Carbon nanotubes synthesis, purification for solar cells and water purification

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Abstract – Carbon Nanotubes were discovered by Iijima in 1991. Then they have been recognized as exciting and fascinating novel material which have specific physical and chemical characteristics and lead to playing a vital role in developing tremendous technological applications. Multi-walled carbon nanotubes, ‘MWCNTs’ were obtained by the arc discharge technique in an atmosphere of Ar and H2 mixture. The catalyst was prepared from a mixture of Ni, Y, Co and Fe. They allow the realization of a quasi-one-dimensional environment for the materials diffused inside, particularly, the case of water inside such nano-channels has recently received consequences. Transport of molecules through molecular pores like nanotubes is essential for many biological and technical applications. The water self-diffusion coefficients help to quantify the state of absorbed water in each system. More loosely bound water yields a higher self-diffusion coefficient, while more tightly bound water yields a lower self-diffusion coefficient. As a novel application we can use the flow of water inside carbon nanotubes as snapshot to measure the pressure inside very soft cells of biological systems when the water goes through its shape by capillary behaviour. Other good application of carbon nanotubes composite is the photovoltaic cells, the most important inspiration is to produce a low cost, renewable energy source which will help to solve the world’s frightening energy crisis, electrical energy from the sun (photovoltaics PV) is considered as one of the mainly future and environmental-friendly source of energy.

Keywords: Carbon Nanotubes (CNTs), Purification, Photovoltaics, Water, Renewable energy.

1. SYNTHESIS OF CARBON NANOTUBES

Soon after the discovery of carbon nanotubes, Ebbesen and al. [1] successfully applied a large-scale synthesis which made extensive investigations on this promising material possible. Further optimization of the carbon nanotube growth technique raised the nanotube yields to above 70%. Nevertheless, nanotube samples of higher purity are strongly needed for many research and application purposes.

There are four main methods to generate carbon nanotubes. Most of them are based on the sublimation of carbon under inert gas. The first method is chemical vapor deposition, ‘CVD’ [2], the second one is the catalytic decomposition of carbon monoxide in a high pressure process, ‘HiPCO’ [3], third method is the one called ‘laser ablation’, (LA) [4] or the solar technique [5-7] and the fourth method is arc-discharge, ‘AD’ [8]. The growth mechanism of nanotubes varies depending on which method is used.

The formation of SWCNTs always needs the presence of rare metals or a transition metal or mixture of them. The catalytic mechanism involves the coordination of metal atoms to the dangling bonds of growing nanotubes, called the scooter mechanism [9]. The transition metal atoms bridging two carbon atoms go scooting around the edge of the nanotube, as it is growing. The common mechanism of growing nanotube is the
growth of an individual SWCNT on a metal nanoparticle substrate. The carbon atoms nucleate on the metal catalyst and grow to several micrometers in length, as is schematically illustrated in figure 1. When the carbon becomes super saturated in the nanoparticle, it starts to precipitate in form of graphitic sheets. Since the edges of the sheet are unstable, the emergence of pentagon defects leads to the formation of a nanotube cap which closes the tube. Closing the nanotube requires considerable distortion of the hexagon and hence of the $sp_2$ bonds [10] (Fig. 1, b-, c-, d- and e-). After the cap is formed, two processes can happen: firstly, more carbon atoms can be inserted into the metal-carbon bonds, leading to the elongation of fullerene to form a single wall nanotube. Secondly, the fullerene cap can continue to grow around the nanoparticle, surround it and then preventing any further growth [11].

![Fig. 1: Root growth mechanism of SWCNT](image)

**Arc discharge technique**

For our experiments, we have used SWCNTs prepared by arc-discharge and purchased from CNI, Houston Texas, USA (HiPCO). [8, 12-22]

The electric arc discharge process is one of the most common methods for nanotube production. This growth technique of carbon nanotubes has been greatly improved in time. This method was introduced for the synthesis of fullerenes. Iijima in 1991 has discovered MWCNTs by using this method, later he discovered SWCNTs by the same method and the metallic nanoparticles. The method is preferred over other methods in that it has high yields of high quality, low defect carbon nanotubes in large batches. It produces SWCNTs using a relatively low-priced and not complex apparatus.

The Krätschmer generator has been used to generate fullerenes. It consists of two carbon electrodes; the thicker cathode, on which the deposit is separated from the thinner anode by ~1 mm. This technique uses high temperatures (about 4000 K), which is needed to evaporate carbon into plasma. The arc discharge method produces both multi- and single walled carbon nanotubes.

As shown in figure 2 a graphitic rod is used as an anode in the reactor for nanotubes. In the rod a hole (3.2 mm diameter, 8.30 mm depth) is drilled, filled with a mix of carbon (65 % by weight) and metal catalyst powder (7% by weight Y and 28% by weight Ni). This rod is loaded into the reactor and acts as the consumed anode for the process. The cathode is a large plate made from high density carbon and is not consumed in the process (Fig. 2).

The chamber is sealed and evacuated. It should be flushed several times with helium.
to expel all the air before being finally pressurized at 500 mbar for the run. A direct current (DC) source is connected to provide 100 amperes at a voltage of 60 volts. The arc is initiated by adjusting the distance between the anode and the cathode maintaining the voltage constant (60 V).

A bright discharge occurs and the anode is consumed. The nanotubes start to grow below 1100 °C. The electrode separation of about 1 mm must be maintained by the operator for the duration of the process which can take about six minutes until the electrode is consumed, and the process must be stopped. The chamber is cooled down by filling it with helium up to atmospheric pressure; and finally the reactor is opened slowly.

Fig. 2: Schema of the SWCNT Krätschmer generator which has been used to produce arc-discharge material and the rod filled with powdered NiY catalysts

Fig. 3: Arc-discharge reactor used for synthesis of SWCNTs
The photographs describe the SWCNT reactor: A) Chamber of the reactor, B) graphitic disc-cathode C) graphitic rod-anode which is filled with catalysts, D) complete view of the reactor.
The purification of the carbon nanotubes is essential to our studies. As we will see later, especially the magnetic metal clusters hinder the NMR investigations. It is necessary to remove as many clusters as possible. Also, in order to study the water absorption by the SWCNTs, it is necessary to open the tubes, which are normally closed directly after the synthesis.

There are many purification techniques; each of them has its own advantages and limitations. Chemical oxidation treatments are conveniently used in large batch production, but they strongly destroy carbon nanotubes layers [15]. Non-destructive methods, such as micro-filtration or size exclusion chromatography purification methods are not practical for a large quantity of SWCNTs [12, 13, 15].

The SWCNT samples that are used in this study were prepared by the HiPCO process in Houston and purified in Max-Planck-Institute for Solid State Research in Stuttgart, Germany.

To purify our samples we have used four purification treatments:

a. Oxidation in air at 350 °C to remove amorphous carbon;

b. Sonication to fracture the metal clusters;

c. Centrifugation to separate the metal clusters from the carbon nanotubes;

d. Acidic treatment, also to remove the metal clusters.

2.1 Oxydation in air

The different types of the batch are put in the oven in air by 350°C for three hours or until 25% weight loss. Most of the amorphous carbon will be removed by converting carbon into carbon oxides.

2.2 Sonication of carbon nanotubes

After the treatment in the oven the material is dispersed (1% weight) in a SDS solution (sodium dodecylsulfate) as a surfactant. The surfactant molecules are surface-active agents, which can modify the particle-suspending medium-interface and prevent the aggregation of particles for a long time. The dispersion is prepared with an ultrasonic probe (Finger ultrasonic generator Up 200S) with 50 Watt at full cycle for one minute. Too long sonication times should be avoided to prevent destruction of nanotubes. The ultrasonic treatment decomposes the metal nanoparticles.

2.3 Centrifugation

Centrifugation is another technique to purify carbon nanotubes. When a container with a suspension of carbon nanotubes is rotated at high speed in a centrifuge (Eppendorf centrifuge 5804), all suspended particles, including the dispersed nanotubes, will be accelerated towards the bottom of the container due to the centrifugal force. However, since different particles in the suspension may have different masses and may sense also different cohesive forces from the solvent, their acceleration is expected to be quite different. For instance, hard particles such as clusters of catalysts should move to the bottom faster than the long, thin carbon nanotube structures, which are subjected to larger cohesive forces and move along more complicated trajectories.

Therefore, with appropriate control of the rotation speed and duration, one may expect that the final suspension will contain more carbon nanotubes than the original suspension. The purity of carbon nanotubes in this way is improved. The procedure is repeated three times with increasing speed and running time (3600 rpm for 1-2 minutes, 5000 rpm for 3 minutes and 15000 rpm for 3 minutes. After each run the precipitate is removed from the container).
3. CHARACTERISATION

3.1 Electron microscopy

By using transmission electron microscopy (TEM) or scanning electron microscope (SEM), it is possible to see that the carbon nanotubes are cylinders of graphene sheet with different structural symmetry. Scanning electron microscopy (SEM) was conducted on a LEO 1530 VP field emission scanning electron microscope equipped with a Phoenix EDX system. Transmission electron microscopy (TEM) analysis was carried out on a Philips CM 200 electron microscope (point resolution of 0.2 nm and acceleration voltage of 120 kV (in MPI Stuttgart).

3.1.1 Microscopy of SWCNTs

Figure 4 shows a scanning electron microscopy (SEM) image of a raw material containing bundles of nanotubes, amorphous carbon and clusters of NiY. Figure 5 shows at a higher resolution an electron microscopy picture of a sample with 20 wt % Fe clusters. Here nicely the carbon nanotube bundles and the metal clusters can be observed. Figures 6-13 show SWCNT material at different purification steps. The purification causes a decrease in bundle size and shortens the tube length.

![Fig. 4: SEM micrograph of raw SWCNT (NiY)](image)

![Fig. 5: TEM picture of a raw SWCNT (Fe HiPCO) with 20 % wt Fe impurity](image)
Fig. 6: SEM picture of the samples with 13wt % NiY impurity (raw sample)

Fig. 7: SEM micrograph of SWCNT (NiY) after first cycle of purification

Fig. 8: SEM micrograph of SWCNT (NiY) after second cycle of purification
Fig. 9: SEM micrograph of SWCNTs (NiY) after the third cycle of purification

Fig. 10: SEM micrograph of SWCNTs (NiY) after heat treatment at 370 °C and centrifugation without any cycle of purification

Fig. 11: SEM micrograph of SWCNTs (Fe pur) after treatment at 370 °C and centrifugation without acidic treatment
Fig. 12: SEM micrograph of SWCNTs (Fe pure) after treatment at 370 °C and centrifugation without acidic treatment

Fig. 13: SEM micrograph of SWCNTs (Fe pure) after treatment at 370 °C centrifugation and many acidic treatments to make the tube shorter

REFERENCES


ICE SD’2011: Carbon nanotubes synthesis, purification for solar cells and... 179


