

Functionalization and Characterization of Multi-Walled Carbon Nanotubes Using Chemical Oxidation Method

Dr. Adawiya J. Haider 

Nanotechnology advanced material research center, University of Technology/Baghdad

Email: Adawiya_haider@yahoo.com

Dr. Mohammad . R. Mohammad

Applied Physics department, University of Technology/ Baghdad

Duha S. Ahmed 

Applied Physics department, University of Technology/ Baghdad

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ABSTRACT

Functionalized MWNTs have been of interest for dispersion enhancement in processing or for chemical modifications. Modification of multiwall carbon nanotubes (MWNTs) by ultrasonication with oxidizing acid mixtures is frequently used to functionalize CNTs. In this work, the functionalization process of MWCNTs involves using a mixture of concentrated sulfuric acid and nitric acid (95% H₂SO₄: 65% HNO₃, 3:1 volume ratio), ultrasonicated at 25°C for 30min. The results confirmed by Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), and Scanning Electron Microscopy (SEM). From the FTIR spectrum, the existence of carboxyl group indicates the functionalization of MWCNTs on the outer surface wall. SEM micrographs show the occurrence of surface modification on the MWCNTs structure. Finally, a well dispersed of MWCNTs colloidal was successfully obtained with less MWCNTs structure collapsed.

توظيف ودراسة خصائص انابيب الكربون المتعددة باستخدام طريقة الاكسدة الكيميائية

الخلاصة

تمتلك انابيب الكربون المتعددة امكانية استخدامه في تطبيقات كثيرة الا انها تواجه محددات في مجال الانتشار وقد وجد ان المعاملة بالاحماض تعزز خاصية اعادة التجميع لانابيب الكربون المتعددة (MWNT). يتضمن البحث عملية توظيف انابيب الكربون المتعددة (MWNT) بمجاميع فعالة مختلفة باستخدام طريقة الاكسدة بالاحماض من خلال استخدام خليط من الاحماض المركزة من حامض الكبريتك وحامض النتريك المركزين (95% H₂SO₄ : 65% HNO₃, 3:1 volume ratio) واستخدام جهاز الموجات فوق الصوتية (ultrasonic) عند درجة حرارة 25°C لمدة 30 دقيقة ويترك ليبرد عند درجة حرارة الغرفة. اما نتائج العمل فيتم اثباته باستخدام تقنيات الفحص منها مطيافية الاشعة تحت الحمراء (FTIR), حيود الاشعة السينية (XRD) وجهاز المسح الالكتروني (SEM). من نتائج مطيافية الاشعة تحت الحمراء FTIR توضح عملية توظيف انابيب الكربون المتعددة (MWNTs) على سطح الجدار. وتظهر صور المسح الالكتروني SEM حدوث تغيرات

في تركيب MWCNTs . واخير يتم الحصول بنجاح على محلول عالق ذات انتشارية جيدة لمادة الكربون النانو تيوب المتعدد (MWNTs) باقل ترسيب للمادة.

INTRODUCTION

Multiwall carbon nanotubes (MWNTs) have been intensively studied for potential applications due to their outstanding physical properties. Since multi-walled carbon nanotubes (MWNTs) and single-walled carbon nanotubes (SWNTs) were discovered by Iijima in 1991 and 1993, respectively [1]. They have been used in many applications, such as field emission devices, nanoelectronics, hydrogen storage, biosensors and delivery systems for drugs, because of their outstanding chemical, physical, electrical and mechanical properties [2].

However, the critical difficulty in applying carbon nanotubes for applications is because of the poor dispersibility and bundling between carbon nanotubes tubules, as affected by the attractive van der Waals interaction among themselves [3]. The improvement of dispersion has become a challenge to maximize the properties of CNTs. In order to overcome self-aggregation, Chemical Modification of Multi-Walled Carbon Nanotubes (MWNTs) is recognized as an efficient method for functionalization, promoting dispersion and surface activation at the same time or utilization of surfactants is regarded as an effective way to improve their wettability and adhesion to host matrix materials[4].

The surface modification of carbon nanotubes through functionalization process is the way to overcome these problems. Carbon nanotubes functionalization with concentrated acid solution of H_2SO_4/HNO_3 mixture and sonicated for several minutes is a process where functional groups (OH, C=O, and COOH) can be introduced on single and multi-walled carbon nanotubes (SWCNTs/MWCNTs) through liquid-phase oxidation procedures [5].

FTIR spectrophotometer was used to confirm the functional groups which formed after chemical modification with mixture of sulfuric acid and nitric acid. Crystallographic structure of the obtained Functionalization (F-MWNTs) will be confirmed by X-ray diffraction (XRD) measurements, while scanning electron microscopy (SEM) will be used for characterization of the morphology of purified MWCNT, F- MWCNT as well as the distribution of nanocrystals on the CNTs surfaces [6].

EXPERIMENTAL METHODS

Functionalization of MWCNTs

In this study, MWCNTs were functionalized by using a mixture of concentrated sulfuric acid (95% H_2SO_4) and nitric acid (65% HNO_3) (3:1). Firstly, 0.1g of as-synthesized (raw-MWCNTs) was treated with 100 mL of (95% H_2SO_4) and (65% HNO_3) (3:1) in flask of 500ml. The flask was vortex for 10min and ultrasonically vibrated in water bath ultrasonic at temperature of 25°C for 30 min. After that, the mixture was diluted with 400 mL of deionized water (D.W) and vacuum-filtered through a 0.22 μm polycarbonate membrane, the solvent was exchanged with H_2O_2 (30% v/v) as reduction reagent and the procedure was identically repeated. The solid was washed with deionized water until the pH of the

filtrate reached approximately 7.0. The solid was then dried under vacuum for 24 h at 25C⁰ to yield the carboxylic acid-functionalized MWNTs (MWNT-COOH).

Finally, the presence of functional groups on the carbon nanotubes was assessed visually by means of the time required to sediment in a polar solvent. For this experiment, 5 mg of CNTs were sonicated (ultrasonic bath) in 6ml of ethanol for 5 min. Then, the CNT-ethanol solution was removed from the bath and the time required for the CNTs to sediment was monitored [5, 7].

Characterization of the F-CNTs

The presence of carboxylic functional groups (O=C–OH and C–OH) on the oxidized MWCNT surface as shown in fig. 1 can be identified by different means. In complementing the dispersion data, the detailed structures and the chemical compositions of as synthesized MWCNTs and functionalized MWCNTs were characterized by using Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), and Scanning Electron Microscopy (SEM). From the FTIR spectrum, the existence of carboxyl group indicates the oxidation of MWCNTs on the outer surface wall and chemical composition and crystallographic structure of functionalized MWCNTs were confirmed by X-ray diffraction (XRD) measurements. The SEM micrographs show the occurrence of surface modification on the MWCNTs structure. The method used in functionalization MWCNTs has created fragmented structure toward the functionalized MWCNTs [3,8].

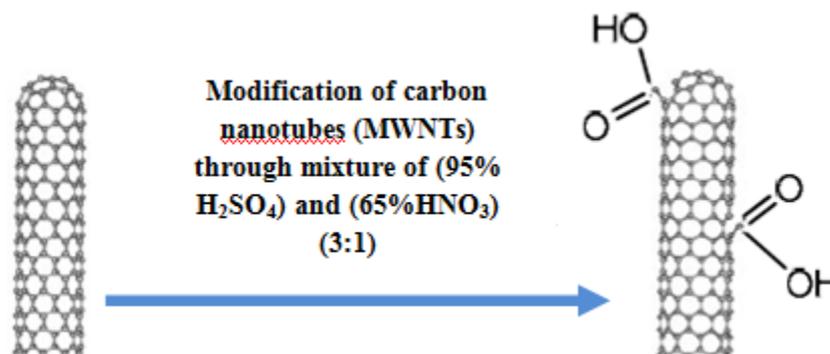


Figure (1) Schematic Diagram of Modification (Functionalization) Mwcnts by Through Mixture of (95% H₂SO₄) and (65% HNO₃) (3:1).

RESULTS AND DISCUSSION

Electron microscopy

Scanning electron microscopy was used to investigate possible MWCNTs fragmentation occurred during acid treatment and used to detect possible morphological changes on MWCNT specimens depending on the severity of each treatment. Figure (2a) shows typical SEM images of the pristine nanotubes (a) as well as those treated with strong oxidants such as sulfuric acid and nitric acid then followed by H₂O₂ as shown in Figure (2b,c). Thus, the treatment of CNTs with strong oxidizing agents causes severe etching of the graphitic surface of the material, leading to tubes of shorter length with a large population of disordered sites [9]. Analysis of

several SEM images of treated MWCNTs allowed reliable length measurements of only a few nanotubes, and all of them were between 1 and 3 μ m, similar to pristine material [5].

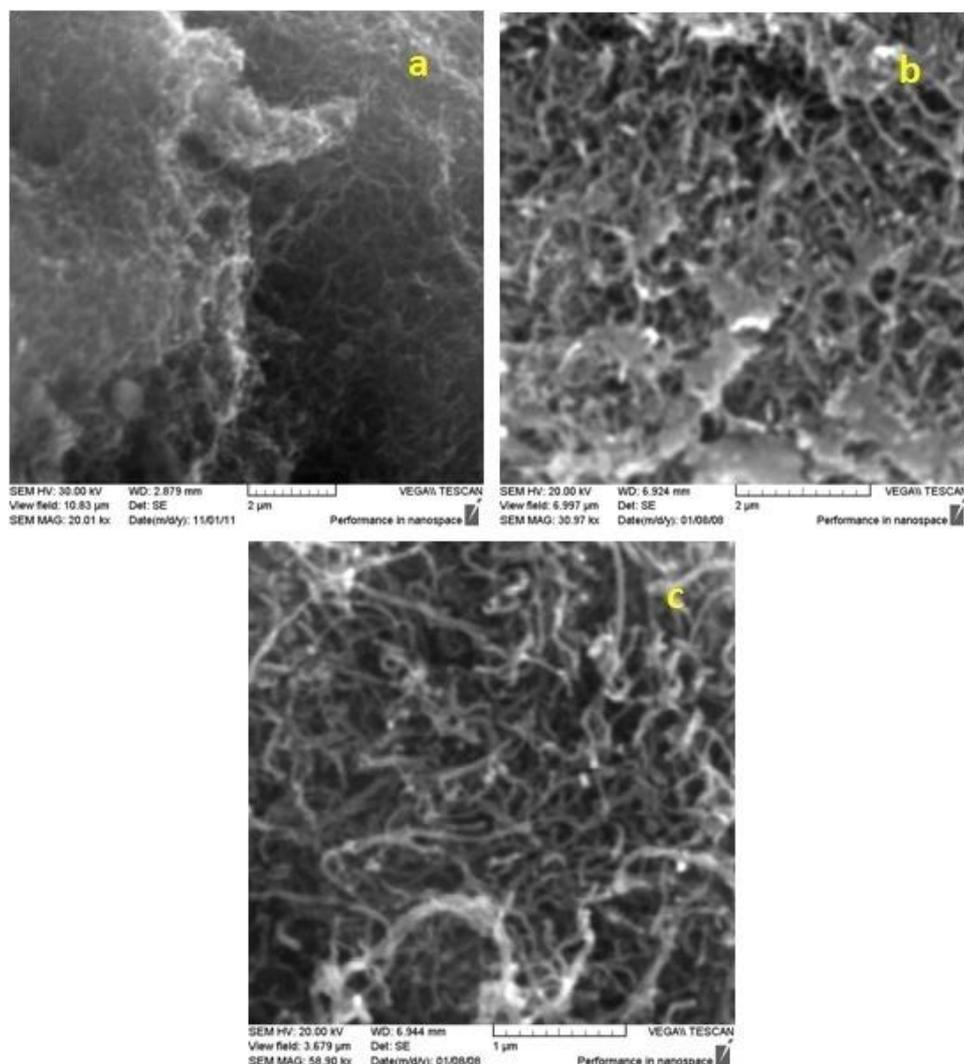


Figure (2) SEM Images of MWCNTs: (A) Raw-MWCNT and (B,C) Functionalized-MWCNT at Different Magnifications.

Infrared Spectroscopy

The IR spectrum confirmed the presence of functional groups in the pristine-MWCNT, MWCNT-COOH due to the oxidation of some carbon atoms on the surfaces of the MWNTs by a mixture of concentrated sulfuric acid and nitric acid in the range 500 to 4000 cm^{-1} is shown in Figure (3 a,b) . The stretching (O=H) vibration occurred at 3408 cm^{-1} in the MWCNT-COOH spectrum Figure (2b), can be assigned to the O-H stretch from carboxyl groups (O=C-OH and C-OH) and the

peak at 2360 cm^{-1} can be associated with the O–H stretch from strongly hydrogen-bonded –COOH [12]. The peak at 1627 cm^{-1} can be associated with the stretching mode of the carbon nanotube backbone (conjugated C=C stretching). Moreover, the peak at 1371 cm^{-1} may be associated to the C–C bond stretch.

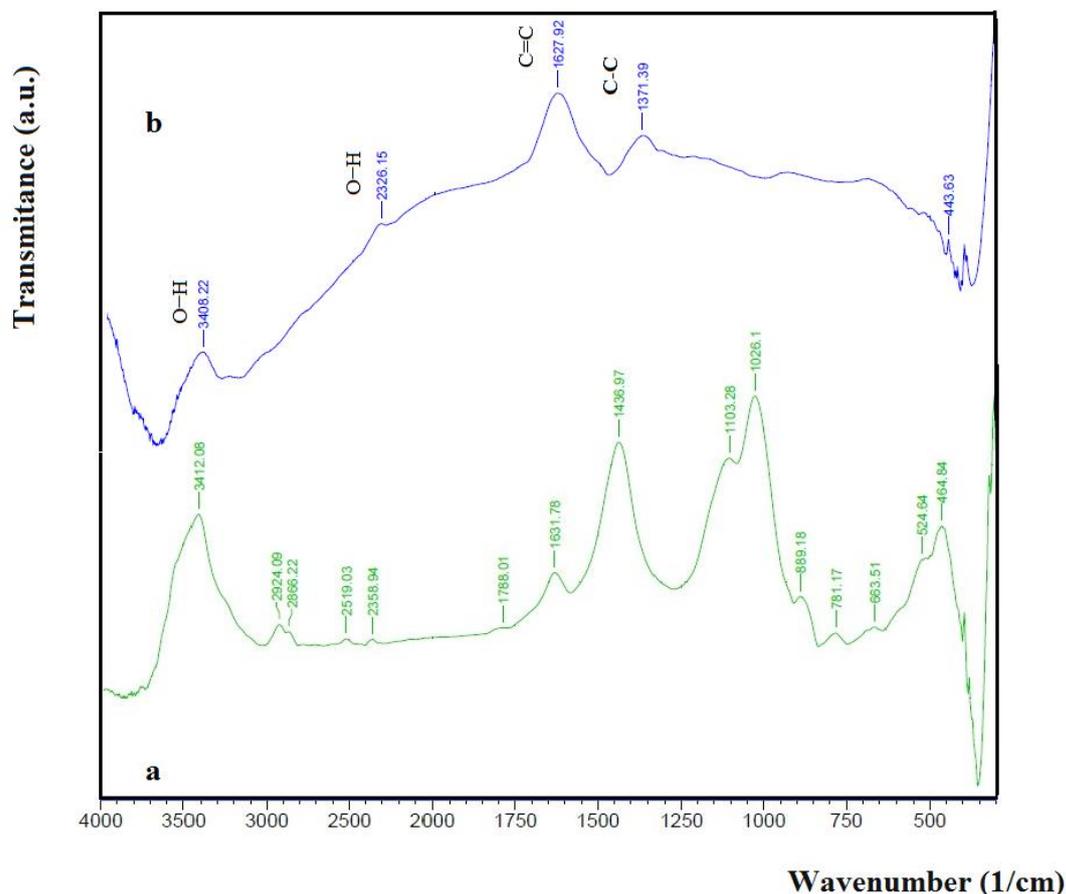


Figure (3) FTIR spectrum for as-synthesized (a) and Functionalized MWCNTs (b).

X-Ray Diffraction Patterns

Figure (4) shows the x-ray diffraction patterns of **as-synthesized** and **functionalized** MWCNTs. As described in the previous works [10, 11], the significant diffraction pattern of as-synthesized MWCNTs is appeared at 2θ of 26° . The 2θ peaks is corresponded to (002) reflection planes or also known as interlayered spacing between adjacent graphite layers, respectively. The (002) reflection peaks was observed at the same 2θ values in both as-synthesized and functionalized MWCNTs diffractions. Interestingly, the intensity of diffraction peak at (002) in acid functionalized MWCNTs was increased as compared to the raw-MWCNTs ($I_r=204$, $I_f=279$) this is an indication of the loosely of the carbon nanotubes floss after the acid treatment and form more ordered CNTs floss in the functionalized MWCNTs.

Furthermore, from XRD patterns of the functionalized MWCNTs samples, it is shows that the XRD patterns are similar to the as-synthesized MWCNTs. From XRD patterns, it can be conclude that functionalized MWCNTs is still had same cylinder wall structure and inter plannar spacing after the functionalization process. Thus, the structure of MWCNTs is protected even after undergone the treatment as confirmed from XRD analysis previously [3].

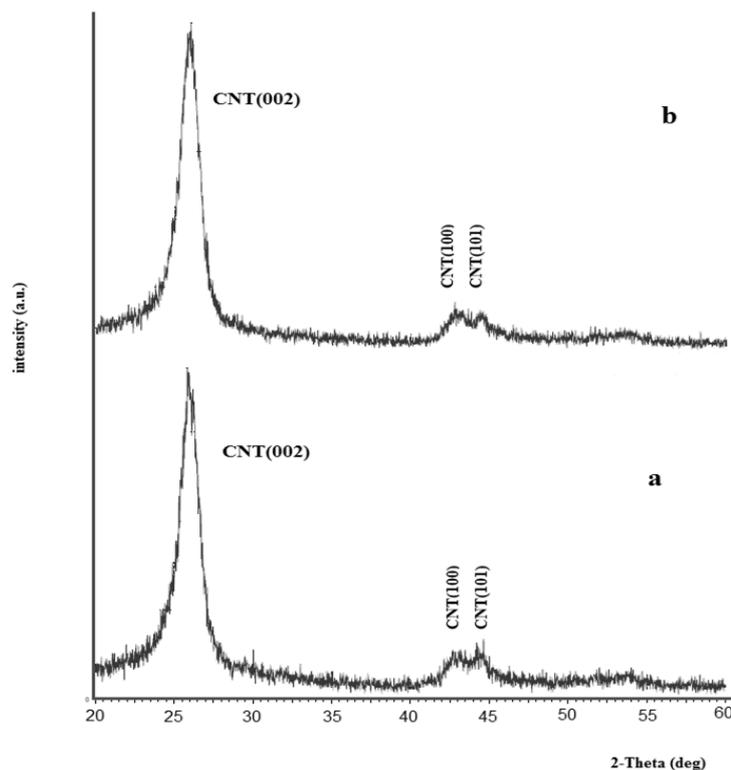


Figure (4) XRD patterns for raw (a) and functionalized MWCNTs (b).

Dispersion Test

The presence of functional groups on the CNT surface can be identified by different means. Among them, the time required for the CNTs to sediment in a polar solvent (ethanol) is a common technique since it is fast, cheap and provides qualitative information. Figure (5a,b) shows photographs of the CNTs\ in ethanol solutions (99%) 72h after sonication 5min [5].

From the observation Figure (5a,b), it shows that the functionalized MWCNTs remained as stable suspension in the ethanol after one week as compared to the as synthesized(raw- MWCNTs), which give unstable suspension after 15min.

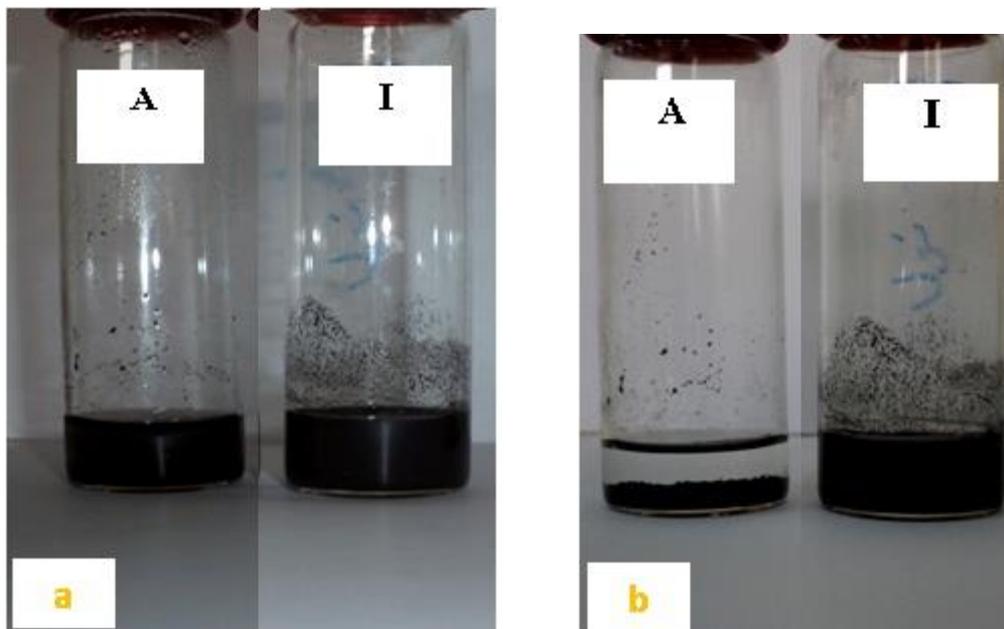


Figure (5) Photograph of MWCNTs in ethanol for : as-synthesized after 15min (a) and functionalized MWCNTs after one week (b).

As the results shows from the dispersion test of MWCNTs in ethanol solutions, stable colloidal form of functionalized MWCNTs dispersion is feasible to obtain due to the presence of functional (COOH, -OH) groups on the surface of the carbon nanotubes led to a reduction of van der Waals interactions among them which promotes their separation and dispersion in ethanol as compared with as-synthesized MWCNTs.

On the other hands, the sonication technique applies during the functionalization, as well as in the dispersion process also gave energetic effect in getting the MWCNTs bundles to start loose [3].

CONCLUSIONS

Functionalized MWCNTs were obtained through treating MWCNTs with chemical oxidation method. Well dispersed MWCNTs were obtained after functionalization due to the generated of the (OH, C=O, and COOH) groups on the surface of the carbon nanotubes. The presences of functional groups on the outer-wall of MWCNTs were successfully form hydrogen bonds with ethanol solutions after sonication 5min. The advantage of sonication method is the simple and easy way for the functionalization of MWCNTs in the acid treatment without severe structure destruction of MWCNTs. Furthermore, stable colloidal system of functionalized MWCNTs has achieved, thus confirmed the effectiveness of this method to disperse MWCNTs.

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