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Influence of surface oxidation on the morphological and crystallographic structure of multi-walled carbon nanotubes via different oxidants

Hassan Khani* and Omid Moradi*

Abstract

In this paper, three kinds of multi-walled carbon nanotubes (MWCNTs) with different diameters (outer diameters: 10 to 20, 30 to 50, and >50 nm) and special surface areas (200, 60, and 40 m^2/g, respectively) were oxidized in commonly used liquid oxidizers: (1) concentrated nitric acid, (2) a mixture of nitric + sulfuric acids (*V*:*V*, 1:3), (3) hydrogen peroxide, (4) a mixture of hydrogen peroxide + sulfuric acid (*V*:*V*, 1:1), and (5) acidic potassium permanganate. Morphology of the pristine and oxidized MWCNTs was characterized by scanning electron microscopy which provides sufficient resolution for direct visualization of their outer diameter distribution. Full width at half maximum (FWHM) in the X-ray diffraction (XRD) investigation of the MWCNT samples before and after the oxidation process was measured. After treatment with oxidants, a clear decrease in nanotube diameters along the tube walls was observed. Decrease in the degree of crystallites started with the FWHM widening of the XRD diffraction peaks. The particle (crystallite) size (d_{002}) calculated by Bragg's law and Scherrer equation increased depending on the kind of oxidants; the procedure can be performed using a mixture of HNO_3 + H_2SO_4 on the surface of the MWCNTs with an outer diameter of 10 to 20nm. However, similar are the diffraction patterns of pristine and oxidized MWCNTs. Therefore, the MWCNTs that underwent oxidation process were able to preserve the first features of their structures, even though some narrowing of outer diameters and decreases in crystallites appeared. Nevertheless, the structure of MWCNTs still remains intact to be used as oxidized nanotubes in most applications.

Keywords: Multi-walled carbon nanotube; Surface functionalization; Morphology; Crystallographic structure

Background

Carbon nanotubes (CNTs) are divided into two types, namely single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs). SWCNTs are a graphite sheet rolled into a cylinder of a few micrometers in length and a few nanometers in diameter. MWCNTs consist of several such cylinders nested inside each other. MWCNTs have attracted great attention as a new kind of nanomaterial since their discovery in 1991. Carbon nanotubes have unique mechanical, electrical, magnetic, optical, and thermal properties. Owing to their inert nature, the nanotubes tend to form bundles with each other and thus do not disperse well in organic matrices in their pristine state. Suitable enhancement of the surface of MWCNTs is thus required in order to optimize their dispersion in the organic matrices. Out of various possible ways to achieve surface functionalization, chemical oxidation means of surface modification are quite common [1-4]. In this case, in typical experiments, MWCNTs with different diameters were oxidized under reflux condition in different oxidants [1-29]. The pristine and oxidized MWCNTs were then investigated with regard to their crystallites and morphologies via X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The objective of this research is to study the morphological and crystallographic structure of oxidized

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Table 1 Average diameters of MWCNTs (narrowing of nanotube diameters during oxidation)

Kind of MWCNTs	Average MWCNT diameters (nm)
Outer diameter = 10 to 20 nm	
Pristine	20.66
Oxidized with HNO_3	16.47
Oxidized with $HNO_3 + H_2SO_4$	14.25
Oxidized with H_2O_2	14.90
Oxidized with $H_2O_2 + H_2SO_4$	19.40
Oxidized with $KMnO_4$	18.71
Outer diameter = 30 to 50 nm	
Pristine	40.70
Oxidized with HNO_3	35.95
Oxidized with $HNO_3 + H_2SO_4$	34.62
Oxidized with H_2O_2	38.34
Oxidized with $H_2O_2 + H_2SO_4$	36.42
Oxidized with $KMnO_4$	38.42
Outer diameter > 50 nm	
Pristine	74.82
Oxidized with HNO_3	47.94
Oxidized with $HNO_3 + H_2SO_4$	50.25
Oxidized with H_2O_2	59.44
Oxidized with $H_2O_2 + H_2SO_4$	50.63
Oxidized with $KMnO_4$	55.63

MWCNT array that will be used as the first step for other functionalization and applications.

Results and discussion

Morphology and crystallographic structure of MWCNTs

SEM

The morphology of MWCNTs before and after oxidation was characterized by SEM. The outer diameter (OD) of the carbon nanotubes varied in the three kinds of MWCNTs (10 to 20, 30 to 50, and >50 nm). The average diameter of MWCNTs before and after oxidation was measured (Table 1). Figures 1, 2, and 3 show the SEM images of MWCNTs. The nanotubes are pure and only carbon nanotubes were observed. After treatment with acids, a clear change in diameter and surface roughness along the tube walls was observed. Through the oxidation process, the diameters of MWCNTs were narrowed down gradually. Table 1 presents the erosion of nanotube surface during oxidation [1-3].

XRD

Figures 4, 5, 6, 7, 8, 9, 10, and 11 show the XRD profiles of the MWCNTs. It can be found that the pristine and oxidized samples possess a structure similar to that of graphite crystal, which indicates that the functionalization process does not change the bulk structure of the MWCNTs. The strongest and sharpest diffraction peak for all samples at around $2\theta = 26.3°$ could be indexed as

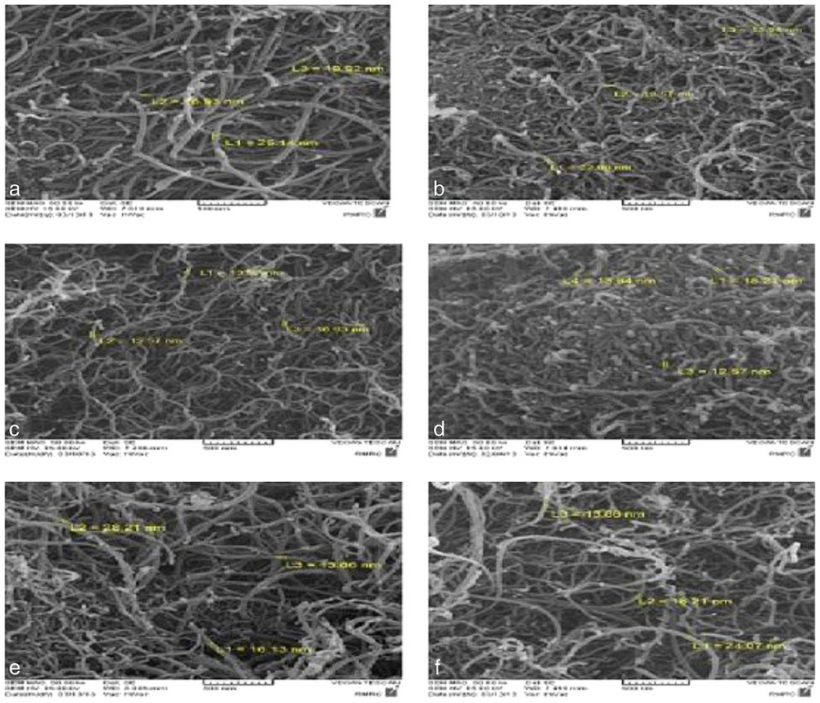

Figure 1 SEM images of MWCNTs with an outer diameter of 10 to 20 nm. (a) Pristine, **(b)** oxidized with HNO_3, **(c)** oxidized with $HNO_3 + H_2SO_4$, **(d)** oxidized with H_2O_2, **(e)** oxidized with $H_2O_2 + H_2SO_4$, and **(f)** oxidized with $KMnO_4$.

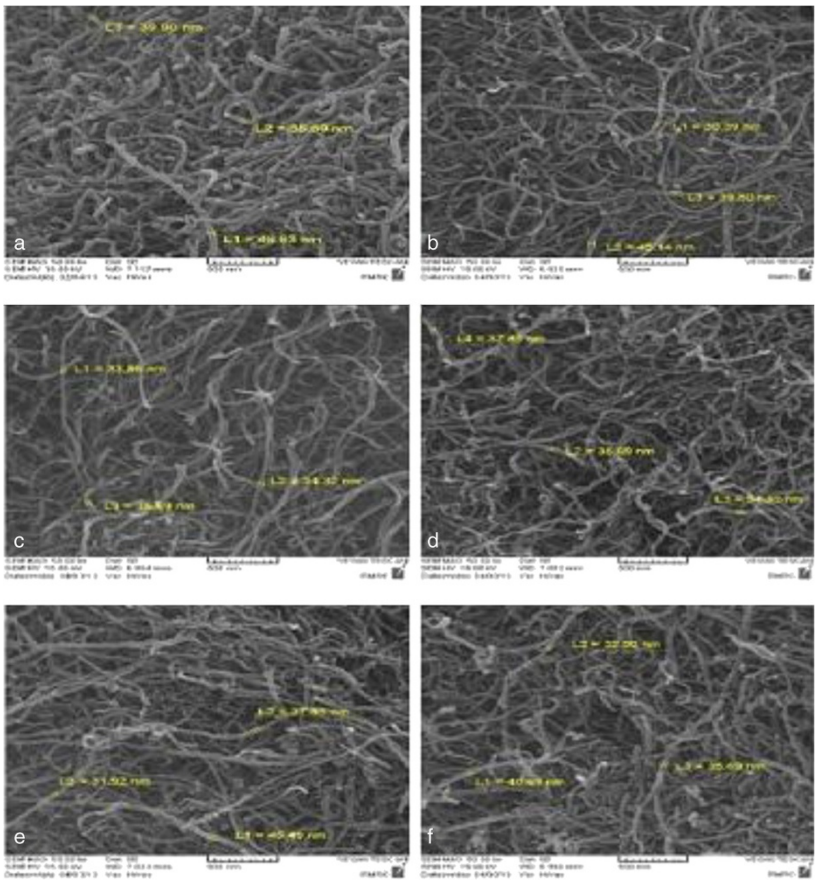

Figure 2 SEM images of MWCNTs with an outer diameter of 30 to 50 nm. (a) Pristine, **(b)** oxidized with HNO_3, **(c)** oxidized with $HNO_3 + H_2SO_4$, **(d)** oxidized with H_2O_2, **(e)** oxidized with $H_2O_2 + H_2SO_4$, and **(f)** oxidized with $KMnO_4$.

the C (002) reflection of graphite. The sharpness of the C (002) peak indicates that the graphite structure of MWCNTs was acid-oxidized without significant damage. XRD was used to measure the crystal size and interlayer spacing. Due to the CNT's intrinsic nature, the main features of the X-ray diffraction pattern of CNTs are close to those of graphite, as shown in Figures 4, 5, 6, 7, 8, 9, 10, and 11. A comparison between Figure 4 and the others shows that a graphite-like peak (0 0 2) is present at approximately 26° in 2θ. Measurements of crystal size (d) can be achieved from this peak (Tables 2 and 3) and the Scherrer equation (Equation 1). As mentioned above, the average crystallite size of the MWCNTs was determined using the XRD patterns, via the well-known Scherrer equation:

$$d = \frac{k\lambda}{\beta\cos\theta} = ? \text{ nm} \quad (1)$$

where β is the full width at half maximum (FWHM), θ is the diffraction angle, λ is the wavelength (1.54 Å), d is the particle (crystallite) size, and k is the Scherrer constant (0.91).

The Scherrer equation is derived from Bragg's law, and it is limited to nanoscale particles only. It is known that a decrease in the order of crystallinity in carbon materials will make the XRD peaks broader. Accordingly, all treated samples had a wider FWHM, which implies that the oxidation of MWCNTs had actually deteriorated the degree of crystallinity. However, amounts of it are very little (Tables 4 and 5) [2,27].

Conclusions

Oxidation of carbon nanotubes was used as a common step in the functionalization process to increase their solubility and compatibility with different materials. However, this procedure should be used with certain caution as it can result in the destruction of the nanotube structure in the case of elevated temperatures and increased oxidation time. In this paper, the structure and morphology of pristine and oxidized MWCNTs were studied using SEM and XRD analyses. SEM examinations on MWCNTs showed that after oxidation process, the diameter of oxidized MWCNTs begin to narrow. However, comparing the SEM images of the pristine MWCNTs and that of

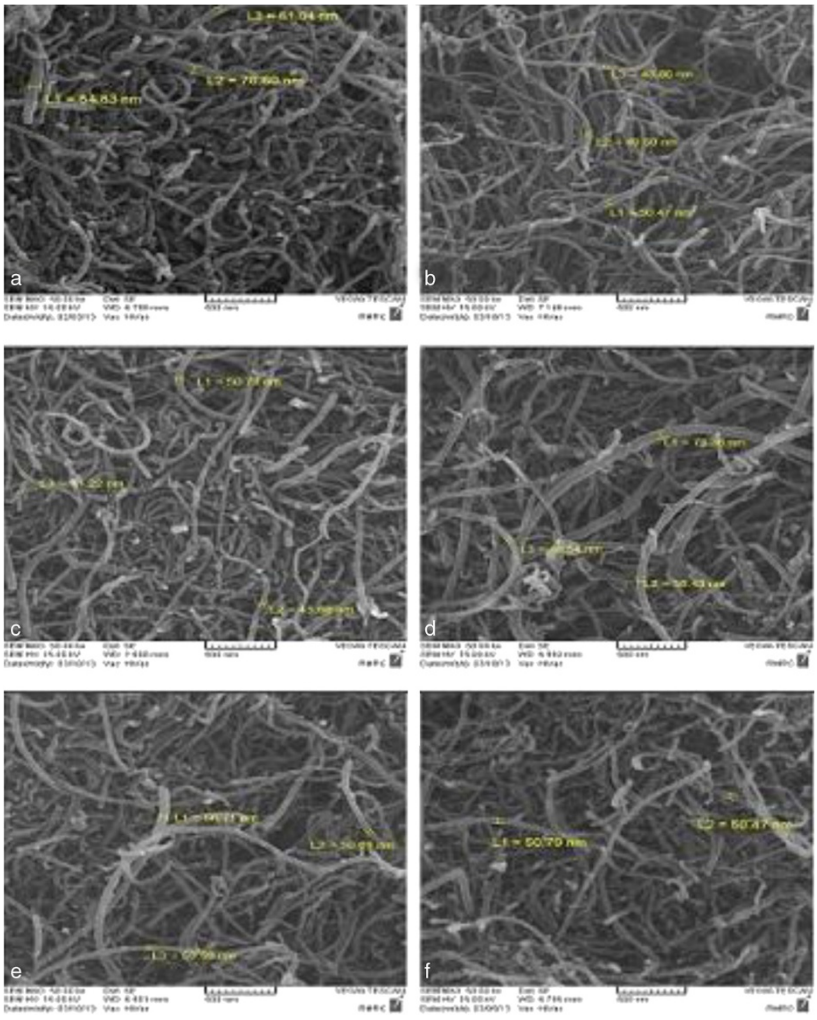

Figure 3 SEM images of MWCNTs with an outer diameter >50 nm. (a) Pristine, **(b)** oxidized with HNO_3, **(c)** oxidized with HNO_3 + H_2SO_4, **(d)** oxidized with H_2O_2, **(e)** oxidized with H_2O_2 + H_2SO_4, and **(f)** oxidized with $KMnO_4$.

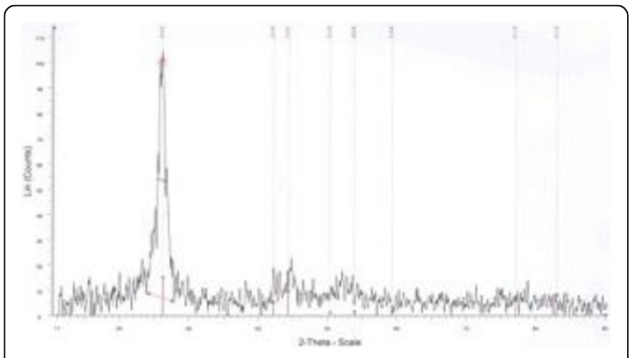

Figure 4 XRD profiles of the MWCNTs (OD = 10 to 20 nm) before functionalization. CuKα, graphite.

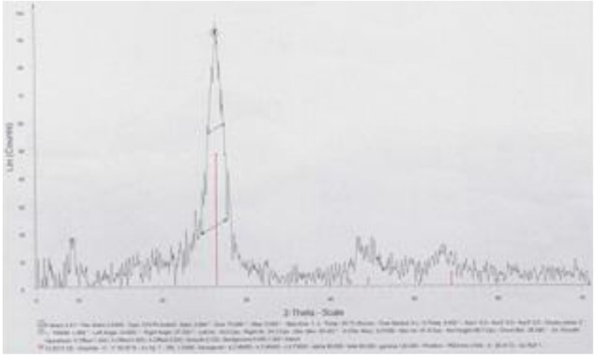

Figure 5 XRD profiles of the MWCNTs (OD = 10 to 20 nm) after functionalization with HNO_3 + H_2SO_4. CuKα, graphite.

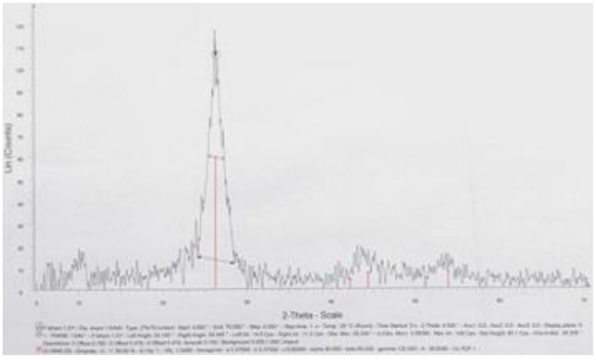

Figure 6 XRD profiles of the MWCNTs (OD = 10 to 20 nm) after functionalization with HNO_3. CuKα, graphite.

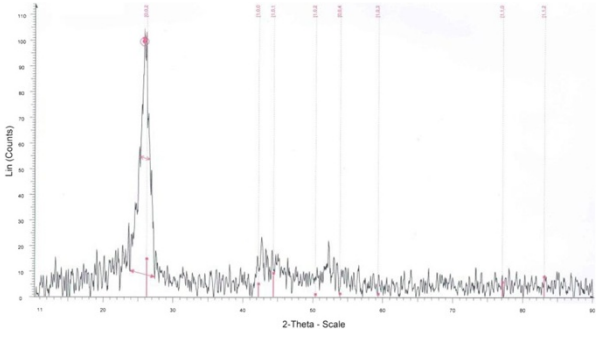

Figure 9 XRD profiles of the MWCNTs (OD = 10 to 20 nm) after functionalization with $H_2O_2 + H_2SO_4$. CuKα, graphite.

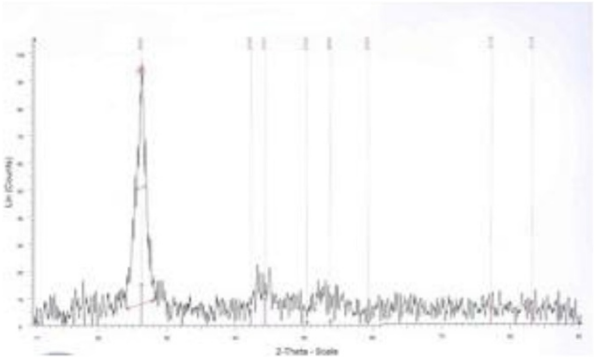

Figure 7 XRD profiles of the MWCNTs (OD = 10 to 20 nm) after functionalization with $KMnO_4$. CuKα, graphite.

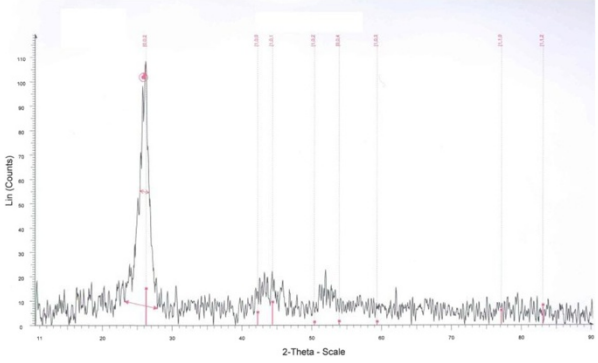

Figure 10 XRD profiles of the MWCNTs (OD = 30 to 50 nm) after functionalization with HNO_3. CuKα, graphite.

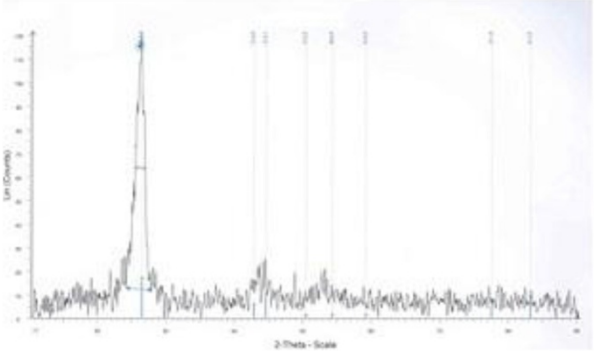

Figure 8 XRD profiles of the MWCNTs (OD = 10 to 20 nm) after functionalization with H_2O_2. CuKα, graphite.

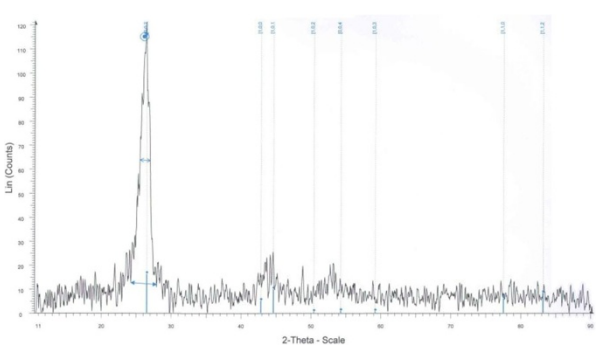

Figure 11 XRD profiles of the MWCNTs (OD > 50 nm) after functionalization with HNO_3. CuKα, graphite.

Table 2 Particle (crystallite) size of MWCNTs with the same diameter and different oxidants

MWCNTs (OD = 10 to 20 nm)	d (C_{002}) (nm)
Pristine	70.07
Oxidized with HNO_3 + H_2SO_4	42.46
Oxidized with HNO_3	43.79
Oxidized with $KMnO_4$	51.903
Oxidized with H_2O_2	58.39
Oxidized with H_2O_2 + H_2SO_4	58.39

k = 0.91 and λ = 1.54 Å.

the oxidized MWCNTs, there are practically no visual differences between them. XRD and SEM analyses revealed that the chemical treatment did not induce structural damages to the nanotubes. According to the XRD patterns, the least damaging oxidation process for creating hydrophilic sites on the hydrophobic surface of MWCNTs can be achieved using acidic potassium permanganate under reflux and mild oxidation of MWCNTs. The XRD patterns were taken to reveal detailed information about the crystallographic structure of MWCNTs. The 2θ ranged from 10° to 90°, where θ is the diffraction angle. The strongest and sharpest diffraction peak for all samples at around 2θ = 26° could be indexed as the C (0 0 2) reflection of graphite. The sharpness of the C (0 0 2) peak indicates that the graphite structure of the MWCNTs were acid-oxidized without significant damage. The crystallite size particle (d_{002}) calculated by Bragg's law changed depending on the kind of oxidants and MWCNTs. It is known that a decrease in the order of crystallinity in carbon materials will make the XRD peaks broader. Accordingly, all treated samples have either a smaller d_{002} or a wider FWHM which implies that the oxidation of MWCNTs had actually deteriorated the degree of crystallinity. Moreover, the process seemed to start with widening the FWHM, followed by shifting the C (0 0 2) diffraction towards lower angles. Furthermore, this phenomenon was more significant with oxidation using the mixture HNO_3 + H_2SO_4. These results show that there were more apparent structural changes after acid oxidation with the mixture HNO_3 + H_2SO_4 according to the SEM images.

Table 3 Particle (crystallite) size of MWCNTs with the same oxidant and different MWCNT diameters

MWCNTs oxidized with HNO_3	d (C_{002}) (nm)
OD = 10 to 20 nm	43.79
OD = 30 to 50 nm	63.7
OD > 50 nm	63.7

k = 0.91 and λ = 1.54 Å.

Table 4 The FWHM width with the same MWCNT and different oxidants

MWCNTs (OD = 10 to 20 nm)	FWHM (C_{002})	2θ
Pristine	1.245°	26.146°
Oxidized with HNO_3 + H_2SO_4	1.958°	26.422°
Oxidized with HNO_3	1.940°	26.245°
Oxidized with $KMnO_4$	1.622°	26.208°
Oxidized with H_2O_2	1.443°	25.808°
Oxidized with H_2O_2 + H_2SO_4	1.480°	26.337°

Methods

Material

Multi-walled carbon nanotube features are listed in Table 6.

Acid treatment of MWCNTs

Separately, three types of MWCNTs (2.0 g) with different diameters were dispersed in a 200-ml solution of 8 M HNO_3 in a round-bottom flask and refluxed at 60°C for 48 h with continuous stirring (200 rpm) and ultrasonicated in an ultrasonic bath (300 W, 50 kHz) to obtain carboxyl functional groups. Upon cooling, the mixture was thoroughly washed with deionized water to remove traces of untreated acid until the pH value was 7, which signifies zero acidity. Then oxidized MWCNTs were filtered through a centrifuge and a polycarbonate filter (Whatman, pore size 0.2 μm). Then the samples were dried at 120°C in a vacuum oven for 24 h. To compare with the oxidation in HNO_3, the same process was performed in a mixture of HNO_3 (50 ml) + H_2SO_4 (150 ml) (*V*:*V*, 1:3), a mixture of H_2O_2 (100 ml) + H_2SO_4 (100 ml) and 18% H_2O_2 (200 ml) at 120°C, and also acidic $KMnO_4$ (200 ml) in 95°C for 48 h. In the case of functionalization in $KMnO_4$, the obtained solid mixture was washed with water, filtered, rewashed with concentrated HCl to remove the produced MnO_2, then refiltered to remove the produced MnO_2, and then refiltered again. [1-4, 11, 18, 23, 29]

Characterization methods

Scanning electron microscopy

To investigate the morphologies of MWCNTs before and after oxidation, the SEM model VEGA (TESCAN, Brno, Czech Republic) with a field emission gun was

Table 5 The FWHM width with the same oxidant and different MWCNT diameters

MWCNTs oxidized with HNO_3	FWHM (C_{002})	2θ
OD = 10 to 20 nm	1.940°	26.245°
OD = 30 to 50 nm	1.367°	26.170°
OD > 50 nm	1.336°	26.013°

Table 6 Multi-walled carbon nanotube features

	Specimen 1	Specimen 2	Specimen 3
Purity	>95%	>95%	>95%
Outer diameter	10 to 20 nm	30 to 50 nm	>50 nm
Special surface area	200 m^2/g	60 m^2/g	40 m^2/g
Preparation method	Chemical vapor deposition	Chemical vapor deposition	Chemical vapor deposition

Table 7 XRD test condition

Parameters	
Reference standard	EN 13925–1:2003
Sample preparation	
With crushing	No
Without crushing	Yes
Radiation	
Cu voltage	40 kV
Current	30 mA
2θ	10° to 90°
Step size	0.05°
Coating time	0.5 s
λ (wavelength)	1.54 Å
k (Scherrer constant)	0.91

used (without gold-coated samples because the diameter of MWCNTs seems bigger with gold coating).

X-ray diffraction

XRD patterns were taken with an X-ray powder diffractometer (model GNR MPD 300, GNR Analytical Instruments Group, Novara, Italy) to reveal detailed information about the crystallographic structure of the material. The radiation used was CuKα with a wavelength of 1.54 Å. The 2θ ranged from 10° to 90°, where θ is the diffraction angle. The test condition is shown in Table 7 [2,27].

Competing interests

Both authors declare that they have no competing interests.

Authors' contributions

H KH carried out the result analysis, participated to draft the manuscript and in the manuscript elaboration, carried out the experiments, and obtained most of the experimental images. O M coordinated the project, discussed the results, and helped to draft the manuscript. Both authors read and approved the final manuscript.

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