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SYNTHESIS OF CARBON NANOTUBES, NANO FIBBERS AND NANO UNION BY ELECTRIC ARC DISCHARGE METHOD USING NACL ACCUSE AS SOLUTION AND FE AND NI PARTICLES AND CATALYSTS

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Abstract: Carbon nanotubes (CNTs), carbon nanofibers and carbon nano onions were synthesized by simple arc discharge between two graphite electrodes immersed in NaCl distilled water solution. Synthesis of CNTs was investigated in NaCl solution with different experimental parameters, such as voltage, current, catalyst concentration and NaCl solution molarities, using Fe and Ni catalysts. Then, Carbon nanofibers were synthesized by using a mixture of Fe and Ni (1.8:0.9 mols %) as a catalyst. The experiments were optimized with using 0.3 molar of NaCl solution and 3 mol% catalyst concentrations. Raw as-produced materials were partially purified by acid treatment and thermal oxidation methods. The carbon nanostructures were characterized by scanning and transmission electron microscope (SEM and TEM).
In this investigation the simple and inexpensive arc discharge in liquid environment method has been used for the production of carbon nanotubes. Other nanostructures as-products were also produced by this method.
Keywords: MWCNTs, Arc-discharge, NaCl Solution, SEM, TEM,

1. Introduction

Ijima observed the new form of molecules in the transmission electron microscope (TEM) images in 1991 [1]. Carbon nanotubes (CNTs) are novel materials. They can be imagined as graphite sheets, are rolled up into seamless cylinders, are arranged in concentric configurations, and consist of one (Single-walled CNTs) or more (Multi-walled CNTs) layers. Due to direction of rolling, CNTs are classified based on chirality's vector into 3 types of armchair, zigzag and chiral nanotubes.

The CNTs can be synthesized by several conventional methods such as: laser ablation [2], chemical vapour deposition (CCVD) [3] and electric arc discharge ([1], [4], and [5]). Fine single-walled CNTs are produced by laser ablation using a carbon source doped with catalysts, and the multi-walled CNTs are formed without catalysts. Electric arc discharge is widely employed in a reduced inert-gas atmosphere (such as argon and helium etc) to

synthesize CNTs and other carbon nanostructures. Large quantities of CNTs were first prepared by this method [6]. In this method, carbon source with Fe, Ni, Co catalysts located at discharge region is vaporized due to discharge heat. The vaporization carry out in a chamber with reduced pressure (~600 mbar), and vapours which include CNTs deposit both on the surface of cathode and on the wall of the chamber. The disadvantages of this method are high temperature of process, reduced pressure and using expensive noble gasses.

Electric arc discharge in liquid environment was first used by Hsin et al [7] in water in 1991 in order to synthesize CNTs. This simplified method does not require expensive noble gases, high temperature furnace and vacuum equipments [8]. Since then, benzene, toluene [9] and the liquid nitrogen ([10]-[12]) were also used as liquid environment. Sano et al produced a fine quantity of carbon nano onions and CNTs from arc discharge in deionised water ([10]-[14]). Arc discharge was not stable in deionised water due to its electrical insulating characteristic. Therefore, salt solution was used as the liquid environment in order to improve electrical conductivity of solution [15]. In the present study, carbon nanostructures were synthesized by using an electric arc discharge in sodium chloride distilled water solution.

2. Experimental

In this work, carbon nanostructures were successfully synthesized by using an electric arc discharge apparatus. The schematic of experimental set-up which was used in this study is shown in Fig. 1.

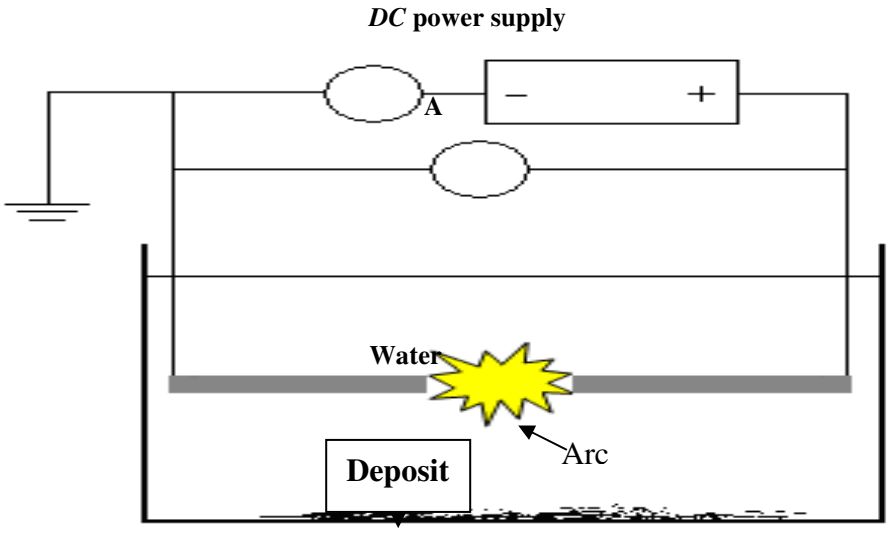


Fig 1 Schematic view of the arc-discharge apparatus

The apparatus consisted of two pure graphite electrodes submerged in 2 Lit of NaCl solutions in a glass container. The diameters of the anode and the cathode were 9 and 11 mm, respectively. Anode was drilled with 3 mm in diameter and 3 cm of the depth and the hole was filled with graphite powder mixed with Fe and/or Ni as catalyst. Electrodes were horizontally immersed into a 6 cm of the depth in an open glass vessel. The cooling ability of NaCl solution is better than deionised water and cheaper than liquid nitrogen. Therefore, it is an ideal liquid environment for synthesizing carbon nanostructures.

Two electrodes were manually touched and after initially arc discharge, separated to approximately 1 mm distance, immediately. Typical run time was 60 s. Most of the products dropped at the bottom of the vestal and few deposited on the cathodes cavity. A little soot was also found on the surface of the liquid. In this study, scanning electron microscope (SEM: Philips XL-30) and TEM were used to examine the morphology of the as-produced materials.

Various experimental parameters, such as voltage, current, catalyst concentration and NaCl solution molarities, were tested when Fe and Ni were used as catalysts. A mixture of Ni and Fe was also used as a catalyst. Voltage varied from 14 to 20V while different NaCl molarities (0.2, 0.25 and 0.3 molar (M)) and catalyst concentrations (1, 3 and mol %) were used for synthesizing CNTs. All experiments were carried out at atmospheric pressure. The initial temperature of solution was 10^{o} C.

Micrographs show that the CNTs, carbon nano fibres (CNFs) and nano onions were synthesized with using this method but No nanostructure was observed in the SEM image of the materials collected materials from the tip of the cathode. These results correspond with previous work [16]. The produced CNTs which had different diameters included many impurities such as catalyst particles and amorphous carbon. Therefore, purification was needed. As-produced materials were partially purified by acid treatment and annealing in an oven.

3. Results

3.1. The effect of Fe catalyst on production

Experimental results showed that produced CNTs by electric arc discharge in NaCl distilled water solution, are mostly multi wall while single walled CNTs were rarely synthesized by this method [17]. Typical TEM image of as-produced CNTs is shown in Fig. 2. In this image, there are many nano-particles, graphite layers which have polyhedron-like structures and few

CNTs that are covered with amorphous carbon layer. The structures of the CNTs that are observed in subsequent TEM and SEM images are clear.

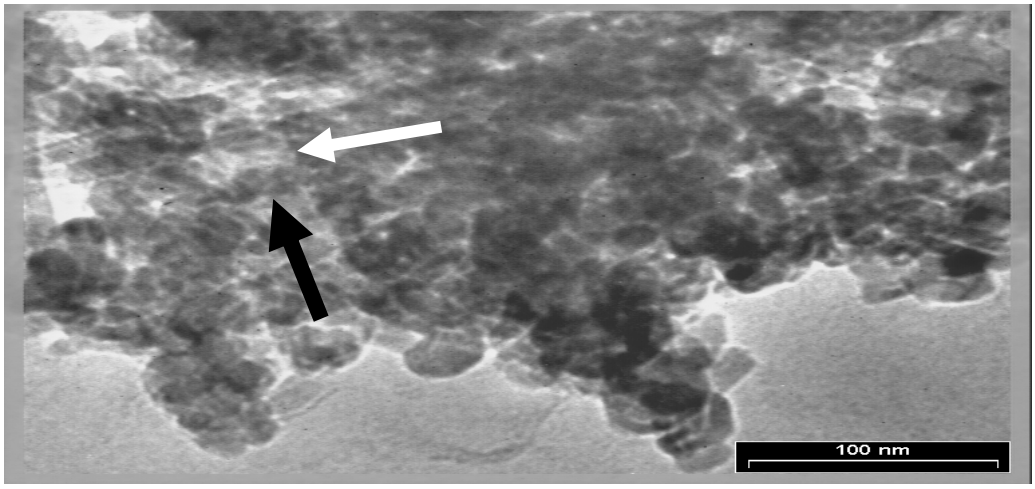


Fig. 2 TEM image of as-produced materials were produced using Fe as a catalyst. Polyhedron-like structures are mostly observed and few CNTs are also indicated by two arrows at the left corner.

The CNTs were mostly grown at the presence of the catalysts, and the quality and quantity of them were improved with suitable catalyst concentration. With 3 mol% Fe catalyst and 0.3M NaCl solution, the optimum nanotubes yield was found at a voltage of 19-20V between electrodes. SEM images of as-produced materials are shown in Fig. 3 and Fig. 4. CNTs have straight walls and clean surface in comparison with products obtained with other catalysts and liquid environments. The amount of impurities (such as amorphous carbon, catalyst particle, and

carbon nano porous) was very high, when voltage was 14V. At high voltages, we could hardly have stable arc. Arc discharge was erratic in the case of 0.2M, and was regular in 0.3M NaCl solution.

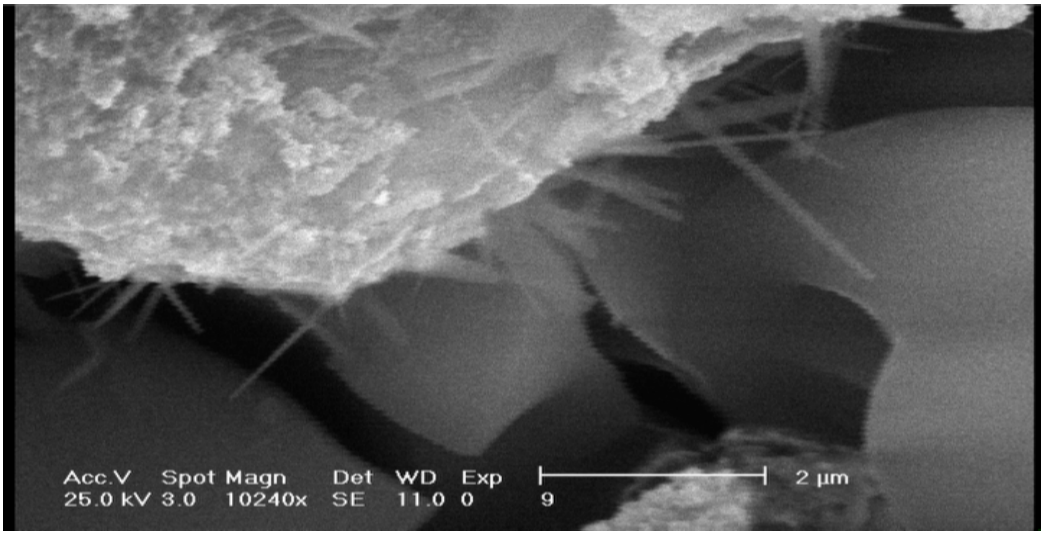
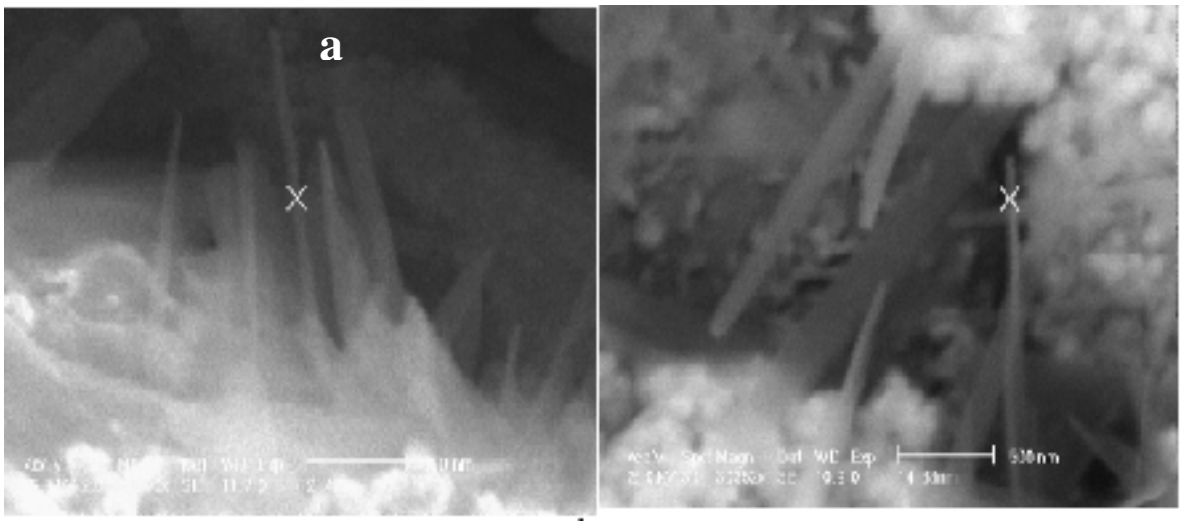


Fig 3 Low magnification SEM image of as-produced materials were obtained with 5 mol % Fe catalyst.

TEM image in fig. 5 shows multi walled CNTs which are grown clearly beside many polyhedron structures. They are typically 100-300 nm in length and 25-30 nm in diameter. In this image, catalyst particles are also observed.



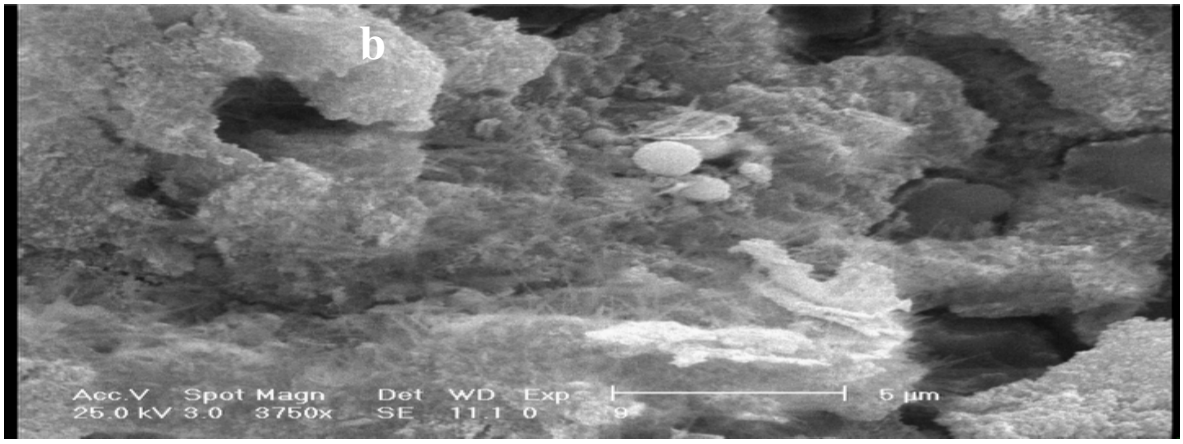


Fig 4 SEM images of as-produced materials a) High magnification image of CNTs,

b) Low magnification SEM image of specimen surface area

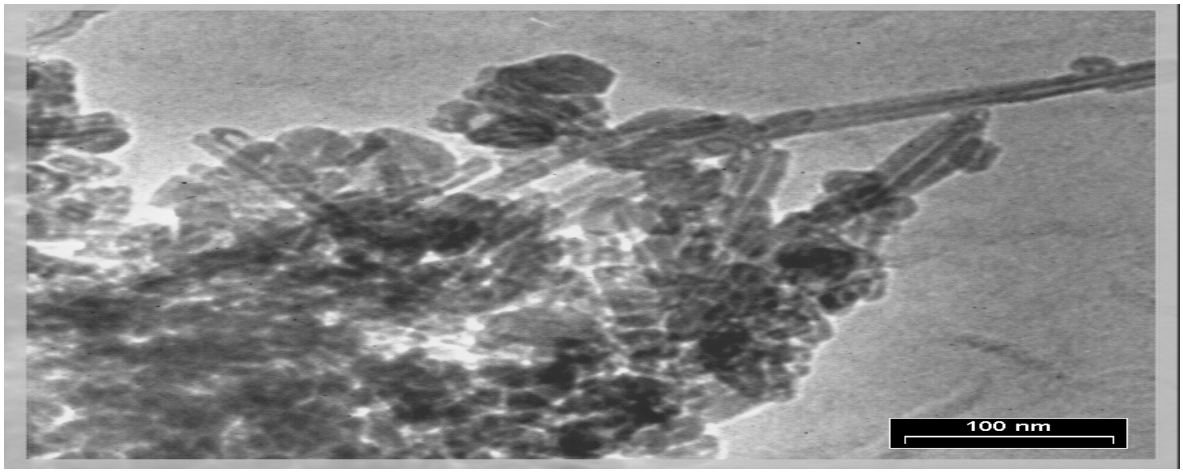


Fig. 5 TEM image of the as-produced multi walled CNTs

3.2. The effect of Ni catalyst on production

In this step, arc discharge apparatus operated in the same way as previously described, with one difference. In this study, Ni (instead of Fe) was used as a catalyst. The raw deposited materials were produced by 3 mol % Ni in 0.32M NaCl distilled water solution and a SEM image of products is shown in Fig. 6. Agglomerated structures of carbon are observed in the right side of the image, beside them many carbon nanostructures were grown. In this image, few CNTs are hardly seen behind the CNFs. SEM image in fig. 7 shows considerable amount of CNTs. Carbon nano onions were also synthesized by electric arc discharge in NaCl solution. Fig. 8 shows a typical TEM image of a carbon nano onion. Carbon nano onion (25

nm in diameter) existed on the surface of the liquid, with well-crystallized wall. The TEM images in Fig. 9. a and b show as-produced materials which were collected from the bottom of the baker. Multi walled CNTs were grown beside catalyst particles and polyhedral structures. The CNTs were typically 15-35 nm in diameter and 100-400 nm in length.

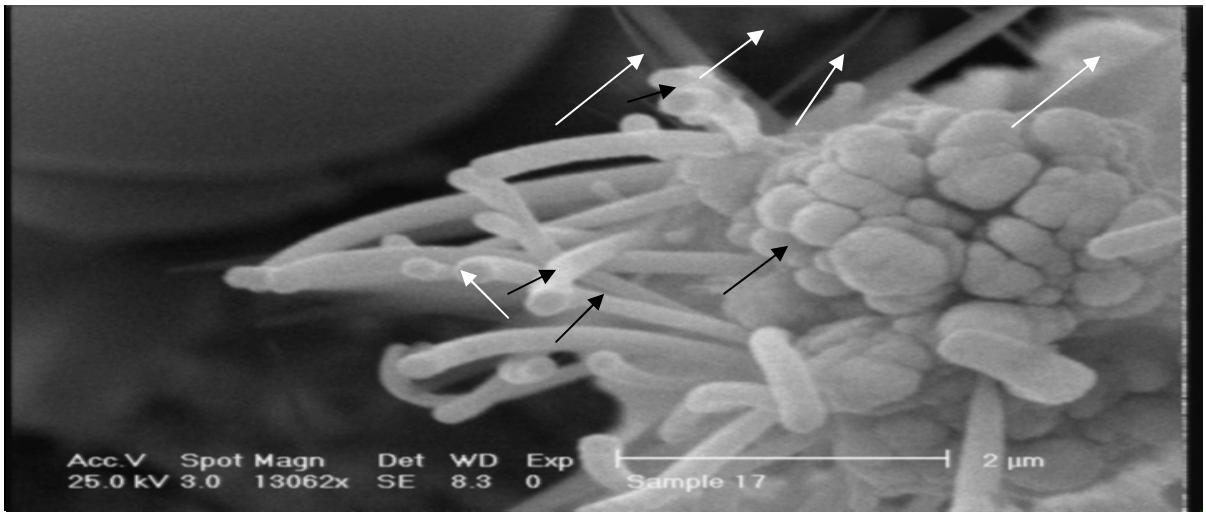


Fig 6 Typical low magnification SEM image of structures were produced with 3 mol% Ni as catalyst in 0.32M NaCl solution. Apparatus worked at 19-20V. A few CNTs are observed behind the CNFs which are indicated by arrow.

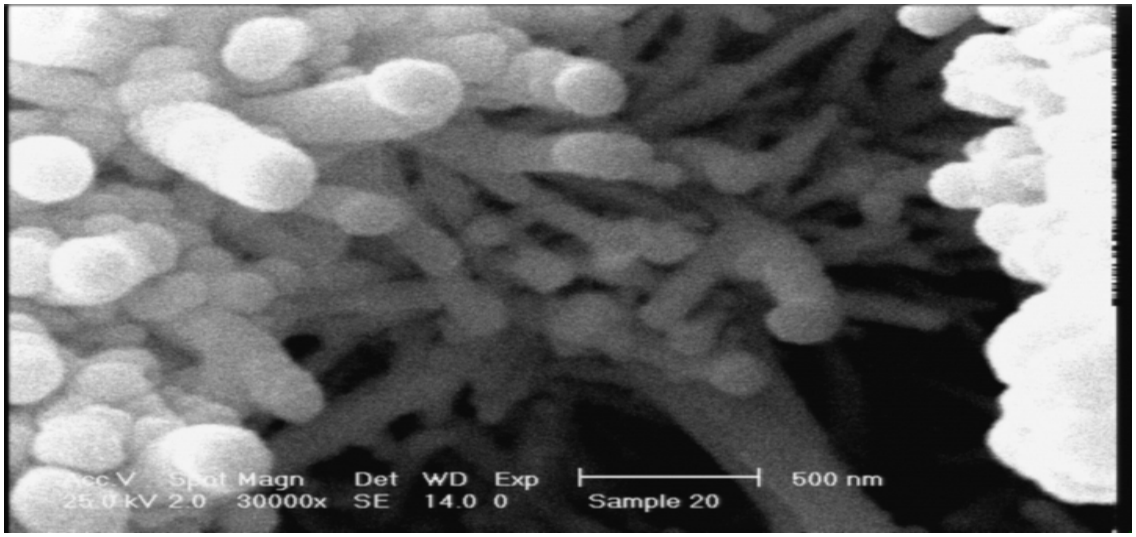


Fig 7 SEM Image shows CNTs which were produced with 3 mol % Ni catalysts in 0.3M NaCl distilled water solution. Apparatus worked at 19-20 V

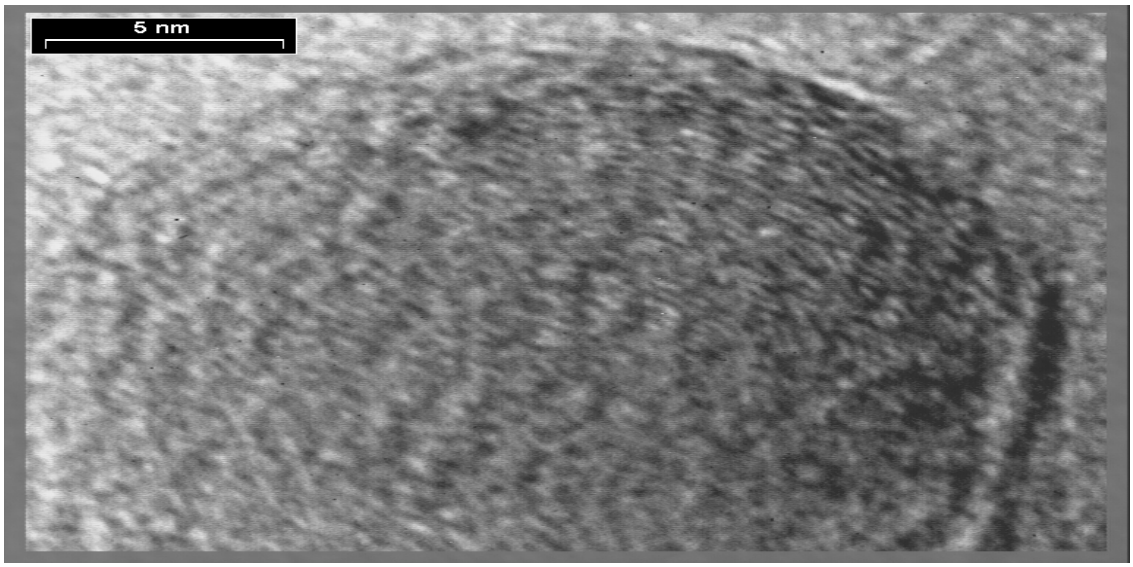
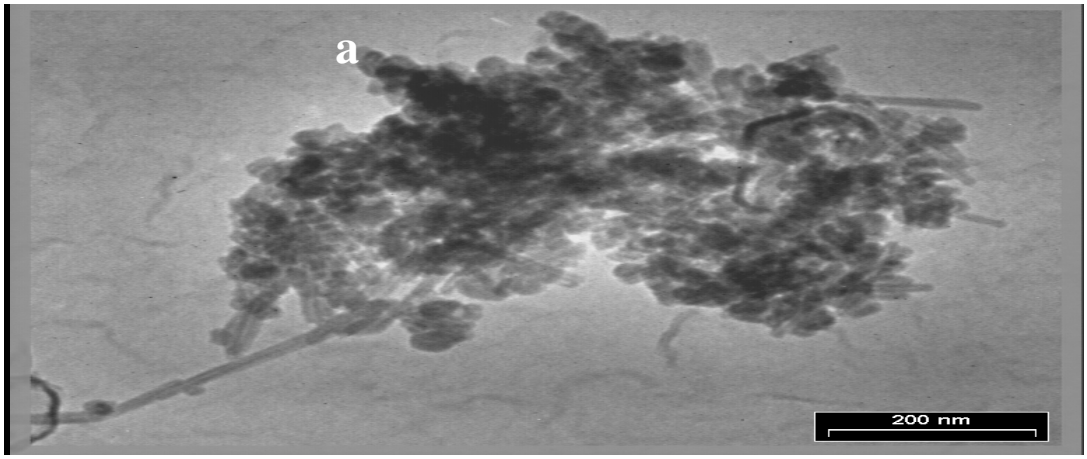


Fig 8 Typical TEM image shows a carbon nano onion which was produced by arc discharge in NaCl solution, as produced materials were collected from the surface of the liquid



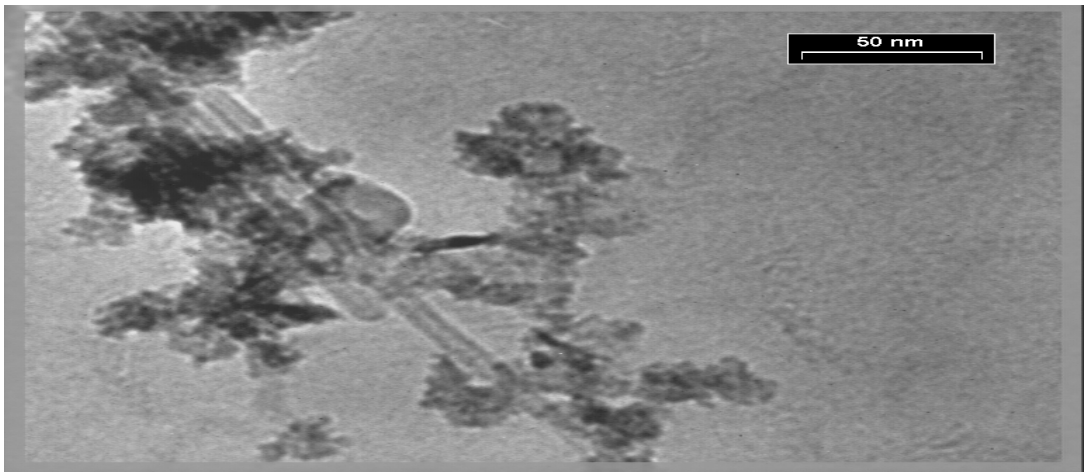
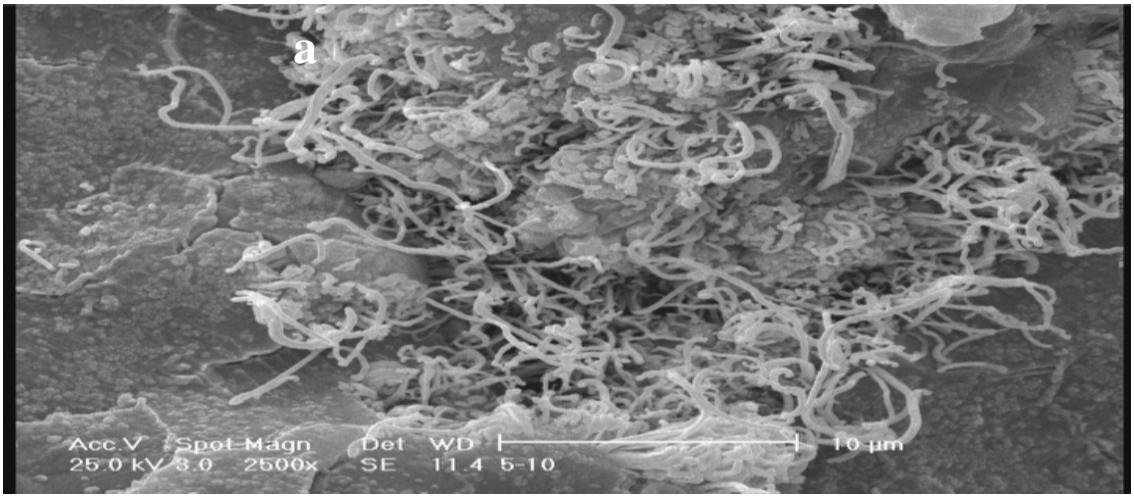


Fig 9 TEM images show CNTs which were synthesized by electric arc discharge in NaCl solution The CNTs were typically 15-35 nm in diameter and 100-400 nm in length.

3. 3. The effect of Fe-Ni mixture on production

CNFs which had High yield were synthesized by electric arc discharge in 0.3M NaCl distilled water solution and using a mixture of catalysts Fe and Ni (Fe : Ni, 1.8: 0.9 mol %). This method with above conditions is Simple and inexpensive for synthesizing CNFs. SEM images of purified samples are shown in Fig. 10. a and b. In these images, CNFs were grown together with the same diameters and oriented directions. They are long and have many defects on their walls and have typically 200-500 nm in diameter and few µm in length.



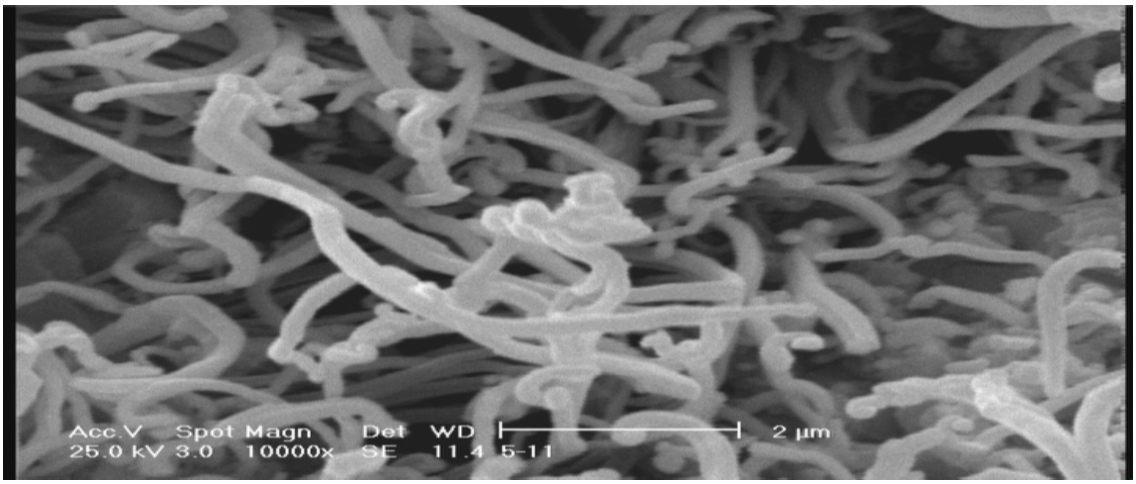


Fig 10 SEM images show CNFs which were produced with a mixture of Ni and Fe as a catalyst. The CNFs dimensions are typically 200-500 nm in diameter and a few µm in length.

4. Purification

Produced raw materials contained considerable amount of impurities such as amorphous carbon and metal catalyst particles. Therefore, purification was required. Raw materials were washed several times in distilled water solution, in order to decrease the NaCl concentration, first as-produced materials was reflux in ethanol (70 wt%) using ultrasonic wave and centrifuged for 4 min in order to remove light impurities. Second, obtained sample refluxed in 0.2M HNO_3 solution (10 ml) for 12 hours, to remove metal catalysts from CNTs, and then, the sample was washed by distilled water solution and dried. Third, obtained materials was transferred to an oven, was heated in atmospheric pressure and 500°C of temperature for 10 min. Fig. 11.a and b show SEM images of purified CNTs. As can be seen from these images, the percentage of CNTs is considerably increased.

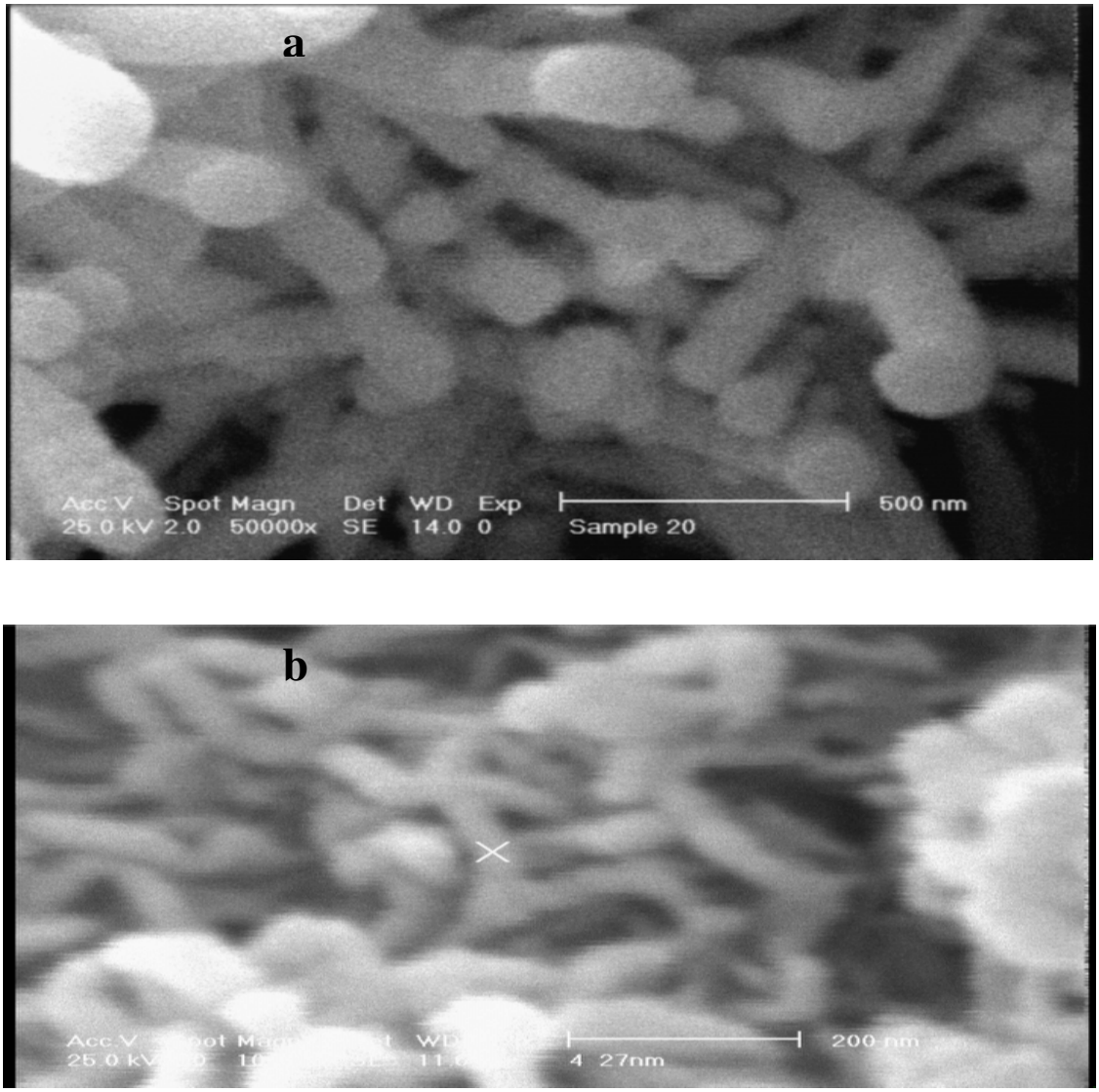


Fig 11 SEM images show as-produced materials which were obtained after purification. a) The CNTs were produced with 3 mol% Ni catalyst and 3M NaCl solution. b) The CNTs were produced with 5 mol% Ni catalyst in 0.25M NaCl solution.

5. Conclusions

Multi walled CNTs were successfully synthesized by DC arc discharge between two graphite electrodes in NaCl distilled water solution, using anode doped with Fe and Ni as catalysts. The experiment was optimized in the condition that NaCl solution concentration was 0.3M and 3 mol% catalyst concentrations. Apparatus worked at voltage of 19-20V with 70A out-put current. TEM and SEM images show that collected CNTs from the bottom of vessel was typically 100-300 nm in length and 25-30 nm in diameter. As-produced materials were

purified and then CNTs cleared. Carbon nano union was also synthesized from the sample which was collected from the surface of the liquid. CNFs were produced by electric arc discharge in 0.3M NaCl distilled water solution with a mixture of Fe and Ni catalysts. CNFs were grown together with similar diameters (200-500 nm) and long length.

Acknowledgements;

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