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Research Article

Purification and Functionalization of Carbon Nanotubes Based on Hydrogen Peroxide

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ABSTRACT:
Maybe the purification process represents large challenges towards use *nanomaterial* in huge applications. Therefore, many efforts have focused on finding ways to get methods able to remove all or at least most impurities from synthesized materials. In this work, the purification process was applied on *MWNTs* which synthesized by *CVDs* techniques without a catalyst. The method depends on using three steps which ended by treatment with hydrogen peroxide as oxidant agent to eliminate unconverted carbon and carbonaceous materials which we predicted mainly produce. *XRD* analysis, *SEM* images, and *FTIR* spectrum were used to evaluate the role that could be achieved in all the steps. The method succeeded in removing most of the impurities and make activation for *MWNTs* without any damages.

Keywords: *MWNTs; H_2O_2; XRD; Functionalization; Impurities*

INTRODUCTION:

The most common carbon nanomaterial's after 1991 were [1] carbon nanotubes CNTs, which represent with single SWNTs and multi-walled carbon nanotubes MWNTs. The structure and distinctive geometry enhance the scientists to understand the amazing properties that pioneered the use of implemented applications and encouraged towards new applications. As we reported in our previous work [2-3] the activity of CNTs in various applications influence directly with the percent of impurities and the strategy of purification. Nikolai et al. [4.] mention that as-prepared CNTs mostly include two sources of impurities, metallic and carbonaceous materials. The metallic commonly behave as a catalyst for precipitation while the carbonaceous materials represent unconverted carbonaceous, amorphous and graphitic carbon, fullerenes and carbon onions [5]. The difficulty of purification represents by the similarity of solubility and physical properties of both the CNTs and the carbonaceous materials. The strategy of purification mainly includes chemical and physical methods. The physical method used to remove carbonaceous materials such graphitic sheets and CNTs groups.Salernitano et al. [6] reported that physical methods maintain the *CNTs* installation, while the interference between the groups mostly causes complicate and reduces the activity. Dillon et al.[7] reported that metal catalyst can be removed chemically when treatment with inorganic acids by reflux or thermal treatment which can enhance the purification process. Generally, the chemical method was more efficient than the physical method to separate the impurities from *CNTs* due to carbonaceous materials are oxidized faster than *CNTs*. Hou et al. reported [8] combination of *physiochemical* methods make the separation and oxidation process together more activity to remove the maximum value of impurities with less damage to tubes. The ratios of metal catalysts and carbonaceous impurities influence directly with the techniques of production. Bernier et al. reported that [9.] *CNTs* as-prepared by arc discharge include high quantities with low purity. The common analysis methods that used to evaluate the *purities* of *CNTs* are scanning *SEM* and *t*ransmittance TEM spectroscopy, Thermogravimetric analysis TGA, Raman spectroscopy, and X-ray diffraction XRD. The Images of CNTs samples obtained from SEM and TEM [10] mostly depend on finding the length, diameters, and the impurities for the synthesized CNTs. The TGA [11] can depend on an evaluation the purifier of synthesized carbon nanotubes, the nature of the tubular surfaces, purified and the types of CNTs. Raman spectroscopy [11-13] extensively employed techniques for the characterization, functionalized and compare purifier of carbon nanotubes by comparing the signal intensity and peak shift. Most of the previous techniques were reported to evaluate the impurities of CNTs while XRD patterns rarely used for this matter. In this work, the synthesized CNTs by chemical vapor deposition method were purified using modified method [12] which depend on predicting the impurity by controlling the condition of precipitation without a catalyst. XRD, SEM and FTIR analysis were used to prove and explain the behavior of CNT filaments during the purification process. The process of purification is depended on use H2O2 as oxidant agent when producing OH free radicals and separation funnel as a re-desperation apparatus. The role of H2O2 can be related to easily convert to H2O without any interference with CNTs as compare with HCl, KOH, H2SO4 and either strong acid or base [13].

EXPERIMENT:

A-Materials

MWNTs prepared by modified CVD homemade on the silica surface as support without catalyst with purity around 56% and the diameter ranging between 8 -32 nm were employed in this study. The Hydrogen peroxide H_2O_2 was purchase from Barcelona, Spain in 30% percent weight. Ethanol with purities (99.93%) was supplied from Alfa, Aesar and distilled water were distilled in our laboratories for five times.

B-Purification

Purification of synthesized MWNTs was carried out with three different agents using H_2O, C_2H_5OH, and H_2O_2 which used in three steps respectively. Figure 1 shows the first step which includes 200 mg of as-prepared MWNTs were treated with 100ml of distilling water for 4 times by desperation with an ultrasonic water bath. In the first step, most of the unconverted carbon will convert to a black solution which removed from the mixture. The second step as shown in figure 2, ethanol alcohol (50 ml) was re-distribute using separation funnel for 15 min which re-uses it for 3 times. Figure 3 represent the third step when re-distribute the product from second step in 100 ml of H_2O_2 at 15° C for 12h with stirring by the magnetic stirrer. The solution allowed to reach room temperature, then heating gradually to 50∘C until complete dissociation most of the hydrogen peroxide. Finally, the sample was filtered and washed with distilled water then dried at 80∘ C for 12h.

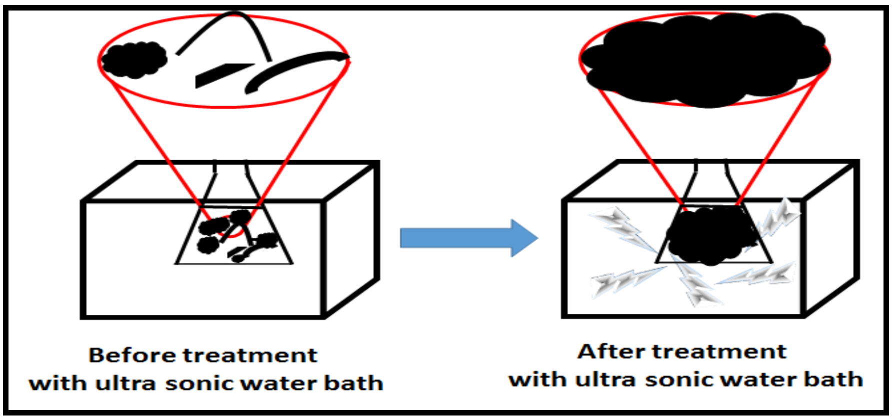

Figure 1: Experiment setup and treatment for ultrasonic water bath with CNTs solution

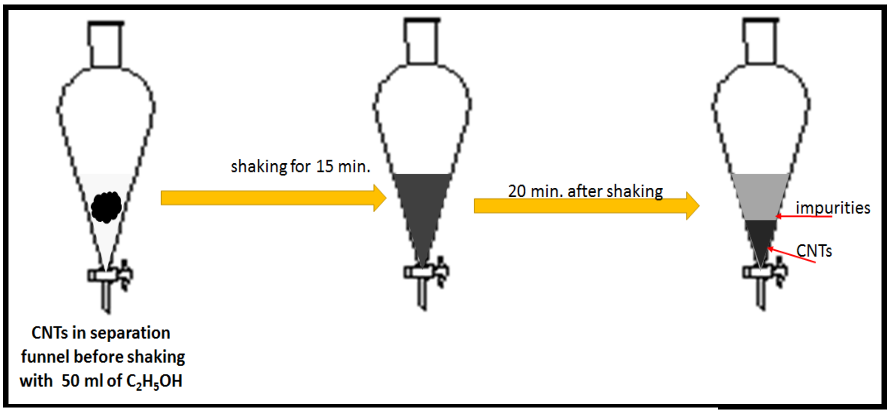

Figure 2: Schematic diagram of treatment ***CNTs*** with ethanol by separation funnel

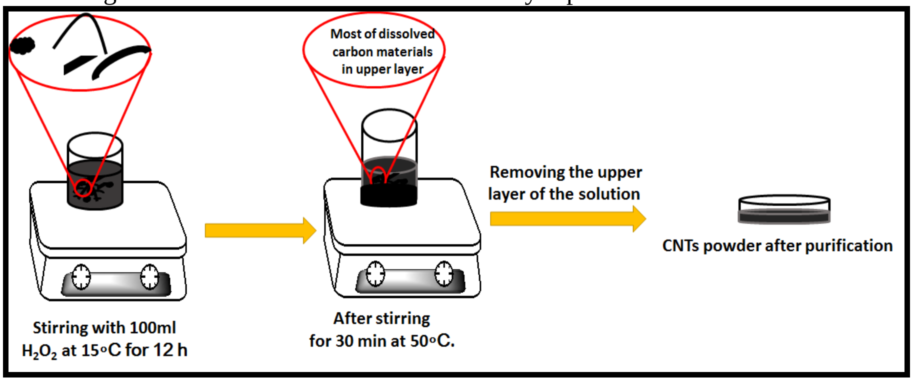

Figure 3: Schematic diagram of treatment CNTs with H2O2 by magnetic stirrer at 15∘C for 12h.

The XRD diffracted patterns were collected at Ni-filtered Cu Kα radiation with 40 kV, 40mA) by (RigakuRotalflex) (RU-200B). To make images for filaments of carbon, field emission scanning electron microscopy (FESEM) measurements were carried out on a JEOL JSM-6700F field emission instrument using a secondary electron detector (SE) at an accelerating voltage of 2 kV. Fourier transfer infrared (FT-IR) spectra were collected on a Shimadzu IRAffinity-1 FTIR Spectrophotometer with a resolution of 4 cm^{-1} and scanned from (400 to 4000) cm^{-1}.

RESULTS AND DISCUSSION:

The as-prepared CNTs in this work of consist of a mixture of MWNTs, and impurities which mostly represent by amorphous carbon, graphite, and unconverted carbon. Actually, the predicted in impurities can be related to conditions of precipitation which made on the support without using a catalyst such as Fe, Mo, Co, or Ni. all the schemes in Figure 4 (a - d) shows two characteristic interlayer spacing of CNTs. The first at $2\theta \approx 25.5$⍰ for C(200) plane, When compared to normal graphite at $2\theta = 26.5$⍰, this peak downward shift due to an increase in the sp2; C=C layers spacing [13-14]. The second peaks at $2\theta \approx 43$⍰, which can be attributed to the diffraction from the C(001) plane of the carbon nanotubes.

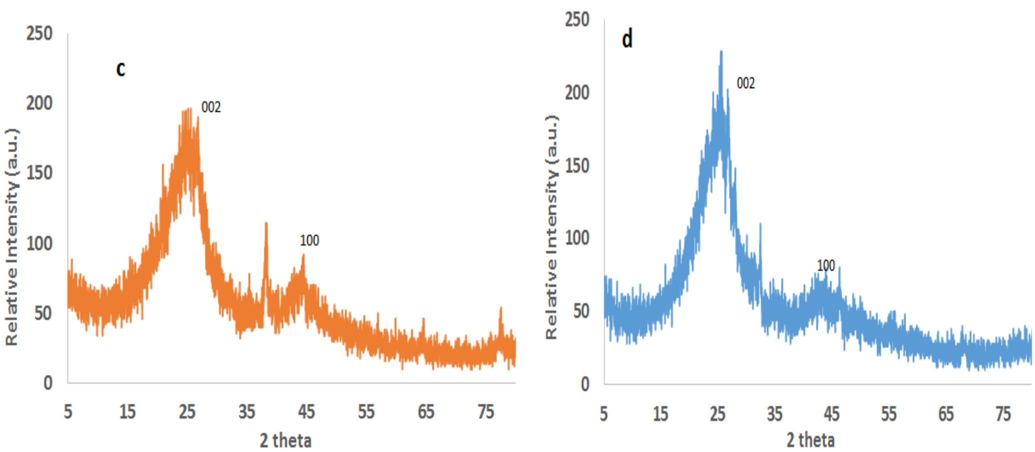

Figure 4: XRD patterns of (a) as prepared MWNTs and after treatment with three steps (b) H_2O (c) C_2H_5OH and (d) H_2O_2.

The existent of these two peaks refer to the graphitic structure of MWNTs which did not destroy during treatment with H2O2 for a long time [15]. The X-ray diffraction patterns were used to determine (D) the average crystallite size (D) estimation with using $2\theta \approx 25$ by the Debye-Scherrer equation [16].

$$D = K\lambda / \beta\cos\theta \qquad (1)$$

Where λ is the X-ray wavelength equal to (0.15405 nm), β is the peak width of the diffraction peak profile at half the maximum height (FWHM) resulting from small crystallite size in radiance, and K is a constant related to the crystallite shape mostly equal to 0.9.

The value of the interplanar spacing between the layers of the tubular structure (d) was calculated using Bragg's Law as shown in equation 2 and 3 [17-18] when n=1 refer to an integral number for the order of scattering light.

$$2d\sin\theta = n\lambda \qquad (2)$$

$$d = \lambda / 2\sin\theta \qquad (3)$$

Table 1, listed the parameters that calculated from equations one and three by using 2theta and the width of the peaks which include particle size and interplaner spacing.

Table 1: Summary of characterized XRD peaks at about 25°, FWHM, particle size D and interplanar spacing d.

Samples	2 theta°	FWHM= β (nm)	D (nm)	d (nm)
As-prepared MWNTs	25.0	0.030	4.68	0.36
H_2O+MWNTs	25.2	0.031	4.53	0.35
C_2H_5OH+MWNTs	25.2	0.031	4.68	0.35
H_2O_2+MWNTs	25.7	0.036	3.94	0.35

From figure 4a to 4d the intensity of second peaks at $2\theta \approx 43$ was decreasing after each treatment which refers to increase the purities during the steps of purification. This result agrees with Rasel et al.[15] and Peng et al. [17] explained decreases the intensity of this speaks to all parts of MWNTs were absolutely parallel to the 002 plane.

The effect of impurities and unconverted carbonaceous materials represent [18] by increasing the roughness on the surfaces of the tubular structure. Therefore the intensity of plane 100 was $2.03 < 3.19 < 4.5 < 5.01$ for H_2O_2, C_2H_5OH, as prepared MWNT, and MWCNTs treated with H_2O respectively.

This refers to H_2O_2 treated MWCNT after two steps of eliminations the impurities had complete elimination most of the impurities as compared to as prepared MWNTs. The maximum value of plane intensity for MWNTs with distilled water as shown in figure 4b which may related to remaining carbonaceous materials that cover most the surfaces of the tubular structure.

The SEM images in figure 5, shows as-prepared CNTs were entangled with amorphous carbon, carbon nanoparticles or unconverted carbon. The images show many agglomerates with high length reach to 2 µm that can be related to many carbonaceous materials forming the large groups. After purification process within three steps, the image of SEM shows clearer of filaments MWNTs as shown in figure 6.

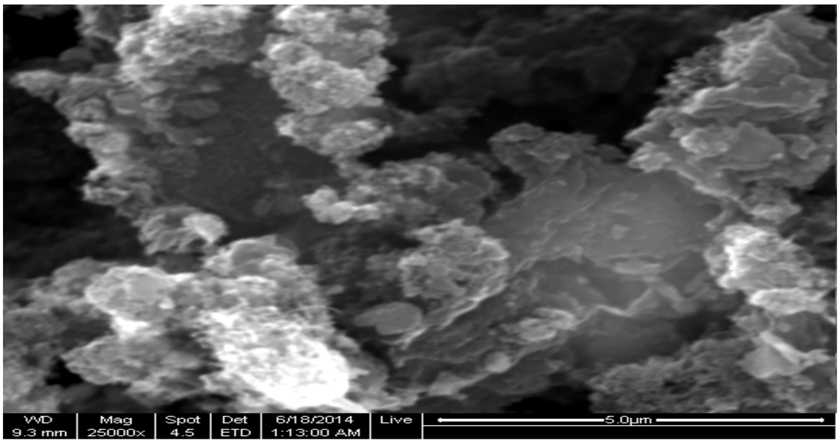

Figure 5: SEM images for as-prepared MWNTs.

In this work, we predict the unconverted carbon represent the main byproduct thus we will depend on use H_2O_2 for many reasons. The first, as compare[19-20] with strong acid or base H_2O_2 did not cause any damage to the tubular structure, in addition, did not produce salts as Cl^-, NO_3^- and SO_4^{-2} which most difficult to remove from solution. The second all the H_2O_2 will convert to H_2O and O_2 gas without any process to remove from solution or CNTs.

The SEM images in figure 6, for the MWNTs after purification shows, remove most of the impurities from the sample which can be referred to succeed the methods of purification.

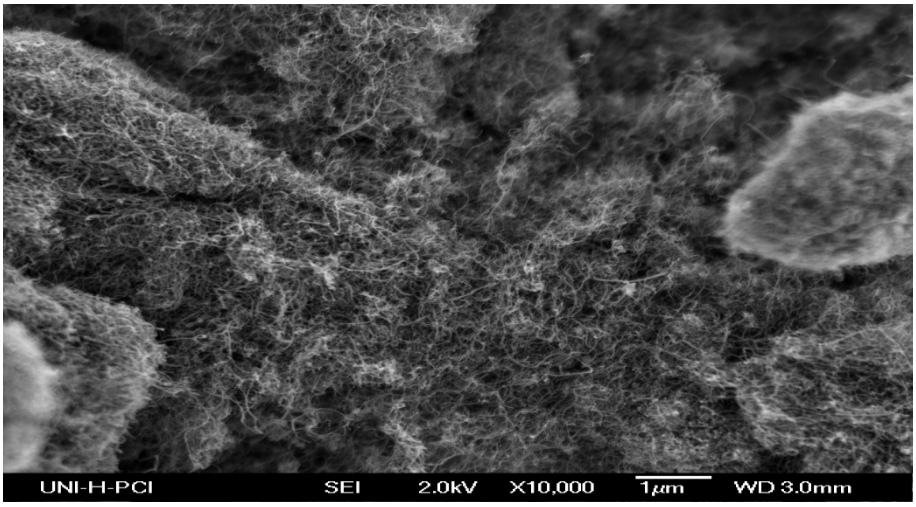

Figure 6: SEM images for MWNTs after purification with three steps.

The FTIR spectra for as prepared MWNTs and after purification with three steps are represented in Figure 7. Many weak [20] peaks that appeared in 1500–3500 cm−1 region in as-prepared MWNTs as shown in figure 7 mostly can be attributed to impurities. After every step of purification, the week peaks were reduced until reach the third step of purification which disappear completely. Figure 8, shows a peak at 3359 cm−1 was assigned to the stretching vibration of hydrogen bonded OH [20] which clear when treated the sample with alcohol and hydrogen peroxide. The intensity of this band was significantly increased and broadened when translating from steps (with C_2H_5OH) to step 3 (with H_2O_2) of purification with H2O2. Indicating the formation of huge –OH groups upon chemical treatments [21]. The peak at 2830 cm−1 which was related to an effect of H2O2 and C_2H_5OH with MWCNTs was assigned to C-H for two types of hybridizations sp2 and sp3 C–H [22]. The peak at 1680 -1650 cm−1 was due to the stretching vibration of C=C [23] and C=O of quinone [24.] that was created on MWCNT surfaces from C_2H_5OH and H_2O_2. The MWNTs after purification include many functional groups such as hydroxyl,carbonyl, and epoxide which represent a perfect active site for many reactions and activities.

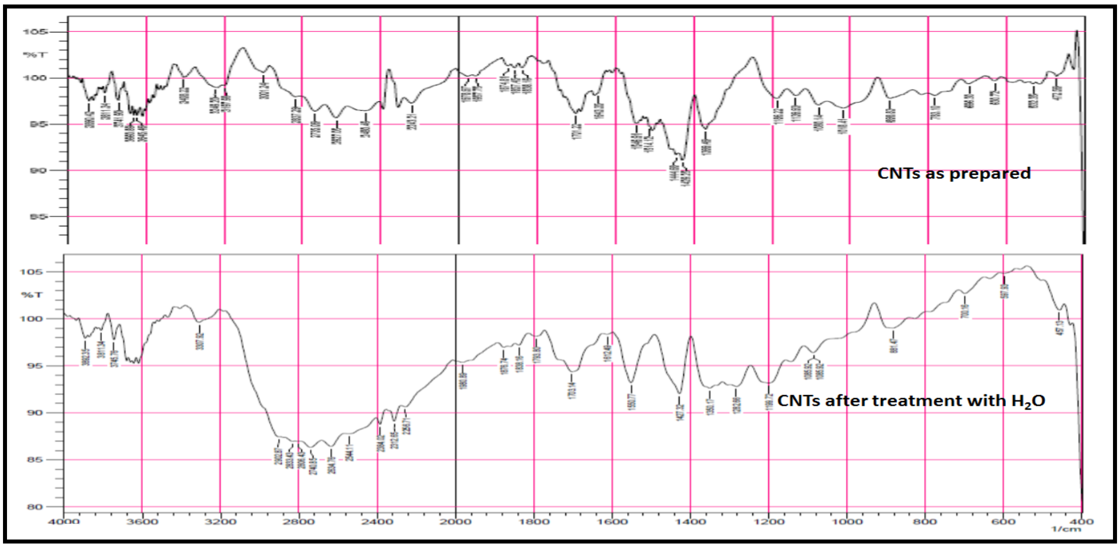

Figure 7: FTIR spectrum for as prepared MWNTs and after treatment with distilled water (first step of purification).

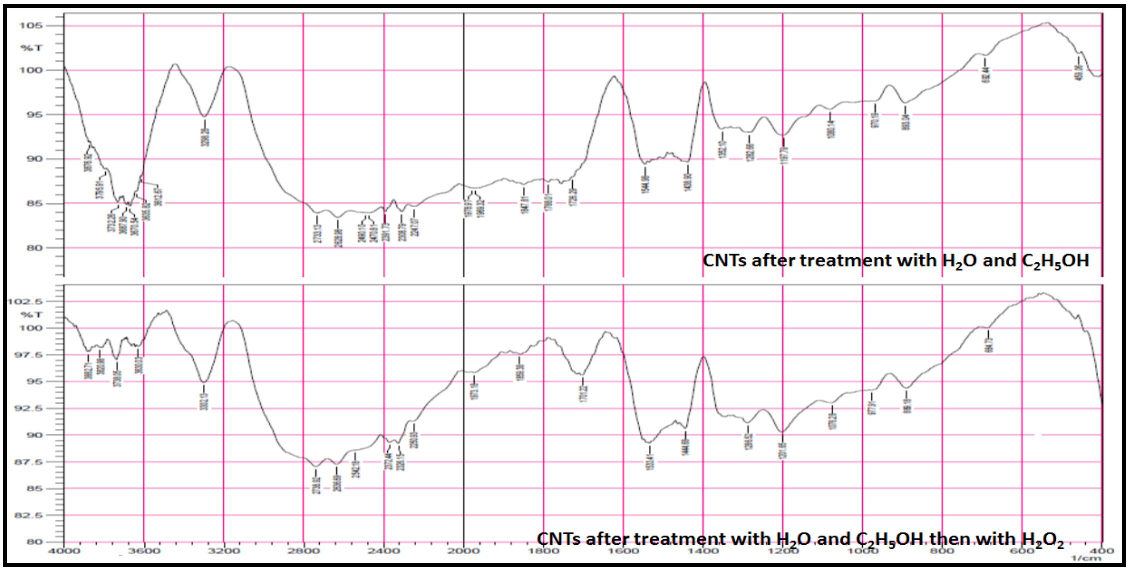

Figure 8:FTIR spectrum for MWNTs after treatment with C_2H_5OH then with H_2O_2 (second and third steps of purification).

CONCLUSION:

The limitations of using carbon nanotubes in many applications represent by the abilities to remove the impurities from the product. The specific strategy of purification was applied successfully to enhance the purities of the product. The first two steps with H_2O and C_2H_5OH eliminate many carbonaceous materials which could be dissolved or make a colloidal solution without precipitation in solution. The third step with H2O2 completes the most important effect when removing many interferences materials which detected by XRD analysis. The images of SEM and XRD analysis shows the change in particle size and interlayer spacing for MWNTs in three steps of purification. The FTIR transmission spectrum prove that process of purification in exist of H_2O_2 were succeeding in make activation the MWNTs as shown with hydroxyl and carbonyl group.

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