Purification Techniques for Cheap Multi–Walled Carbon Nanotubes

Ahmed. M. Abbas2, Firas H. Abdulrazzak1, Israa M. Radhi2, Ahmed I. AbdulLatif1, Takialdin A. Himdan2, Falah H. Hussein3, 4

1Chemistry Department, College of education for pure science, Diyala University, Diyala, Iraq
2Chemistry Department, College of education for pure science Ibn al-Haytham, University of Baghdad, Baghdad, Iraq
3Pharmaceutics Department, College of Pharmacy, Babylon University, Hilla, Iraq
4Al-Mustaqbal University College, Najaf, Iraq

Abstract. Multi-walled carbon nanotubes from cheap tubes company MWCNT-CP were purified by alcohol / H2O2 / separation funnel which is simple, easy and scalable techniques. The steps of purification were characterized by X-ray diffraction, Raman spectroscopy, scanning electron microscopy SEM with energy dispersive of X-ray spectroscopy EDX and surface area measurements. The technique was succeeded to remove most the trace element from MWCNT-CP which causing increase the surface area. The ratios of impurities were reduced to less 0.6% after treatment by three steps with losing less than 5% from MWCNT-CP.

Keywords. Cheap tube, Separation funnel, H2O2, surface area, EDX.

1. Introduction
Since the reported literature of carbon nanotubes CNTs by Lijima [1] huge efforts were done towards benefited from extraordinary physiochemical properties [2]. The specific behavior of CNTs can be related to amazing structure with hybridization and verities, in types which could be single SWCNT, double DWCNT, few FWCNT, and multi walled carbon nanotubes MWCNT [3]. CNTs can synthesize by different techniques [4] such fragment flam deposing FFD, chemical vapour deposing CVD, laser ablation LA, and arc discharge AD [4]. Generally the process of synthesized CNTs produces many impurities from many sources, such the substrate of precipitation, catalyst, unconverted carbon and the method of purification [4]. The abilities for using CNTs in any applications influence and limit with electrical properties, number of walled with nature of the surface and ratios of impurities [4, 5]. The impurities [6] could be unconverted carbon, adsorbs liquids, remaining of support and metals, which used as active sites for precipitation. The impurities may reduce or increase specific properties of CNTs thus the sensitivity and selectivity should be varied. For example, electrical applications influence with purities of CNTs such cationic or anionic species causing change the sensitivity of carbon nanotubes when the fabrication of sensors for different molecules [7]. Many strategies were depending to remove
the impurities from the product such using strong oxidant agent [8] or high temperature [9]. All methods succeed to remove the impurities or at least most of impurities, but the bad news [10] is higher ratios of CNTs will be damaged by these methods. Thus the strategies were trying to reduce the influence of strong reagent and high temperature. The common ways [11] used dilute solutions from that reagent with lowering the temperature and looking for new materials with new instruments for this purpose. The developers did not solve all the problems for purifications because there is a trace element which still with CNTs, thus we still needed for more methods for more activity. In this work MWCNTs produce from a cheap tub company by CVDs which include Mo, Co and carbonaceous materials such amorphous carbon, and Nano capsules as impurities were purified. The methods of purification depend on oxidation/separation technique to eliminate the impurities. The purification process includes two sections which analyzed by X-ray diffraction XRD, Raman spectroscopy, scanning electron microscopy SEM and surface area measurements.

2. Materials and Method
Multi-walled carbon nanotubes MWCNTs were purchased from cheap tube Inc., USA, the product specifications, refer that MWCNTs was fabricated by chemical vapor deposition. Hydrogen peroxide was supplied from Barcelona, Spain with 30% percent weight and Ethanol (99.85%) from Hyman, England. The method of purification actually represents modified for our works in this field [12, 13] which include two sections as shown in Figure 1 and 2: the first with methanol, while the second with hydrogen peroxide. The first section was dispersed MWCNT-CP in 100ml of methanol with stirring for 2h., after that filtration and washing the product with distilled water then thermal treatment at 90°C for 4h. The second section includes five steps: (1) treatment the MWCNT-CP which produce from the first section with 100ml of H2O2 at 20°C with stirring for 2h., (2) allowed for the mixture to reach for room temperature with stirring. (3) Shaking the product by separation funnel for 15 min., then allowed to separate the mixture. (4) The precipitation was shaking with 100ml of distil water before thermal treatment at 90°C (A). (5) The solution which produces from step 3 was diluted with 75 ml of distilled water than complete the treatments as step 4 (A). Both steps 4 and 5 were produce black suspension (B) on the float of solution which represent the impurities of the sample. Step 4 and 5 were repeat twice with the same conditions to produce MWCNT-CP after purification.

Figure 1. Treatment of MWCNT-CP with H2O2 when (A) refer to mixture before shaking and (B) the mixture after shaking.
3. Results and Discussion

A (Riga Rotalflex) (RU-200B) X-ray diffractometer was used to analysis the crystallography of MWCNTs using Cu Kα radiation for 0.15405 nm, between 5° -75° with a scan rate of 5°/min and the resolution 0.02°. Sentara infinity 1 Broker was used to analysis Raman spectroscopy at 530 nm, light leaser with intensity 2m W for 5 lops per 2s and resolution equal to 3-5 cm. Scanning electron microscopy SEM measurements were carried out on a JEOL JSM-6700F and energy dispersive X-ray spectroscopy EDX were performed at 200 kV with an ultrahigh resolution pole piece 4 μm. The Micromeritics ASAP 2020 was used with apply The Brunauer–Emmett–Teller (BET) to measure surface area. Preliminary analysis for MWCNT-CP were done by XRD analysis, which shown in Figure3 with five peaks at 16.4°, 25.7°, 44.3°, 44.7°, 64.4° and 77.9°. The first peak referred to the graphite structure of planar orientation [14] while the two peaks at 25.7° and 44.3° were related to the tubular structure of Nano carbon [15]. The peaks at 44.7° and 77.9° [16] were related to Molybdenum and 64.4° for Co [17] mostly use as catalyst for precipitation MWCNT. Figure 3 shows that ethanol did not cause change in morphology of MWCNT-CP, just limited to increase the intensities of the two peaks of CNTs as compared with impurities.
The XRD analysis for the sample after treatment with second section were reported in Figure 4, which shows clear change for all peaks. The two characterized peaks of MWCNTs raises with high intensity while the peaks of impurities were removed and some of them disappear. The impurities of MWCNT-CP were signed with C and can be seen in the upper part of Figure 4, which shows high intensity for Mo, Co and remaining carbon.

Figure 5 refers to Raman spectroscopy for all samples in all the steps of purification. The two characteristic peaks of MWNTs show higher intensity for G band at 1585 cm⁻¹ with increasing purities as compare with D band at 1340 cm⁻¹. Increase the intensity of the G band refer to high graphitic for the surface which cleaned after purification. The SEM images in Figure 6 for the MWCNT-CP with diameter 35nm to 90 nm while the average of length 1.3 μm- 2.8 μm.
Figure 5. Raman spectroscopy for MWCNT-CP after treatment with ethanol then H₂O₂ for one times, twice and impurities of MWCNT-CP

Figure 6. SEM images for MWCNT from cheap tube

Figure 7. EDX analysis for MWCNT-CP before purification
Figure 7 and 8, refer to EDX analysis for MWCNT-CP before and after treatment with ethanol respectively when shows removed 1.4% of the element from the sample which may adsorb on outer and end of the tubes. After treatment by hydrogen peroxide in stirring then two times with separation funnel the EDX analysis in Figure 9, for MWCNT-CP were succeed to remove 95% from Mo and Co. Figure 10, refer to EDX analysis for suspension (B) that floated which consist of carbon materials with MWCNT-CP whom responsible to remove many species of impurities mostly by adsorption [18]. The surface area for the samples through the purification process were measured which shows 449.381 m²/g for MWCNT-CP before purification. After purification the sample shows 346.908 m²/g after one treatment with H₂O₂ while the value reduces to 317.537 m²/g after twice treatment with H₂O₂. The surprised result was the value of surface area for remains materials with high ratios of impurities when shows 620.240 m²/g. The mases of samples after every steps were measured which refer to reduce the impurities for less 0.6% with losing 5% from MWCNT-CP when used this techniques.

Figure 8. EDX analysis for MWCNT-CP after treatment with ethanol

Figure 9. EDX analysis for MWCNT-CP after the process of purification
4. Conclusion
Purification techniques by oxidation/separation method were succeed to make cheap Multi-Walled Carbon Nanotubes more purified. The efficiency of method is supported by experimental analysis of the Raman spectrum, SEM, EDX and surface area. The evidence confirms that MWCNT-CP were become more purified when treated with C2H5OH/H2O2/separation due to remove the impurities from the sample. Methanol played important roles when removed and washed the MWCNTs in the first section. This technique can be used to make purification for most of CNTs which synthesized by different methods.

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