

## Characterization of Amide and Ester Functionalized Multiwalled Carbon Nanotubes

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Multi-walled carbon nanotubes (MWCNT) were functionalized by different functional group *via* amidation and esterification process. The MWCNT were treated with  $H_2SO_4/HNO_3$  first to introduce carboxylic acid functional group on the surface of MWCNT. This carboxylic group was used as reaction precursor in the functionalization. There are two functionalizing reactant were used which is dodecylamine,  $CH_3(CH_2)_{11}NH_2$  and 1-octadecanol,  $CH_3(CH_2)_{17}OH$ . Electron microscopy revealed that the morphology of amide and ester functionalized MWCNT exhibit decrease in their diameter size due to insertion of amide and ester functional group. Raman measurements showed that G-band (graphitic structure) of amide and ester functionalized MWCNT slightly shifted downfield about  $6-8\text{ cm}^{-1}$  due to presence of new functional group on the surface of MWCNT. Multi-walled carbon nanotubes attached to organofunctional element have greater flexibility for further usage in various application fields such as nanocomposite material, biology and chemical sensor and environmental monitoring.

**Keywords:** Multi-walled carbon nanotubes, Amidation, Esterification, FESEM-EDX analysis.

### INTRODUCTION

The potential of carbon nanotubes (CNTs) in chemical, mechanical, electrochemical sensing application, nanocomposite material and environmental monitoring is nowadays are incontrovertible [1-5]. Carbon nanotubes (CNTs) can be categorized into two group depending on their number of walls, which are single walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT). Multi-walled carbon nanotubes consist of multiple rolled layers (concentric tubes) of graphene and distance of interlayer in MWCNT is close to the distance between graphene layers in graphite, approximately  $3.4\text{ \AA}$  [6]. The production of MWCNT are less challenging compared to the SWCNT, such as number of catalyst used and range of operating temperature, thus the MWCNT are more favourable in variety of industrial application. The monitoring of hazardous substances requires device that must be fast response, reproducible, stable, sensitive and selective to detect various pollutants in a simple and efficient method [7]. Carbon nanotubes are the most suitable candidate due to their high surface area, nanosize and good conductivity. However, the most

challenging in applied CNTs as sensor material are the poor dispersibility, low interaction with analytes and high inertness [8]. van der Waal's forces are more effective in causing the agglomeration of smaller particles. Functionalization is the one of several ways to improve these weaknesses of CNTs [9]. There are few type of functionalization such as non-covalent functionalization, covalent functionalization, functionalization using physical chemistry such as mechanochemical reaction and electrochemical reaction and outerwall/innerwall functionalization [6]. In this paper, amide and ester functional group were attached using covalent functionalization. This functionalization beside improve the properties of CNTs, it is also enhancing the solubility of CNTs in common solvent by the presence of functional group on the surface of CNTs [10]. The functionalized ester and amide of MWCNT were analyzed using field emission scanning electron microscopy (FESEM), energy dispersive X-ray microscopy (EDX) and Raman spectroscopy.

### EXPERIMENTAL

Multi-walled carbon nanotube with a carbon content 95 % purchased from Nanostructure & Amorphous Materials, Inc

(USA) were used as received without any pre-treatment and its outside and inside diameters were 10-20 nm and 5-10 nm, respectively. Nitric acid (65 %) and sulphuric acid (98 %) were supplied by Merck Company (Germany). Dodecylamine [ $\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2$ , 99 %] and 1-octadecanol [ $\text{CH}(\text{CH})\text{CHOH}$ , 99 %] as functionalizing reactant also were supplied by Merck Company (Germany). All chemical reagents are analytical grade and were used as received.

**Carboxylation of as received MWCNT:** 2.0 g of multi-walled carbon nanotubes (MWCNT) were mixed in a beaker with a ratio 3:1 mixture of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ . Then, the mixture was sonicated at 70 °C for 120 min. After sonication process done, the black solid was collected, washed several times and filtered. Finally, the end product was dried in vacuum oven at 80 °C for 24 h. This product was labelled as MWCNT-carboxylic. Carboxylic functional group was used as reaction precursors in the amide and ester functionalization.

**Amidation and esterification:** In a 50 mL beaker, 0.5 g of dodecylamine/1-octadecanol was melted on a hot plate at 80 °C for about 30 min, 1.0 g of MWCNT-carboxylic was added and sonicate at 70 °C for 30 min before few drops of sulphuric acid,  $\text{H}_2\text{SO}_4$  as catalyst were put together. The mixture continues sonicate for 5.0 h. After the reaction end, the mixture was washed and filtered several times. Finally, the functionalized product was dried in vacuum oven at 80 °C for 24 h. This product was labelled as MWCNT-amide/MWCNT-ester.

**Characterization analysis:** The morphology of as received MWCNT, MWCNT-carboxylic, MWCNT-amide and MWCNT-ester were analyzed using field emission-scanning electron microscopy (FESEM) model JEOL 7600F. All of four samples were coated with platinum, Pt for 30s first before examined under microscope. Elemental composition of MWCNT-carboxylic, MWCNT-amide and MWCNT-ester were determined by energy dispersion X-ray (EDX) analysis. Images were recorded with an accelerating voltage of 5.0 kV and Raman measurements were conducted with a 532 nm laser with a confocal microscope of Renishaw InVia system.

## RESULTS AND DISCUSSION

**Field emission-scanning electron microscopy (FESEM):** FESEM images of morphology of as received MWCNT, MWCNT-carboxylic, MWCNT-ester and MWCNT-amide were showed in Fig. 1(a-d), respectively. From the Fig. 1(a), it showed clearly that as received MWCNT exhibit 20-30 nm of diameter size with few agglomerations. After carboxylic functionalized, the diameter size slightly increased up to 40 nm due to insertion of new functional group as expected. It can be seen also that the roughness of the side walls is attributed by defect sites with carboxyl groups on the surface [11]. When the MWCNT-carboxylic were further functionalized with octadecanol and dodecylamine, the diameter size around 20-

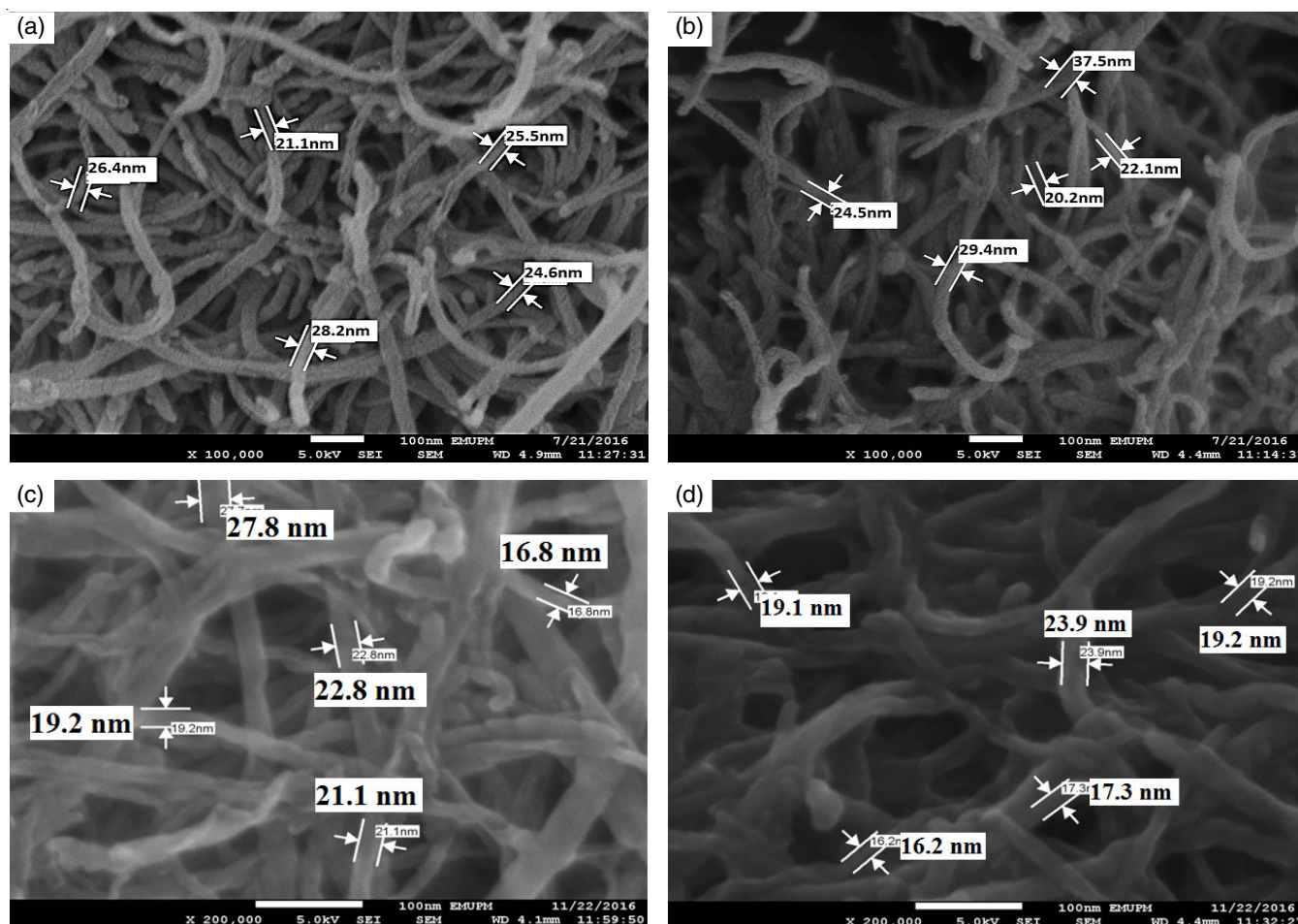


Fig. 1. (a) as received MWCNT (b) MWCNT-carboxylic (c) MWCNT-ester (d) MWCNT-amide

30 nm but further characterization need to be done to confirm attachment of amide and ester functional group.

**Energy dispersion X-ray analysis (EDX):** Energy dispersion X-ray analysis (EDX) analysis is to determine the existence of oxygen, nitrogen and carbon element. It was conducted on several zones on all of four samples. The main elements and concentrations found in a representative analysis are listed in Table-1. The largest element in the as-received MWCNT is carbon. For MWCNT-carboxylic and MWCNT-ester, oxygen content is the main interest due to presence of carboxylic and ester functional group and it showed that percentage of oxygen content increased after carboxylation and esterification treatment. As in MWCNT-amide, percentage of nitrogen content appeared due to presence of amide functional group. This result confirmed that carboxylic, ester and amide functional group successful attached on the surface of MWCNT.

TABLE-1  
EDX ANALYSIS OF AS RECEIVED  
MWCNT AND FUNCTIONALIZED MWCNT

Element	Multi-walled CNT(MWCNT) (%)			
	As received MWCNT	MWCNT-carboxylic	MWCNT-ester	MWCNT-amide
C	96.64	92.06	93.20	80.80
O	2.98	7.19	6.80	10.94
N	–	–	–	8.26

**Raman spectroscopy:** Raman spectra of as-received MWCNT, MWCNT-carboxylic, MWCNT-ester and MWCNT-amide are displayed in Fig. 2. Raman spectroscopy is a very important tool and highly sensitive for the characterization of

carbon-based nanostructures morphology. Raman spectra can be categorized into two prominent peaks that correspond to the characteristics of MWCNT; the first peak at about  $1350\text{ cm}^{-1}$  (D band) deriving from disordered graphitic structures and the second peak at about  $1580\text{ cm}^{-1}$  (G band) deriving from concentric cylinders of graphite layers [12]. Whereas, the ratio of peak intensity of the D-band and G-band ( $I_D/I_G$ ) indicated the amount of defect sites on the MWCNT. Table-2 summarized the value of  $I_D/I_G$  of as received MWCNT and functionalized MWCNT. As can be observed in Raman spectrum, the characteristic peaks of as received MWCNT, named the D band at  $1346\text{ cm}^{-1}$  and the G band at  $1588\text{ cm}^{-1}$ , approximately, are identified. When carboxylation of MWCNT was performed, these characteristic peaks can still be identified, proving that the acid treatment does not damage the structure of MWCNT. However, when the MWCNT-carboxylic was further functionalized with ester and amide, the G band shifted downfield about  $6\text{--}8\text{ cm}^{-1}$  compared to the MWCNT-carboxylic. This slightly shifted due to ester and amide functional group on the surface of MWCNT. Comparing the ratio  $I_D/I_G$  values of as received MWCNT and MWCNT-carboxylic, it is observed that after functionalization, the ratio values increase as expected (Table-2). The oxidation of MWCNT breaks some of its bonds and inserts chemical groups that can be interpreted as defects on the structure [13]. But, after ester and amide functionalization, the values decreasing. It is proven that the inner graphitic layers of MWCNT were not affected by the functionalized amide and ester and still kept their highly oriented structure. This is inline with the lower intensity of D-band (level of defects in the sample) of MWCNT-ester and MWCNT-amide compared to the MWCNT-carboxylic.

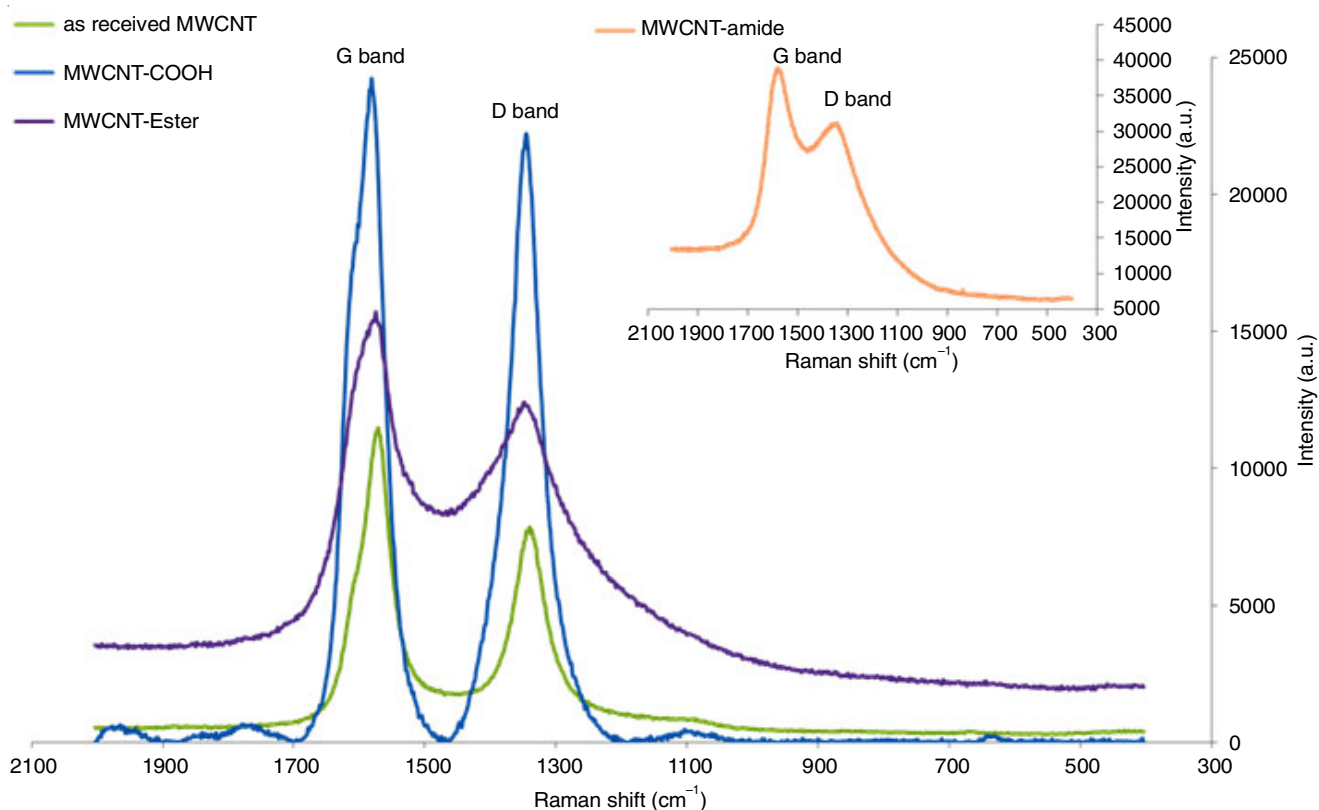


Fig. 2. Raman spectra of as received MWCNT and functionalized MWCNT

TABLE-2  
I<sub>D</sub>/I<sub>G</sub> OF AS RECEIVED MWCNT AND  
FUNCTIONALIZED MWCNT

MWCNT	G band (cm <sup>-1</sup> )	D band (cm <sup>-1</sup> )	I <sub>D</sub> /I <sub>G</sub>
As received MWCNT	1588	1346	0.85
MWCNT-carboxylic	1586	1347	0.96
MWCNT-ester	1579	1350	0.80
MWCNT-amide	1581	1360	0.80

## Conclusion

A methodology of functionalization of multi-walled carbon nanotubes *via* amidation and esterification has been demonstrated. Two different functionalized reactant containing different functional groups were introduced onto the surface of MWCNT after carboxylation of the MWCNT surface. Carboxylation was used as reaction precursors for further modification by creating defects and also adding large amount of oxygen-containing group on the surface of MWCNT. Multi-walled carbon nanotubes were functionalized with amide and ester group using sonication method and several characterizations were performed to analyze the attachment of carboxylic, ester and amide functional group. FESEM, EDX and Raman analysis have provided an evidence of this modification which lead to the changes of diameter size, existence of new element composition and successful attached new functional groups. The surface modification of MWCNT could significantly improve dispersibility and enhance interfacial interaction between the MWCNT and analytes. Therefore, functionalization becomes an important step, which will facilitate the effectiveness of MWCNT in their application.

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