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Preparation and characterization of multiwall carbon nanotubes decorated with zinc oxide

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ABSTRACT

Multiwall carbon nanotubes MWCNTs were synthesized then decorated with ZnO. The decorated ZnO was grown on the surface of MWCNTs via simple wet chemical route. The prepared MWCNTs/ZnO composite was characterized by X-ray diffraction, EDS, HRTEM, FTIR as well as thermal analysis. Zinc oxide with about 30 nm as confirmed by HRTEM and XRD could be described as wurtzite hexagonal crystalline structure. The HRTEM results showed that the MWCNTs were uniformly decorated with ZnO nanoparticles with nearly no agglomeration. The co-operative behavior between MWCNTs and ZnO gives rise to the production of advanced functional materials with a wide range of applications.

Keywords: MWCNT decoration, Nano metal oxides, HR-TEM and Thermal analysis.

INTRODUCTION

Nanotechnology is the science of manipulation of matter on atomic and molecular scales in order to obtain materials with specific and enhanced properties. A key challenge in nanotechnology is the assembly of nanoparticles with different physical and chemical properties in order to obtain composite materials with tunable nanostructural properties [1]. Carbon nanotubes (CNT's) have attracted considerable attention in recent years and become the subject of intense research activity worldwide not only due to its fascinating high electrical and mechanical properties, but also for its outstanding, thermal, magnetic, and optical properties [2]. These excellent properties endow this novel carbon material with varied nanotechnology applications, including gas sensors, field emission devices, molecular diodes, magnetic and ceramic composites [3- 5]. The assembly of isotropic nanoparticles onto one-dimensional (1D) architectures represents an important step towards the integration of nanoparticles into nano devices. In particular, nanoparticles of one material can be assembled on a 1D nanostructure of a different material to form unique and interesting hybrid nanomaterial systems. Recently, carbon nanotubes (CNTs) have been used as templates or scaffolds for the hybrid assembly of nanoparticles [6]. Modification of CNTs has been paid a great deal of interest as a fascinating model system for fundamental scientific research with the potential technological applications. In particular, fabrication of CNT-based devices modified with metal oxides is more applicable than non-modified devices. Up till now, various metal oxides such as TiO₂, SnO₂, ZnO, Fe₂O₃, MnO₂ and RuO₂ have been reported to modify CNTs [7-13]. The aromatic ring system of CNTs [14] can be disrupted by the application of oxidation reagents, such as HNO₃ or a mixture of H₂SO₄/HNO₃, and therefore

nanotubes can be functionalized with groups such as hydroxyl, carboxyl or carbonyl that are necessary to anchor guest species such as metal ions to the tube [15, 16]. As a result, most of the properties of the guest can be synergistically combined with those of the host to yield composite materials with superior characteristics. As it is well known, CNTs have a strong tendency to agglomerate due to their nanosize and the resultant high surface energy. However, the grafting of chemical functionalities, e.g. carboxylates, on the surface of CNT imparts negative charges, and hence creates the electrostatic stability required for colloidal dispersion [17, 18]. One can divide these reported synthesis methods into two main categories: those that are based on (1) the dispersion of CNTs in a metallic precursor solution followed by a chemical synthesis step (i.e., hydrothermal, microwave synthesis, or ultrasonication) or (2) the functionalization of CNT sidewalls with organic ligands followed by the physical or chemical attachment of nanoparticles [19]. Nowadays finding a simple and low-cost approach to modify CNTs with the metal oxides nanoparticles is still an active research.

In the present work, MWCNTs will be prepared then decorated with nano ZnO using the simple wet chemical method with high loading ratio. The prepared samples will be characterized by XRD, EDS, HRTEM, FTIR and thermal analysis respectively.

MATERIALS AND METHODS

2.1. Chemicals

Zinc acetate, oxalic acid purchased from Al-Nasr company- Egypt and functionalized high purity multi wall carbon nanotubes (F-MWCNTs). The high purity F-MWCNTs were synthesized by the floating catalyst chemical vapor deposition (FCCVD) method and the details can be found elsewhere [20]. All of these chemicals were used without any further purification.

2.2. Decoration method

For F-MWCNTs decoration with ZnO two precursors were prepared separately and one of them was added to the other drop wise. A 200mg of F- MWCNTs was suspended in 50ml of distilled water using ultrasonic waves for 10 min. 1.65 gm of Zinc acetate was dissolved in 50ml of distilled water and added to F-MWCNTs solution and stirred for 5 min. 3.15 gm of oxalic acid dissolved in 100ml distilled water solution was added drop wise to the above precursors and stirred for 1hr at 80°C. The precipitated dark gray powder was filtered, washed several times, with distilled water until PH value reached 6.5-7. After that the powder was collected and dried at 60°C overnight. Finally this powder was calcinated at 400°C for 2hrs. The calcination temperature was decided based on thermal analysis data.

2.3 Characterization techniques

X-ray diffraction (XRD) measurements were performed using Philips XRD Powder diffractometer (PW3050/60) with Cu K α radiation ($\lambda = 0.15406$ nm).

Energy Dispersive X-ray (EDX) analysis was carried out with Philips (Inspect S, FEI Company, Holland) Scanning Electron Microscope (SEM) operated at 30kV.

High Resolution Transmission Electron Microscopy (HR-TEM) examination was conducted on a Philips (FEI Tecnai G2 S-Twin) High Resolution Transmission Electron Microscope operated at 200kV.

Fourier Transform Infrared Spectroscopy was measured on FTIR (VERTEX 70, Bruker Optik GmbH, Germany).

Thermal analysis (TGA and DSC) data were recorded with a DTA-TGA thermal analyzer (STD-Q 600) in the temperature range 25–720°C under nitrogen flow at a rate of 30/min.

RESULTS AND DISCUSSION

3.1. XRD results

In order to understand the structure of the MWCNTs/ZnO composite, powder XRD has been recorded. Fig.1 shows the XRD pattern of the MWCNTs decorated with ZnO nanoparticles. It can be seen that the diffraction peaks of the pattern at $2\theta = 23.3^\circ - 26^\circ, 41.5^\circ - 43.8^\circ$ are assigned to (002), (110) planes of MWCNTs [20-23]. By combining the XRD and HRTEM analysis of nanotubes, Kiang et al. [24] found that the (002) reflection peak shifts from 26.60°

for graphite (inter-shell spacing of 0.335 nm) to 26.18° – 22.77° for carbon nanotubes, corresponding respectively to 0.34–0.39 spacing; While the other diffraction peaks of the composite match well with hexagonal wurtzite ZnO (JCPDS Card No. 79-0205) [22]. The XRD pattern indicated that ZnO consisted of pure phase, and no characteristic peaks were observed for other impurities which indeed confirms that the synthesized composite contain pure ZnO. The sharp peaks demonstrated that ZnO in the samples were well crystallized [25]. The size of the ZnO nanoparticles was estimated from the full width at half maxima (FWHM) of the [101] diffraction peak on the basis of the Scherrer formula are about 35 nm.

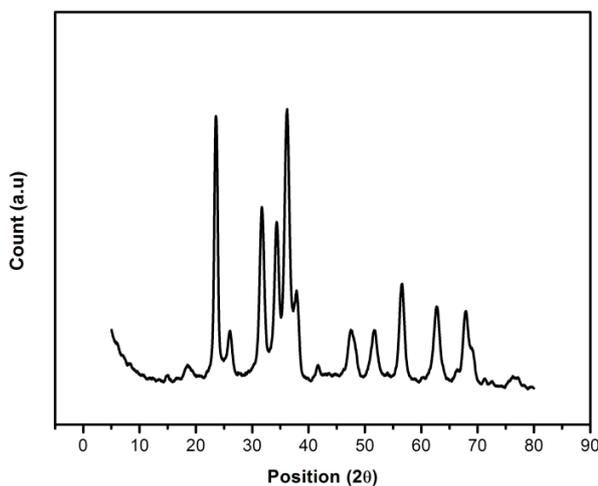


Fig. 1 XRD pattern for MWCNTs/ZnO composites

3.2. EDS analysis

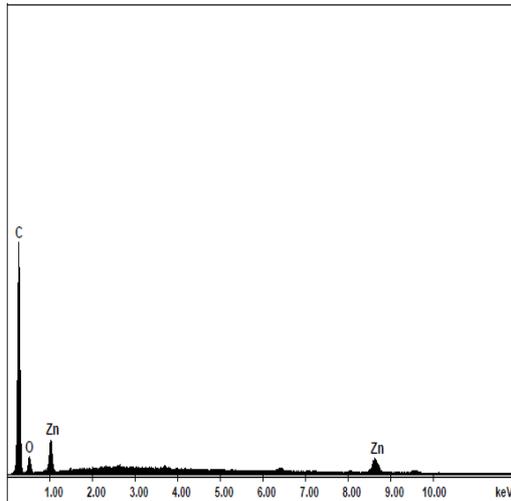


Fig.2 EDS analysis of MWCNTs/ZnO composites

In order to confirm the elements present in the resultant MWCNTs/ZnO composite, an EDS analysis was performed. As depicted in fig. 2 the EDS analysis reveals the presence of Zn, O and C which emphasize the successful of decoration process with ZnO nanoparticles. Also there is no any catalyst in the composite. This due to removing all of the catalyst used in the MWCNTs synthesizes during the purification process. Also the successful washing of the resultant composites removes other impurities which may resulted from the reaction of oxalic acid and zinc acetate.

3.3. HR-TEM

Figure 3 shows the HRTEM images of the obtained ZnO/MWCNTs composite. The images show the formation of spherical ZnO nanoparticles on the surface of MWCNTs. Also the images revealed the homogeneous dispersion of uniform ZnO nanoparticles along the surface of MWCNTs with relatively high particle density, without the formation of any noticeable agglomeration, this indicates the efficiency of the rather simple route employed for their preparation [18, 26, 27]. Also it is clear that there were no any other materials on the surface of MWCNTs except ZnO which verifies the results obtained from XRD and EDS analysis. As can be seen from the HRTEM images (Fig. 2) the estimated size of ZnO nanoparticles was about 30nm. The observed particle size was found to be in a good agreement with that obtained from XRD result.

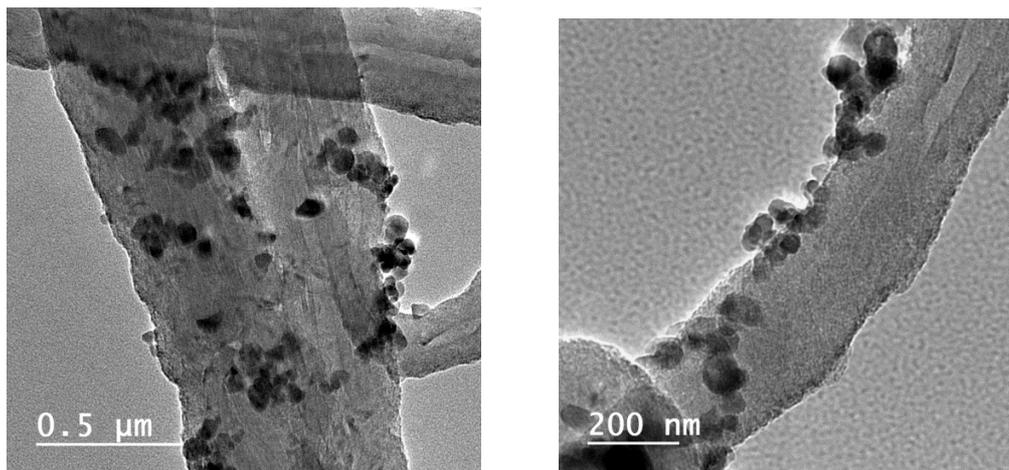


Fig. 3: HRTEM of the ZnO/MWCNTs composite

3.4. FTIR measurement

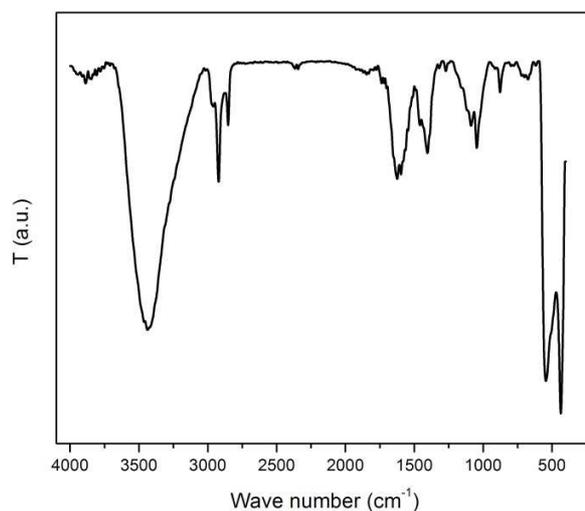


Fig. 6. FTIR spectra of MWCNT/WO₃ nanocomposite

In the present study the FTIR is utilized in order to analyze the possible bonding between the decorated structure and the surface of the MWCNTs. In other words, FTIR in this study could be a means providing an observation about the interactions at the surface during the possible adsorption of nanoparticles and to determine the structure of the adsorbed species. Fig. 6 presents the FTIR spectrum of MWCNTs/ZnO composites. The spectrum shows a broad band at 3435 cm⁻¹, which refers to the OH stretching of the hydroxyl group that can be ascribed to the oscillation of

carboxyl groups (O=C-OH and C-OH) [20]. The bands at 2938 and 2852 cm^{-1} are assigned as the stretching vibration of C-H bonds [28]. The carbonyl characteristic band is also observed around 1618 cm^{-1} and can be assigned to the carbonyl group from quinine or ring structure [29]. Intense band at 1397 cm^{-1} is due to O-H deformation of C-OH group. Two bands were observed at 538 and 437 cm^{-1} , the first one may be associated with oxygen deficiency and/or oxygen vacancy (VO) defect complex in ZnO; while the second band corresponds to the E2 mode of hexagonal ZnO which is described as Raman active [30].

3.5. Thermal analysis

Thermal analysis (DSC and TGA) can be considered as an effective tool because of its ability to determine the amount of nano metal oxides on the surface of MWCNTs also the optimal temperature of heat treatment or calcination can be specified. Fig. 4 represents the DSC and TGA curves for ZnO/MWCNTs composite before calcination. The DSC and TGA curve shows an endothermic peak at 147°C, which is accompanied by a small weight loss of 17% primarily due to the removal of water ($\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{ZnC}_2\text{O}_4 + 2\text{H}_2\text{O}$, the theoretical weight loss is 19.05%). This result indirectly proves that the as-synthesized product is $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. The endothermic peak at 395 with the corresponding weight loss of 33%, can be attributed to the decomposition of acetate groups ($\text{ZnC}_2\text{O}_4 \rightarrow \text{ZnO} + \text{CO} + \text{CO}_2$, the theoretical weight loss is 38.09%) [31] after calcination at 400°C for 2 hrs. The endothermic peak has disappeared as shown in fig5. The amount of ZnO nanoparticles on the surface of MWCNTs was estimated from TGA curve to be 75% by weight.

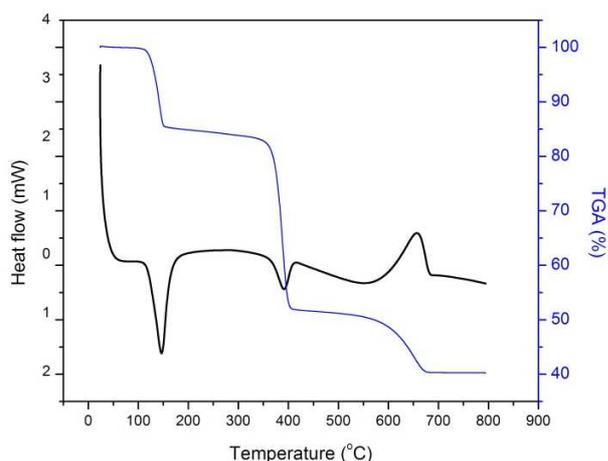


Fig. 4: DSC and TGA curves for ZnO/MWCNTs composite before calcination

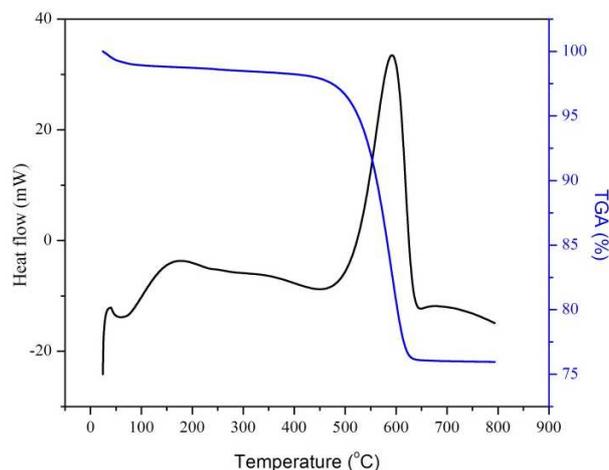


Fig. 5: DSC and TGA curves for ZnO/MWCNTs composite after calcination

CONCLUSION

The simple wet chemical route was used for the decoration of the surface of MWCNTs with ZnO nanoparticles. The obtained results indicated that the ZnO nanoparticles were distributed uniformly on the surface of MWCNTs with negligible agglomeration. HR-TEM results indicate that, the average size of the ZnO nanoparticle is about 30 nm. In the XRD pattern, the sample was observed to have high purity without any impurities. FTIR data confirms the formation of ZnO nanoparticles on the surface of MWCNTs. Collecting these data one can conclude that the decorated MWCNT was achieved with simple method which could be dedicated in many applications.

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