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Preparation and Characterization of Multiwall Carbon Nanotubes Decorated with Copper Oxide

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Abstract

Multi-walled carbon nanotubes (MWCNTs) are special form of carbon nano materials with amazing applications in many areas of research.MWCNTs were synthesized by anAtmospheric Chemical Vapor Deposition (ACVD) system then decorated on their surface with Copper Oxide (CuO) nanoparticles via the hydrothermal method. The prepared un-purifiedMWCNTs and purified MWCNTs were characterized by High Resolution Transmittance Electron Microscope (HRTEM), Xray Diffraction (XRD) and Raman spectroscopy. As well as the CuO/MWCNTs nanocomposite was characterized by HRTEM, XRD, Fourier Transform Infra-Red Spectroscopy (FTIR), Thermogravimetric Analysis (TGA) Differential Thermal Analysis (DTA) and Raman spectroscopy. The results demonstrated the distribution of CuO nano particles on the surface of MWCNTs as well as the particle size, which was around 43 nm. The prepared nanocomposite has high thermal stability with adequate well quality. The combination of CuO nanoparticles and MWCNTs gives rise to the production ofa new composite with a wide range of applications.

Keywords: MWCNTs, CuO, Nanocomposite, TGA and XRD.

1. Introduction

In recent years, carbon nanotubes(CNTs)have become an interesting topic of scientific research due to their excellent remarkable properties of mechanical, electrical, chemical, and physical properties, as well as their high thermal stability and high surface area. These unique properties have directed CNTs toward a wide range of applications in several fields of nanoscience and nanotechnology[1-3]. MWCNTs are considered a concentric assembly series of (n) single wall carbon nanotubes(SWCNTs) where (n) higher than 2 and there is no limitation for the higher value [4,5].Arc discharge, laser ablation, and chemical vapor deposition (CVD) are the three main methods for producing CNTs [6,7]. CVD seems to be the most suitable method for industrial use due toitshigh yield, high quality with different specific properties, and relatively low temperature unlike other techniques. In addition,the CVD method offers aneasy fabrication scale that harvests CNTs in different forms and shapes (powder, film, coiled, andstraight) [8]. Synthesizing process of CNTsvia CVD depends on the pyrolysis of hydrocarbon sources over acatalyst for the deposition of carbon cloud in a certain site in the furnace tube [9]. Since most of synthesizing methods of CNTs produce lotsof impurities such as amorphous carbons, graphitic carbon, fullerenes, carbon onions and catalyst metals, the applications of CNTs depend on their purity [10]. Several techniques havebeen evolved for CNTs purification. Chemical purification techniques introduced oxygenated function groups such as carboxylic groups (-COOH) which is taken into consideration as serving the chemistry surface of nanotubes [11].The catalyst particles can beremoved by chemical purification during treatment with

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inorganic strongacids via refluxing or thermal treatment, which enhances the purification process [12]. Functionalization process plays an important role which facilitating loading nanoparticles on the CNTs surface and permits formation of several chemical function groups on CNTs surface [13,14]. Recently, researchers used molecular modelling to study theoretically the structure and properties of carbon nanomaterials. They are applying molecular modelling to understand the structure and behaviour of functionalization on nanotubes that lead to the well and suitable applications in many areas of research [15,16].

The combination of (CNTs) and nano particles (CNTs/NPs) leads to a successful integration of the properties of the two components in a new variety of applications [17,18]. The new composite (CNTs/NPs) has extraordinary new properties which combine the dual unique properties of CNTs and NPs. Meanwhile, the combination occurs by covalent or non-covalent bonds between the CNT surface and the covered nanoparticles(NPs)[17].Thiscombination might be obtained by attaching NPs of metals (Ag, Au, Pt, Pd, Rh, etc.) to the external surface of CNTs [19]. Metal oxides (MOs) nanoparticles are also the most important and interesting class of material science. These MOs are formed on the CNTs surface as continuous amorphous, single crystalline films with discrete thickness and with different shapes and sizes such as nanorod, nanowire, etc [20].

Serious researchhas been developed to study the interactions of different MOs with CNTs surface. Mesoporous peapodswere designedas Co_3O_4/CNT electrode by using a controllable nano casting process. The new material offers high specific capacity, cyclic performance, and excellent rate capacity [21]. Researchersprepared a nanocomposite from ZnO/MWCNTs by using simple chemical methods during dip and dry process and by applying ionic layer reaction and adsorption. The electrochemical analysis of ZnO/MWCNTs showed the nanocomposite represented a good electrode for charge storage application [22].Synthesized MWCNTs decorated with zinc oxide (ZnO) by using simplewet chemical route methods. They obtained ZnO with anaverage size of 30 nm and it has a high purity without any impurities [23].CuO is P- type semiconductor that has band gap energy (1.2-1.7 eV). CuO is characterized by high chemical stability, easy synthesizing from several sources, low cost, nontoxic, and has a photocatalytic property. The main disadvantage of CuO is that it has a thin band gap, which causes recombination of the photogenerated (electrons-hole pairs) where the holes and electrons come back to each other quickly. The composite CuO/CNTs add interesting electrical, mechanical, chemical, and physical properties which solve numerous defects in pure CuO [24-26]. Khashan et al Studied the preparation and characterization of decorated CNTs with different ratio of CuO nanoparticles by using laser ablation [27]. Yang et al Synthesized MWCNTs with CuO in nano leaves shape as plate form by using chemical precipitation methods. They observed that the nanocomposite has a remarkable property for glucose sensing [28].

In this study, MWCNTs were synthesized by ACVD system that produces a high yield of MWCNTsat a low cost. The MWCNTs were purified and functionalized via concentrated acid treatment. The distribution of CuO nanoparticles on the surface MWCNTs was achieved through the usage of hydrothermal treatment method where the most advantages of hydrothermal treatment method that produce uniform nanoparticles under controlling their size and shape. The prepared samples werecharacterized by different characterization techniques.

2. Experimental

2.1. Materials

Different chemicals and reagents were used for MWCNTssynthesizing, purification and decorations.Cobalt Nitrate hexa hydrate [Co $(NO_3)_2$. $6H_2O$] was purchased from AlphaChemica. Iron Nitrate Nona hydrate [Fe $(NO_3)_2.9H_2O$] was obtained from Guangdong Guangzhou Chemical Factory Co, Ltd. Magnesium Oxide [MgO] with purity of 99% from Prolabo Company. Sulfuric acid [H_2SO_4] was obtained from Scharlau, European Union.Nitric acid [HNO_3]was obtained from Caroler European Union. Cupric acetate monohydrate[$(CH_3COO)_2$ Cu.H_2O] was obtained from LobaChemie. Ethanol [C_2H_5OH] was obtained from Chem-lab and Sodium hydroxide [NaOH] was purchased from Germany, EMD, Millipore corporation.All chemicals and reagents were used as it received without any further purification or treatment.

2.2. Synthesis of Materials

2.2.1. Catalyst Preparation

The bi-metallic Fe-Co Catalyst was prepared by the impregnation method.Firstly;3.62 g of $Fe(NO_3)_2.6H_2O$ and 2.47g of Co $(NO_3)_2.9H_2O$ were dissolved in 50 ml of distilled water then 10g of MgO was added slowly under continuous stirring for 1 h at room temperature.Subsequently the mixture was drying at 120ºC for 2 h. Eventually; the resultant catalyst was calcinated at 550ºC.

2.2.2. MWCNTs Synthesizing

MWCNTs were synthesized by using an APCVD system. The APCVD system consist of various tools, gas cylinders, and instruments, that were being carefully connected to each other to achieve safe and perfect operation. In a typical run, 0.5 g offresh catalyst was placed inside the middle of reaction chamber. The furnace temperature was set at 750 º C,

meantime thenitrogen was allowed to flow at a rate of 30ml/min. Once the required temperature is reached, acetylene gas is allowed to flow at a rate of 200 ml/min.The MWCNTs weredeposited over catalytic particles for 30 min.Eventually, the Acetylene flow was interrupted, while keepingnitrogento flow continuously upon cooling to room temperature. The deposited carbonaceous material on the walls of quartz tube as a thin black film was collected.

2.2.3. MWCNTs Purification andFunctionalization

1 g of un-purifiedMWCNTs were refluxed in 150ml of 3:1 mixture of concentrated HNO_3 and H_2SO_4 solution, then sonicated in a water bath for 30 min. Subsequently,the mixture was continuously stirred for 2 h at 200ºC, then left in the concentrated acid mixture at ambient conditions for additional 24 h. Thoroughlywashed with distilled water several timesuntil neutralization, then dried at 70°C for 24 h.

2.2.4. Synthesizing CuO/MWCNTs Nanocomposite:

The CuO NPs were grafted onto the external surface of MWCNTs by hydrothermal route. Two solutions were prepared separately and mixed then transferred to hydrothermal cell.40 mg of MWCNTswere suspended in 50 ml absolute ethanol viaultrasonicfor 30 min. a 300 mg of cupric acetate was dissolved in50 ml ethanolat room temperature. The MWCNTssuspensionwaspoured on cupric acetate solutionthen allowed to stir for an additional 1h. The second solution is an oxidizer, containing 100 gm of NaOH in 50ml ofdistilled water was added drop by drop to the above solution undercontinuous stirring for 4 h. Finally, the mixture was transferred toa 50ml Teflon-lined sealed stainless-steel autoclave and maintained at 150ºC under autogenous pressure for4 h. The autoclave was cooled down naturally to room temperature,then washed thoroughly and calcinated at 350ºC for 2 h.

2.3. Characterization Techniques

The shape and size of un-purified, purified MWCNTs and CuO/MWCNTs nanocomposite were studied by HRTEM JEM-2100.

The crystalline structure was determined by XRD diffractometer with a secondary monochromatic wavelength of Cu (λ=1.542Aº) at 45 K.V., 35mA, and scanning speed of 0.02/sec.

Raman spectroscopy has been utilized to observe the structure and to confirm the SP^2 hybridization state in the graphitic structure. The spectra were collected by (Bruker SENTERRA) with a (ND-YAG) laser source and with a wavelength of 532nm.

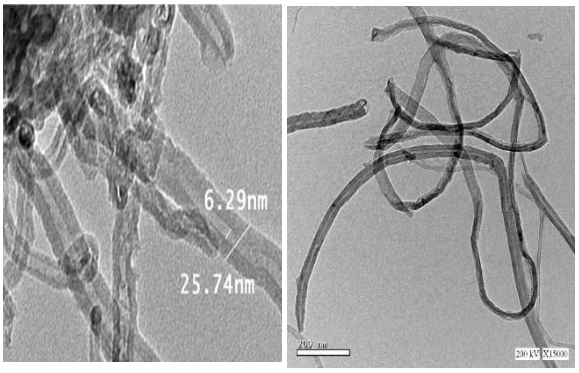
Also, purified MWCNTs and CuO/MWCNTs nanocomposite was examined byTGA-DTA measurements by STDQ-600 thermal analyser from room temperature up to 1000ºC under air atmosphere.

FTIR spectroscopy has been utilized to detect the functional groups on the surface of purified MWCNTs and the functional groups of nanoparticles on the surface ofpurified MWCNTs. The spectra were collected by (FTIR Vertex 70 Bruker optics model device).

Results and Discussion

2.4. MWCNTs Characterization

Figure 1ashows the HRTEM images of un-purified and purified MWCNTs. The HRTEM image of the un-purified MWCNTs shows that some catalyst particles are located at the end cab of MWCNTs. The catalyst particlesappear as a dark spot. The location of the catalyst particlesat the end of the cab suggests that the mechanism of reaction is root growth due to strong interaction between support catalyst (MgO) and metallic particles (Fe_2O_3, CoO) [29].The HRETM micrograph of purified depicted in fig. 1confirmed the hollow core structure of MWCNTs beside that the absence of amorphous carbon is clearly confirmed. The inner and outer diameter of MWCNTs were measured to be 6 nm and 25.7 nm respectively. After the purification process, the dark spots were absent this was due to the elimination of the catalyst particles.



(a) **(b)**

Fig. 1. HRTEM images of MWCNTs; a) before purification and b) after purification.

The XRD patterns of un-purifiedand purified MWCNTs are presented in figure 2. The diffraction peaks at 2θ=26.3ºand 44.7º are indexed to(002) and (100) planes which are attributed to the hexagonal graphite structure. The structure of the MWCNTs has confirmed using XRD measurements.

Whencompared to graphene, MWCNTs have (002) peak which might be weakly and broadened. Thus, asymmetric behaviour may be occurring due to the existence of multiple crystalline samples which consistof at least two crystalline sheets. Also, it is difficult to be isolated individually due to the graphite particles are stacked and wrapped in MWCNTs[30]. Therefore, the diffraction peaks of the XRD pattern of figure 2 confirm the formation of MWCNTs. The XRD pattern of un-purified MWCNTs exhibited sharp peaks at 2θ= 38.3°, 45°, 62.3°, 64.9° and 78°. The diffraction peaks at 38.3°, 45° are indexed to (002) and (101) diffraction planes of MgO respectively. The diffraction peaks at 62.3°, 64.9° are assigned to (214) and (300) diffraction planes iron oxide (Fe_2O_3) respectively. The diffraction peaks at 2θ=78° corresponded to (222) and indicated to the presence of CoO. For purified MWCNTs the diffraction peaks of catalyst particles disappeared due to the purification process using strong acid. The characteristic diffraction peaks corresponding to the (002) plane wasobserved at 2θ=26.3° and 25.9° for un-purified and purified MWCNTs respectively.Thisshift in peak position could be due to the removal of carbon impurities which existed between MWCNTs layers [31]. The XRD results confirm the formation of MWCNTs as proved by HRTEM.

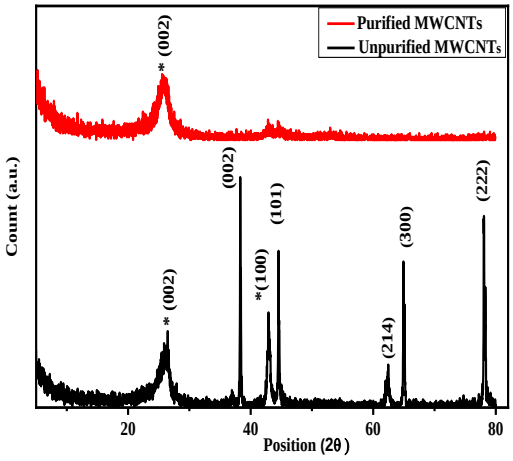


Fig. 2. XRD patterns of purified and un-purified MWCNTs.

The Raman spectra of figure 3 exhibits three Raman shifts for both un-purified and purified MWCNTs. The Raman shifts at 1566cm^{-1}, 1338cm^{-1}, 2677cm^{-1} is related to G, D, 2D bands respectively.The high energy mode is called G band and corresponds to the tangential vibrations of carbon atoms (C=C) which lie at 1566cm^{-1}, this band related to SP^2hybridization of all carbon materials [32]. The G band for purified MWCNTs is sharper and narrower than for un-purified MWCNTs indicating the removal of catalyst particles, which resulted in inducing some defects to the outer surface of MWCNTs [32,33]. The quality and purity of the crystalline structure of MWCNTs is obtained from the ratio of integrated intensities of D band and G bandi.e.I_D/I_G [34]. It was know that, the higher crystalline lattice of nano tubes, the lower I_D/I_G ratio.The I_D/I_G for un-purified and purified MWCNTs sample equal to0.85 and 0.6 respectively.The above mentioned results indicate that the un purified MWCNTs have an inherent defects during their synthesizing. After purification the I_D/I_G decreased, which means that there is an improvement in the quality of the sample. In addition, the good advantage is that it is possible to obtain well purification without damage.

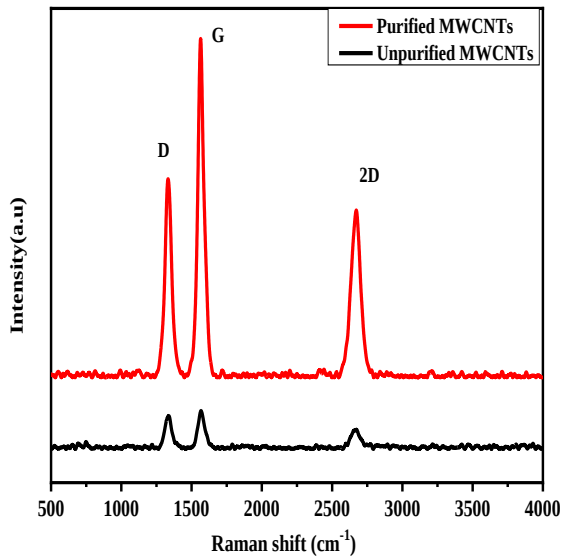


Fig. 3. Raman spectra of purified and un purified MWCNTs.

2.5. Characterization of CuO/MWCNTsNanocomposite

Figure 4 displays the HRTEM images of CuO/MWCNTs. The HRTEM images demonstrated that the CuO nanoparticles are attached to the external surface of MWCNTs. Additionally,CuO nanoparticles are coated on the tubular structure of nanotubes with strong adhesion between the CuO nanoparticles and MWCNTs.

The XRD diffraction pattern of CuO/MWCNTs is presented in figure 5. The diffraction peaks at 2θ=26° and 43.6° are indexed to (002) and (100)planes of MWCNTsrespectivelyas elucidated earlier in fig. 2. The characteristic peaks at 2θ=35.7°, 38.4°,61.3° and 74° are indexed to (-111), (111), (113) and (311) are due to the monoclinic structure of CuO phase[35]. The pattern at 2θ= 44° and 50.9° are corresponding to the cubic phase of Cu [36]. No additional peaks belonging to any impurities were detected in the XRD diffraction patterns demonstrated the high purity of CuO/MWCNTs nanocomposite. The particle size of CuO nanoparticles was estimated by

Debby Scherrer's equation and found to beabout 43 nm [37].

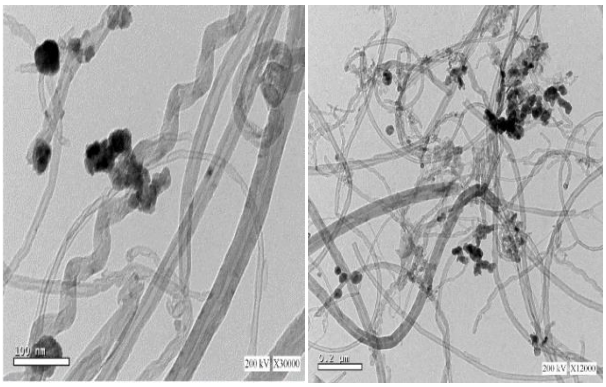


Fig.4. HRTEM images of CuO/MWCNTs nanocomposite.

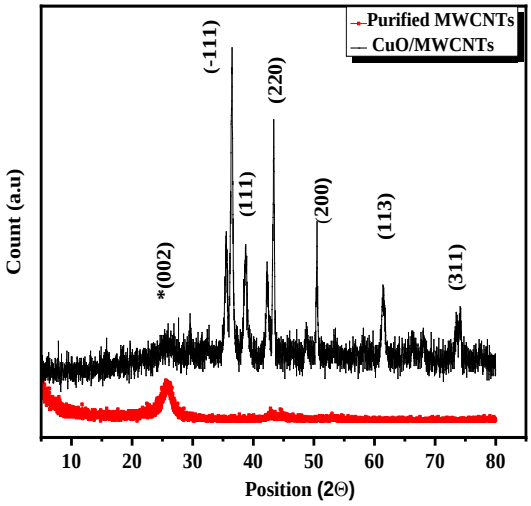


Fig. 5. XRD pattern of CuO/ MWCNTs and purified MWCNTs.

The FTIR spectra of the CuO/MWCNTs nanocomposite confirm the presence of CuO on the surface of MWCNTs as depected in figure 6. The broad band at 3435 cm^{-1} associated with the stretching of –OH group of adsorbed water. The bands at 2858cm^{-1}-2924cm^{-1} are assigend to assymmetric and symmetric stretching vibration of C-H in $–CH_3$ and CH_2 group respectivly. The band at 1628cm^{-1} associated with C=C of SP^2 hypridization in nanotubes ring [38]. The band at 1115-1060cm^{-1} attributed to C-O stretching vibrations in the carboxylic groups[39]. The band at 1714cm^{-1} which refers to C=O in the carboxylic groups and the two bands at 1115cm^{-1}-1060cm^{-1} attributed to C-O. It was recognized that the carboxlic group is removed by the reduction reaction. However, due to the low reduciblity of Cu^+ there are some epoxy group or hydroxy group present on MWCNTs surface which cause an increase in C-O stretching vibration bands. This reason confirms the reduction of MWCNTs by cuprous ions to form CuO nanoparticles [40]. Swamwar NV et al in 2012 confirm that the characteristic peaks of Cu-O appear at 400-600cm^{-1} [41]. In this spectra,the additional observed bands at 447cm^{-1}, 606 cm^{-1} is due the stretching vibration mode of Cu-O in the monoclinc structure of CuO.

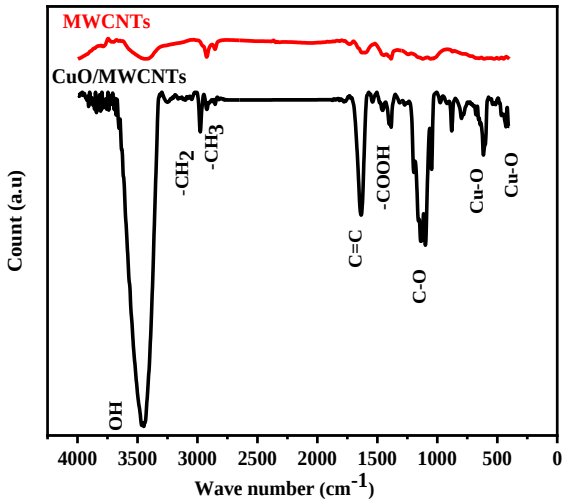


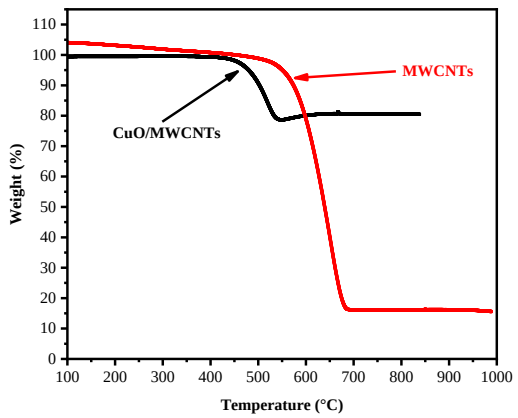
Fig. 6. FT-IR spectra of Purified MWCNTs and CuO/MWCNTs nanocomposite.

The thermal analysis (TGA and DTA) curves of purified MWCNTs and CuO/MWCNTs nanocomposite are presented in figures7a and 7b respectively.

The TGA curve of purified MWCNTs exhibitsaresidual weight due to the presence of somemetallic particles inthe carbon cage or between the inter shell layers of MWCNTs. It is so difficult to remove the metallic particles residuebecause of the graphitic structure is highly resistant to the oxidation process. Therefore, any influence of additional oxidation may cause damageto MWCNTs surface [42]. However, the purified MWCNTs have high purity, high thermal stability, and fewer defects as confirmed earlier by HRTEM and XRD measurements. The DTA thermogramof the purified MWCNTs ischaracterized by an endothermic peak from 532 °C to 711°C.

The TGA curves of the nanocomposite CuO/MWCNTs showed weight loss of about 22% which is attributed to the oxidation of MWCNTs. Theamount of CuO nano particles were estimaied from TGA measurment. The loading ratio was estimated to be 78% of CuO on the surface of MWCNTs . The DTA curve for CuO/MWCNTs showed an endothermic peak at 523 ºC which refers also to the oxidation of MWCNTs. It was shown that the oxidation temperature of MWCNTs was shifted toward lower temperaturemight be because of the catalytic role of CuO, presence of NaOH in solution, and the effect of hydrothermal treatment. The results showed good agreement with HRTEM , XRD and FTIR measurments.

Fig. 7a. TGA curves of purified MWCNTs and CuO/MWCNTs nanocomposite



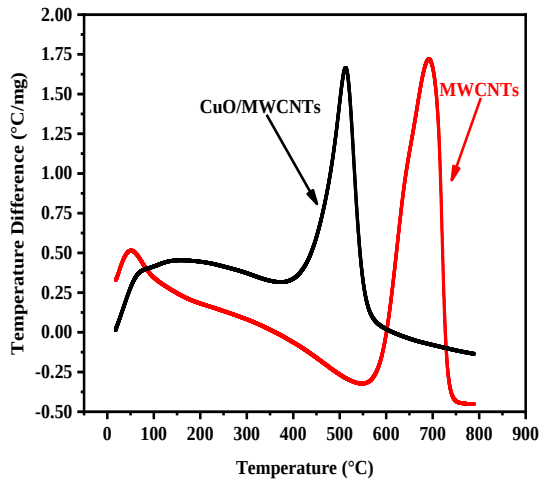


Fig. 7b. DTA curves of purified MWCNTs and CuO/MWCNTs nanocomposite.

The Raman spectra of CuO/MWCNTs is illustrated in figure 8. The Ramanshifts around 1566cm^{-1}, 1338cm^{-1},and 2677cm^{-1} corresponded to G (the graphite band), D (disorder band), and 2D (second order harmonic) bands of MWCNTs respectivly. According to group theory, there are three Raman active modes of CuO, at 228cm^{-1} , 333cm^{-1} and 697cm^{-1} corresponding to one A_g, and two B_g modes which are related to the vibration modes of CuO structure[43]. The I_D/I_G of CuO /MWCNTs is 0.9 which is higher than purified MWCNTs (0.6). This means that there are some defects that affect the graphitic structure of MWCNTs. Increasing D, G intensitiesare related to the partial reduction of MWCNTs when they are decorated with CuO[43, 44, 45, 46].The above results confirm the presence of CuO on MWCNTs surface.

Fig. 8. Raman spectra of CuO/ MWCNTs nanocomposite and purified MWCNTs.

4. Conclusion

In this work, the MWCNTs were synthesized by theAPCVD system. The CuO nano particles were attached to the external surface of MWCNTs via hydrothermal rout. The purified MWCNTs and CuO/MWCNTs nanocomposites were characterized using different techniques including XRD, HRTEM, FTIR, DTA, TGA and Raman. The results obtained by the above-mentioned characterization techniques confirmed the successive functionalization process of MWCNTs where XRD confirms the elimination of the catalytic particles from MWCNTs surface. The FTIR proved the formation of carboxyl groups on the MWCNTs surface. The CuO/MWCNTs nanocomposite was synthesized by hydrothermal rout. The HRTEM demonstrated the presence of CuO nanoparticles on outer surface of MWCNTs. The particle size of CuO was calculated by Debye Scherrer's equation and found to be43nm. The TGA-DTA demonstrated the high thermal stability of nanocomposite. Raman spectra confirm the presence of CuO nanoparticles where the characteristic three modes (A_g,2B_g) of CuO are observed.

5. Conflicts of interest

"There are no conflicts to declare".

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