SYNTHESIS AND APPLICATION OF CNT BASED ENERGY STORAGE AND CONVERSION DEVICES

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Abstract

Carbon nanotubes (CNTs) are one-dimensional tubular structures of carbon that have attracted much attention due to their potential to be used in various fields like energy storage/conversion devices, biosensing devices, drug delivery systems to name a few. Their excellent electrochemical properties like electron mobility, electrical and thermal conductivity, and high surface area make them good material for use in energy storage and conversion materials. The most promising research in the synthesis and applications of CNTs toward energy conversion and storage is highlighted along with limitations faced in mass production.

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ABSTRACT

Carbon nanotubes (CNTs) are one dimensional tubular structures of carbon that has attracted much attention due its potential to be used in various fields like energy storage/conversion devices, bio sensing devices, drug delivery systems to name a few. CNTs possess qualities of a good thermal conductors as well as insulators depending on its crystal direction. They are excellent conductors of heat along their axis but act as insulators in lateral direction. Their excellent electrochemical properties like electron mobility, electrical and thermal conductivity, and high surface area make them a good material for use in energy storage and conversion materials. Several synthetic strategies like arc discharge; Laser Ablation, Chemical Vapor Deposition (CVD), pyrolysis, flame synthesis etc. have been used for mass production of CNT reinforced composite materials. The study shows CVD technique as the most suitable technique for mass manufacturing due to the low cost of experimental setup. The most promising research in the synthesis and applications of CNTs toward energy conversion and storage ishighlighted along with limitations faced in mass production.

NOMENCLATURE

CNT Carbon Nanotube SWCNT Single walled carbon nanotube MWCNT Multi walled carbon nanotube CVD Chemical Vapor Deposition LIB Lithium ion battery SC Supercapacitor TCF Transparent conducting film

INTRODUCTION

Pure carbon exists in nature in the form of diamond and graphite. Besides graphite and diamond several allotropes of carbon has been developed or discovered. Carbon nanotubes (CNTs) are one such allotropes of carbon in which hexagonally oriented carbon atoms (graphite sheets) roll up to make a tubular or cylindrical structure. These nanotubes are characterized by diameters of the order of nanometers and lengths up to few microns. These structures were first reported by Ijima in 1991 who discovered multi walled carbon nanotubes (MWCNTs) by arc-discharge method. Nanotubes can be classified into single walled carbon nanotubes (SWCNTs) and multi walled carbon nanotubes (MWCNTs) depending on the number of cylindrical carbon walls. CNTs are also characterized by a vector called chiral vector that indicates how the carbon atoms are rolled up. Since their discovery, a tremendous amount of research has been done to study different optical, mechanical, electrical and thermal properties of CNTs and how they can put into application. Several techniques of CNT synthesis and carbon growth mechanisms for its mass production have also been studied extensively. Several synthetic strategies like arc discharge, laser ablation, chemical vapor deposition (CVD), pyrolysis, flame synthesis have been successfully developed. Among these synthesis processes, arc discharge, laser ablation and CVD methods are commonly used for mass production of CNTs and nanotube blended materials. Despite a huge progress in CNT research over the years, we are still unable to produce CNTs of well-defined properties in large quantities by a cost-effective technique. The root cause of this problem is the lack of proper understanding of the CNT growth mechanism. This study will mainly cover the various applications of CNTs in energy sector.

CARBON NANOTUBES IN ENERGY STORAGE AND CONVERSION APPLICATIONS

Portable and renewable energy storage technology has gained considerable attention in recent years. Lithium-ion battery (LIB) and Super capacitor (SC) are two main technologies that has been greatly studied and improvised to meet the growing challenges of energy sector. Rapid development of microelectronics and continuous miniaturization of the devices require novel LIBs and SCs with high energy densities and large power delivery capabilities. CNTs being one of the most reliable and sought after nanomaterial has been greatly utilized as electrode materials to improve the storage capacity and efficiency of LIBs and SCs.

Lithium ion Batteries

Lithium ion batteries (LIBs) have emerged as an interesting novel energy storage device for diverse applications due to its superior energy density compared to other battery technologies. Application of LIBs ranges from portable electronic devices to electric vehicles (as viable alternatives to combustion engines). Among the many rechargeable battery technologies, LIBs are low cost, safe, and have minimal side reactions while offering the best energy, voltage, capacity, and tap density. For all these reasons, extensive research has been concentrated toward the design and development of high performance electrode materials. Fig 1 shows the operating principle of LIBs. The electrical energy produced by LIBs is a result of two processes, namely charging and discharging. Li ions are transported from the cathode to the anode by a non- aqueous electrolyte during charging. The difference in lithium chemical potential of the two electrodes causes this process to occur [Sandeep et al.,2018]. When discharged, Li-ion is inserted from the electrolyte electrochemically reducing the cathode and simultaneously oxidising the anode. Thus, an electric current flows throughout an external circuitry to run an electronic device. Specific energy (Wh/kg) and Power density (Wh/L) are two parameters that express the performance of an LIB. Higher the specific energy, higher the energy content of the battery. This is enhanced by availability of large number of charge carriers per unit volume of the electrode to ensure high specific charge (Ah/kg) and high and low redox potentials at the cathode and at anode, respectively, to ensure high cell voltage. CNTs, which have a 1D tubular structure, with its enriched chirality, large surface area and high electrical and thermal conductivity, are of excellent use in electrochemical energy storage devices like LIBs. They also ensure reversible Li-intercalation and extraction without destroying the material structure, large contact area with electrolyte, and increased Li-ion insertion/removal rates through short transport pathways compared to other conventional materials. CNTs have excellent electrochemical properties. Compared to the conventionally used graphite electrodes, CNTs can store more number of Li ions in the spaces between hexagonal carbon rings. Also the diffusion rate of Li into CNT enriched electrodes is lesser compared to the graphite electrode. This results in lower power density. CNTs eliminate the use of binders on electrodes owing to its ability to grow on various current collectors and greater adhesion properties. The well-formed connection between CNTs and current collectors and high mechanical flexibility and stability, significantly increases the specific capacity and stability of binder-free electrodes. Both SWCNTs and MWCNTs can be used as LIB anodes, either by simply depositing them onto a current collector or by directly growing them onto a catalyst-pre-modified current collector. LIB anodes using SWCNT is found to have the highest reversible capacity of lithium insertion amongst carbon based materials. Apart from acting as 1D electrode materials and binders, 3D porous structured, CNT/ graphene hybrids such as CNT/GO (graphene oxide) presents good performance as LIB electrodes [Yi Li et al.,2019]. These hybrid materials are also used as both active and current collectors. CNTs/graphene hybrids can also be used as the conductive substrates to load metal oxides with high theoretical Capacity.

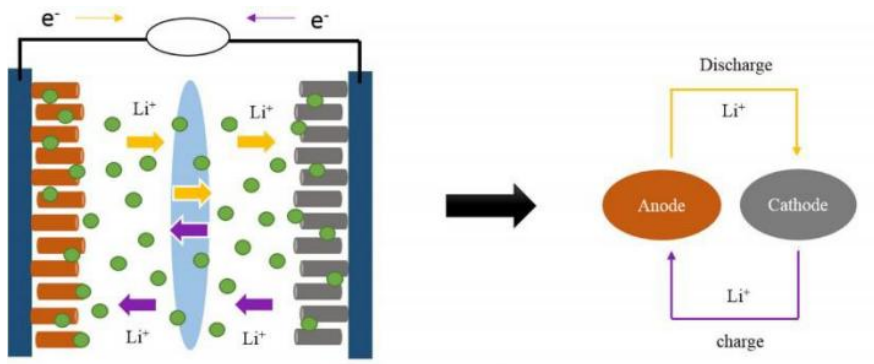

Figure 1: Schematic for the working principles of LIBs [Sandeep et al., 2018]

Supercapacitors

As discussed previously, CNTs have excellent electron conductivity, large surface to volume ratio and outstanding electrolyte accessible capability. For these mentioned reasons, CNT based electrodes exhibit good electrochemical performance and has proven to be critical in enhancing the performance of electrochemical capacitors or supercapacitors. They are found in diverse fields of applications such as consumer electronics (e.g., mobile phones, camera, and toys), medical appliances, transportation, electrical utilities, and defense systems. In comparison to other energy storage systems, supercapacitors offer rapid charging, higher power density (10 kW/kg), excellent reversibility (90%- 95%), longer cycle life, higher columbic efficiencies, lack of maintenance, and operational safety. There are two different types of supercapacitors, namely, electrical double layer capacitors (EDLCs) and pseudo-capacitors. EDLCs contain two electrodes and the charges get accumulated on these electrodes. The charge separation between the electrodes results in energy storage. Thus, materials with large surface area and good conductivity are required for high performance EDLCs. Pseudo- capacitors transfer charges by redox reaction that takes place between electrode and redox material on the surface of electrode. Both SWCNTs and MWCNTs have been widely investigated as effective supercapacitor electrodes with high surface areas to support aqueous and non-aqueous electrolytes. CNT/graphene hybrid 3D structures are also used to increase the performance of supercapacitors. These hybrids can be used in two ways in a supercapacitor. They can be applied directly as electrodes for electrical double layer capacitors (EDLCs). CNT/graphene hybrids are also used as highly conductive skeleton for loading pseudocapacitive metal oxides and sulphides[Yi Li et al.]. The requirement of high energy density without sacrificing the power density is difficult to be obtained using pure CNT electrodes as they store charges based on a physical process. Thus pseudocapacitive active materials like conductive polymers and MeOx, in combination with CNTs are used to modify its properties.

Transparent conducting films

Transparent conducting films or TCFs are optically transparent conducting films. They can be used in thin film photovoltaic cells, in organic LEDs and in liquid crystal displays (LCDs). The challenge of making TCF flexible led to the utilization as a potential material of carbon-based nanostructures. The conventional TCFs consist of tin oxide doped with indium [ITO] and tin oxide doped with fluorine [FTO]. A TCF material should be selected carefully to balance the optical transmittance and electrical conductivity. CNTs, because of its excellent flexibility and high optical transmittance are used as alternatives to conventional ITO and FTO conducting films [Sandeep et al, 2018]. CNT based TCFs are fabricated in both dry and wet conditions. Dry process of CNT based TCF fabrication include the famous arc discharge, laser ablation and CVD techniques while wet processes include spray pyrolysis, spray coating, spin coating, screen printing etc.

SYNTHESIS OF CARBON NANOTUBES

Major manufacturing techniques employed for fabrication of CNTs are Arc discharge, Laser Ablation and Chemical vapor deposition (CVD). The principle behind all these techniques is to provide a carbon source, either in solid, liquid or gaseous state, enough energy to produce carbon atoms. The difference in energy source used is the basic difference between all these synthesis strategies.

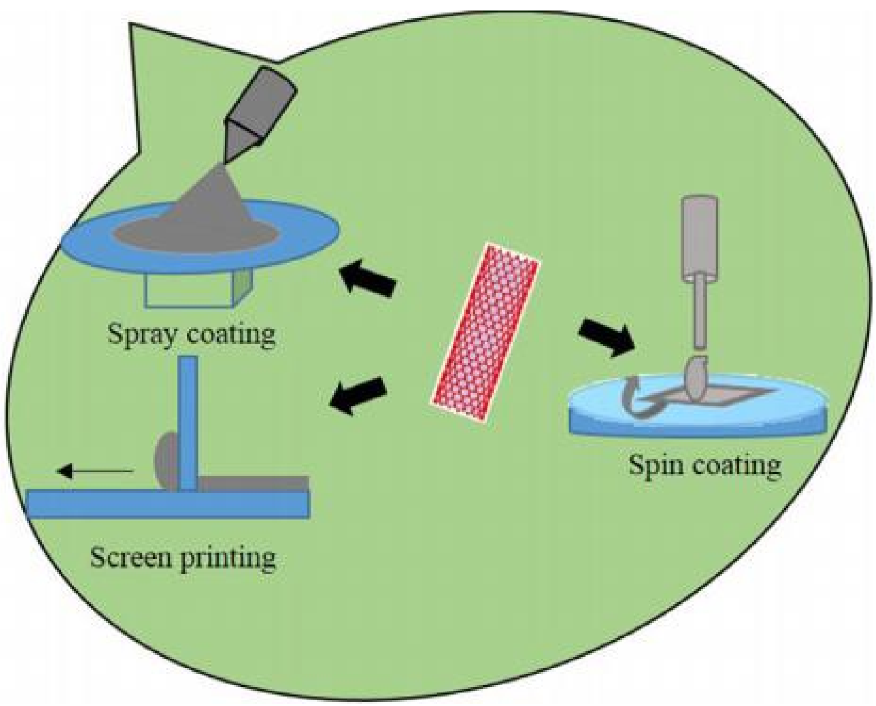

Figure 2: Wet processes for CNT-based TCFs fabrication [Sandeep et al., 2018]

Arc discharge

Electric current is used as the energy source in arc discharge synthesis of CNTs. The method uses temperatures usually above 1700°C and obtains CNT growth with fewer structural defects. The arc-discharge method was the first method by which CNTs were produced. The setup consist of a furnace, graphite electrodes, a stainless steel vacuum chamber, a water cooled trap and high voltage power supply. The two graphite electrodes are placed in a case filled with inert gas at low pressure and subject to arc vaporization, end-to-end with a slim clearance of almost 1 mm. A DC current of 50-100A at a potential difference of almost 20V will achieve this high-temperature arc discharge. The arc usually exceeds 3000oC which helps to vaporize the plasma in carbon atoms. When anode material is used for the doping of metal catalyst-graphite rods, soot-like SWCNTs are achieved. Researches have been done by varying the current source to AC and bipolar sources delivering currents at various peak frequencies. It is found that the soot production rate (SWCNT production rate) increases with increase in current supplied. However, the quality of SWCNTs almost remains the same. MWCNTs are found deep inside cathode deposits and on the top surface. Researches have proven that a hydrogen arc obtained by using a gas that contains hydrogen in place of inert gas is more effective due to its high temperature and high activity.

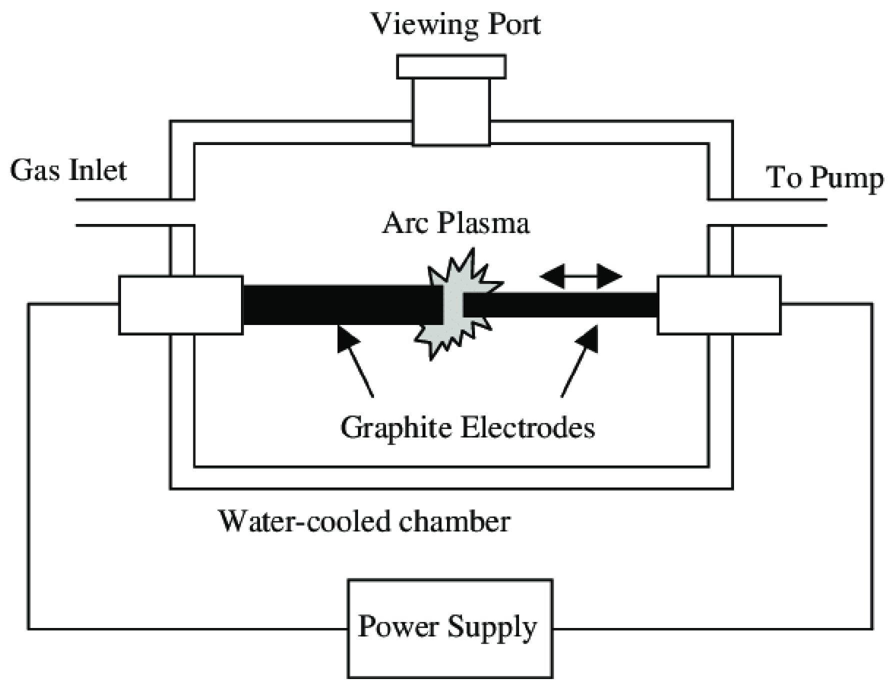

Figure 3: Schematic of Arc Discharge Method [Rajesh et al., 2014]

Laser Ablation

High intensity laser light act as energy source to excite carbon atoms in laser ablation technique. Laser beam like YAG or CO2 vaporizes a graphite target under high temperature in an inert atmosphere. Carbon species are produced by the laser. These species are swept from a high temperature zone to a water cooled copper collector by the flowing inert gases. The reaction temperature determines the quality & yield. Small amounts of transition metal such as Ni, Fe or Co when added to the carbon target, SWCNTs are produced. Various parameters like catalyst composition, growth temperature, nature of gases & gas pressure, average nanotube diameter and size distribution can be varied by varying the laser used. Carbon atoms and molecules condense from these vaporized species to form large carbon clusters. Catalysts which also start to condense, but rather slowly, attaches to these carbon clusters. The tubular structured carbon molecules from this form SWCNTs. This process of CNT growth continues until conditions have cooled sufficiently so that carbon atoms can no longer diffuse through or over catalyst surface particle. This growth also gets hindered as the size of catalyst particles become too large. Selective Laser Melting (SLM) is another technique used for fabricating CNT reinforced Al nanocomposites[Dongdong et al, 2019]. This material is used to prepare Aluminium metal matrix which are used in combination with phase changing materials for energy storage. This process uses laser based additive manufacturing technique. Both arc discharge & laser ablation techniques are very expensive due to the high power equipment so they are mainly used for SWCNTs production. These methods also produce small quantities of CNTs with a lot of impurities.

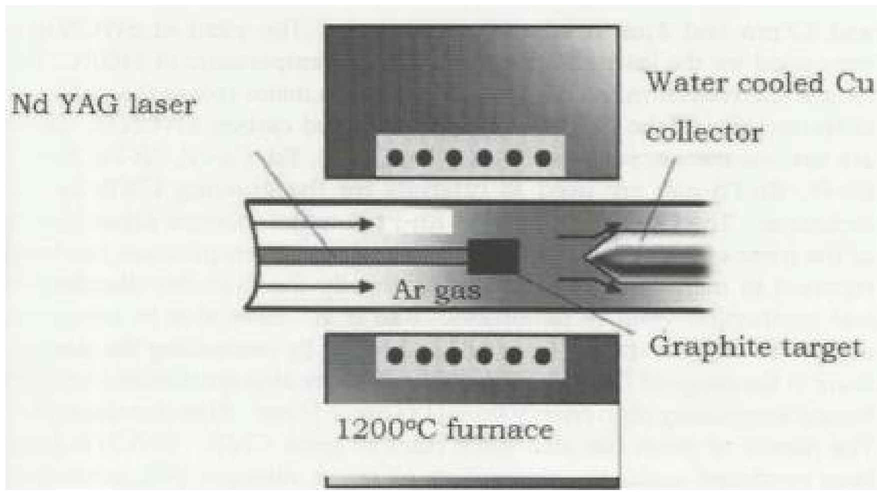

Figure 4: Schematic of Laser Ablation Method [Rajesh et al., 2014]

Chemical Vapor Deposition (CVD)

The best and the most used technique for mass production of CNTs is chemical vapor deposition. This is mainly because of the lower temperatures involved in CVD and greater ability to control the nanotube size by changing catalyst particle size. The catalyst particles act as a surface for carbon precursor decomposition and CNT formation. A carbon source in gaseous phase is passed over an energy source like a resistive heating coil to energize the gaseous atoms. By controlling the catalyst particle size, catalyst concentration, pressure, growth time, growth temperature and gas flow rate, CNT molecules with required properties can be grown on catalyst surface. Generally, for**Figure 5: Schematic of Chemical Vapor Deposition [Rajesh et al., 2014]**

Other techniques

1. Spray pyrolysis

In spray pyrolysis, the carbon precursor and the synthesis of

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MWCNTs, low catalyst material are both pumped into the temperatures (600-900 C) are preferred and temperatures around 900°C-1200°C yield SWCNTs. This high temperature requirement for SWCNT fabrication is due to its higher heat of formation which is attributed to its small diameter that results in a higher strain energy and curvature. The diameter of nanotubes is directly linked with the size of catalyst particles used. Varying the catalyst composition and coating catalyst particles on various substrates to know the characteristics of the resulting CNTs formed has been an area of research in the past decade. Several CNT hybrid materials are prepared through CVD technique to increase electrochemically active surface area and the fast electron/ ion transfer. CVD method provides large production yield at lowest prices. However, CVD technique imparts more deficiencies in the fabricated CNT material. The CNTs can be extracted from the final product by a purification process, before being used for specific applications.reactor at the same time. The injection CVD process is another name for it. It has an advantage over the traditional CVD approach in that liquid hydrocarbon and catalyst can be added continuously into the reaction zone, resulting in MWCNT output that is both inexpensive and semi- continuous [Annubhawi et al., 2017]. Liquid additives are also monitored and regulated.

Flame synthesis

Flame synthesis provides a method for direct growth of nanotubes over large area substrates. Continuous and quick heating is involved. Inherently, flames provide either oxidizing or carbon-rich conditions, allowing metal-oxides or carbon materials to expand easily [Hua et al., 2019]. It can also be used in conditions without any confinement, allowing for scalability and high deposition rates.

Mechanical Ball Milling

Fine particles with a homogeneous size distribution can be produced by milling balls, and both wet and dry powders can be grinded at a low cost. Nanotubes are ground into extremely fine powders using the ball milling process. The collision between the tiny rigid balls in a hidden container generates localised high pressure during the ball milling process. Usually, ceramic, flint pebbles and stainless steel are used. Selected chemicals are used inside grinding container to include functional groups onto CNTs.

CONCLUSIONS

The detailed study conducted above shed light onto numerous issues faced by present technologies that are used to manufacture CNTs. The findings can be listed as:-

- Fabrication of CNTs of the given diameter is still not possible due to catalyst particle size limitations.
- Controlling the number of walls of MWCNTs is another issue. It still remains a huge task to synthesis thick MWCNTs with more than six carbon cylinders.
- Chirality control remains one of the most sought after areas of research.
- Recycling of waste materials is another efficient, cost-effective, and green alternative for large-scale production of CNTs.
- The most widely used cost effective method for mass production of CNTs is the CVD method despite the imperfect CNTs it produces.

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