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Thermal stability investigation of decorated multi wall carbon nano tubes (MWCNT) with TiO_2 nanoparticles

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Abstract

The aim of the current research is concentrated on the modification of multi-walled carbon nanotubes (MWCNT) using TiO_2 nanoparticles at rutile phase. In order to elucidate the role of TiO_2 content on photocatalyst behavior of MWCNTs, the hybrids were prepared with different amounts of TiO_2 nanoparticles. the opening and functionalization of MWCNTs were carried out by oxidation with nitric acid solution. The samples were characterized by Fourier Transform infrared (FT-IR) spectroscopy, transmission electron microscopy (TEM), and thermogravimetric analysis (TGA). FTIR results show that functional groups such as carboxylic and hydroxyl groups have been successfully attached to the surface of nanotubes after acid treatment. The attaching these oxygen containing groups lead to easy dispersion of CNTs in polar solution. TEM results of oxidized MWCNTs illustrated opening of MWCNTs at the end tips. The micrographs taken from the modified carbon nanotubes prove that the surface of MWCNTs is decorated with nano-sized TiO_2. The TEM results revealed that the average size of TiO_2 nanoparticles which modified MWCNTs were 20nm. TGA results confermed that there was no obvious weight loss between 300 and 400°C, therefore there is no amorphous carbons in the raw samples The results obtained from thermal behavior of modified CNTs revealed that the hybrid with highest amount of TiO_2 had the higher temperature of decomposition.

Keywords: Physical behavior, MWCNT, TiO_2, Thermal stability

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1- Introduction

In the recent years, the investigation of carbon nano tubes (CNTs) and CNT containing different nano particles have been paid a great deal of attention due to fantastic properties of CNTs such as mechanical, electrical conductivity and high aspect ratio [1]. Up to now, various metal oxides such as TiO_2 [2, 3], SnO_2 [4, 5], ZnO [6], Fe_2O_3 [7, 8] and MnO_2 [9] have been reported to modify CNTs. Modification of CNTs with this nanoparticles lead to high potential for applications in particular devices for example in functional and biomedical devices [1].

Titanium dioxide (TiO_2) is a semiconductor with wide bandgap which mainly used as photocatalyst, due to its exceptional properties such as antibacterial activity, non toxicity, high efficiency. TiO_2 has three different morphologies: rutile (tetragonal), anatase (tetragonal) and brookite (orthorombic). The several factors such as temperature and dopant are important in morphology transformation of TiO_2. All three crystalline morphologies include of several TiO_6 octahedras which arrangement of them is different [10].

CNTs and titanium dioxide (TiO_2) composite materials have attracted attention of researchers in relation to the treatment of contaminated water and air. Tasviri et al[11] obtained TiO_2-coated carbon nanotubes which were functionalized with amine groups. Bouazza et al [2] have coated Multi-walled carbon nanotubes with TiO_2 layer by sol–gel method. Chen et al [3] investigated the fabrication of CNTs–TiO_2 composites by hydrolysis. They observed that the formation of TiO_2 and its compounding with CNTs happened almost simultaneously. Silva et al [12] combined TiO_2 with multi-walled carbon nanotubes by means of an acid-catalyzed sol–gel method to produce composite catalysts with different CNTcontents to be used in water treatment processes. Zein and Boccaccini[13] investigated the coating of MWCNTs with TiO_2 by three-step purification and functionalization process combining oxidation in air that caused high purification of the MWCNTs and modification the surface of MWCNTs with TiO_2. Jitianu et al[14] Synthesized carbon nanotubes-TiO_2 nanocomposites and investigated the photocatalytic activity of TiO_2. Their results showed that the photocatalytic activity of CNTs-TiO_2 nanocomposite is higher than that of TiO_2.

Yu et al[15] reported that functionalized CNTs enhanced the band gap of mesoporous TiO_2 and decreased the recombination of e^-/h^+ pairs. Meanwhile functionalized CNTs have oxygen containing groups such as hydroxyl that increased OH^- radicals. Therefore they observed that photocatalytic activity of mesoporous TiO_2 using carbon nanotubes was increased.

Xie et al [16] studied the Enhancement Visible-Light-Driven Photocatalytic Activity of Carbon Nanotube/TiO_2 nanohybrids and reported that the as prepared hybrids show good dispersity and uniformity of CNTs. in addition they observed that photocatalytic activity of hybrids on the degradation of rhodamine B (RhB) in water was 1.5 times greater than that of TiO_2 nanoparticles under visible-light irradiation.

However in the last studies, modification of MWCNTs with TiO_2 has been investigated but no previous research done in the thermal stability of which. Therefore the main purpose of this research is functionalization and decoration the surface of the MWCNTs with TiO_2 nano particles and investigation the thermal behavior of them.

2- Materials and Experimental

multi-walled carbon nanotubes (MWCNTs, 95.9% purity, diameter: ~ 40-60 nm, length: ~ 5-15µm), Tetra chloride titanium ($TiCl_4$, M= 189.79, 99%, Merck), Nitric Acid (HNO_3, M= 63, 65%, Merck) and Hydrochloride Acid (HCl 37 wt.%, Merck) were used for synthesis CNT-TiO_2. A typical experimental procedure was described as follows. Firstly, the opening and functionalization of MWCNTs were carried out by oxidation with nitric acid solution at room temperature for 2h in an ultrasound bath and 2h in magnetic stirrer at high speed. then the treated MWCNTs were filtered and washed several times with distilled water until the PH of the filtrate has reached 7 and dried at 90 ºC for an overnight. Secondly A certain amount of $TiCl_4$ was added to 100ml of distilled water, followed by adding a little HCl (37 wt.%) to the distilled water before $TiCl_4$ was dissolved in the water. The addition of a small amount of acid is only for reducing the hydrolysis of $TiCl_4$ 75mg of acid treated MWCNTs were dispersed in this solution using ultrasound bath for 2h. The mixture was stirred for 22h at room temperature and then raised temperature to 80°C and the mixture was stirred for 3h then filtered, dried at 80 ºC for 1 h and calcinated at 370 ºC for 3h.

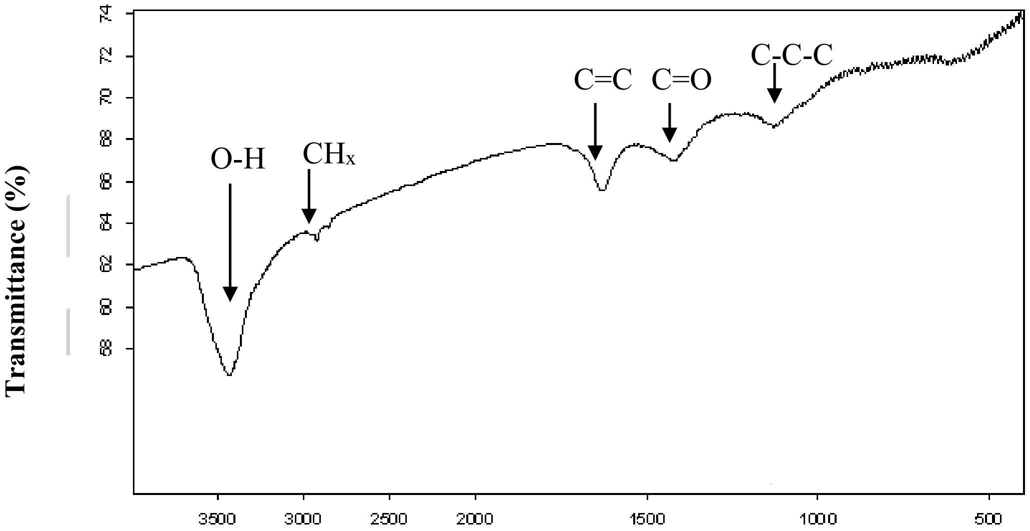
FTIR measurements were carried out on a Tensor 70 Fourier transform infrared spectrometer. Thermal Gravimetric Analysis (TGA) were carried out on Shimadzu (TGA50) thermal analyzer under air flow at the heating rate of 10 ºC /min to obtain information on the decomposition and the burning properties of carbon nanotubes and impurities present in it. The temperature of the sample was varied from room temperature to 1000 ºC. The transmission electron microscopy (TEM, LEO 912AB) was used to investigate the quality of modification.

3- Results and discussion

3.1 Functional Group Analysis

FTIR spectra of pristine and functionalized MWCNTs in the range of 400-4000 cm^{-1} are shown in (Figure 1) and (Figure 2) respectively. As can be seen in Figure 1 the pristine CNTs show absorbance bands around 1100 cm^{-1} could be attributed to the stretching vibration of C−C−C group [7]. The absorbance band at 1405-1465 cm^{-1} is assigned to the stretching vibrations of CH_2 groups. Absorbance band around at 1627 cm^{-1} could be attributed to the stretching frequencies of the C=C bonds of MWCNTs. The absorptions at 2923 and 3441 cm^{-1} is related to the CH_2 and hydroxyl groups on the surface of MWCNTs respectively.

The infrared spectra of functionalized MWCNTs indicate that the absorptions at 1744 and 3442 cm^{-1} are evidently related to the presence of carboxylic and hydroxyl groups, resulting from oxidation of nitric acid. The attaching these oxygen containing groups lead to easy dispersion of CNTs in polar solution such as water [17]. In addition of carboxylic acid and hydroxyl groups, two peaks at 2853 and 2923 cm^{-1} are attributed to the stretching vibrations of the symmetric and asymmetric CH_2 groups, respectively. Absorbance band around at 1636 cm^{-1} could be attributed to the stretching frequencies of the C=C bonds of MWCNTs. The peak at 2360 cm^{-1} corresponds to the C–O bonds.



Wave number (cm^{-1})

Figure 1. FTIR spectra of pristine MWCNTs.

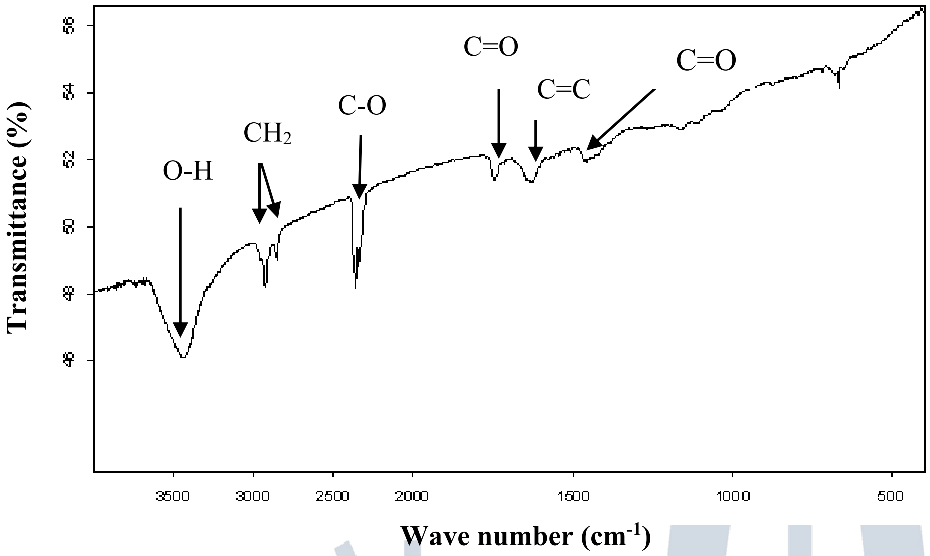


Figure 2. FTIR spectra of functionalized MWCNT

3.2 TEM Study

The TEM microphotographs of the oxidized MWCNTs and MWCNTs-TiO_2 are shown in (Figure 3) and (Figure 4) respectively. Figure 3 illustrated opening of MWCNTs at the end tips. In the oxidation process, the oxidant successively attacked active sites (the hexagon electrophilic attack), providing the main contribution to the surface oxides and opening end of tubes [18]. As can be seen in Figure 4, the TiO_2 nanopartiles attach to the surface of functionalized MWCNTs. Decoration of the outer surface of MWCNTs can de describe as below.

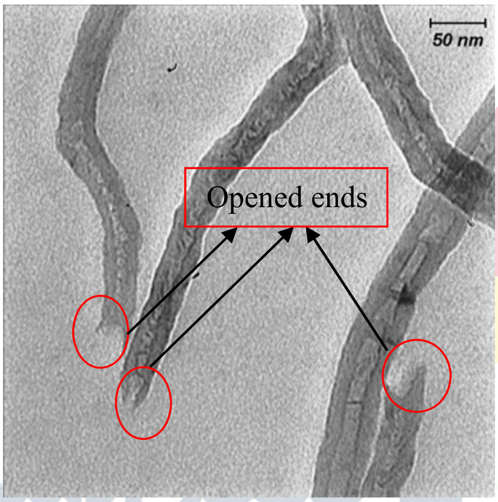


Figure 3. TEM image of opened of MWCNTs.

At first, after oxidation of MWCNTs in nitric acid, functional groups produced on the surface of MWCNTs which act as specific sites for the nucleation of metal particles [17]. Then, the titanium ions in the solution which produced by hydrolyses of $TiCl_4$ are adsorbed to the surfaces due to the electrostatic attraction. Finally, TiO_2 nanocrystals are in-situ formed on the outer surface of MWCNTs. The TEM results revealed that the average size of TiO_2 nanoparticles which modified MWCNTs were 20nm.

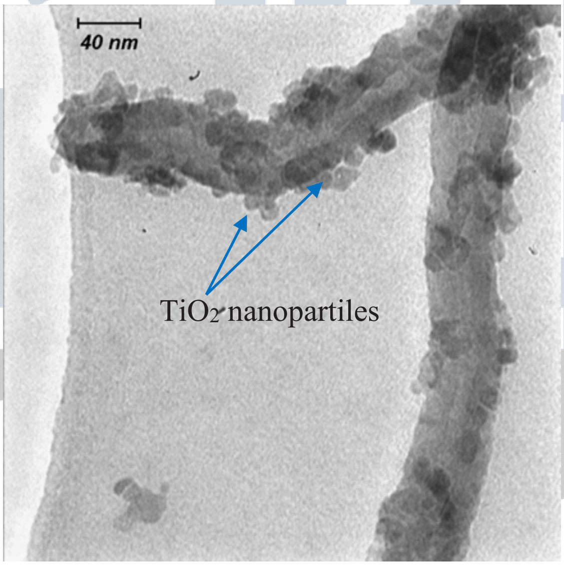


Figure 4. TEM image of MWCNTs-TiO_2.

3.3 Thermal Stability

Figure 5 and Figure 6 show the TGA and TDGA graphs of the pristine and oxidized MWCNTs respectively. All the results are obtained under the same conditions described in the Experimental section. As shown in the TGA graph (Figure 5), in the raw MWCNTs the weight loss started at 603°C, and continued rapidly by increasing the temperature until 800°C which stable region appeared. As can be seen, there is no obvious weight loss between 300 and 400°C, therefore there is no amorphous carbons in the raw samples because the combustion of amorphous carbon occurs between 300 and 400 °C whereas combustion temperature of CNTs is between 400 and 700°C [13]. The residual mass of pristine MWCNTs at temperature above 800°C is 4 wt% which related to the catalyst used in synthesizing the MWCNTs thus the purity of raw MWCNTs is 96%. Its known that, the decomposition temperature of MWCNTs depends on the thermal stability of functional groups which attach to the surface of CNTs [18]. The TGA curve of oxidized MWCNTs shows that the burning temperature starts at 628°C and the stable region occurs at nearly 825°C.

From DTGA graph (Figure 6) observed that the temperatures of the maximum rate of weight loss (or oxidation) for oxidized and raw MWCNTs are 698 and 671°C. As seen from data, the maximum rate of weight loss took place at higher temperature when the samples were acid-treated. As mentioned in the FTIR analysis, the surface of pristine MWCNTs contains active sites such as $-CH_2$ which improve the thermal stability or oxidation resistance of MWCNTs, because as reported by Chiang et al [18] in the initial stage of oxidation, the oxidant attack to active sites that exist on the surface of CNTs and it lead to thermal stability of oxidized CNTs. It's known that the burning temperature of CNTs with small diameter is lower than CNTs with large diameter. As mentioned in the experimental section, the diameter of MWCNTs varied in the range of 40-60nm. Therefore in the DTGA graph after the maximum rate of weight loss there is region which the DTGA amount approximately maintain constant that attributed to MWCNTs with larger diameter.

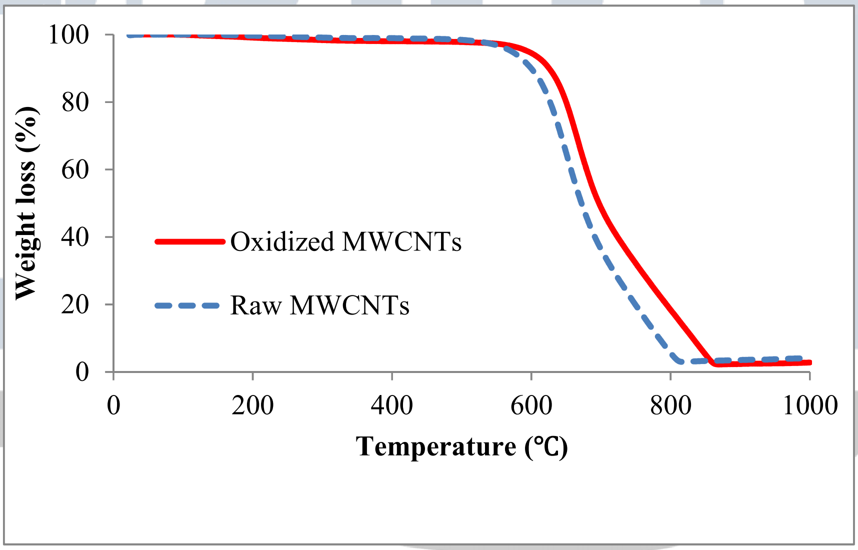


Figure 5. TGA graph of the pristine and oxidized MWCNT.

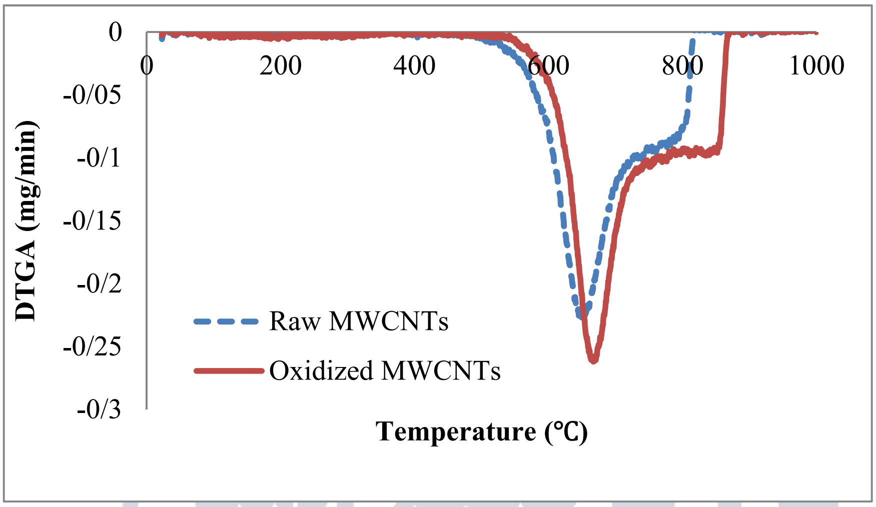


Figure 6. TDGA graph of the pristine and oxidized MWCNT.

The TGA graph of TiO_2 and modified MWCNTs with TiO_2 nanoparticles observed in Figure7. The results show that the thermal stability of decorated MWCNTs with TiO_2 nanoparticles depends on the amount of TiO_2 nanoparticles which attach to the surface of MWCNTs. As the ratio of TiO_2 to CNT in the modified MWCNTs is increased, the thermal stability is increased too. This is due to nature of TiO_2 nanoparticles. Its known that titanium dioxide is as a ceramic material that are stable up to 1000℃. Whereas CNTs start to burn at 400℃ therefore by loading of TiO_2 in the CNTs the decomposition temperature shift to right. As can be seen from Figure 8. T(-10%) which attributed to the temperature that 10% weight loss of each samples occur increase by increasing of TiO_2 amount of modified MWCNTs.

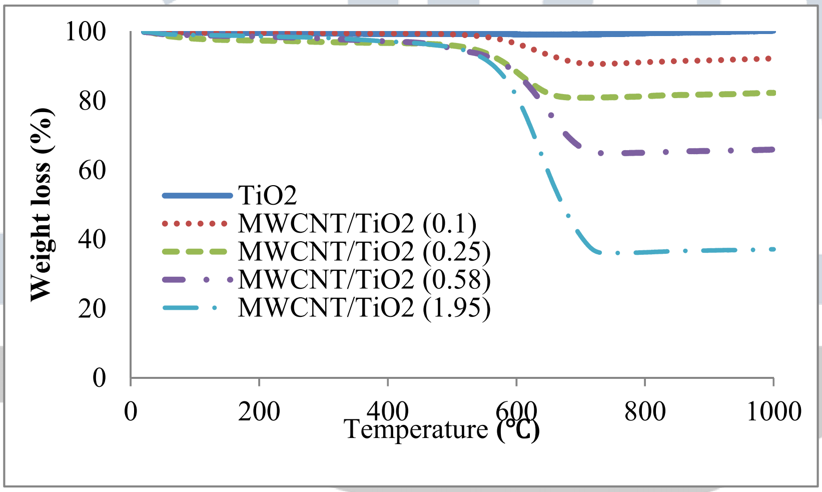


Figure 7. TGA graph of TiO_2 and modified MWCNTs with TiO_2 nanoparticles.

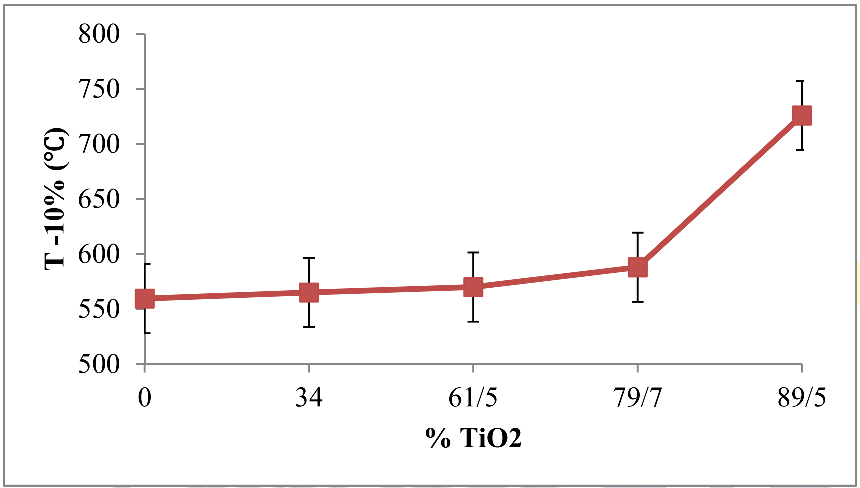


Figure 8. Dependence of T(-10%) to TiO_2 amount of modified MWCNTs.

4- Conclusions

In summary, we have synthesized the hybrids of MWCNTs/ TiO_2. The acid treatment plays a critical role in functionalization, decomposition temperature of MWCNTs and modification of MWCNTs. According to the TEM results, TiO_2 nanoparticles successfully attach to the outer surface of functionalized MWCNTs. Thermal stability of as prepared hybrids confirmed that with increasing amount of TiO_2 nanoparticles on the outer surface of MWCNTs, the decomposition temperature of hybrids increases.

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