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PREPARATION AND CHARACTERIZATION OF HIGH QUALITYSINGLE-WALLED CARBON NANOTUBES USING ARC DISCHARGE TECHNIQUE

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Single-walled carbon nanotubes (SWNTs) were obtained by the arc discharge technique in an atmosphere of Ar and H_2 mixture. The catalyst was prepared from a mixture of Nickel and Yttrium, which allow the realization of a quasi-one-dimensional environment for the materials diffused inside. The SWNTs have been purified by oxidation and centrifugation techniques the SEM provide a fast and reliable feedback in the development of purification techniques. The SWNTs have been characterized using AFM/STM techniques. The diameter of SWNTs is about 1.4nm and several hundreds of nm long. Moreover, the different electronic properties of nanotubes gaps have been observed. The SWNTs have shown a semiconducting behavior. The spatially resolved CITS of a SWNTs strand on a SiO_2 surface show a variation of tunneling probability along the long axis of the carbon nanotube.

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1. Introduction

Carbon Nanotubes were discovered by Iijima in 1990. Soon after the discovery of carbon nanotubes, Ebbesen and Ajayan [1] successfully applied a large-scale synthesis which made extensive investigations on this promising material possible.

For the time being, carbon nanotubes have been recognized as exciting and fascinating novel material which has specific physical and chemical characteristics. Therefore, Carbon nanotubes play a vital role in developing tremendous technological applicationssuch as photovoltaic, sensors, filters for cleaning contaminated drinking water, and other applications. Further optimization of the carbon nanotube growth technique raised the nanotube yields to above 65 %. Nevertheless, nanotube samples of higher purity are strongly needed for many research and application purposes. Different techniques have been used to generate carbon nanotubes, most of them are based on the sublimation of carbon under inert gas, such as, chemical vapor deposition (CVD) [1, 2], the catalytic decomposition of carbon monoxide in a high pressure process (HiPCO) [3, 4], ‘laser ablation (LA) method [5] or the solar technique [6-8], and arc-discharge (AD) [9]. The growth mechanism of nanotubes varies depending on which Method is used. The formation of SWNTs always needs the presence of rare metals, transition metal or the presence of their mixture. The catalytic mechanism involves the coordination of metal atoms to the dangling bonds of growing nanotubes, called the scooter mechanism [10]. The quality and the purpose of CNT application depends on their purity after production. Different types of method were used to purify the CNT. Among other purification techniques, Chemical oxidation treatments are conveniently used in large batch production, but usually this kind of treatment strongly destroy carbon

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nanotubes layers [11]. On other hand, Non-destructive methods, such as micro-filtration or size exclusion chromatography purification methods are not practical for a large quantity of SWNTs [12].

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 SWNT on a metal nanoparticle substrate. The carbon atoms nucleate on the metal catalyst and grow to several micrometers in length. 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 [13]. 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 [14].

In this work, the SWNTs have been produced by a low cost method, purified and characterized. The production was done using Arc Discharge Technique. Oxidation and Centrifugation methods were used to purify the CNTs. The carbon nanotubes were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). In particular, the structural electronic properties where investigated with AFM/STM and current image tunneling spectroscopy (CITS) techniques.

2. Material and methods

In the presented work, SWNTs have been prepared by arc-discharge [15-18]. The electric arc discharge process is one of the most common methods for nanotube and fullerene production. This method has been attracted by many researchers for production of carbon allotropes. As this method has high yields of quality and low defect carbon nanotubes in large batches it has been preferred over other methods. Using this method the SWNTs can be produces 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 disc cathode with 13 cm diameter, on which carbon rod is separated from the thinner disc anode by ~1 mm. This technique uses high temperatures (about 3850 K), which is needed to evaporate carbon into plasma. The combined plasma of Nickel and Yttrium are more stable than the individual plasma source of these metals [19. 20]. The arc discharge method produces fullerene, multi- and single walled carbon nanotubes. The chamber is sealed and filled with Nobile gas as nitrogen and argon. It should be flushed several times with nitrogen to expel all the air. Some batches have been pressurized at hundreds of mbar for the run to control the diameter of the produced tubes. A direct current source is connected to provide 90-120 amperes at a voltage of 45 volts. The arc is initiated by adjusting the distance as described before between the anode and the cathode maintaining the voltage constant (45 V). A bright discharge occurs and the anode is consumed. The electrode separation of about 1 mm must be adjusted 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.

The purification of the carbon nanotubes is essential because the metal clusters block the carbon nanotubes from both sides directly after the synthesis, which prevent its application purpose. In the current work, two purification techniques have been used to purify the carbon nanotubes from metal cluster inter or intra. Each purification process passed through several stages as described below.

In this process and to purify the carbon nanotubes, most of the amorphous carbon have been removed by the oxidation in oven’s air. The sample material were placed in the oven for three hours with temperature of 375°C and until 30% of the weight has been lost. Most of the amorphous carbon will be removed by converting carbon into carbon oxides. After treating the material in the oven, a sonication process has been applied to damage the metal cluster. The treated material is dispersed (1% weight) in a solution of sodium dodecyl sulfate (SDS) or NaDs lauryl sulfate as a surfactant. The surfactant molecules are surface-active agents that can prevent the aggregation of particles and can modify the particle-suspending medium-interface. The dispersion is prepared with an ultrasonic probe with 50 Watt at full cycle for one minute. According to the sonication process and to prevent the destruction of nanotubes, too long sonication time has been avoided and the ultrasonic treatment decomposes the metal nanoparticles.

Centrifugation is another efficient purification technique for carbon nanotubes. In this method, the sample of carbon nanotubes is placed in the container and rotated at high speed in a centrifuge. Since the particles in the sample have different masses and cohesive forces, then all the particles in the sample will be accelerated toward the bottom at different time. For instance, hard particles such as clusters (less cohesive forces) should move to the bottom faster than carbon nanotubes (larger cohesive forces). 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. To assure the quality and the purity of carbon nanotubes the procedure is repeated three times at different speed and running time (4000 rpm for 90 seconds, 5000 rpm for 90 seconds and 15000 rpm for 90 seconds).

3. Results and discussion

XRD Analysis

The material has been subjected to XRD measurements at different preparations stages. The XRD patterns were recorded in 2 theta geometry using STOE diffraction system equipped with a Cu target (wavelength 1.54 A°).The purpose of the XRD measurements is to see the signal of metal oxides during the cleaning process. Figure 1 show The XRD results of raw SWCNTs (green curve), the purified material (violet curve) that heated up to 375 C^{o}, and the material that subjected to centrifuge for purification (red curve). The diffraction peaks of which the lines are indicated (26^{o}, 36°, 43°, 52°, 62° and 76°), five of these intense peaks correspond of NiY carbide. Due to carbide inside the SWCNT, whose diameter is bigger for high NiY ratios, the carbide peaks are more intense for higher NiY ratios in the precursor powder. The peak at ~43° corresponds to the diffraction peak of graphite and is also present in nanotubes. Moreover, the behavior of the XRD spectra shows that NiY particles are not quickly released in the purification process of the first cycle, and the reason can be explained by NiY particles are enclosed in the hollow channel of the nanotubes or encapsulated in other carbon material.

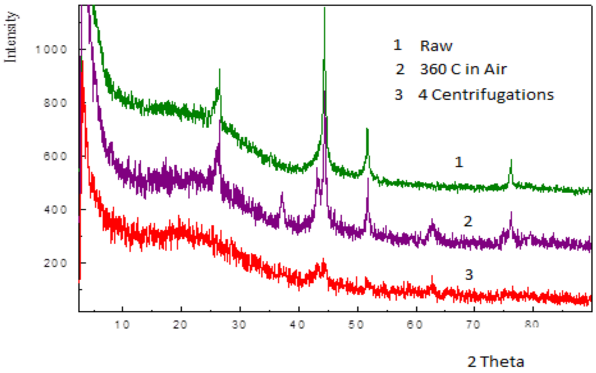


Fig. 1. Shows the XRD spectrum of SWNT for different stages of purification by powder X-ray diffraction. The first curve (green) belongs to raw SWCNTs, second (violet) to heat treated by 360°C and third (red) to centrifuge four times.

SEM Electron Microscopy

By means scanning electron microscope (SEM), it is possible to observe directly the formation of CNT and the efficiency of the preparation method. It is possible also to have an indication of the grade of purity attained. SEM analysis was conducted on a LEO VP field emission scanning electron microscope equipped with a Phoenix EDX system.

Figures 2 shows SWNT samples before and after the purification process with SEM. In the SEM images shown in Figure 2a, the bright areas are thought to be due to agglomerated metal particles. They appear to be gathered into clusters and associated with a carbon nanotube. They are clearly removed by the cleaning process as shown in Figure 2b. In the cleaned sample there are no traces of the metal particles.

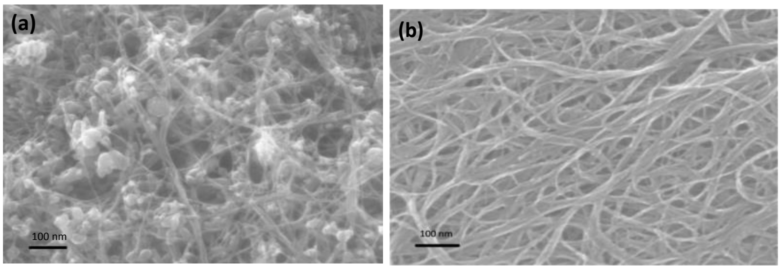


Fig. 2: a) SEM micrograph of the raw SWNT, b) SEM micrograph of SWNTs after the purification processes.

STM and AFM measurements

The sample has been prepared under ambient condition by evaporation of aqueous solutions (10-9 M/L) of the respective carbon nanotube on a clean highly oriented pyrolytic graphite (HOPG) substrate. To perform the STM measurements the tunneling current was between 5-100 pA, the bias voltage was in range of ± 50 mV to ± 100 mV, the frequency was between 2-5 Hz, the resolution was 256 × 256 points for topography and 128 × 128 in the current image tunneling spectroscopy (CITS) measurements, the scan range of voltages was from –1 to 1 V relative to the tip potential, and the tunneling resistances were sited to order of 2 GΩ. A tip of Pt-Ir (90/10) has been used of mechanical wire cut of diameter 0.25mm. All figures of STM, CITS, and AFM have been produced using the WSxM program [21]. 3-D map of current, voltage, and position has been produced by acquiring the IV-curve at every pixel of the image. Figure 3.a shows a STM topographic that indicates well dispersed bundles of SWNT and aligned closely in parallel. The heights of SWNTs are about 1.4nm and several hundreds of nm long. Moreover, the electronic nature of nanotubes has been described with the I-V curve, as shown in figure 3.b. Furthermore and to clarify the electronic nature of the nanotube, the electrical mapping of the junction region was obtained via current image tunneling spectroscopy (CITS) in which a full I-V spectra was acquired at each pixel in the imaging mesh, providing a dense array of both electronic and topographic information associated with the entire scanned area as shown in figure 3.a. These Spectra were considered to correspond to semiconducting SWNT [22].

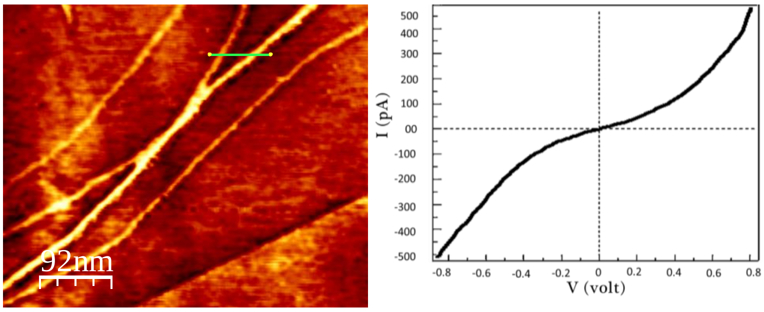


Fig. 3: (a) Topographic STM image of SWCNT sample on HOPG substrate at room temperature with tunneling current pA and the bias voltage mV. Scan area nm. (b) I–V curve recorded over carbon nanotubes sample in part a.

For the investigation of the prepared SWNTs in insulating substrates, the carbon nanotubes were deposited on the SiO_2 flat surface and characterized by combined STM/AFM devices. Two point measurements were used to characterize the electrical transport properties of carbon nanotubes on insulating surface. One point, which is electrode, is metallic tip connected to the tuning fork sensor and another electrode is gold that was evaporated using shadow mask technique [23]. To perform the AFM analysis, the prepared carbon nanotubes has been deposited as a drop on SiO_2 surface and left in the air until the solvent has been evaporated. The AFM/CITS has been used to study the distribution, concentration and the preparation quality of the carbon nanotubes on insulating substrates.

The images in Figure 4.a and 4.c show the topography of nanotubes that have been taken by FM-AFM mode at voltage bias 500 mV. The analysis shows a height of nanotubes about 8 nm and apparent width of 20 nm as shown in Figure 4.b. By considering the standard size of nanotubes about 1.5-2 nm and the current diameter measurements, this will indicate that, the measured structure is a bundle of nanotubes. Figure 4.c shows the current image of the carbon nanotube deposited on SiO2 surface. The dark background of the image refers to SiO_2 surface. The enhanced contrast of the nanotubes was related to the electrostatic forces present in the system.

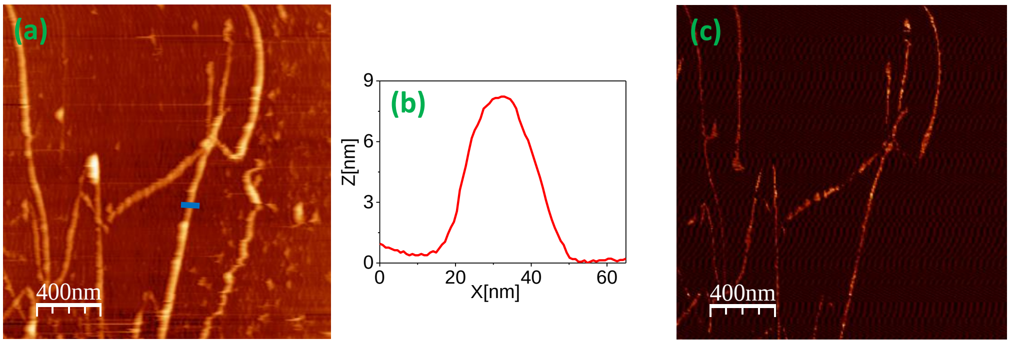
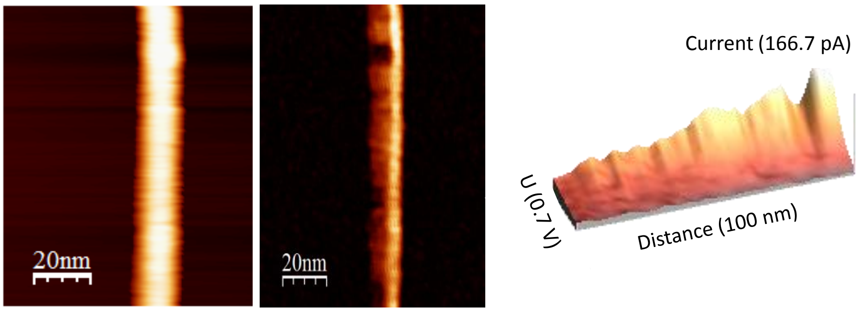


Fig. 4: a) AFM topography image. b) Profile Dimension of the blue line in Figure 3a. c) The image of the carbon nanotube deposited on SiO2 surface with voltage bias of 500 mV.

In order to determine the change in the conductivity, the scan size has been reduced to increase the resolution of AFM images. In Figure 5 the images have been taken with electrode above the top of the image. 2D and 3D current image can be clearly seen in Figure 5.b, where the upper side corresponds to the part of the nanotube closer to the gold electrode. Figure 5.c represents the current versus the length of carbon nanotube, that taken from Figure 5.b, at voltage bias of 700 mV. The investigation shows that the current is increasing with the length of carbon nanotube, and this is a good evidence for conductivity within the nanotubes. The same behavior has been observed in previous studies for carbon nanotubes prepared using different techniques [24-26].



a) b) c)

Fig. 5: a) AFM topography b) 2D and 3D current image of the nanotube with voltage bias of 500 mV, Δf = 9 Hz, and amplitude = 0.5 nm. c) current versus length at voltage bias of 700 mV.

4. Conclusion

We have demonstrated a method for synthesizing Single-walled carbon nanotubes (SWNTs) using the arc discharge technique in an atmosphere of Ar and H_2 mixture using catalyst prepared from a mixture of Nickel and Yttrium. The produced The SWNTs have been purified by oxidation and centrifugation techniques. The SEM technique provides a fast and reliable feedback in the development of purification techniques. The STM/AFM techniques have been successfully applied to study the structure and the electronic properties of carbon nanotubes on conducting and insulating surfaces. After establishing an electrical contact to the nanotubes, the structure and conductivity of the carbon nanotubes could be mapped simultaneously. A detailed analysis of the local conductivity along the carbon nanotubes reveals a linear increase in resistance with the distance from the gold contact. These results reveal that the fabricated single wall carbon nanotubes by arc discharge technique could eliminate several processing parameters currently used for SWNT fabrication. Most importantly, this process can produce well-dispersed, clean and straight SWNTs, rather than bundled and deformed SWNTs coated with metals and amorphous carbon nanoparticles. The high-quality low cost carbon nanotubes prepared in this work may find their application in many areas from various devices to electrical fillers for conducting composite materials.

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