallic precursors such as ferrocene, iron (II) phthalocyanine (FePc), iron pentacarbonyl, nickelocene and cobaltocene to nucleate the growth of nanotubes. Non-carbonaceous compounds, such as FeCl3, are also reported to be promising catalyst precursors for growing ACNTs. In most cases, a carbon source must be added in excess to increase the carbon-to-catalyst ratio and prevent high levels of metal impurity in the CNTs [05]. Aromatic hydrocarbons such as xylene, toluene, benzene and naphthalene [04] are often used along with ferrocene because of their chemical structure similarities [04] and the fact that most of the aromatic hydrocarbons can dissolve ferrocene easily. However, the use of heavy hydrocarbons such as aromatic hydrocarbons and cyclohexane is not suitable because heavy hydrocarbons will deposit on the reactor wall in a low-temperature zone [06]. As a result, lighter hydrocarbons such as acetonitrile , ethylene [06], acetylene and alkanes are commonly used. In addition, tree products such as turpentine oil and camphor are also used as carbon sources for synthesising ACNTs.

After many years of research, FC-CVD has been modified with the goal of growing ACNTs of better quality and alignment. In general, there are two major types of reactors used for FC-CVD, namely double-furnace and single-furnace reactors. In the double furnace setup (Fig. 2), the first furnace is responsible for the vaporisation and sublimation of the catalyst precursor, while the second furnace is kept at a high temperature for the catalysts to assemble and nucleate the growth of CNTs. One of the drawbacks of this process is the steep temperature gradient that exists between the two furnaces, which makes it difficult to maintain the same evaporation rate throughout the entire process. As for the conventional single-furnace setup, only one high-temperature furnace is required. The mixture of the catalyst and carbon feedstock (liquid phase) is first evaporated using a heater before it is introduced into the reactor. The problem with this approach lies in controlling the uniformity of the catalyst particles inside the reactor. Aerosol-assisted carbon deposition has been developed to overcome this shortcoming. Jeong et al. used an ultrasonic evaporator to atomise a mixture of ferrocene and xylene. The mixture was then carried into a single-furnace reactor by a carrier gas. Spray pyrolysis with the use of a spray nozzle to atomise the mixture supply coming into the reactor has also been reported [03]. The growth of CNTs from FC-CVD has been suggested to occur in two different ways. First, the active metals must deposit on the substrate before the growth of CNTs can take place. Li et al. [07] found that CNTs could be grown from an iron film deposited on substrate that contained different sizes of iron nano particles. The larger iron particles were responsible for producing the carbon atomistic species, which were required for subsequent growth of the CNTs. Meanwhile, the smaller iron particles were more catalytically active because of their higher surface energy. However, the study of Huang et al. [08] found that the growth of nanotubes started on the active catalyst at the floating stage. These authors provided more convincing proof than did the previously mentioned authors. In their study, four substrates were placed at different locations in the reactor with temperatures ranging from 200 _C to 900 _C. Nanotubes were found on the substrate in the temperature range of 200 _C to 300 _C.

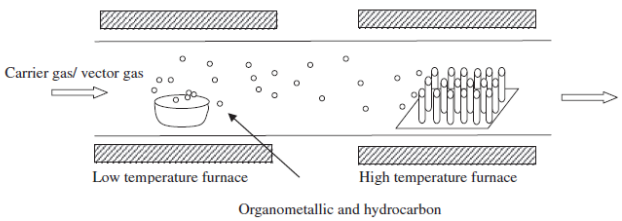


Fig. 2 – Scheme showing the double-furnace setup used in the organo-metallic/hydrocarbon co-pyrolysis process.

It is known that this range of temperature is too low for growing nanotubes. Furthermore, nanotubes were found on Au-coated wafers, but Au is not a good substrate for growing CNTs. Besides, the U-shaped nanotubes (Fig. 3) are believed to grow in the floating phase and then become hooked on the substrate, forming a U shape as a result of the flowing gas. The thermal pyrolysis method is attracting considerable attention for the synthesis of ACNTs because of its exceptionally low cost and ease of scaling up to mass production [04]. The ACNTs can be grown on flat substrates and also on cylindrical substrates such as the wall of a tube reactor. Moreover, ACNTs are also reported to grow on spherical substrates consisting of 50% SiO2, 30% Al2O3, and 20% ZrO2 with a diameter of 700 lm (Fig. 4) [06].

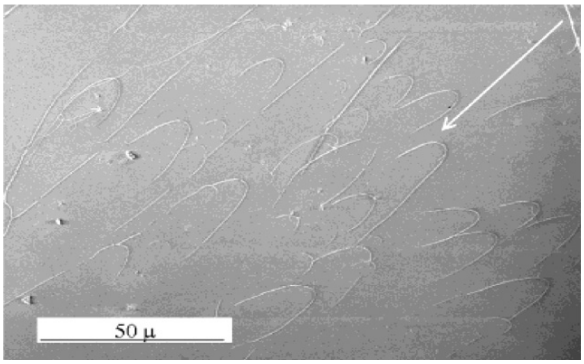


Fig. 3 – U-shaped CNTs (the arrow indicates the flow direction) [08].

2.2. Flame Synthesis:

Flame synthesis is another single-step method that is capable of producing ACNTs. It involves the direct combustion of hydrocarbon in the presence of an oxidiser. The CNTs are normally grown directly on an alloy substrate, such as catalytic rod-like probes, grids or plates. The use of metal–organics such as iron pentacarbonyl , ferrocene or metal nitrate dissolved in fuel [13] has been reported. So far, ACNTs have only been reported to grow on alloy substrates.

Flame synthesis is a very energy-efficient process because the fuel itself is a source of heat and carbon. The temperature achieved can be as high as 1600 K, which is hard to achieve with CVD in a conventional furnace.

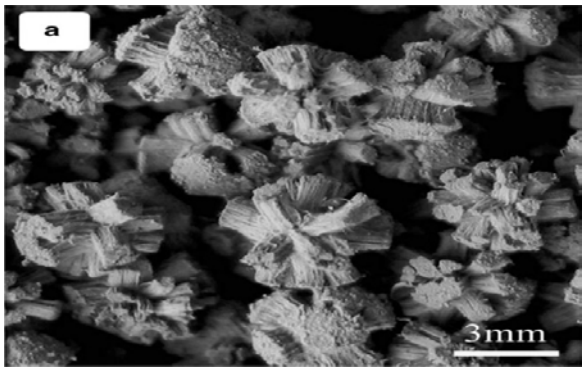
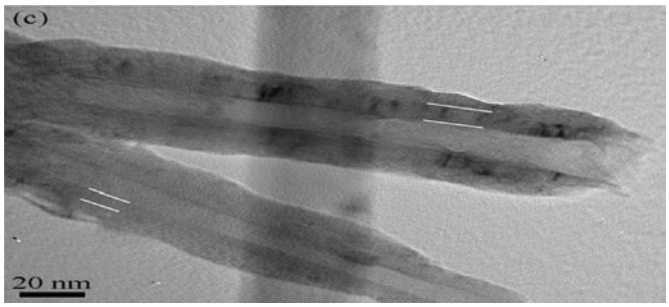


Fig. 4 – Vertically aligned CNTs grown on a spherical substrate approximately 700 lm in diameter [06].

For ACNT synthesis over a large area, it is more economical to use flame rastering and multiple flames to achieve a controllable residence time and the desired flame region [11]. The production efficiency and yield per energy input is lower than that of CVD, making this method suitable for industrial production [11]. Additionally, flame synthesis is a simple one-step method that without substrate preparation. However, complex substrate preparation has also been reported for flame synthesis. The growth mechanism of ACNTs in the flame synthesis of hydrocarbon can be divided into three main steps. First, the hydrocarbon fuel is pyrolysed in the preheated zone to form hydrocarbon species, which will be the carbon source for the CNTs, while the metal particles form on the surface of the alloy. The hydrocarbon species diffuses onto the catalyst at an appropriate temperature and is then absorbed by the catalyst to nucleate the growth of CNTs.



(Fig. 5 – A TEM image of the CNTs in which the inner layers appear to be organised graphene sheets and the outer layers resemble amorphous carbon deposits. White lines indicate the interface of the graphene sheet and amorphous carbon [02].)

The choice of the catalyst is the main consideration for the production of the ACNTs. An

alloy is always selected because of its lower melting point and higher solubility for carbon compared with pure metal. From our review, a majority of the ACNTs are reported to be grown on alloys containing Ni, along with Fe and Cr [12]. It is believed that the formation of nickel oxide contributes to the growth of CNTs. Nevertheless, the alignment still depends on the density of the metal nano particles, which serve as catalysts. Pan et al. [12] studied different kind of alloys using an ethanol flame and the authors found that pure Ni and pure Fe only produced CNTs and CNFs, respectively. They proposed a ‘‘hollow-core mechanism’’ for Ni. The diffusivity of carbon at the exterior surface of Ni is more rapid than in the interior of Ni nano particles, resulting in the growth of CNTs with a hollow core in the ethanol flame synthesis. In contrast, a ‘‘solid core mechanism’’ applies to Fe because carbon can easily diffuse through the Fe particle to form CNFs. The solubility of carbon in Ni particles was higher compared with Fe particles, so carbon would precipitate more rapidly in Ni. Hence, long, dense and well aligned CNTs are obtained in the presence of Ni. The regions of the flame in which ACNTs can be grown are very limited. Different locations have different carbon species concentrations and temperature profiles, which determine the morphology of the CNTs formed. The formation of CNTs usually happens in the visible orange soot zone of a normal diffusion flame. Yuan et al. [11] found that the yellowish flame was the best place for the CNTs to grow. They suggested that the temperature distinguished the carbon radical species that contributed to the formation of CNTs. Higher temperatures were promoting the formation of CNTs over soot. In another study by Yuan et al., the authors found that the yield, diameter and height of CNTs increased with the sampling height from the nozzle and the temperature.

Counter flow diffusion flames may provide a stable one dimensional reaction zone. There are studies based on the methane flame model (Fig 6(a)) proposed by Beltrame et al. [14] that predict the temperature profile and major carbon species, as shown in Fig 6(b). CNTs are grown 8–9.5mm from the fuel nozzle. ACNTs are only found when an electric field is introduced [09]. Merchan-Merchan et al. [09] found that highly ordered vertical ACNTs were grown in the region 8.5–10.0mm from the fuel nozzle. Xu et al. [10] successfully produced ACNTs with a methane flame seeded with acetylene without the electric field.

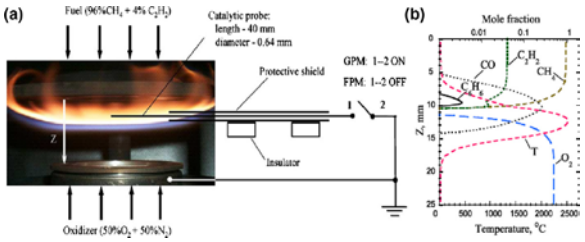


Fig. 6 – (a) A schematic of the experiment set-up using a counter flow diffusion flame proposed by Beltrame et al. and (b) the numerical predictions of temperature and major chemical species.

The breakup of the alloy surface induced by the carbide formed the catalyst nano particles that were responsible for the growth of the CNTs. The high density of the catalytic nano particles formed facilitated the growth of denser CNTs and provided vertical support for the nanotubes. In some other studies [09], the counter flow diffusion flame was also seeded with acetylene, but no ACNTs were synthesised, which might be the reason why Xu et al. [10] conducted the synthesis process at a higher temperature and why this condition enhanced the formation of catalytic nano particles that could grow CNTs, as compared with those reported in [09].

Flame synthesis is less popular than CVD. There are several shortcomings to this method. The apparatus for the flame synthesis, especially the burner, is complicated so that the morphology of the flame can be controlled. The gaseous fuels must be injected safely and carefully. The main drawback to this method is the poor quality of the ACNTs obtained.

From our review, the majority of the produced ACNTs are not straight, except for those synthesised with the aid of an electric field. The bean-sprout–like bundles containing encapsulated particles at the tips of the nanotubes, as shown in Fig. 7, are always found. In addition, a certain amount of CNFs is present in the array of ACNTs, which limits the application in certain fields.

The formation of CNTs in the sooting region also enables the deposition of carbon other than graphitic carbon on the wall. The lengths of ACNTs that are synthesised in the flame synthesis method are relatively short compared with those synthesised from CVD. The study, optimization and application of ACNTs synthesised by the flame synthesis method is limited. From our review, no articles addressed the mechanism of the formation of catalyst nano particles, and characterisation

techniques to determine the crystal phases of the catalyst have not been reported. The actual growth mechanism of the CNTs synthesised from the flame synthesis method is still unclear.

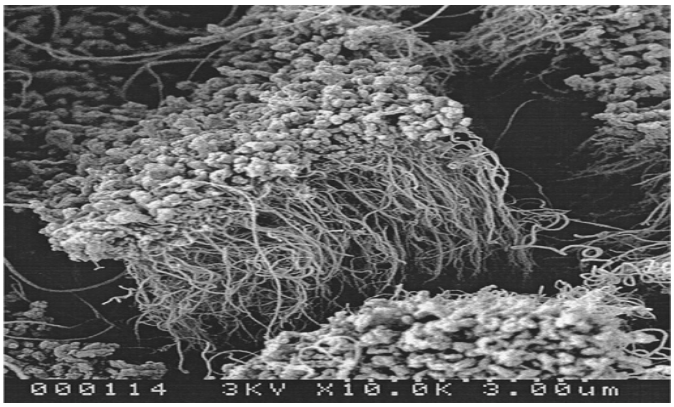


Fig. 7 – An SEM image of bean-sprout–like bundles of well aligned CNTs with catalyst nano particles lifting off at the tip of the CNTs [11].

The poor structure and alignment of ACNTs synthesised by this method have seriously limited the application of ACNTs. However, the low operating cost and scalable production enable ACNTs to be applied as a catalyst support and composite reinforcing material, which do not require ACNTs with perfect alignment and high crystallinity.

Conclusion:

Few of the various methods/techniques have reviewed and discussed to grow horizontally and vertically aligned CNT arrays. The parameters are interdependent for growing ACNT's and make challenges for the synthesis of ACNT's. The preparation of the catalyst that is used to grow ACNTs is even more complicated. Consideration needs to be given to the coupling of the catalyst/substrate/buffer layers. However many methods have been explored to grow ACNTs, every method has its own flaws. None of the method really fulfills the requirement of being cost effective, rapid, and easy to mass produce. The research on the production and applications of ACNTs is ongoing, and there are still many challenges and mysteries waiting to be discovered and answered.

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