CHAPTER 2

Background and previous Studies

2.1 INTRODUCTION

Nanoscience is one of the most promising branches of physics that can open a new area in the developing technology. This is due to the ability of changing the materials physical properties to meet the required need. Thus, nanoscience and its basic selection beside applications for carbon nanotube are exhibited here.

2.2 Nano science

The term nano stands for the length scale which is equal to 10^{-9} meter. Nano particles are those particles that have dimensions in the rang (1-300 nm) , where 1nm = 1nano meter = 10-9 meter .The bulk matter can be converted to nano material by dividing them to isolated aggregates of non interacting particles with sizes in the range (1-300 nm)[22]. Such participles , can no longer obeys classical laws , but obeys quantum laws on expect nano particles to have new physical properties compatible with quantum laws . These new properties strongly dependent on the nano size, shape , structure and concentration.

The nano materials comprise having different shapes and structure. Nano particles may have spherical shape, or may be in the form of rods or hollow tubes or sheets, their size ranges from 1 to 300 nm. These particles may be deposited on a solid substrate or may be dissolved in liquid [24].

2.3 Preparation of nanoparticles

The selection of appropriate method for the preparation of nanoparticles depends on the physicochemical character of the polymer and the drug to be loaded. The primary manufacturing methods of nanoparticles from preformed polymer includes:

2.3.1 Emulsion-Solvent Evaporation Method:

This is one of the most frequently used methods for the preparation of nanoparticles. Emulsification-solvent evaporation involves two steps. The first step requires emulsification of the polymer solution into an aqueous phase. During the second step polymer solvent is evaporated, inducing polymer precipitation as nanospheres. The nano particles are collected by ultracentrifugation and washed with distilled water to remove stabilizer residue or any free drug and lyophilized for storage [23]. Modification of this method is known as high-pressure emulsification and solvent evaporation method. This method involves preparation of a emulsion which is then subjected to homogenization under high pressure followed by overall stirring to remove organic solvent [22].The size can be controlled by adjusting the stirring rate, type and amount of dispersing agent, viscosity of organic and aqueous phases and temperature [22,23]. However this method can be applied to liposoluble drugs and limitation are imposed by the scale up issue.

2.3.2 Double Emulsion and Evaporation Method:

The emulsion and evaporation method suffer from the limitation of poor entrapment of hydrophilic drugs .Therefore to encapsulate hydrophilic drug the double emulsion technique is employed, which involves the addition of aqueous drug solutions to organic polymer solution under vigorous stirring to form w/o emulsions. This w/o emulsion is added into second aqueous phase with continuous stirring to form the w/o/w emulsion. The emulsion then subjected to solvent removal by evaporation and nano particles can be isolated by centrifugation at high speed. The formed nanoparticles must be thoroughly washed before lyophilisation [22].In this method the amount of hydrophilic drug to be incorporated, the concentration of stabilizer used, the polymer concentration, the volume of aqueous phase are the variables that affect the characterization of nano particles [24].

2.3.3 Salting Out Method:

Salting out based on the separation of a water-miscible solvent from aqueous solution via a salting-out effect [22]. Salting-out is based on the separation of a water miscible solvent from aqueous solution via a salting-out effect. Polymer and drug are initially dissolved in a solvent which is subsequently emulsified into an aqueous gel containing the saltingout agent (electrolytes, such as magnesium chloride and calcium chloride, or non- electrolytes such as

sucrose) and a colloidal stabilizer such as polyvinylpyrrolidone or hydroxyethylcellulose. This oil/water emulsion is diluted with a sufficient volume of water or aqueous solution to enhance the diffusion of solvent into the aqueous phase, thus inducing the formation of nanospheres. Several manufacturing parameters can be varied including stirring rate, internal/external phase ratio, concentration of polymers in the organic phase, type of electrolyte concentration and type of stabilizer in the aqueous phase. This technique used in the preparation of PLA, Poly(methacrylic) acids, and Ethyl cellulose nanospheres leads to high efficiency and is easily scaled up[24]. Salting out does not require an increase of temperature and therefore may be useful when heat sensitive substances have to be processed. The greatest disadvantages are exclusive application to lipophilic drug and the extensive nanoparticles washing steps.

2.3.4 Emulsions- Diffusion Method:

This is another widely used method to prepare nanoparticles. The encapsulating polymer is dissolved in a partially water-miscible solvent (such as propylene carbonate, benzyl alcohol), and saturated with water to ensure the initial thermodynamic equilibrium of both liquids. Subsequently, the polymer-water saturated solvent phase is emulsified in an aqueous solution containing stabilizer, leading to solvent diffusion to the external phase and the formation of nanospheres or nanocapsules, according to the oil-to-polymer ratio. Finally, the solvent is eliminated by evaporation or filtration, according to its boiling point. This technique presents several advantages, such as high encapsulation efficiencies, no need for homogenization, high batch-to-batch reproducibility, ease of scale up, simplicity, and narrow size distribution. Disadvantages are the high volumes of water to be eliminated from the suspension and the leakage of water-soluble drug into the saturated-aqueous external phase during emulsification, reducing encapsulation efficiency. Several drug- loaded nano particles were produced by the technique, including mesotetra (hydroxyphenyl) porphyrin-loaded PLGA (p-THPP) nano particles, doxorubicin-loaded PLGA nano particles, and cyclosporine (cy-A-); loaded sodium glycolate nanoparticles [23].

2.3.5 Solvent Displacement / Precipitation method:

Solvent displacement involves the precipitation of a preformed polymer from an organic solution and the diffusion of the organic solvent in the aqueous medium in the presence or

absence of surfactant. Polymers, drug, and or lipophilic surfactant are dissolved in a semi polar water miscible solvent such as acetone or ethanol. The solution is then poured or injected into an aqueous solution containing stabilizer under magnetic stirring. Nano particles are formed instantaneously by the rapid solvent diffusion.

The solvent is then removed from the suspensions under reduced pressure. The rates of addition of the organic phase into the aqueous phase affect the particles size. It was observed that a decrease in both particles size and drug entrapment occurs as the rate of mixing of the two phase increases. Nano precipitation method is well suited for most of the poorly soluble drugs. Nanosphere size, drug release and yield were shown to be effectively controlled by adjusting preparation parameters. Adjusting polymer concentration in the organic phase was found to be useful in the production of smaller sized nanospheres through restricted to a limited range of the polymer to drug ratio.

2.4The fullerenes

Until 1985 it was generally believed that solid elemental carbon occurs in two different crystalline phases: diamond and graphite. Diamond is in thermodynamic equilibrium at very high temperatures and pressures; it occurs, nevertheless, as a metastable phase under atmospheric pressure and at room temperature. The bonding of carbon atoms in a graphene plane is very strong (covalent bonds), whereas the bonding between two graphene layers is weak (Vander Waals bonds). In 1985 an important breakthrough in carbon research was realized by the work of Kroto et al., which resulted in the discovery of large family of all carbon molecules, called 'fullerenes'. They can be crystallized as molecular crystals, which are thus a third form of crystalline elemental carbon. The fullerenes are closed cage carbon molecules with the carbon atoms tiling spherical or nearly spherical surfaces, the best known example being C_{60} with a truncated icosahedral structure formed by 12 pentagonal rings and 20 hexagonal rings .The coordination at every carbon atom in fullerenes is not planar but rather slightly pyramidalized, with some SP^3bonding present in the essentially SP^2 carbons. C_{60} molecular structure shows that every pentagon of C_{60} is surrounded by five hexagons. The key feature is the presence of five-membered rings, which provide the curvature necessary for forming a closed-cage structure. In 1990, Kratschmer et al [2]. Found that the soot produced

6

by arcing graphite electrodes contained C_{60} and other fullerenes. It was the ability to generate fullerenes in gram-scale quantities in the laboratory, using a relatively simple apparatus that gave rise to intense research activity on these molecules and caused a renaissance in the study of carbon.

2.5Discovered carbon Nanotubes

In that the chamber would have been evacuated rather than filled with a small pressure of Helium. The resulting films were largely amorphous, but contained small, partially graphitized regions which contained some unusual structures. These structures included discrete graphitic particles apparently made up of concentric closed shells, tightly curved around a central cavity. One of these structures, reproduced in his 1980 Journal of Microscopy paper, is clearly a nanotube, and Iijima confirmed its tubular nature using tilting experiments. But he did not explore these structures in detail, and suggested that the curved layers were probably due to sp3 bonding, rather than, as we now believe, the presence of pentagonal rings. There are other examples of structures resembling 'Iijima-type' multiwalled nanotubes scattered throughout the pre-1991 carbon literature. In some cases these structures might be contaminants on the carbon films used to support the samples . It has also been claimed that an image in a 1976 paper by Agnes Oberlin and colleagues contains an image of a single-walled tube. While this may be true, the authors did not recognize its significance at the time.

Work by theoreticians also anticipated the discovery of carbon nanotubes. For example,Patrick Fowler of Exeter University described theoretical studies of small cylindrical Fullerene molecules in early 1990 [1, 2] . Two groups of American theorists, one at the Naval Research Laboratory, Washington DC [3], and one at the Massachusetts Institute of Technology submitted papers on the electronic properties of fullerene tubes just a few weeks before Iijima's paper appeared in Nature. Last, but not least, the highly imaginative British chemist David Jones, under his pen-name Daedalus, ruminated about rolled-up tubes of graphite in The New Scientist in 1986[4].

2.6　*Carbon Nanotubes*

By rolling a graphene sheet into a cylinder and capping both end of the cylinder with a half of fullurene molecule a carbon nanotube is formed. Harry Kroto discovered C60 molecule in 1985 [2]. Type of carbon nanotube is determined by the number of the concentric graphene layers.

2.7　*Type of Carbon Nanotubes*

Carbon nanotubes are categorized as single wall carbon nanotubes and multi wall carbon nanotubes. If carbon nanotube contains one graphene layer, it is named single wall nanotube (SWNT); whereas if it contains two or more concentric layer, it is called multi wall carbon nanotube (MWNT).

2.7.1 Single- Wall Carbon Nanotube (SWNT)

A single-wall carbon nanotube (SWNT) is defined by a graphene sheet rolled into a cylindrical shape with a diameter of about 0.4-10 nm and lengths extending up to several microns. If we ignore two ends of carbon nanotube and focus on the large aspect ratio of the tube, carbon nanotubes can be considered as one-dimensional nanostructures with axial symmetry and they have excellent properties because of this symmetry[1,2]. Depicted in figure 2.7.1.

2.7.2Multi -Wall Carbon Nanotube (MWNT)

The second type consists of tubes made of more than one concentric graphene cylinders coaxially arranged around a central hollow with a constant interlayer spacing, which is nearly equal to 0.34 nm *(Dresselhaus, et al. 2001),* graphite layer spacing, and called multi-shell or multi-wall carbon nanotubes (MWNT) and MWNTs consist of 2 to 30 concentric graphene, diameters of which range from 2.5 to 100 nm. MWNTs are stronger than SWNTs, but they have more defects than SWNTs *(Dai, 2002).* Depicted in figure2.7.1.
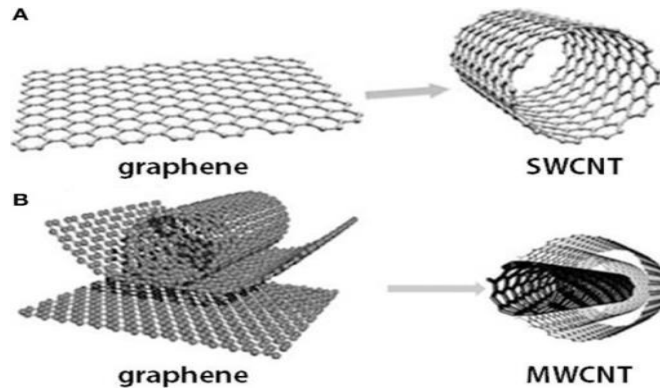
Figure 2.7.2 SWNTs and MWNTS Schematic Diagram [1]

2.8 Synthesis of carbon nanotubes

The major methods of synthesis of carbon nanotubes are Arc discharge method, Laser ablation method and Chemical Vapor Deposition CVD Method.

2.8.1 Arc discharge method

The synthesis of single-wall carbon nanotubes are made with arc discharge method *(Iijima 1991)*. This method has been used for, multiwall nanotubes, and ropes of single-wall nanotubes[1]. The growth of carbon nanotubes happens on carbon (graphite) electrodes by applying direct current (DC) in an inert gas such as argon or helium [2]. Figure 2.8.1 illustrates the arc-discharge setup with large concentration of amorphous carbon and CNTs.
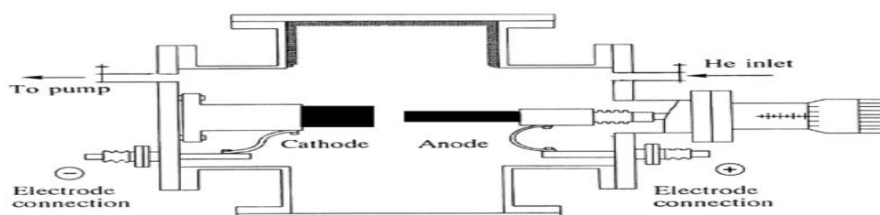

Figure 2.8.1 Cross sectional view of a arc generator [1]

This figure shows two high-purity graphite electrodes of 5-20 mm diameter separated by 1 mm. A voltage of 20-25 V is applied across the electrodes and a dc electric current of 50-120 A flows between the electrodes. Thus the temperature reaches to about 4000ºC, anode vaporises and condenses on the cathode surface, so the length of anode decreases with increasing the formation of carbon nanotubs. During the process both electrodes are cooled with water and the arc is generally operated in He atmosphere at low pressure between 50-700 mbar. Using this technique carbon nanotubes synthesis can be done with or without catalyst in order to produce multi-wall carbon nanotubes and single-wall carbon nanotubes, respectively [2].

No catalyst need for multi-wall carbon nanotube production, and nanotubes are found in bundles in the inner region of the cathode deposit and are roughly aligned in the direction of electric[7]. Iijima used this technique to produce first multi-wall carbon nanotube in 1991, and these nanotubes had 2 to 50 walls. However, many products also used this technique such as fullerenes, amorphous carbon and graphite sheets [8]. By heating the growth material in oxygen environment, graphitic particles can be oxidized and purification is provided, but oxidation also removes an substantial amount of nanotubes. When one of the graphite electrodes (anode) contains a transition metal catalyst particles such as Fe, Co, Ni, single wall carbon nanotubes can be synthesized using arc discharge method. First single-wall carbon nanotube synthesis by arc discharge method using Fe as a catalyst was reported in 1993 by *Iijima and Ichihashi,*. In the same year Bethune et al. also synthesized single- wall carbon nanotubes with this method, but using Co as a catalyst.

2.8.2 Laser ablation method

The first carbon nanotube produced by laser ablation method was reported by Guo [1]. This method utilizes an intense laser pulse [1]or a continuous laser *(Maser, et al. 1998)* to ablate a Co-Ni/graphite composite target. The target is placed in a tube furnace heated to 1200ºC. When this target vaporizes, a cloud of C, C_2, C_3 and catalyst vapors was observed, then cloud condenses, and the small amount of carbon species come together to form a larger one. The vaporized catalysts prevent the closing of these carbon molecules into cage structure, so the growth process is finished with the formation of a single-wall carbon nanotube [2],. During the laser ablation, an inert gas (generally helium or argon) flow take place in the growth

chamber and provides grown of carbon nanotube collected on a water-cooled cupper collector as shown in figure (2.8.2).
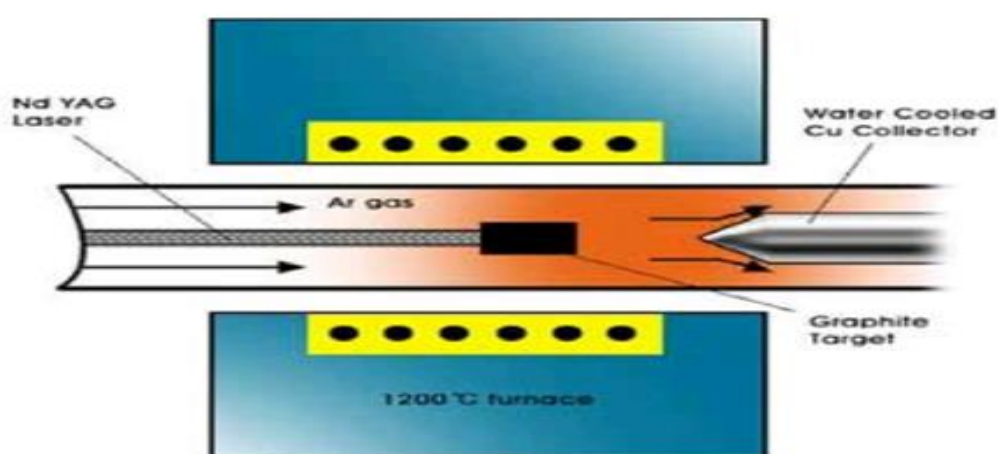

Figure 2.8.2.Schematic illustration of a laser ablation apparatus [2].

2.8.3 Chemical Vapor Deposition CVD Method

Chemical Vapor Deposition method is useful at lower temperature, and the CNTs obtained from both with arc discharge and laser ablation methods are tangled ; thus purification is not evident for these methods. The general nanotube growth mechanism in a chemical vapor deposition process through the dissociation of hydrocarbon molecules over the transition metal nanoparticles, dissolution and saturation of carbon atoms in these nanoparticles. This technique was utilized to grow multi-wall carbon nanotubes till 1993 *(Yacaman, et al. 1993i).*

11

Some different CVD techniques have been developed for carbon nanotube growth such as plasma enhanced CVD, thermal CVD, alcahol catalytic CVD, laser assisted CVD and aerogel supported CVD. Carbon nanotube growth includes two main steps; the first one is the catalyst preparation and the other one is the nanotube growth on this catalyst. In order to synthesis nanocatalyst particles, a thin film layer can be used by annealing or a catalyst can be synthesized by some chemical methods. At the first step, prepared catalyst sample is placed in a quartz tube which is in a furnace and the temperature is set to a desired point. During the increase of the temperature to the set point, an inert gas flow takes place through the tube to prevent the oxidation of samples. When the furnace reaches to the desired temperature a preannealing can be done with H_2 to reduce catalyst nano particles from oxide form to metal form. The other step is sending hydrocarbon gas to the system as a carbon precursor. Generally used hydrocarbon gases are CH_4, C_2H_4, C_2H_2, C_6H_6 for carbon nanotube growth [2]. During growth process, hydrocarbon gas decomposes and carbon deposits onto the catalyst. Carbon has a low solubility in these metals at high temperature and therefore the carbon precipitates to form cabon nanotubes. The key parameters in nanotube growth by CVD are the catalyst system, temperature, composition and the flow rate of the carrier and hydrocarbon gases[1,2,3]. In CVD method Fe, Co, Ni transition metals or their alloys are used as catalyst to synthesize carbon nanotubes. As support, inorganic porous materials such as silica (SiO_2), alumina (Al_2O_3), zeolites and magnesium oxide (MgO) are generally used *(Liu, et al. 2004)..*
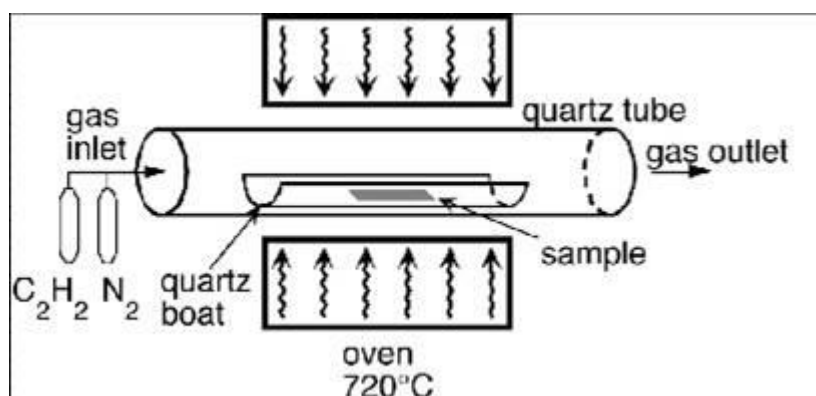

Figure 2.8.3 The schematic illustration of CVD system *[14]*

2.9 Purification

carbon nanotubes can be purified by separating nanotubes from non-nanotube impurities included in the raw products, or from nanotubes with undesired numbers of walls. The impurities are amorphous carbon, catalysts, catalyst supports[4,5,6,7], carbon nanoparticles, and unwanted nanotubes such as a small amount of MWNTs in a raw SWNT sample, or SWNTs in DWNT samples There are two purification techniques : dry methods and wet methods[2]

2.9.1 Dry Methods

The dry methods of purification selectively remove, through gas-phase oxidation, amorphous-carbon species due to their higher reactivity compared to that of carbon nanotubes. The easiest method is air oxidation at certain temperature, originally developed for the purification of MWNTs produced by either CVD or arc-discharge methods [1,3].

For SWNTs, due to their higher reactivity than MWNTs, the reaction conditions need to be adjusted from simple air oxidation to improve the selectivity of oxidation and to improve the purification yield. For example, Zimmerman et al. [7] reported a gas-phase purification method incorporating Cl2, H2O, and HCl gaseous mixtures for SWNTs grown from pulsed-laser vaporization. SWNTs grown from the arc discharge method can be purified by oxidizing in air at 350 ◦C or 470 ◦C, [7].For example, HiPCO nanotubes can be purified using wet air (or wet Ar‑O2) oxidation, at 180‑300 ◦C [4]. A scalable method to effectively purify HiPCO nanotubes was also developed by Smalley᾽s group at Rice University by adding a step to convert metal oxide in raw samples after mild oxidation to $C_2H_2F_4$ or SF6 to form a metal fluoride that can be easily removed by HCl treatment[8].

2.9.2Wet Methods

 In the wet methods purification is done by using solution to treat nanotubes, and can be used alone or together with dry methods. Nitric acid (HNO_3) is the most commonly used wet method for purification, as it is straightforward, inexpensive, and effective in removing metal catalysts and amorphous carbon from large quantities of raw material. For example, as-prepared SWNTs grown by laser-ablation techniques are known to have long bundles of SWNTs with few defects. They can be purified using nitric acid treatment [1]. In a typical run [1], raw SWNTs are refluxed in 2.6M HNO_3 for 45 h. After repeated filtration steps and maybe also centrifugation steps, highly purified nanotubes can be obtained. This method is also widely adapted for the purification of nanotubes prepared by other methods with a small variation in acid concentrations. Wet purification methods can

also be combined with dry oxidation methods. For example, Dillon et al. [2] have reported a nondestructive, scalable, three-step purification process that yields materials with 98% purity. Their method contains a dilute nitric acid (3M HNO_3) reflux for 16 h, functionalized, and redistributes the nonnanotube fractions, so as to form a uniform and reactive coating on the SWNTs. Additionally, other methods, including different chromatography methods Haddon ' s group at UC Riverside discovered that ultracentrifugation at different speeds can be a very effective method for the purification of SWNTs made by the arc method [1]. The method is capable of large scaleup at low cost .

2.10   Carbon nanotubes Application

Carbon nanotubes have attracted the fancy of many scientists worldwide. The small dimensions, strength and the remarkable physical properties of these structures make them a very unique material with a whole range of promising applications[21]. In this review we describe some of the important materials science applications of carbon nanotubes. Nanotubes can be used in the electronic and electrochemical applications, nanotubes as mechanical reinforcements in high performance composites, nanotube-based field emitters, and their use as nanoprobes in metrology and biological and chemical investigations, and as templates for the creation of other nanostructures. Also; carbon nanotubes are being

considered for energy production and storage. Graphite, carbonaceous materials and carbon fiber electrodes have been used for decades in fuel cells, battery and several other electrochemical applications
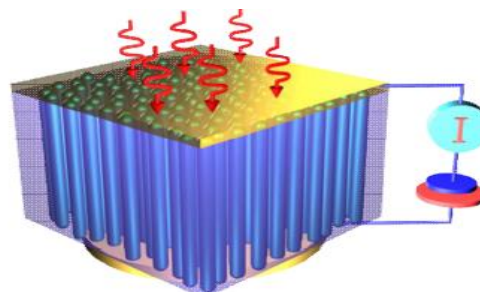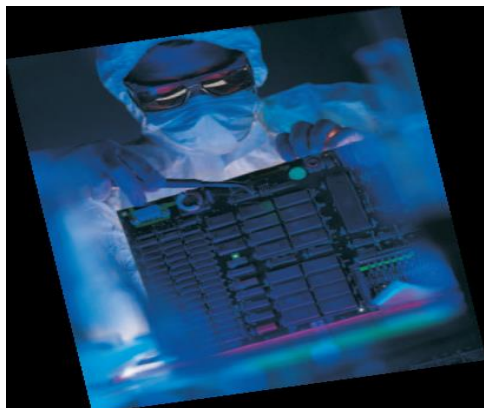

Fig.1 Schematic drawing of the photoconductivity measurement in Ge nanowire array inside AAO.

Figure 2.10 Carbon nanotubes application in Electronic & Semiconductor Device material

Challenges and potential for Carbon Nanotube Applications have come a long way since their discovery in 1991. The structures that were first reported in 1991 were MWNTs with a range of diameters and lengths. These were essentially the distant relatives of the highly defective carbon nanofibers grown via catalytic chemical vapor deposition. The real molecular nanotubes arrived when they were found accidentally while a catalyst (Fe, Co) material was inserted in the anode during electric-arc discharge synthesis. For the first time, there was hope that molecular fibers based purely on carbon could be synthesized and the excitement was tremendous, since many physical properties of such a fiber had already been predicted by theory. It was really the theoretical work proposed on SWNTs and the availability of nanoscale technology (in characterization and measurements) that made the field takes off in 1991. As a novel material, fullerenes failed to make much of an impact in applications. It seems, from the progress made in recent research, that the story of nanotubes is going to be very different. There are already real products based on nanotubes on the market, for example, the nanotube attached AFM tips used in metrology. The United States, Europe and Japan have all invested heavily in developing nanotube applications. Nanotube-based electronics tops this list and it is comforting that the concepts of devices (such as room-temperature field-effect transistors based on individual nanotubes) have already been successfully demonstrated. As in the case of most products, especially in high technology areas, such as nano-electronics, the time lag between concept demonstration and real products could be several years to decades and one will have to

15

wait and see how long it is going to take nanotube electronics to pervade high technology. Other more obvious and direct applications are some of the bulk uses, such as nanotube-based polymer composites and electrochemical devices. These, although very viable applications, face challenges, as detailed in this review. What is also interesting is that new and novel applications are emerging, as for example, nanotubes affecting the transport of carriers and hence luminescence in polymer-based organic light-emitting diodes, and nanotubes used as actuators in artificial muscles. It can very well be said that some of these newly found uses will have a positive impact on the early stages of nanotube product development.

As a conclusion; this review has described several possible applications of carbon nanotubes, with emphasis on materials science-based applications. Hints are made to the electronic applications of nanotubes which are discussed elsewhere. The overwhelming message we would like to convey through this chapter is that the unique structure, topology and dimensions of carbon nanotubes have created a superb all-carbon material, which can be considered as the most perfect material that has ever been fabricated. The remarkable physical properties of nanotubes create a host of application possibilities, some derived as an extension of traditional carbon example fiber applications, but many are new possibilities, based on the novel electronic and mechanical behavior of nanotubes. It needs to be said that the excitement in this field arises due to the versatility of this material and the possibility to predict properties based on its well-defined perfect crystal lattice. Nanotubes truly bridge the gap between the molecular realm and the macro-world, and are destined to be a star in future technology.

2.11Optical and Electrical Properties of Matter

The optical properties include absorption, transmission and reflection. The electrical properties include energy gap ,and electric permittivity which is related to the refractive index.

2.11.1 Absorption

The intensity of the net absorbed radiation is dependent on the character of the medium as well as the path length within. The intensity of transmitted or non-absorbed radiation continuously decreases with distance x that the light traverses:

$$I_T = I_o e^{-\beta x}$$ …………………………………………………..…….. (2.11.1)

Where is the intensity of the non-reflected incident radiation and ß the absorption Coefficient (in mm^{-1}), is characteristic of the particular material; furthermore, varies with wavelength of the incident radiation. The distance parameter x is measured from the incident surface into the material. Materials that have large values are considered highly absorptive.

2.11.2Transmission

The phenomena of absorption, reflection, and transmission may be applied to the passage of light through a transparent solid. For an incident beam of intensity I0 that impinges on the front surface of a specimen of thickness l and absorption coefficient, the transmitted intensity at the back face IT is

$$I_T = I_o (1 - R)^2 e^{-\beta l}$$ …………………………………………….. (2.11.2)

Where R is the reflectance; for this expression, it is assumed that the same medium exists outside both front and back faces. Thus, the fraction of incident light that is transmitted through a transparent material depends on the losses that are incurred by absorption and reflection. Again, the sum of the reflectivity R, absorptivity A, and transmissivity T, is unity according to Equation (2.11.1). Also, each of the variables R, A, and T depends on light wavelength. This is demonstrated the transmission.

2.11.3 Reflection

When light radiation passes from one medium into another having a different index of refraction, some of the light is scattered at the interface between the two media even if both are transparent. The reflectivity R represents the fraction of the incident light that is reflected at the interface, or

$$R = \frac{I_R}{I_o} \qquad \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \text{(2.11.3.1)}$$

Where I_0 and I_R are the intensities of the incident and reflected beams, respectively. If the light is normal (or perpendicular) to the interface, then

$$R = \left(\frac{n_2 - n_1}{n_2 + n_1}\right)^2 \qquad \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \text{(2.11.3.2)}$$

Where n1 and n2 are the indices of refraction of the two media. If the incident light is not normal to the interface, R will depend on the angle of incidence. When light is transmitted from a vacuum or air into a solid s, then

$$R = \left(\frac{n_s - 1}{n_s + 1}\right)^2 \qquad \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \qquad \text{(2.11.3.3)}$$

because the index of refraction of air is very nearly unity. Thus, the higher the index of refraction of the solid, the greater the reflectivity[20].

2.11.4 Absorption coefficients

Much of the information about the properties of materials is obtained when they interact with electromagnetic radiation. When a beam of light (photons) is incident on a material, the intensity is expressed by the Lambert-Beer-Bouguer law:

$$I = I_o \exp(-\alpha d) \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \text{(2-11.4.1)}$$

If this condition for absorption is met, it appears that the optical intensity of the light wave, (I), is exponentially reduced while travelling through the film. If the power that is coupled into the film is denoted by I0, gives the transmitted intensity that leaves the film of thickness d.

(α) Is called "absorption coefficient". From (1) it follows that

$$\alpha = -\frac{1}{d} \, Lin\left(\frac{I}{I_o}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2\text{-}11.4.2)$$

It is clear that α must be a strong function of the energy hν of the photons. For hν < Eg (direct), no electron hole pairs can be created, the material is transparent and α is small. For hν ≥ Eg (direct), absorption should be strong. All mechanisms other than the fundamental absorption may add complications (e.g. "sub band gap absorption" through excitons), but usually are not very pronounced.

Optical transmission measurements were carried out to determine the film thickness, the wavelength dependence of the refractive index and optical absorption coefficient. The optical constants were determined from the optical transmission measurements using the method described by Swanepoel [16].

The transparent substrate has a thickness several orders of magnitude larger than (d) and has index of refraction (n) and absorption coefficient (α = 0). The index of refraction for air is taken to be n0 =1. In the transparent region (α =0) the transmission is determined by n and s through multiple reflections. In the region of weak absorption α is small and the transmission begins to decrease. In the medium absorption region α is large and the transmission decreases mainly due to the effect of α. In the region of strong absorption the transmission decreases drastically due almost exclusively to the influence of α. If the thickness d is uniform, interference effects give rise to the spectrum.

The electric conductivity σ is given in terms of current density (J) and electric intensity (E) by

$$J = \sigma \, E = (\sigma_1 + i \, \sigma_2)E) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.11.4.3)$$

The electric permittivity ε) is also given in terms of flux density D as

$$D = \varepsilon E = \varepsilon_0 E + P = \varepsilon_0 (1 + X) \, E = \varepsilon_0(1 + X_1 + iX_2)E = (\varepsilon_1 + \varepsilon_2)E \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.11.4.5)$$

Thus the absorption coefficient is given by using

$$J = \frac{\partial P}{\partial t} = (X_1 + iX_2)(-i\omega E) = = (\sigma_1 + i \, \sigma_2)E \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2.11.4.6)$$

$$\sigma_1 = \omega X_2 \qquad\qquad \sigma_2 = - \omega X_1$$

$$\alpha = \frac{\sigma 1}{c \, n1}$$ .... (2.11.5.6)

where n_1 is refractive index .

2.11.6 Determination of Band Gaps

The fundamental absorption is related to band-to-band or to exaction transition, which are subjected to certain selection rules [17]. The transitions are classified into several types, according to the band structure of a material. The relation between absorption coefficient and optic band gap for direct transition (k=0) is given by Tauc equation [18]:

$$\sqrt{\alpha h \nu} = B(h\nu - E_g^{opt})$$ .... (2.11.6.1)

And for indirect transition $(k \neq 0)$ the relation becomes

$$\alpha(h\omega) \propto \frac{(\hbar\omega - E_{gap})^2}{\hbar\omega}$$ .... (2.11.6.2)

From the αhv versus hv one obtains Eg and B parameters. B is also a useful diagnostic of the material since it is inversely proportional to the extent of the tail state (Δ E) at conduction and valance band edges.

2.11.7 Refractive index

Light that is transmitted into the interior of transparent materials experiences a decrease in velocity, and, as a result, is bent at the interface; this phenomenon is termed refraction. The index of refraction n of a material is defined as the ratio of the velocity in a vacuum c to the velocity in the medium or

$$n = \frac{c}{\upsilon}$$ .... (2.11.7.1)

The magnitude of n (or the degree of bending) will depend on the wavelength of the light. This effect is graphically demonstrated by the familiar dispersion or se parathion of a beam of white light into its component colors by a glass prism. Each color is deflected by a different amount as it passes into and out of the glass, which results in the separation of the colors. Not only does the index of refraction affect the optical path of light, but also, as explained shortly,

it influences the fraction of incident light that is reflected at the surface. Just as Equation (2.11.7.1)

defines the magnitude of c, an equivalent expression gives the velocity of light in a medium as

$$\nu = \frac{1}{\sqrt{\varepsilon\mu}} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (2.11.7.2)$$

Where ν and are, respectively, the permittivity and permeability of the particular substance. From Equation (2.11.7.1), we have

$$n = \frac{c}{\nu} = \frac{\sqrt{\varepsilon\mu}}{\sqrt{\varepsilon_o\mu_o}} = \sqrt{\varepsilon_r\,\mu_r} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (2.11.7.3)$$

Where and are the dielectric constant and the relative magnetic permeability, respectively. Because most substances are only slightly magnetic, and

$$n \cong \sqrt{\varepsilon_r} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (211.7.4)$$

Thus, for transparent materials, there is a relation between the index of refraction and the dielectric constant [19].

2.12 Previous Studies

In the work done by E.R. Edwards [3] and others X-ray photoelectron spectroscopy was used to analyze multi-walled carbon nanotube(MWCNT) surfaces .Before X-ray examination non-oxidative and oxidative purification treatments for the sample was made in liquid-phase. The MWCNT were produced by pyrolysis of camphor and ferrocene, that provides a high yield but with highiron contamination (~15% wt). The elimination and/or oxidation of iron nanoparticles were monitored by Fe2p and O1s core level. Oxygen-based functional groups attachment was also examined by C1sfitting. The effectiveness of each treatment in iron removal was evaluated by thermogravimetric analysis (TGA) and atomic absorption spectroscopy). The integrity of the MWCNT structure was verified by Raman spectroscopy and transmission electron microscopy. A purity degree higher than 98%was achieved only with non-oxidative treatments using sonification process. Treatments with non-oxidative concentrated acids are more efficient to iron removal from MWCNT inner. The combinationof non-oxidative acid with ultrasound facilitates the ion permeation through graphitic wall and iron corrosion is supposed to occur inside tubes. Thus iron is released without destroying the MWCNT surface in ionic form. MWCNT produced from camphor and ferrocene mixtures with ~15% of iron in their composition were successful purified by conventional liquid phase techniques at a purity degree upper to98%. XPS analysis showed attachment of carboxylic groups on MWCNT surface and iron oxidation after treatments with H_2SO_4:HNO_3. In this case the iron particle was accessed by the liquid by means of graphitic wall corrosion. Concentrated HNO_3 also promoted partial oxidation of iron without damaging significantly tube walls. Maybe this treatment has attacked only some amorphouscarbon or more disordered graphitic sites, and the metallic iron was not accessed totally. However, treatments with non-oxidative concentrated acids are more efficient to iron removal from MWCNT inner. The combination of non-oxidative acid with ultrasound facilitates the ion permeation through graphitic wall and iron corrosion is supposed to occur inside tubes. Thus iron is released without destroying then MWCNT surface in ionic form.

In a paper published by Muhammad Ali Turgunov [4] in collaboration with others.A mixture of sulfuric acid and nitric acid WERE used for surface modification of multiwall carbon nanotubes (MWCNTs) was performed by. Pristine MWCNTs, vacuum heating dry MWCNTs, and vacuum freezing dry MWCNTs were prepared. The results showed that, acid

treatments give more carboxyl groups on the surface of the MWCNTs. In addition, vacuum freezing dry treatment provides less damaged MWCNTs than vacuum heating dry treatment.

Three types of the MWCNTs were examined. Vacuum freezing dry treatment was led to less damage and more interaction with the MWCNTs. The existence of carboxyl groups was verified from Fourier transform infrared spectroscopy.. The presence of defects but no disruption of graphitic structures was observed on the surface after acid treatment. Scanning electron microscopy showed that acid treated MWCNTs had less agglomeration than pristine MWCNTs. Acid treatment would be effective candidate for surface modification of the MWCNTs.

In the work done by M. Stancu [5] and other authers different techniques was used for the purification of multiwall carbon nanotubes (MWCNT) obtained by the AC arc discharge method. The multiwall carbon nanotubes was purified toeliminate the metal catalyst and amorphous carbon. The metal catalyst was removed by treatment with different acids. Subsequently, we have applied two different methods for removing also the amorphous carbon. The first approach for the purifying of the MWCNT was the weak oxidation performed by refluxing the MWCNTs in strong acid for 6 hand the second method was the oxidation with air for 10 minutes. The samples were analyzed using FE-SEM (Field).The results obtained shows that purification procedure is dependent on the method of synthesis of carbon nanotubes. In this paper we report asimple procedure to purify multiwall carbon nanotubesobtained by the AC arc discharge method. Metal catalyst and also amorphous carbon were oxidized by refluxing in acids including hydrochloric acid and nitric acid.Oxidation in air at 550oC removes disordered carbon, but does not eliminate the D-band. The purification procedure consisted in refluxing in different acids followed by airoxidation to obtain highly pure MWCNT samples.for better manipulation of the material and use in the fabricationof novel composites. After each treatment, the functionalizationyield, namely the density of carboxyl and hydroxyl functional groups on the graphitic network, was quantified by means of XPS and titration measurements. Oxidation with nitric acid under extreme conditions (reflux) increases the defect population/formation on the CNTs due to length shortening, as verified by XPS and Raman spectroscopy. Application of a piranha solution showed much lower oxygen content compared to nitric acid oxidation and the absence of additional defects on the graphitic surface. Use of non-acidic treatments such as the mixture

of NH_4OH and H_2O_2, facilitates the complete removal of disordered carbon from the MWCNT specimens as confirmed by thermo gravimetric analysis.

Microwave was used by Fu-Hsiang Ko [8] and others for purification of MWNTs. The microwave-assisted heating in 5mL of nitric acid eliminates impurities, such as amorphous carbon, carbon nanoparticles, and metals, from (MWNTs). Heating the closed reaction vessel under microwave irradiation at 160_C for 30min is a very effective means of purifying the MWNTs. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images confirm that these reaction conditions are beneficial for removing the impurities and ensuring that the MWNTs remain intact. In contrast, a purification temperature of 180_C provides too strongly oxidizing conditions that destroy the MWNTs. The ratio of the G and D bands in the Raman spectra also confirms that a temperature of160_C is optimal. The defect peak that we observed in the differential thermogravimetry (DTG) analysis of the raw material was not present after microwave purification. The presence of metal impurities in the MWNTs can be reduced significantly when using this method.

X-ray photoelectron spectroscopy (XPS) and energy dispersive spectroscopy (EDX) were used to characterize MWCNTs by many authors'. Six commonly used wet chemical oxidants (HNO_3, $KMnO_4$, H_2SO_4/HNO_3, $(NH_4)_2S_2O_8$, H_2O_2,and O_3) were evaluated in terms of their effects on the surface chemistry and structure of MWCNTs using a combination of analytical techniques. oxidation, while chemical derivatization techniques used in conjunction with XPS allowed the concentration of carboxyl, carbonyl, and hydroxyl groups at the surface to be quantified for each MWCNT sample. Our results indicate that the distribution of oxygen-containing functional groups was insensitive to the reaction conditions (e.g., w/w% of oxidant), but was sensitive to the identity of the oxidant. MWCNTs treated with $(NH_4)_2S_2O_8$, H_2O_2, and O_3 yielded higher concentrations of carbonyl and hydroxyl functional groups, while more aggressive oxidants (e.g., HNO_3, $KMnO_4$) formed higher fractional concentrations of carboxyl groups. IR spectroscopy was unable to identify oxygen-containing functional groups present on MWCNTs, while Raman spectra highlighted the frequently ambiguous nature of this technique for measuring CNT structural integrity. TEM was able to provide detailed structural information on oxidized MWCNT, including the extent of sidewall damage for different oxidative treatments.

Covalent surface functionalization of multi-walled carbon nanotubes (MWCNT)s with different naturalamino acids was successfully carried out under microwave irradiation. The process is fast, one-pot, simple and resulted in a high degree of functionalization as well as dispensability in organic solvents. Surface func-tionality groups and morphology of MWCNTs were analyzed by Fourier transform infrared spectroscopy, diffuse reflectance ultraviolet–visible spectroscopy, thermo gravimetric analysis, X-ray diffraction, field emission scanning electron microscopy, and transmission electron microscopy. The results consistently confirmed the formation of amino acid functionalities on MWCNTs which is available for further chemistry, while the structure of MWCNT has remained relatively intact. These results illustrate a direct pathway to functionalize MWCNTs for building nanostructures. The amino acid-functionalized MWCNT scould be easily dispersed in common organic solvents.

Conclusions In a simple, low cost, efficient, and environmental-friendly method involving the use of microwave technology, MWCNTs were functionalized by several natural amino acids. The occurrence of amino acid functionalization of the nanotubes has been confirmed by the use of several methods usually used in materials science. The attached amino acid groups are expected to improve the interaction between the modified MWCNTs and polymer molecule chains, and the terminal hydrophilic carboxyl groups can be avail-able for further chemistry and covalent binding with variety of monomer and polymer matrices in the processing and fabriccomposites and fibers, ceramics for tissue engineering, and implants in orthopaedics and dentistry. Modification with amino acids resulted in significant debundling of the MWCNTs, which allows stable dispersion in common polar organic solvents. The amino acid-functionalized MWCNTs, prepared in this work by an easy and inexpensive one-step method, can be valuable pre-cursors for peptide synthesis and targeted drug delivery, design and fabrication of nanocomposites and fibbers, and other biomed-ical and engineering applications. As one of the most important biocompatible and biodegradable materials, amino acid incorpo-rating with CNT will grant improvement of compatibility and may promise multipurpose in biomedical systems and bio nanomateri-als. The amino acid-functionalized MWCNTs, prepared in this workby a simple and inexpensive one-step procedure, can be valuable precursors for targeted drug delivery, design and production of nanocomposites and fibres, and other biomedical and engineer-ing applications. Further reaction of the MWCNTs

with the amine groups is being currently investigated. Addition of various carbon materials Into lead-acid battery electrodes was studied and examined by Rotem Marom and others , in order to enhance the power , improve cycle life and stability of electrodes in lead acid batteries. High electrical-conductivity, high-aspect ratio, good mechanical properties and chemical stability of((MWCNT), unmodified and modified with carboxylic groups) position them as viable additives to enhance the electrodes' conductivity, to mitigate the well-known sulfation failure mechanism and improve the physical integration of the electrodes.

In this study, the -effect of incorporation of carbon nanotubes (CNT) to the positive and the negative active materials in lead-acid battery was studied .The prototypes is in a configuration of flooded cells, as well as gelled cells. The cells were tested at 25% and 30% depth-of-discharge (DOD). The positive effect of the carbon nanotubes (CNT) utilization as additives to both positive and negative electrodes of lead-acid batteries was clearly demonstrated and is explained herein based on microscopic studies. We have demonstrated that addition of CNT produced by commercial companies to both lead negative electrodes and lead dioxide positive electrodes in lead acid batteries pronouncedly improve the cells performance and doubling the cycle life of practical batteries.

The introduction of the CNT is done in the early stage of electrodes preparation, mixed with the lead precursors in laboratory cells. Hence, formation leads to a uniform integration of the CNT in both the lead and the lead dioxide particulate matrices of the electrodes, at their final pristine form (before cycling) and during the periodic charge discharge cycling.

We also demonstrate in small scale experiments that using modified CNT with carboxylic groups can lead to further improvement in performance. Cells comprising electrodes containing MWCNT functionalized with carboxylic groups exhibited longer cycle life than cells which electrodes contained usual CNT from commercial sources.

Addition of MWCNT into the active mass of industrial manufactured electrodes (both negative and positive electrode) clearly extended the cycle life of SLI type flooded batterie.

The improvement observed is well correlated with teardrop analysis of cycled cells that showed cycled electrodes containing CNT develop much smaller crystals of lead sulfate compared to cycled (CNT free) reference electrodes. Hence, it is clear that the presence of CNT enable much better accessibility of the active mass to the electron transport processes during cycling, due to their physical properties (high aspect-ratio, thin, flexible, robust and

stable electronically conducting agents). Initial studies demonstrated that CNT derivative with hydrophilic functional groups such as carboxylic groups can serve as better additives to lead-acid batteries electrodes than regular CNT, probably due to a better adhesion to their active mass.

Agathe Figarol and group stayed [15] carbon nanotubes (CNT) and nano-graphite (NG) are graphene-based nanomaterials which share exceptional physicochemical properties, but whose health impacts are unfortunately still not well understood. On the other hand, carbon black (CB) is a conventional and widely studied material. The comparison of these three carbon-based nanomaterials is thus of great interest to improve our understanding of their toxicity. An acid functionalization was carried out on CNT, NG and CB so that, after a thorough characterization, their impact son RAW 264.7 macrophages could be compared for a similar surface chemistry (15 to 120 µg·mL−1nanomaterials, 90-min to 24-h contact). Functionalized nonmaterial's triggered weak cytotoxicity similar to the pristine nanomaterials. Acid functionalization increased the pro-inflammatory response except for CBwhich did not trigger any TNF-α production before or after functionalization, and seemed to strongly decrease the oxidative stress. The toxicological impact of acid functionalization appeared thus to follow a similar trend whatever the carbon-based nanomaterial. At equivalent dose expressed in surface and equivalent surface chemistry, the toxicological responses from murine macrophages to NG were higher than for CNT and CB. It seemed to correspond to the hypothesis of a platelet and fiber paradigm.

This physicochemical and toxicological study was designed with two main objectives: the determination of the cellular impact of the acid functionalization of three different carbon-based nanomaterials, and the cellular impact of these nanomaterial morphology at equivalent surface chemistry. It was demonstrated that acid functionalization hasthe same impact whatever the carbon-based nanomaterials: no significant impact on cytotoxicity, enhancement of the pro-inflammatory response, and a decrease in oxidative stress. Carbon black however made an exception, as no pro-inflammatory response was seen before or after functionalization. At a similar dose in the surface and a similar surface chemistry, nano

graphite showed higher cellular response than carbon nanotubes and even higher than carbon black. Further investigation shaves to be carried out to determine if there is a link with the internalization mechanisms and possible frustrated phagocytosis. Carbon-based nanomaterials do not have the same toxicity potential according to their morphology and crystallinity, and it has to be pointed out that the safest one here is considered as a possible carcinogenic to humans. This emphasized the need for further studies on the toxicity of carbon nanotubes and graphene, especially their impacts for a long term exposure.

C. Denktas stayed with team work [17]   Dielectric properties, conductivity mechanisms and current voltage characteristics of Multi Wall Carbon Nanotube (MWCNT) doped and pure Liquid Crystal (LC) material was investigated using impedance spectroscopy method in the frequency range of 100 Hz to 15 MHz. Liquid crystalline material, 4-[4-((S)-Citronellyloxy) benzoyloxy] benzoic acid (CBBA) as a host material and MWCNT was used as doping material in this study. In order to observe the effects of doping MWCNT into LC on dielectric properties, an MWCNT material was doped into CBBA structure with 1 wt%. Real part of dielectric constants (30), imaginary part of dielectric constant (30 0), i.e. dielectric loss, dissipation factor/dielectric loss tangent(tan$d$) were obtained for the pure and doped LC samples. In addition, dielectric strength (D 3ds), negative dielectric anisotropy (D 3da), absorption coefficients (a) and relaxation times (t) were calculated from the empirical data. IeV characteristics of pure LC and doped LC structures were carried out at micro-current levels by current$e$voltage measurements.

In this study, dielectric and electrical properties of CBBA liquid crystal material doped with MWCNT were investigated. In investigated samples, doping concentration of MWCNT in pure liquid crystal CBBAwas chosen to be 1 wt%. Firstly dielectric constant (ε_0), imaginary part of the complex dielectric constant (ε00) and the energy loss tangent, were studied by using DST. Dielectric anisotropy is calculated to be negative for pure and MWCNT doped materials. Doping MWCNT in CBBA decreased the dielectric anisotropy whereas it increased threshold voltage. Loss tangent decreases with increasing frequency for MWCNT doped CBBA and pure LC materials, both. The absorption coefficients a and relaxation times

28

twere calculated for investigated samples. It was found that doping MWCNT into CBBA liquid crystal decreased relaxation time whereas it increased absorption coefficient.AC conduction mechanisms determined from angular frequency dependent conductivity plot. Both samples have two conduction mechanisms such that CBH is active at low frequency regime and SLPL is active at high frequency regime. It is shown that the effect of doping material MWCNT seems to be more dominant in low frequency regime. It is also noteworthy to observe that a small amount of MWCNT doping causes an increase in conductivity values by the order of almost hundred times.

Capacitive deionization (CDI) has attracted significant attention for the next generation water treatment due to its low energy consumption and environment friendly properties incomparison to widely established methods [20]. For CDI technology to move forward, however, the development of carbon electrodes having superb electro sorption behavior is essential. In this study, we demonstrate the functionalization of carbon nanotubes (CNTs) via acid treatment shows enhanced electrochemical characteristics and effectively improves the wettability of the acid-treated CNTs (a-CNTs) via the addition of oxygen functional groups, leading to a higher electric double layer capacitance. Furthermore, defect formation in a-CNTs increases the conductivity and decreases the mass transfer resistance during CDI operation. CDI measurements confirmed a 270% increase in performance of a-CNTs in contrast to pristine CNTs (p-CNTs), attributable to the improved characteristics outlined above.

The present work demonstrates the electrosorption preference e of actions to functionalized CNTs. The acid treatment effectively enhanced the electrochemical capacitance of CNTs, following the addition of oxygen functional groups on a-CNTs' surface. It was shown in XRD results that a-CNTs have more crystalline structure, even after defect formation during chemical functionalization. The physical changes associated with the acid treatment (e.g. shortening of CNTs, defect formation, and opening of capped ends) improved access of the ions to the CNT surface, increasing available sites for adsorption. This led to improved CDI performance of a- CNTs in terms of ion removal efficiency and capacity when compared with p-CNTs. The findings of this work can provide evidence on the potential of functionalized CNTs in the water desalination and softening applications. Functionalized CNTs can be

Combined with other carbon materials, or with metal and metal oxides with high specific capacitance and stability in aqueous solutions, to further improve its performance in CDI.