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Synthesis of Carbon Nanomaterials in Deionized Water with and without Catalyst Using Arc Discharge Technique

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Abstract

Simple and economical technique was used for synthesis of carbon nanomaterials without using vacuum equipment. The used technique implied an arc discharge between two pure graphite rods with different diameters submerged in deionized water at room temperature. These were also investigated with a new type of metal catalyst process for the first time. Plasma arc discharge was produced using D.C power supply with current (30-90 amp.) and voltage (30-50volt). The nanomaterials were produced in the form of nanoparticles (floated), nanotubes and nanofibers (sank), and carbon nanocolloidal (dispersed) through the water. The results of these experiments were examined by high resolution optical microscope, scanning electron microscope SEM and transmission electron microscope TEM. The results revealed different types of carbon nanomaterials.

Keywords: Arc Discharge, Carbon Nanotubes, TEM, Carbon Nanofibers.

تحضير مواد نانوية في الماء اللاأيوني مع وبدون محفز بتقنية قوس التفريغ الكهربائي

الخلاصة

تم إستخدام طريقة بسيطة وإقتصادية لتحضير مواد كاربونية نانوية وبدون الإستعانة بأجهزة تفريغ الغازات. تحوي التقنية المستخدمة قوس التفريغ الكهربائي بين قطبين من الكرافايت النقي ذات أقطار مختلفة مغمورة في ماء لاأيوني بدرجة حرارة الغرفة. تم إستخدام أقطاب من الكرافايت محشوة بنوع جديد من المحفز المعدني للتحري عن التراكيب الناتجة وبنفس تقنية القوس الكهربائي. تم توليد القوس الكهربائي بالإستعانة بمجهز قدرة مستمر ذي تيار يتراوح بين (30-90) أمبير, وبفرق جهد يتراوح بين (30-50) فولت. كانت المواد الكاربونية الناتجة مصنفة كجزيئات نانوية طافية وانابيب وألياف كاربونية نانوية مترسبة في قعر الحاوية وعالق كاربوني نانوي عالق في الماء. تم فحص التراكيب الناتجة من التجارب بالمجهر البصري عالي القدرة التحليلية, والمجهر الإلكتروني الماسح والمجهر الإلكتروني النافذ. لقد أظهرت نتائج هذه الفحوصات أشكال عديدة مختلفة من المواد الكاربونية النانوي

Introduction

Carbon nanotubes (CNTs) have recently attracted great interest as new nanomaterials due to their excellent mechanical, electrical, and chemical characteristics. Considerable efforts has been expended searching for potential applications of CNTs in a world wide range of scientific fields, such as electronics, biology, medicine, energy ,materials engineering and aero science [1, 2]. CNTs were first reported by Iijima in carbonaceous deposits on the cathode obtained during the D.C. arc discharge process of a graphite

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electrode in helium gas [3].To synthesize carbon nanotubes various methods have been developed, including three main techniques: Chemical vapor deposition (CVD), specifically the catalytic decomposition of a suitable hydrocarbon, is considered as the best method towards a large-scale production of carbon nanotubes (CNTs) with low costs, and simple equipment [4, 5, and 6]. Laser ablation method [7], and finally arc discharge method [8]. Among the three methods of preparing CNTs, arc discharge is the most practical for scientific purposes because the method yields highly graphitized tubes due to the high temperature process, also the relatively low cost of production [4].Large quantities of CNTs were first prepared by Ebbesen and Ajayan [9], using arc discharge in a helium atmosphere at ca. 60kPa. Discharges in liquid media were also investigated as a route to carbon nanomaterials: e.g., C_{60} from a spark discharge operating at 10 -20 kV in toluene or benzene [10], fullerene fragments via a glow discharge in $CHCl_3$ vapor [11], and CNTs from a low-voltage contactauto-regulated arc discharge in aromatic hydrocarbons. Other nanoparticles have also been formed in liquid media by electrochemical or plasma discharge, e.g., fine silver powders [12] and CNTs [13]. Sundaresan and Bockris [14] studied the behavior of a carbon arc discharge in water; however they focused their attention solely on cold fusion, rather than carbon nanostructure production. In the reaction system using arc discharge in liquid can synthesize varieties of nanotube-family materials [15, 16, 17, and 18]. When graphite electrodes are used with water as liquid, multi-walled carbon nanotubes and carbon onions were produced [14, 15, 16]. When liquid nitrogen was used instead of water, single-walled carbon nanohorns were produced [18]. The liquid hosting the arc plasma has the roles to realize rapid quenching of the carbon vapor emitted from consumable anode, and to determine the gas components of the bubbles which appear at the arc zone. After knowing the possibility to obtain such series of nano-materials, it becomes important to understand the mechanism of the relevant reaction field to control the purity and structure of these products. For this purpose, some efforts were carried out and we can find some progress in the literature. For example, the influence of the components of electrodes and liquid [16, 18, 19], discharge pattern (pulse or continuous, D.C or A.C) [20, 21], pressure [21], and flow dynamics of liquid [22] were investigated previously. One such morphology is the petal-like sheet that is identical to that obtained by Ando et al. [23]. Arc discharge in deionized water with an open vessel is extremely simple and cost effective compared he arc discharge in low-pressure hydrogen environments [23, 24 and 25].

This work describes the production of CNTs at different morphologies fabricated by using arc discharge in deionized water in open vessel at an ambient atmosphere.

Experimental

The apparatus used in this work is shown in Figure (1). Two high purity graphite electrodes (99.9%) with different diameters (3mm, 6mm, 12mm) were used in arc discharge technique. The anode and cathode electrodes were connected to the positive and negative terminals of a D.C. power supply Al-aqsa company, Iraq (100A, 30V), respectively. Both electrodes were submerged in 3liter volume Pyrex beaker filled with 2 liters of deionized water at room temperature. to tThe depth of the electrodes was 10cm bellow the water level. One side of the graphite electrodes handle was kept fixed (cathode), and the other (anode) controlled manually using a micrometer system to regulate the distance between the electrodes.

Experimental procedure

The arc discharge was generated between two pure graphite electrodes in deionized water. These electrodes were emerged in deionized water to the depth of 10 cm, and they were horizontally aligned on the same axis with about 1 mm gap. One of the brass electrodes holders was free to move, forward and backward using a micrometer, which enables proper electrodes gap adjustment during arc discharge (Fig.1). The power supply is turned on the anode electrode is then moved gradually towards the cathode electrode using a manual micrometer. Once the electrodes are in touch to generate the discharge, the anode turned red hot subsequently, the anode electrode is moved backwards to maintain the gap about 1mm .simultaneously, the plasma in a semispherical shape is formed. When the arc discharge stabilized, the rods are kept at about 1mm apart while the carbon deposited on the cathode. The power supply is turned off after 10-20 min. and left for a while for cooling.

Figure (2) shows an experimental plasma formation with different sizes. Nokia digital camera (3.2MP) was used to capture images, as shown Figure (2A, B, C, D, E, &F).The larger sphere plasma in Fig. (2F) was settled at high temperature around 3500K.This temperature value has been estimated previously by many workers [26, 27]. The plasma sphere is filled with gas bubbles such as (H_2, CO) [17, 27]. It can be seen that the purpose of water is to increase the speed of quenching process of carbon growth. Accordingly, deionized water acts as a quenching media for the nucleation and growth of carbon nanomaterial.

Characterization

The Characterization of the nanomaterials were studied by high resolution optical microscope (Olympus BX51M with CCD camera Kruss DCM35), transmission electron microscope TEM (Philips – CM12), and field emission scanning electron microscope (FESEM) (Geminr-Supra^{TM}40VP).

The main parameters which play significant role in this technique are, control of arcing current and the increment of water temperature. Arc discharge in water is rather a difficult choice because of high arc fluctuation, due to small arc gap, and progressing decrease of water transparency caused by carbon particles dispersed in water.

Carbon nanomaterials were produced using new soluble salts catalyst of $FeCl_3$ and ethanol. Small amount of $FeCl_3$ powder (0.05M/0.2433g) was dissolved in ethanol. The liquid solution containing the catalyst in salt form was mixed with graphite powder (ratio: 3/1) resulted in a new paste material. A hole was drilled through the anode rod of 6mm diameter, 10mm long .The size of the hole was 3mm diameter and 15mm depth .The resulted paste was filled the anode's hole and then dried at 100°C in oven.

Results and discussion

Arc discharge was generated in graphite rods .Anode rods with 3 and 6 mm diameters of graphite were used. Graphite rod of 6mm and 12mm diameter were used as cathode. In such experiment, the diameter of the anode is especially important because only the anode is consumed by arc discharge process. It is noteworthy that the discharge in water is erratic, thus it is critical to control precisely the arc gap in order to run upon ignition to avoid arc disruption. The electrodes gap was maintained (0.1cm) during the experiment. Optimum arc performance was achieved at current of 30-90 A, with a voltage drop of 5-15V as shown in Table (1).

The electrical power of the arc discharge in water was estimated as a maximum value (750 W) and minimum value (350 W). The discharge duration, associated with the anode feeding distance (1cm) was 10-20 minutes. The average feeding rate was in the range 0.5-1 mm/min. The experimental data of catalytic and non catalytic process are presenting a non linear input power as shown in Table (1) &Table (2). This is considered to be a new behavior for arc discharge method, which it has not been mentioned elsewhere.

Figure (3) shows a high resolution optical microscope micrographs for sank particles at the bottom of water .These are preliminary images indicate the formation of carbon networks with different diameters and shapes. The real structures of the same materials were investigated using transmission electron microscope TEM, and magnifications of 19000x and 25000x.This will be seen in figure (6).

Optimum plasma, spherical and homogenous was successfully achieved with stable temperature. Consequently, high quality carbon nanoparticles have been produced as it is shown in Figure (4). This Figure shows SEM micrographs at different magnifications (800, 1000&1200) X for the floated carbon nanoparticles collected from water surface using field emission scanning electron microscope (FESEM). This shows agglomeration of carbon nanoparticles .The average size of carbon nanoparticles was estimated to be around 20nm , which is comparable to the particles produced by other workers [28] using arc discharge technique .

The graphite rod (cathode) structure was investigated using scanning electron microscope (SEM). Figure (5) shows the SEM micrographs of the cathode after the arc discharge process. It has been mentioned previously that the arc discharge is produced at very high temperature [26, 27] .The high temperature effect on a nanostructure of graphite electrodes structure is shown in Fig. (5A). these can be seen as a result of layers graphitized at very high temperature as shown in Fig. (5B, C). This is confirmed by other workers [29].

Another set of experiments was obtained using metal catalyst method. The experimental data is shown in Table (2). The structures of the produced materials were investigated using TEM, at accelerating voltage 80kV, and magnifications of 19000x, and 25000x. Figure (6) shows the produced nanomaterials micrographs investigated by (TEM). Different structures can be identified in this figure like, carbon nanocoils, the so called bamboo-like carbon within sliced in-between and also the tube with layer of amorphous carbon outside the tube. These are in accordance with many workers [30]. Table (3) summarizes the sizes and the shapes of carbon nanotubes as shown previously in Figure (5) , indicated by the arrows .In contrast to single wall nanotubes (SWNT) and multiwall nanotubes (MWNTs) , bamboo-like carbon nanotubes (BCNTs) have regularly occurring compartment-like graphite structures inside the nanotubes. It is proved that the same catalyst which is used with CVD method gives the same results [31].

Conclusions

Arc discharge techniques in deionized water using arc discharge experiments produce variety of carbon nanomaterials without catalyst. Various kinds of carbon nanotubes using a new process of metal salt catalyst were also presented. Production of SWCNT with this technique was achieved .The products also show different shapes and sizes of CNT's. We believe that the different shapes and sizes are due to the differences of the catalyst shapes and sizes. That is what researchers look for.

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Table (1): Experimental arc discharge data without catalyst.

Exp.1 Arcing time: 10min Dimensions: 6mmx50mm									
V/volt	12	7	9.5	8	8.3	8	7.8	7	
I/Amp	50	35	90	70	71	40	46	50	
Exp.2 Arcing time: 15 Dimensions: 6mmx50mm									
V/volt	14	4.5	7	8.6	9	9	8	7.7	8
I/Amp	45	60	60	78	80	85	88	69	86
Exp.3 Arcing time: 10 min Dimensions: 3mmx50mm									
V/volt	7.5	7.6	7.8	8.2	7.8				
I/Amp	80	84	80	75	81				
Exp.4 Arcing time: 10min Dimensions: 3mm, 6mm x50mm									
V/volt	8.1	8.6	8.4	8.5	8.2	7.9			
I/Amp	75	65	68	75	77	83			
Exp.5 Arcing time: 25 min Dimensions: 6mmx50mm									
V/volt	9.1	8.8	7.9	7.5	7.2	9.3	9.2	12.1	10.2	9.6
I/Amp	45	65	88	93	95	65	68	55	60	68
Exp.6 Arcing time 10 min Dimensions: 6mmx50mm									
V/volt	6.9	6.4	5.7	5.6	6.3	5.1	7	6.5	5.9	6.3
I/Amp	73	80	95	87	75	88	60	75	90	85

Table (2): Experimental arc discharge data with catalyst.

Exp.1 Arcing time: 10 min Dimensions: 6mmx50mm										
V/volt	11.3	10.9	10.0	*9.8*	*9.7*	*9.3*	*8.9*	*9.1*	*8.7*	*7.7*
I/Amp	34	37	40	*51*	*66*	*70*	*67*	*74*	*75*	*76*
Exp.2 Arcing time 10 min Dimensions: 6mmx50mm										
V/volt	12.3	11.5	10.7	*10.0*	*9.9*	*9.3*	*9.2*	*9.0*	*8.8*	*8.6*
I/Amp	36	39	38	*42*	*48*	*49*	*50*	*59*	*66*	*78*

Table (3): Types and sizes of carbon nanomaterials pointed in Figure (6A, B).

Pointed arrow No.	Tube diameter (nm)	Type of nanocarbon	Figure (6)	Shape / Type
1,2,3	≈ 63nm,11nm,7nm,	CNF's	A	Bamboo-like
4,5,6	≈ 7nm, 35nm, 42nm	CN coils	A	*SWCNT-Coiled ≈ 1* µm *long* *SWCNT-Coiled-long, with coil diameter ≈ 40nm*
7,8,9	≈ 22nm,32nm,45nm	Carbon nano belts	B	
10,11	≈ 70nm,78nm	CNF's	B	Greater than ≈ 3µm long

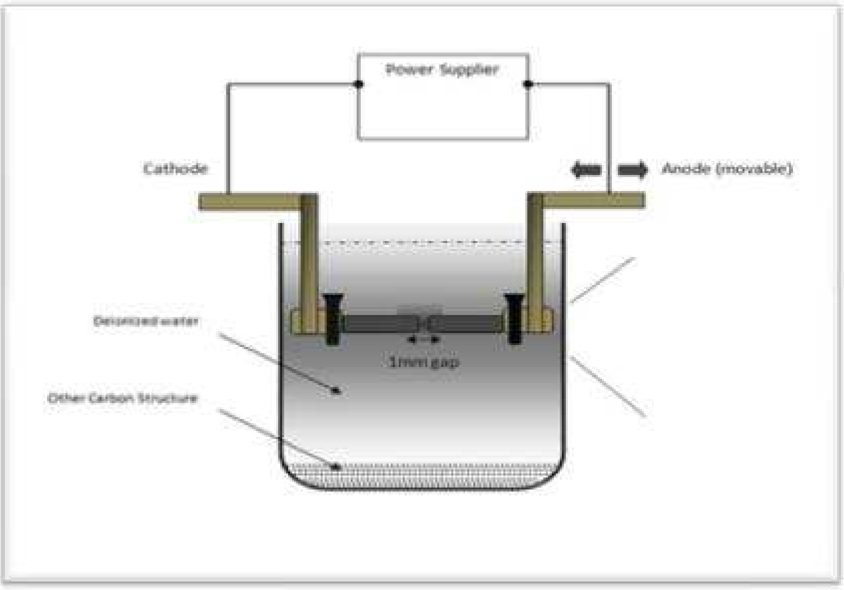
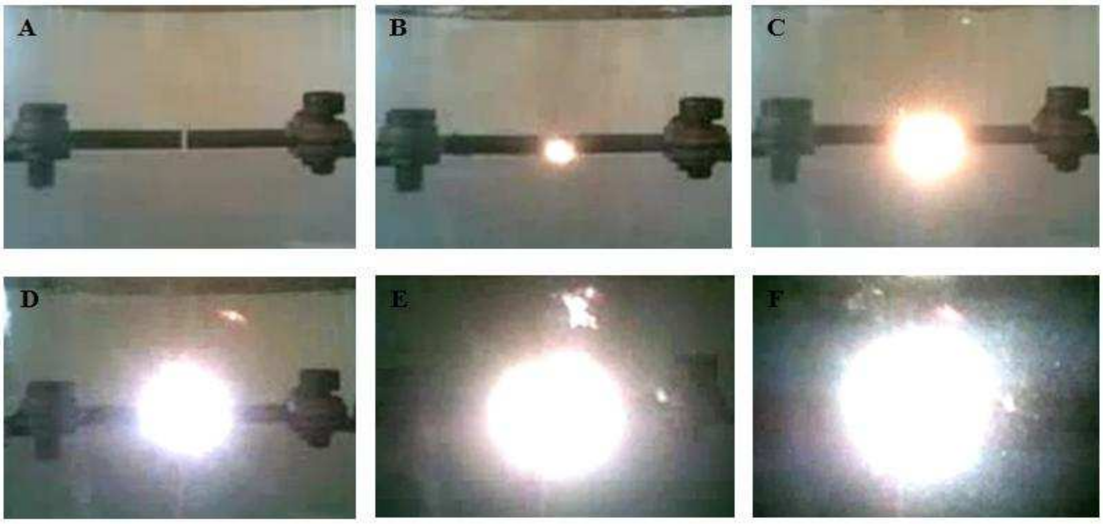


Figure (1): Schematic of the apparatus used for arc discharge in water



deionized water

Figure (2A, B, C, D, E, and F): Steps of spherical plasma generation using Arc discharge of 12mm electrodes in water (scale 1: 4)

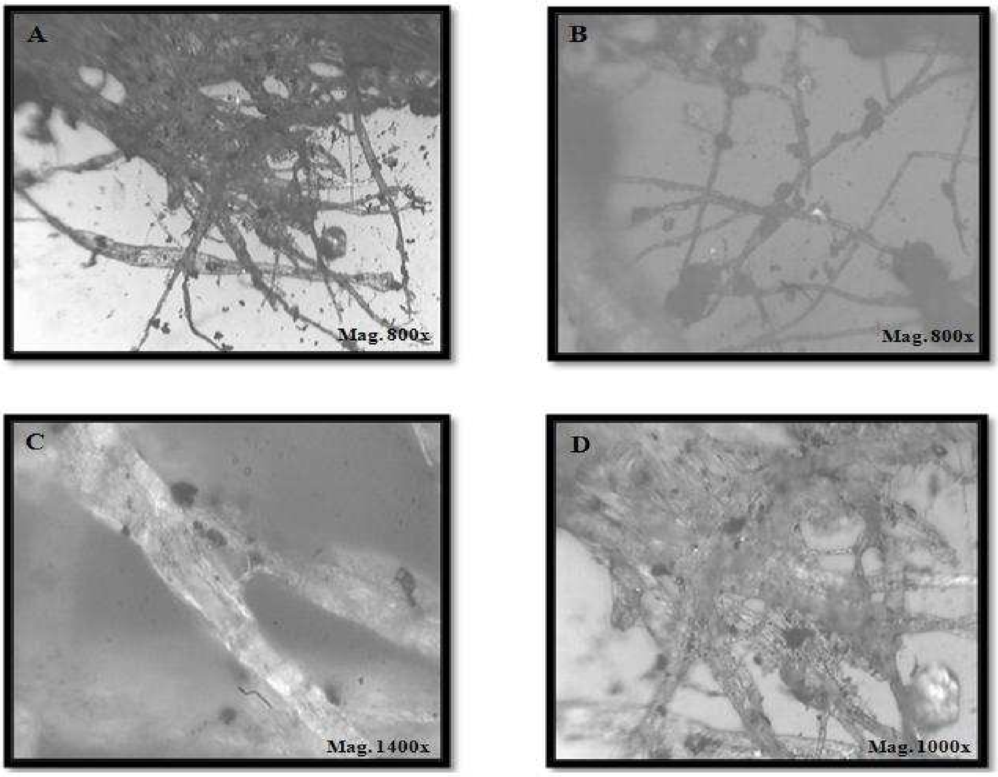


Figure (3): Optical microscope micrographs of the resulted carbon network structures

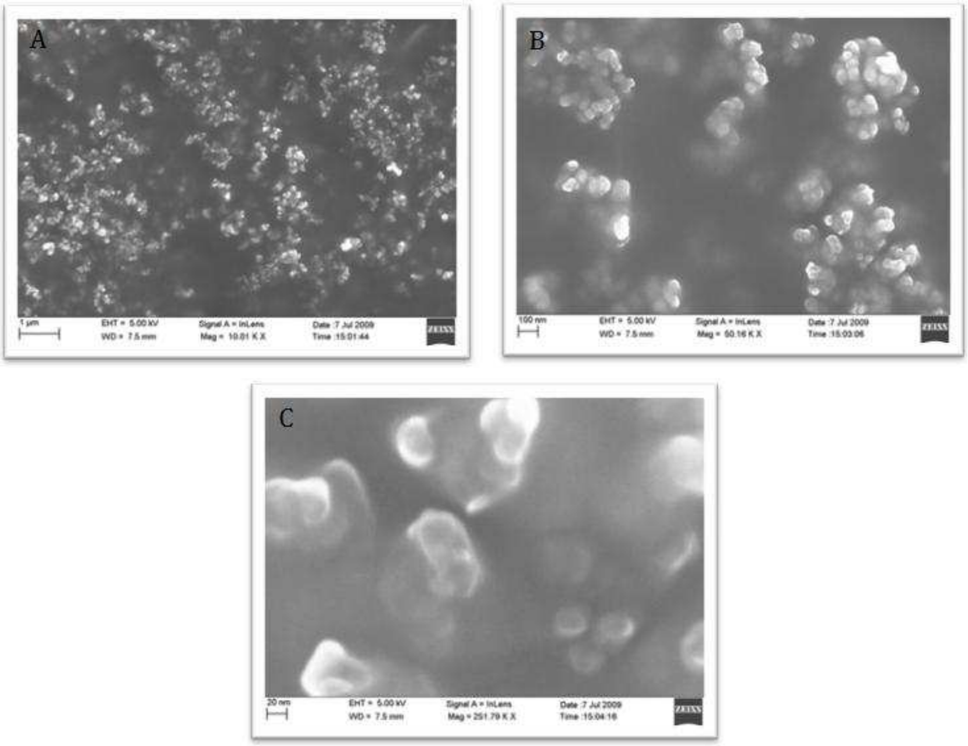


Figure (4): SEM micrographs of the floated carbon nanoparticles on water surface

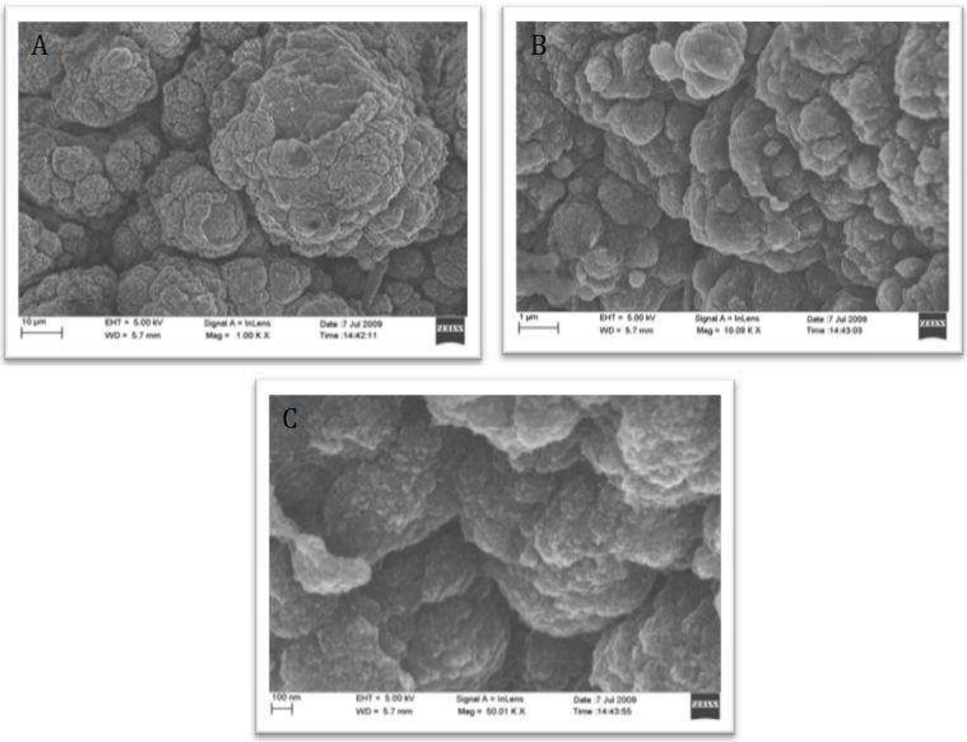


Figure (5): SEM micrographs for cathode electrode used in arc discharge

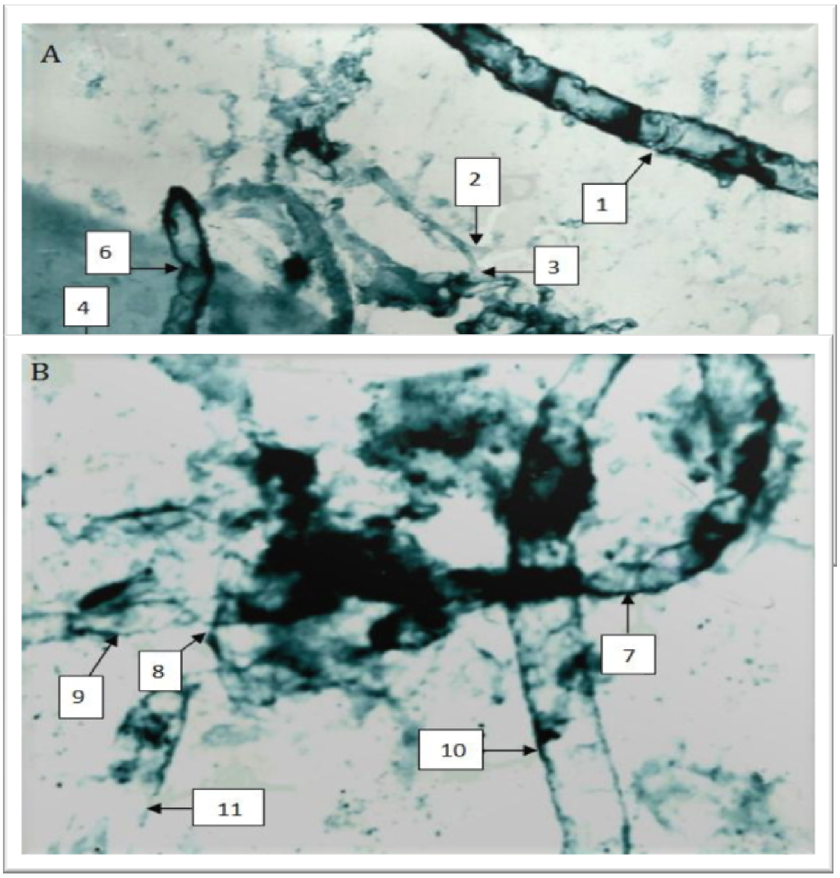


Figure (6): TEM micrographs of the synthesized carbon nanostructure using catalyst; (A) Magnification: 25,000x, (B) Magnification: 19,000x