THE SYNTHESIS AND APPLICATIONS OF CARBON NANOTUBES FROM NATURAL GAS

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ABSTRACT

Carbon Nanotubes are newly discovered carbon; it is fullerene related structures but a fullerene's carbon form a sphere while a nanotube is cylindrical. According to theoretical predictions of carbon nanotubes, the tubular fullerene, may possess extraordinary physical and chemical properties. Due to its unique properties, carbon nanotubes have found a variety of potential applications in advance technologies; including nanoelectronics, biomedical, electromagnetics, electrochemical, composite, mass storage, etc. They provide an alternative to current technology to achieve better performance and smaller sizing in numerous applications. It brings technologies of all area to the edge and beyond expectation in the past. This paper will cover the outstanding properties of carbon nanotubes and the applications of carbon nanotubes.

Keywords: Carbon Nanotubes, Utilization of Natural Gas, Application.

1 INTRODUCTION

In the past century, the discovery of fullerenes has outburst the research activity in the field of carbon. However, in 21th century, with the discovery of carbon nanotubes by Sumio Iijima, NEC electron microscopist, research attention has been devoted to synthesizing, commercialization and application of high quality carbon nanotubes.

Carbon nanotubes name derives from their size; they are on the order of only a few nanometers in diameter and their length can be millions of times greater than their width. They are actually tubular nanostructures, where graphite sheet was rolled into cylinder of nanosize tube. They are found both in single walled (SWNT) with the smallest diameter synthesized is around 0.3 to 1 nm; and multi-walled (MWNT) with largest diameter range up to few hundred nanometers. Their outstanding chemicals and physical properties have attracted researchers' interests. Their potential applications were in advance technologies namely: electronics, biomedical, new composite, electrochemical devices, mass storage and others.

These materials are often prepared by the methods of arc-discharge, laser beam evaporation of graphite and chemical vapor deposition of hydrocarbon. Chemical vapor deposition has been developed as the most fruitful method for the large scale production of CNT (Qian, et. al., 2003). However, the absolute yield of CNTs is still relatively low to this date. Yet, catalysis technology is strongly believed that it is a potentially powerful tool for controllable synthesis, for well tailored CNT either in diameter, wall thickness or well crystallized structures. Recently, hydrocarbon decomposition reaction was revealed as most economical process due to its low energy input to produce hydrogen and also CNT (Zein, et. al. 2004$_a$).

Through the thermal catalytic reaction, hydrocarbon is decomposed into hydrogen and filamentous carbon. Generally, carbon atoms generated by dissociative chemisorption of hydrocarbon on particular edges of the metal particle diffuse to the opposite planes and crystallize there as continuous graphite-like structure. Methane, which is the most abundant resource among all hydrocarbons, is an ideal source for production of highly graphitized CNT because of its kinetic stability at high temperature.

2 CARBON NANOTUBES PRODUCTION FROM NATURAL GAS

Above 80% of the hydrocarbon fraction of natural gas is methane; natural gas conversion is actually intended for methane conversion. The large amount of inexpensive, easily attainable deposits of natural gas creates an attractive prospect for the energy source. The presently known reserves of natural gas exceed that of crude oil by factor of about 1.5 (Dry, 2002). The total natural gas reserves in the Asia and Oceania is 441.73 trillion cubic feet while the total natural gas reserves in the world is 6076 trillion cubic feet reported by Oil and Gas Journal (EIA, 2004). Many of the natural gas reserves are located at remote areas, making economical use difficult because of the high cost of transporting the gas. Because of the low value of natural gas, much of this gas is re-injected into the reservoir or is flared.

Malaysia has substantial natural gas reserves. At the beginning of 2004, Malaysia proved reserves were estimated at 75 trillion cubic feet. About 60% of marketed natural gas production is consumed domestically and three quarters of which is used for electricity generation. The country largest gas field is in Kinabalu, in eastern Malaysia, which it is the region second largest Liquefied Natural Gas (LNG) exporter, accounting 14% of total world trade in LNG in 2002.

In the past decade, methane decomposition is an alternative route of hydrogen production from natural gas, where clean fuel (Zein, et. al., 2003) can be obtained through single step reaction without further purification process. Currently, the major problem in methane decomposition is to develop an appropriate utilization of large amount of well tailored CNT co-produced with hydrogen. In this case, supported-Nickel catalyst is well known for its effectiveness for well crystalline CNT (Takaneka, et. al., 2004). Moreover, Ni doped with Mn reported to give lowest activation energy (Zein, et. al., 2004_a; 2004_b).

The gas phase reaction that uses methane as raw material, at the temperature range from 773K to 1273K depends on the type of catalyst in the fixed bed (Takaneka, et. al., 2003, Wang, et. al., 2002, Ermakova, et. al., 1999; 2001). CNT is produced few minutes after the reaction started till the catalysts were deactivated (Moulijn, et. al., 2001). CNT produced under certain reaction condition from either bimetallic catalyst or catalyst with metal doping with defined catalyst preparation method will give different morphology (Wang, et. al., 2002, Piao, et. al., 2002) and yield (Ermakova, et. al., 1999; 2001, Takaneka, et. al., 2003, Qian, et. al., 2004).

Therefore, production of CNT should base on its advance area of application. Definitely, CNT used for bio-medical appliances and nano-electronics differs significantly in their properties. Hence, is important to review area of CNT possible and potential used for better tailoring of CNT synthesizing in future work!

3 CNT PROPERTIES

CNT is merely nanoscopic thread, made of pure carbon as regular and symmetric as crystals, these exquisitely thin, impressively long macromolecules have been the object of intense scientific study for the past decade. Just recently, they have become a subject for engineering as well. CNTs' extraordinary properties include: superlative resilience, tensile strength and thermal stability—have fed fantastic predictions of microscopic robots, dent-resistant car bodies and earthquake-resistant buildings. Most surprisingly is that CNT is stronger than steel where CNT modulus Young is hundred times greater than steel of the same weight.

What makes these tubes so stable is the strength with which carbon atoms bond to one another, which is also what makes diamond so hard. In diamond the carbon atoms link into four-sided tetrahedra, but in nanotubes the atoms arrange themselves in hexagonal rings. One sees the same pattern in graphite, and in fact a nanotube looks like a sheet (or several stacked sheets) of graphite rolled into a seamless cylinder.

Comparing SWNT properties to other material, one can see that CNT properties are really amazing that enable its applications in many advance technology that attracted numerous researchers interest. SWNT density is 1.33 to 1.4 g/ cm^3; it is approximately half the density of aluminium. Its tensile strength is 45 billion Pa where high strength steel alloys break at about 2 billion Pa. Besides, CNT can be bent at large angles and restraightened without damage whereas metal and carbon fibers fracture at grain boundaries. SWNT can carry current up to capacity of 1 billion amps/ cm^2 but copper wires burn out at about 1 million amps/cm^2. Comparing field emission, SWNT can activate phosphorous at 3 V if electrodes are spaced 1 μ apart, but Mo tips require fields of 50 to 100 V/ μm and have very limited lifetimes. Although pure diamond is well known as good heat transmission at 3320 W/m·K, SWNT is predicted to be as high as 6000 W/m·K at room temperature. Additionally, SWNT is stable up to 2800 ^{0}C in vacuum, 750 ^{0}C in air; but, metal wires in microchips melt at 600 to 1000 ^{0}C. Withstanding the mentioned amazing properties of CNT, cost of a gram of SWNT is approximately USD 1500; gold market price is about USD 10 per gram (Collins, et. al., 2000, Dresselhaus, et. al., 2000, Dekker, et. al., 1999).

Thus, in time, CNT may yield not only smaller and better versions of existing devices but also novel one that wholly depends on the extreme of nanoparticles. Nevertheless, with so many avenues of development under way, it seems clear that it is no longer a question of whether CNT will become useful components of the future but merely the applications and timing.

4 CNT APPLICATIONS

4.1 APPICATION OF CNT IN BIOMEDICAL

With the development of human kind intellectual spirit and quality of living, it is also important to pay attention to health. Therefore, advance field of CNT applications also include biomedical application of CNT that gives better and precise results to the effect of medicine in human body. CNT is predicted to become important in vaccine delivery (Marc, et. al., 2003). More significant, CNT is also aimed to involve in nano-mechanics as nanotubes actuator (Minett, et. al., 2002). Existing properties of CNT is their ability to efficiently convert electrical energy into mechanical energy, i.e., actuation. Nanotube actuation is caused by the geometrical expansion of C-C covalent bond cause by charse transfer into nanotube. The ability to actuate, in addition to their high strength (approx. 1TPa), make macro scale sheets of CNT ideal for artificial mucles (Boughman, et. al., 1999).

CNT is also applicable in synthesizing gelatin. CNT is used to prepare novel hybrid gelatin hydrogel. With added CNT, stability of hybrid hydrogel can be maintained and to enhance the mechanical property of hydrogel.. Its demonstrated application is in protein concentrating (Li, et. al., 2004) eg. *Albumin human serum.*

Besides, Balavoine et. al. reported that MWNT is used for helical crystallization of protein. Mattson et. al. (2000) looked at the advantages of the shape and exceptional ridiaity of CNT for the growth of embryonic rat brain neurons on MWNT. Other researchers had studied immobilized biological species on both SWNT and MWNT for biosensor and bioreactor system.

4.2 APPLICATION OF CNT IN ELECTRONICS

CNT can play the same role as silicon does in electronic circuits, but at a molecular scale where silicon and other standard semiconductors cease to work. Although the electronic industry is already pushing the critical dimensions of transistors in commercial chips below 200 nm, i.e., about 400 atoms wide, engineers still face large obstacles in continuation of this miniaturization. Wires and functional devices tens of nanometers or smaller in size could be made from nanotubes and incorporated into electronics circuit that work faster and on much less power than those existing.

CNT is applied in nanoelectronics as Carbon Nanotube-based Field Emmision Transistors, CNT-FETs (Repetto, et. al., 2004). Their small dimensions make them a suitable instrument to analyze quantum phenomena and their particular structure gives them an extreme strength both to electrical and mechanical stresses. After fabrication of FET from CNT, the only step forward is to produce integrated circuits, i.e., p- and n-type transistors (Avouris, et. al., 2002). Hoenlein, et. al. (2003), concluded that FET from CNT outperform the best silicon FET devices in all transistor characteristics. IBM claims that earlier in 2001, it found a way to produce arrays of CNT transistors on wafer. IBM had also created the first logic circuit using a single CNT transistor (Johnson, et. al., 2002). Collins et. al. (2000) found that gate electrode can change the conductivity of the nanotube channel in FET by a factor of one million or more, comparable to silicon FET.

Appenzeller et al. (2000) concluded that the achievable electrical performance of CNT FET in a 'planar cylinder' geometry can be expected to be comparable to state-of-the-art silicon FET. Baughman, et. al. (2002), silicon technology is so entrenched that it will take an overwhelmingly compelling new technology to replace it. However, CNT-FET technology is in its infancy and is by no means comparable to the mature silicon technology. CNT do not yet qualify, but the potential payoff is so great that this research is amply justified from commercial viewpoint.

Combination of carbon nanotubes with different band gaps could behave like light-emitting diodes and even nanoscopic lasers (Collins, et. al., 2000). Woo et. al. (2001) fabricated organic light emitting diodes with SWNT. The device made with SWNTs in the buffer layer shows a significant decrease in the electroluminescence as compared to that of the device without the SWNTs. Also, the lower power dependence of the current at low applied voltages implies that the injected holes are initially trapped by SWNTs.

Today, CNT has been commercially applied in flat panel display. Levenson, et. al. by marrying a paradigm shifting technology to current-day cathode ray tube (CRT) display manufacturing and assembly techniques. Staring from very low resolution in light emitting diodes (LED) product, CNT electron emission for display field emission applications, now can not be denied appears as high resolution, large-format televisions at homes. Samsung which has been working on flat panel CNT display introduced its first product in late 2003 (Ouellete, et. al. 2003). Field-emission displays can offer wide viewing angles, and they are inherently less power-hungry than plasma displays, making them cheaper to operate. With these advantages, companies like Motorola and Sony are also aggressively pursuing field-emission display technology using nanotubes, concurrent with improvement in liquid crystal displays and the emerging organic and polymeric light emitting diodes display.

Also, to this date batteries used in about 60% of cell phones and notebook computers contain carbon nanotubes. They fulfill their function by making the battery last longer, making it more recyclable, and improving the energy delivery.

4.3 APPLICATION OF CNT AS COMPOSITE

CNT composite is the first commercial application of CNT in area of new material, use as electrically conducting component in polymer composites (Baughman, et. al., 2002). The nanofiber morphology of CNT allow electronic conductivity to be achieved while minimizing degradation of other performance aspects, such as mechanical properties and the low melt flow viscosity needed for thin wall molding applications. CNT composites is widely applicable in automotive gas lines and filters, where it dissipates charge buildup, that can lead to explosions, and better maintains barrier properties against fuel diffusion than plastics filled with carbon black.

Also, some General Motors cars are already included conductive plastic automotive parts, where CNT is added (Collins, et. al., 2000). Such plastic can be electrified during painting so that the paint will stick more. Therefore, avoids separate painting and associated color mismatch. Smoothness of the surface finish provides an advantage over other conductive filters (Baughman, et. al., 2002).

Eikos, Inc., has patent coverage on CNT composites for shielding of electromagnetic radiation from cell phones and computers. It is a potential lucrative application (Glatkowski, et. al., 2001). Uniformly dispersion of CNT into plastics can potentially provide structural materials with dramatically increased modulus and strength.

4.4 APPLICATION OF CNT IN ELECTROCHEMICAL DEVICES

Baughman, et. al.(2002) reported that high electrochemically accessible surface area of porous CNT arrays, combined with their high electronic conductivity and useful mechanical properties, CNT are attractive as electrodes for electrochemical devices. Super-capacitors which have giant capacitances and electromechanical actuators where CNT is used may eventually be used in robots. Due to the separation of the electrode in capacitor is in nanometers compare to original dielectric capacitor of micrometer separated, very large capacitances result from high CNT surface area accessible to the electrolyte. Therefore, energy is stored by charge injection of only a few volts (Baughman, et. al., 1999) applied in super-capacitors which can be used for applications that require higher power capabilities than batteries and ordinary capacitors, such as hybrid electric vehicles and electromechanical actuators.

4.5 APPLICATION OF CNT IN HYDROGEN STORAGE

CNT have been long heralded as potentially useful for hydrogen storage; for fuel cells that power electric vehicles or laptop computers. Hydrogen is important fuel mainly in three applications: In nickel-hydride battery, in which hydrogen is combined as a metal hydride; in spark ignition engine powered car; and in a fuel cell. Hydrogen can be converted to electricity with emission of only water with very high efficiency. The most significant news come from the world wide vehicle corporations such as Ford, GM, Toyota, Hondo, etc., that the development of proton exchange membrane fuel cell electric vehicles has made great progress. For conventional porous carbon, the hydrogen uptake is proportional to its surface area and pore volume. However, high hydrogen adsorption capacity can be only obtained at very low temperature. In contrast, in spite of its relatively small surface are and pore volume, CNT show surprising high hydrogen storage capacity that embarked scientist great interest on this aspect (Cheng, et. al., 2001).

4.6 APPLICATION OF CNT IN SENSOR AND PROBES

Baughman, et. al. (2002) claimed that possible chemical sensor application of non-metallic CNT. The main advantages are the miniature size and the correspondingly small amount of material required for a response. Seiko Instruments collaboration with Daiken Chemical Co., Ltd produces CNT scanning probe tips for atomic probe microscopes. CNT mechanical robustness and low buckling force dramatically increase probe life and minimize sample damage during repeated hard crushes into substrates. The nanoscale diameter of CNT also gives better resolution in comparison to conventional nanoprobes.

Baughman, et. al.(2002) implies that CNT based gas discharge tubes may also soon find commercial use for protecting communications network against power surges. Another more challenging application is microwave generation by improving the lifetime of CNT emitter under very high current (500 mA/ cm^2).

5 CONCLUSION

An impressive advancement of CNT applications in diverse area has been done since the past decade; for the decade of future, additional progress is likely when CNT applications, as advance material in miniature devices, breakthroughs will reach commercial application. Independent of the outcome of the ongoing races to exploit nanotubes applications, CNT have provided possibilities in nano-technology that were not conceived in the past.

Other CNT application which is demonstrated and on its pathway to the market includes chemical and genetic probes, i.e., to tag strand of DNA, mechanical binary memory, i.e.,non-volatile RAM, nanoweezers, supersensitive sensors, ion storage, sharper scanning microscope, super-strong materials.

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