Preparation and Characterization of MWCNTs-Chitosan Composite

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Abstract

The present work aims to prepare Multi-walled carbon nanotube acid (MWCNTs-COOH) by using fragments Flam Deposition technique (FFD), grafting CNTs with Chitosan (CS) to prepare (CS-OMWCNTs) composite. Each of the following techniques is used to characterize the components of composite x-ray diffraction (X-RD), Fourier Transform Infra Red (FT-IR), Raman spectra, Field emission scanning electron microscopy (FESEM), transmitted electron microscope (TEM), and Laser Particle Size Analyzer technology. The results of the laser particle size analyzer showed that the particle size ranged between (87.8-403.3). Pattern of XRD showed that its diffraction spectrum contains crystalline materials with a good atomic arrangement of atoms with graphite, while SEM microscopy revealed that the average diameter of the tube was 40 nm. Raman Spectroscopy showed ID/IG ratio of 0.6, which means a lower degree of distortion in the compositional structure of the carbon nanotube. As for TEM technology, it showed the attachment of carbon nanotube to the surfaces of chitosan. FT-IR showed the active groups present on the surface of carbon nanotube such as (COOH, OH)

Key words: CNTs; Chitosan; XRD; FESEM; TEM

1. Introduction

Environmental pollution increased rapidly with the development of industries in our life. The biggest challenge for the researchers in an environmental field is the pollution in our life. Adsorption is one of the methods widely used in removing pollutants from aqueous solutions due to the low cost and high efficiency. One of the good adsorbed surfaces is CNTs composites. Carbon nanotube was first discovered in 1991. CNTs are a 1D hollow cylinder-shaped nanomaterial that is synthesis from graphite papers. The hybridization of carbon nanotube is of the type sp2 of carbon atoms hybridized. It results from the rolling of the 2D sheets of graphite with the hybridization of sp2 and forms a tubular structure. The π-π interaction is another feature of graphite. CNTs form have good heat conductivity properties making them applicable in optics, electrochemistry, and nanotechnology.

There are types of carbon nanotubes, including single-walled, multi-walled, two-walled, and few-walled, which are classified according to the number of graphene layers that make up the cylinder. SWCNTs have a diameter of (1-2) nm. The cylinder formed by rolling the graphene sheet is sealed at both ends by a cap made of Hemi-fluorine, meaning half of the
fluorine ball. Depending on the diameter and on the charity l atom, a metallic or semiconducting band is formed. Carbon atoms in equivalent sites are in the form of a hexagonal aromatic ring, while the flat atoms on the sides are in the form of pentagonal rings.

MWCNTs consist of many graphene layers with an outer diameter of (2-100) nm, while the length is up to some micrometer. MWCNTs feature high rigidity, strength, tenacity, and high flexibility. The multi-walled carbon nanotubes feature high rigidity, strength, tenacity, and high flexibility. The distance between the layers was (0.34-0.39) nm, while the length ranges from nanometer.

Carbon nanotubes are synthesized in some methods, including (laser ablation, vacuum arc deposition, chemical vapor deposition, and chemical flame fragmentation). Characterization CNTs by (FT-IR, Raman, SEM, XRD, and TEM).

Chitosan is considered one of the most used natural biopolymers consisting of linear polyacrylate with an amino group derived from actin. Grafting carbon nanotubes to chitosan enhances the mechanical properties and dispersion of carbon nanotubes in the chitosan matrix depends on the degree of de-acetylation.

The compound(CS-MWCNTs) properties improved significantly compared to those of chitosan only. The functional groups in carbon nanotubes such as carboxyl and hydroxyl lead to the dispersion of the carbon nanotubes in the chitosan matrix.

2. Material and experimental work

2.1 Materials

The coal which was used as a source of carbon and kerosene were purchased from the local market. Dimethylformamide (DMF) was supplied by Alpha. Chemika with purities 98%. Hydrogen peroxide was obtained from Scharlau (30% percent weight). Sulfur powder (98%) was purchased from CDH. Chitosan (deacetylation 95.7%) was obtained from (SHAANXI SANGHERB BIO.TECH INO.)

2.2 Experimental work

Synthesis of Multi-walled carbon nanotube (MWCNTs). MWCNTs were synthesized by the chemical fragments flame deposition method, which involved taking 10 g of coal and mixed with 3 g of pure sulfur, the mixture was placed at the bottom surface of muffle furnace. The furnace was installed at a temperature of 90°C. By the passage of nitrogen gas at a flow rate 25 cm³/min, after the furnace reached the required temperature, 1 mL of kerosene was added into the mixture, then the flame was used. The combustion process begins and is accompanied by the precipitation process on the upper surface of the furnace. After that, the heating is stopped as the nitrogen gas continues and the furnace is left to cool down. In this step, the sedimentation process is completed, after which the precipitate is collected.

Purification for Multi-walled carbon nanotube (P-MWCNTs). The pre-prepared multi-walled carbon nanotubes were purified, 0.1 g of MWCNTs were taken and placed in a 100 mL beaker, 50 ml of pure H2O2 at a concentration of 30% was added. Leave the mixture for three days at a cooling temperature of 4°C. The mixture was extracted and left to room
temperature, the mixture was heated to 50 °C with continuous stirring for 30 min, the mixture was separated in a separating funnel for 15 min. The MWCNTs were dried at 60°C for 6h.

**Synthesis of oxidized multi-walled carbon (OMWCNT).** OMWCNTs were prepared by taking 0.1 g of P-OMWCNTs mixed with sulfuric acid and nitric acid in a ratio of (1: 3 v/v) respectively. 0.1 g of MWCNTs was taken with 50 mL of the above-mentioned acids, and mixed in an Ultrasonication device. For a period of 3h at a temperature of 40°C, the mixture is left to room temperature and then 100 mL of deionized water are added to it. The OMWCNTs are washed with distilled water using a centrifuge until it reaches a nearly neutral pH, and it is dried at a temperature of 60°C for a period of 6h.

**Synthesis of CS-MWCNTs Composites.** 0.5g of chitosan particles were taken and dissolved in 20 mL of DMF solution and left for 24 h, OMWCNTs were dispersed in 20 ml of deionized water in an ultrasonication for 30 min. The dispersed OMWCNTs were slowly added to the chitosan solution with continuous stirring for 6h at 40°C, CS-MWCNTs are dried at 50°C for 6h.

### 3. Characterization techniques

Characterization of the crystal structure of the sample using (XRD, Simens D500, UK), scanning electron microscopy (SEM, Sigma VP,UK) gives information about surface morphology, Raman spectroscopy at 532 nm wavelength used to evaluate the carbon nanotube structures by ID. / IG, Transmission Electron Microscopy (CM 120, UK) provides a more accurate picture of the tube structure, FT-IR(Shimadzu 8500, Japan) shows the active groups present in carbon nanotubes, and the laser particle size analyzer technology (Brookhaven 90 plus, USA) for measuring the size of nanoparticles.

### 4. Results and discussion

**Laser Particle Size Analyzer:** The size distribution of the prepared MWCNTs with a temperature of 90°C as shown in (Fig. 1), these results showed that the size of the nanoparticles from (87.8-403.3 nm). The increase in the size of the nanoparticles is a result of the accumulations that occur between the layers of carbon nanotubes which attributed to Van der Waals force. Values between layers and also increased temperature has the effect of dispersing carbon nanotubes, causing accumulation between layers.
Figure (1) the laser particle size analyzer for the prepared carbon nanotubes

X-ray diffraction analysis: The results of the prepared and characterized sample by the technique of X-ray diffraction (XRD) as shown in (Fig.2). This figure showed that there is a crystal structure with peaks observed at $2\theta = 26^\circ$ and $43^\circ$ which attributed to (002) and (100), respectively. On that note, there are new peaks which are $2\theta = 54.3^\circ$, $77.5^\circ$, due to (004) and (110) respectively. These peaks mentioned above symbolize the tubular graphene structure, examination between some other peaks that are attributed to the presence of amorphous carbon which showed weak peaks $^{32,33}$. 

Figure (2) X-ray diffraction of the prepared carbon nanotubes

**Raman analysis:** structure of the prepared sample in (Fig.3) shows that two condensed graphene strips appeared in 1345.95 cm\(^{-1}\) and 1588.30 cm\(^{-1}\) corresponding to beams D and G, respectively, the D domain is represented by the hybridization of SP\(^3\) of the carbon atom on the structural structure of the carbon nanotubes CNTs, the G band is related to the hybridization of SP\(^2\), which is a defect in the graphene structure that forms the carbon nanotubes, the presence of both D and G confirmed the presence and formation of multiple carbon nanotubes. Walls, MWCNTs, ID / IG ratio is very important to study the extent of formation of carbon nanotubes and their defects related ID / IG was calculated and was equal to 0.6. This ratio indicated that the resulting carbon has few walls, i.e. it is a mixture of few and multi-walled walls, and indicates a low degree of deformation on the walls of the tube structures\(^{34}\).
**Figure (3) Raman spectra of prepared carbon nanotubes**

**SEM analysis:** Figure 4 represents the image of carbon nanotubes, which shows the presence of bundles of carbon filaments, the diameter of the beams ranging from (40-100 nm) and with lengths ranging between (1-3) micrometers and it is mostly composed of a group of filaments of carbon nanotubes. Multiple walls on each other, It can also be observed that many carbon compositions that belong to the non-metamorphic carbon material that appeared in the form of diffuse circular masses with diameters ranging from (7-200 - nm)\textsuperscript{35}. 

\[ \frac{I_D}{I_G} = 0.6 \]

\begin{tabular}{c|c}

| Raman shift (cm\textsuperscript{-1}) | Intensity (counts) |
|--------------------------------------|--------------------|
| 1345.96                              | 400                |
| 1588.30                              | 375                |
| 2810.56                              | 350                |
| 2927.83                              | 325                |
| 3827.83                              | 300                |
| 4000.00                              | 275                |
| 4300.00                              | 250                |
| 4600.00                              | 225                |
| 4900.00                              | 200                |
| 5200.00                              | 175                |
| 5500.00                              | 150                |
| 5800.00                              | 125                |
| 6100.00                              | 100                |
| 6400.00                              | 75                 |
| 6700.00                              | 50                 |
| 7000.00                              | 25                 |
| 7300.00                              | 10                 |
| 7600.00                              | 5                  |
| 7900.00                              | 0                  |
\end{tabular}
The process of chitosan denaturation with carbon nanotubes to prepare a binary compound that represents chitosan / CNT, which was examined using a scanning electron microscope and as shown in Figure. 5. The new composition after Chitosan denaturation with carbon nanotubes showed that the last structures can increase the surface area through the transformation of large-scale structures into structures of a smaller size, as shown in the figure (5). It can also be seen that the carbon nanotubes helped to disperse the organic compounds of chitosan, which could increase the effective groups on the surface.

Figure (4): Image of the prepared scanning electron microscope

Figure (5): Scanning electron microscope image of chitosan with prepared carbon nanotubes
TEM analysis: The transmission electron microscope gives a more accurate picture of the prepared tube structure. Figure 6 shows the image that belongs to the prepared carbon nanotubes and presence the clusters of the prepared carbon nanotubes as a result of accumulations occurring between the carbon nanotubes in the image of the enlargement strength of 200 nm. The 90 nm was more pronounced for the carbon nanotubes, the darker black regions were the nanotube aggregations and the lighter areas were evidence of the presence of amorphous carbon atoms.

Figure (6) TEM of an image of the prepared carbon nanotubes has different enlarging power (A) 200 nm enlargement power and (B) 90 nm magnification power

In Figure 7, the image of the process of denaturing chitosan with carbon nanotubes and with different enlargement power. It was shown that there is a strong bond between carbon nanotubes and chitosan on the outer surface. At 50 nm enlargement, the lighter regions return to the chitosan nanotube, while the darker black regions are due to the carbon nanotubes, and this association helps to increase the surface area and dispersion of the carbon nanotubes and provide more effective groups on the surface.

Figure (7) An image of the prepared carbon nanotubes with chitosan having different enlarging power (A) 200 nm magnification power and (B) 50 nm magnification power
FT-IR: Figure 8 illustrates the FT-IR technique for pure (P-MWCNTs) and activated carbon nanotubes (MWCNT-COOH). The top peak at 3373.73 cm\(^{-1}\) belonging to OH-hydroxyl was found and produced from the carboxyl group associated with the aromatic ring of the activated carbon nanotubes, either 1734.42 cm\(^{-1}\) is the peak belonging to C = O in the carboxyl group, while the two peaks at 1616.40 cm\(^{-1}\) and 1543.10 cm\(^{-1}\) refer to C = C for the ring, while each of 1346.36 cm\(^{-1}\) and 1225.63 cm\(^{-1}\) belong. These values refer to the C-O for the carboxyl group\(^{39}\).

![Figure (8) FT-IR for carbon nanotubes](image)

5. Conclusion

In this study, local coal was used as a source of carbon atoms in presence of sulfur and kerosene to increase the inflammation process during the deposition of chemical flame fragments at a temperature of 90ºC and the presence of nitrogen gas to prevent the oxidation process. Various techniques have been used to diagnose the prepared carbon nanotubes (XRD, FESEM, TEM, Raman, FT-IR, and Laser particle size analyzer). These techniques reveal that the prepared sample has multiple carbon nanotubes (MWCNT) with a diameter of 40 nm and the structure of the crystalline material. With a perfect arrangement of atoms compatible with the structure of graphene. The ID / IG intensity ratio is 0.6. The current study indicates the possibility of using local coal as a source for the synthesis of carbon nanotubes.

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