

Modification of Carbon Nanotubes Surface Using Different Oxidizing Agents

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Carbon nanotubes (CNTs) were initially discovered at Japan in 1991 by Somui Ejeema, from that date CNTs were synthesized using different methods. In addition their physical and chemical properties were studied extensively [1,2]. However, researchers were directed their attention towards synthesis and purification of these materials as they can play important roles in wide range of applications in both industrial and environmental fields [3,4]. The main source of CNTs is the graphite which normally exists as sheets with hexagonal structure for carbon atoms. These sheets can be rolled up into cylindrical shape due to the presence of Van der Waals forces to produce tubular structure with nano scale radius with length of some micrometer scale. Due to this structure CNTs can be considered as an elongated hallow fullerene [5]. Generally, as a result of this structure of CNTs, it shows robust mechanical, electrical, thermal, and optical properties as well as large surface area with high adsorption ability which makes these materials to be a good candidate to remove many types of pollutants from air, water and soil. Generally CNTs consist of layers of graphite sheet with a thickness of one carbon atom with sp² hybridization [6]. According to number of these layers CNTs can be classified into single- walled CNTs (SWNTs), Double -walled carbon nano tubes (DWCNs), and Multiwalled CNT (MWNTs).

Initially, graphite is used as a starting material in the preparation of CNTs, in this context the first attempt was performed by Brody in 1865. He used sulfuric acid with potassium permanganate as oxidizing agents. After that a mixture of nitric acid and sulfuric acid was used by Hummer in 1896. In 1907, Staundmuier added nitrate to above mixture to increase the efficiency of oxidation process. The present study describes oxidation of MWCNTs using a mixture of HNO₃, H₂SO₄ and H₂O₂.

Figures 1-3 summarize the progress of oxidation of neat CNTs with time by using different oxidizing agents.

Effect of oxidation processes on the structure and morphology of MWCNTs was investigated by using non-oxidation MWCNTs as described before [7,8]. X-ray diffraction (XRD) was used to follow the changes in the patterns for MWCNTs.

XRD patterns (Figure 4) shows that both non-oxidized MWCNs and that oxidized with different oxidation agents are almost similar.



Figure 1: The Progress of Oxidation of MWCNTs using ${\rm HNO}_{\rm _3}$ 69.7% (from left to right).



Figure 2: The Progress of Oxidation of MWCNTs using $\rm H_2O_2$ 30% (from left to right).



Figure 3: The Progress of Oxidation of MWCNTs using $\rm H_2SO_4$ 98% (from left to right).

This indicates that crystalline structure of carbon nanotubes doesn't change significantly upon oxidation processes [9-11]. The relative changes in the peaks intensities, probably arises from the presence of different functional groups after oxidation of CNTs, this can lead to agglomerate of CNTs over each other which gives some changes in peaks intensities [12].

FTIR spectrophotometry was used to study the functional groups on the surface of CNTs after oxidation processes for neat MWCNTs using HNO_3 , H_2SO_4 and H_2O_2 as oxidizing agents. Figure 5 shows FTIR spectra for neat and different oxidized forms of CNTs.

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Figure 4: XRD patterns for neat and oxidized MWCNTs using different oxidizing agents.



FTIR spectra for neat and oxidized CNTs, shows that hydrogen peroxide has low ability in oxidation of CNTs. This observation arises from weak band that is assigned to absorption of hydroxyl group which appears around 3500 cm⁻¹ [13,14]. Also FTIR spectra shows a weak band around 1650-1750 cm⁻¹ which is assigned to absorption of carbonyl group in the oxidized CNTs with H₂O₂ [15-18]. On the other hand, oxidation of CNTs with nitric acid and sulfuric acid gave more intense peaks for both hydroxyl group around 3500 cm⁻¹ and carbonyl group around 1650-1750 cm⁻¹.

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