Methods on Preparation of Single Walled Carbon Nanotubes Review

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Abstract

Carbon nanotubes are a kind of material with special chemical structure and excellent physical properties, demonstrating great application prospects in the fields of electronics, physics and chemistry. In this paper, some preparation methods of single walled carbon nanotubes were reviewed, and the advantages and disadvantages of these methods were discussed, and the newest methods of single walled nanotubes productions were reviewed.

Introduction

Carbon nanotubes CNTs used in the research fields of mechanics, optics, electronics and biology, they are theoretically distinct as a cylinder fabricated of rolled up graphene sheet, where exist in with two phases: single walled carbon nanotubes SWCNTs and multi walled carbon nanotubes MWCNTs [1], different types of tubules can be formed by rolled graphene sheet as shown in figure(1), where the graphene is wrapped represented by a pair of indices (n,m) which is can be classified of CNTs as armchair (n=m), zigzag (m=0), or chiral (all others). Single walled carbon nanotubes SWCNTs exhibit all three structures armchair(n=m), zigzag (m=0), or chiral (n,m)) arrangements while multi walled carbon nanotubes MWCNTs exhibit only(armchair or zigzag)[2], they are directly effect on electrical properties of nanotubes, since carbon nanotubes have the sp2 bonds between the individual carbon atoms, they have a higher tensile strength than steel and Kevlar. So that, theoretically, SWCNTs may really have hundreds of times of a tensile strength stronger than steel. Elasticity is another property of carbon nanotube, it can bend, kink, twist, and finally buckle without damaging the nanotube when exposed to high force and press sitting and great axial compressive forces, and under very physically powerful forces presses, it is possible to temporarily deform to shape of a nanotube. In the structure of the nanotube some of the defects existed such as defects in atomic vacancies or a rearrangement of the carbon bonds can weaken a nanotube's strength.
Methods of Carbon Nanotube Synthesis

There were various ways of prepared CNTs some of these are arc discharge, laser ablation, and chemical vapor deposition (CVD) [1], summarized of the various methods are in figure (2)[2]. Each of them has some advantages and disadvantages for some of these shown in table (1) which resulting in different growth. The most suitable synthesis process proved from CVD to produce CNTs which controlled characteristics, such as length, diameter and number of walls. due to the high temperatures and pressures required, CNTs synthesizing remains costly and difficult.
Table 1: advantages and disadvantages of three most common CNTs synthesis methods [1]

<table>
<thead>
<tr>
<th>Method</th>
<th>Arc discharge</th>
<th>Laser ablation</th>
<th>CVD</th>
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<tr>
<td>advantages</td>
<td>Both SWNT or MWNT produced, Yield rate greater than 75%, Method is simple, inexpensive, high quality nanotubes.</td>
<td>Both SWNT or MWNT produced, Yield rate greater than 75%, Relatively high purity, Synthesis at room temperature.</td>
<td>Both SWNT or MWNT produced, Yield rate greater than 75%, method is simple method, low temperature, high purity, large-scale production, aligned growth possible.</td>
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<td>disadvantages</td>
<td>High temperature, required purification, tangled nanotubes</td>
<td>Limited method limited to the lab scale, crude product purification required</td>
<td>Synthesized CNTs and MWNTs are usually defects</td>
</tr>
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Arc Discharge for SWNTs Synthesis

In 1993 Iijima and Bethune used Arc discharge in condition 50–500 Torr CH4/Ar or Helium gas >2500°C with the catalyst Fe or Co in carbon which is first confirmed SWCNT production.

A higher temperature uses in electric arc discharge technique (above 1,700°C) for CNTs synthesis which typically cause the expansion of CNTs with defects fewer structural in comparison with other methods. high-purity graphite (6 to 10-mm optical density) water-cooled electrodes with diameters between 6 and 12 mm and separated by 1 to 2 mm in a chamber filled with helium (500 torr) at sub atmospheric pressure (helium can be replaced by hydrogen or methane atmosphere) see figure (3) [1,3].
Laser ablation

In 1996 Thess et al. used Laser ablation in condition of 500 Torr Ar Furnace at 1200°C (target at >2500°C) Ni/Co in Carbon which is which is First laser ablation, high yield [3,4]. Transition-metal/graphite composite rods put in direct laser vaporization which is produced single-walled carbon nanotubes (SWCNTs) in a heated flow tube in the condensing vapor. Apparatus of the oven laser-vaporization to figure (2)[3] which is the same as that used to produce metallofullerenes and fullerenes [3],

Chemical Vapour Deposition (CVD)

In 1996 Dai et al. used CVD CO in condition 1.1 atm at 1200°C with the catalyst Mo, Co/Ni which is First SWCNT CVD growth.
In 1998 Kong et al. used CVD CH4 in condition 1.25-atm inlet at 1000°C with the catalyst Fe/Al2O3 which is first patterned-substrate growth.

In 1999 Cassell et al used CVD CH4 in condition 1.25-atm inlet at 900–1000°C Fe/Mo/Al2O3 which is First large-scale bulk CVD synthesis of SWCNT.

In 1999 Nikolaev et al. used CVD (HiPco) CO in condition 10 atm at 1200°C with the catalyst Fe (CO)5 which is vapor demonstration of HiPco SWCNTs (later P ~ 30–50atm).

In 2000 Vander Wal et al. used Flame N2/Ar/air + C2H2 or C2H4 at 900–1400°C in flame Metallocene which is first flame synthesis of SWCNTs.

In 2000 Kitiyanan et al. and Bachilo et al. used CVD CO in condition 1 atm at 700°C with catalyst Co/Mo/silica Demonstration of CoMoCAT: diameter control in bulk catalyst.

In 2001 Li et al. used CVD CH4 in condition 1 atm at 900°C with catalyst Fe/Ferritin Diameter-selective substrate synthesis from predefined nanoparticles.

In 2001 Ural et al. used Zhang et al. used CVD CH4 + H2 in condition 1 atm at 900°C with catalyst Fe/Mo/silica which is First aligned SWCNT growth: E-field alignment (substrate aligned in 2002).

In 2002 Maruyama et al. used CVD C2H5OH or CH3OH in condition 5–10 Torr 550–900°C with catalyst Fe/Co (Co/Mo) which is First growth from alcohol; low temperature; first proposition of amorphous carbon etchant (OH) during growth.

In 2002 Kim et al. used CVD CH4 + H2 + C2H4 in condition 1 atm at 900°C with catalyst Fe/Ferritin which is First aligned SWCNTs (>400 μm)

In 2003 Huang et al. used CVD CO + H2 in condition 1 atm at 900°C with catalyst Fe/Mo Aligned SWCNTs from gas flow utilizing fast heating and tip growth (>1 mm)

**Plasma Enhanced Chemical Vapour Deposition (PECVD)**

In 2003 Kato et al. used PECVD CH4 + H2 in condition 500 mT at 550–850°C with catalyst Fe/Co/zeolite which is first PECVD of SWCNTs, in 2004 Li et al. used Remote ECVD CH4 + Ar in plasma in condition 500 mT at 550–750°C with catalyst Fe Preferential low T growth of semiconducting SWCNTs in PECVD, it can be shown in figure (5)
In 2004 Murakami et al. used CVD C2H5OH in Ar/H2 at 800°C with catalyst Co/Mo. First vertical SWCNT films (<15 μm tall) were produced.

2004 Hata et al. used CVD C2H4 + Ar + H2O in condition 1 Atm at 750°C with catalyst Fe, Co/Mo, Fe/Mo. 2.5-mm vertical SWCNT growth; ultrahigh yield; controlled use of H2O as an etchant [3].

In 2010, D. W. Lee and J. W. Seo [5] were presented a simple chemical method without using any pressure treatment in order to produce CNTs in liquid solution at 70°C from graphite powder. The steps of this method shown in figure (6).[5]

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**Figure 5**: Schematic of a remote radiofrequency PECVD system

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<table>
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<tr>
<th>a</th>
<th>5.0g of graphite (99.995% purity) slowly added to a mixture of (25ml) fuming nitric acid and (50ml) sulfuric acid</th>
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<tr>
<td>b</td>
<td>the mixture down to 5°C in an ice bath for 30 minutes</td>
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<tr>
<td>c</td>
<td>25.0g of potassium chlorate slowly added while stirring for 30 minutes due to a lot of heat was produced, special care must be took</td>
</tr>
<tr>
<td>d</td>
<td>heated up to 70°C for 24 hours, then placed in the air</td>
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<td></td>
<td>precipitated of most graphite on the bottom but reacted carbons were floating, then transferred floating carbons into DI water (1ℓ)</td>
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<td></td>
<td>stirring it for 1 hour</td>
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<td></td>
<td>the sample was dried after the solution filtrated, then steps b and c were repeated 4 times</td>
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**Figure 6**: Steps of preparation of carbon nanotubes.
In 2011 J. Prasek et al [2] reported that in the last few years the CVD and PECVD techniques are most utilized methods, they mentioned methods for uniform vertically aligned CNTs synthesis using catalyst deposition as well as utilizing method, where a nonporous anodized aluminium oxide used as a pattern for selective CNTs grown in lithographic. In 2016 a useful knowledge lead from the review related to general overview, preparation methods, types and applications of CNTs. They have recommended to little understanding of the basics for the interaction of nanoparticles with living cells, organs and organisms. A conceptual understanding of biological responses to nanomaterials is needed to develop and apply safe nanomaterials in drug delivery in the future. In 2018 D. Janas, [7] reviews the aims of demonstrate the state-of-the-art for all the mainstream methods in order to sorting CNTs (preferential synthesis, selective destruction, (di)electrophoresis, selective destruction, ultracentrifugation, chromatography, aqueous two-phase extraction and (co)polymer isolation). It is concluded that the catalyst system such as CoMo catalyst (for preferential (6,5) synthesis) and he trys to introducing species addition, may be production of other chiralities. The presence of impurities is the general problem of CNTs produced which is usually influence the final properties of CNTs as a material used in some special application. Therefore, this problem can be found in several papers’ purification techniques for CNTs include: Acidic and oxidation, thermal treatment, filtration, annealing, ultrasonication and other [2].

**Conclusion**

SWCNTs can be preparation from different most utilized methods are CVD and PECVD, the catalyst selection which is used in production SWCNTs is very important factor, they are different form of SWCNTs grown on a substrate by CVD. A conceptual understanding of biological responses is needed to nanomaterials as CNTs in developed many applications and safe in drug delivery in the future.

**References**