



## The Chemical Functionalization of Multi-wall Nanotubes with Methyl 2-(2-amino-4-oxothiazol-5(4H)-ylidene) Acetate and Phenylhydrazine

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### ABSTRACT

In this paper, the chemical functionalization of carboxylated multi-walled carbon nanotubes (MWNT-COOH) by Methyl 2-(2-amino-4-oxothiazol-5(4H)-ylidene) acetate (MWNT-Amide) and latter modification by phenylhydrazine for producing thiazole derivative (MWNT-Thiazole) have been investigated. All products were characterized by FT-IR, Raman spectroscopy, SEM, elemental analysis, TGA, DTG. These functionalizations have been chosen due to active sites of carbonyl and C=C groups in MWNT-Amide and the creating thiazole derivative on the MWNTs for future application.

**Key words:** Nanotube carbon, Thiazole derivative, Functionalization, TGA.

### INTRODUCTION

The discovery of carbon nanotubes (CNTs) by Iijima<sup>1</sup> have been attracting much attention from chemists and scientists owing to their electronic, mechanical, optical, and chemical characteristics<sup>2-3</sup>. One of the driving forces in the development of new classes of novel nanomaterials for applications in biology and medicine have been functionalization chemistry during the past decade<sup>4-5</sup>. The chemical functionalization of CNTs involves the generation of chemical moieties on their surface for subsequent alignment. These surface modifications play an important role for application of nanotubes in composite, sensors and many other fields. Thus, extensive research has been focused

on the surface modification of CNTs which can be cited esterification<sup>6</sup>, addition of free radicals<sup>7</sup>, oxidation<sup>8</sup>, amidation<sup>9-11</sup>, hydrogenation<sup>12</sup>. In previous papers, we have investigated the functionalization of MWNTs with 1,2-phenylenediamine<sup>9</sup>, 2-aminophenol<sup>10</sup> and urea derivatives<sup>11</sup>. In this paper, we investigated the functionalization of MWNT-COOH with Methyl 2-(2-amino-4-oxothiazol-5(4H)-ylidene) acetate to producing thiazole derivative (MWNT-Thiazole) through the reaction with phenylhydrazine. Synthesis route of modified MWNT-COOH was shown in Fig. 1. The products were characterized by FT-IR, Raman, SEM, TGA, DTG and elemental analysis.

## EXPERIMENTAL

All reagents and solvents (thionyl chloride, phenylhydrazine, THF and DMF) from Merck Chemical Inc. and MWNT-COOH (%95 purity, 20-30 nm, Netvino Co., Ltd) were purchased and used as received. Methyl 2-(2-amino-4-oxothiazol-5(4H)-ylidene) acetate are prepared from the reaction thiourea with dimethylacetylenedicarboxylate (DMAD)<sup>13</sup>. Fourier transform infra red (FT-IR) spectrum was recorded using KBr tablets on a Thermo Nicolet Nexus 870 FTIR spectrometer. Raman spectra recorded on VARIAN-CARY 100 spectrometer. Scanning Electron Microscope (SEM) was used to study the morphology of the MWNTs. SEM measurement was carried out on the XL30 Philips Electron Microscope. Elemental analyses of C, H, N were performed with a SERIES (II) 2400 from Perkin Elmer Co. USA. The samples investigated by thermal gravimetric analysis (NETZSCH TG 209 F1 Iris) in the N<sub>2</sub> (10°C/min).

### Preparation of MWNT-Amide (2)

100 mg of the MWNT-COOH were suspended in 15 mL thionyl chloride (SOCl<sub>2</sub>) and 1 mL dimethyl formamide (DMF). The mixture was then stirred at 70 °C for 30 h under reflux. Subsequently, the residual SOCl<sub>2</sub> was removed by reduced pressure distillation to yield the acylchloride-functionalized MWNT (MWNT-COCl). 80 mg of MWNT-COCl were mixed with 200 mg of Methyl 2-(2-amino-4-oxothiazol-5(4H)-ylidene) acetate in 25 ml DMF and the reaction mixture was stirred at 90 °C for 72 h. Then, the mixture was cooled to room temperature, filtered and washed thoroughly with DMF, ethyl alcohol and THF. Subsequently, the black solid was dried at room temperature for 6 h under vacuum condition.

### Preparation of MWNT-Thiazole (3)

40 mg of the MWNT-Amide was sonicated in 15 ml phenylhydrazine for 15 minutes gave out a homogeneous suspension. Then, the mixture was stirred at 80°C for 72 h. After cooling to room temperature, the reaction mixture was separated by centrifugation and washed thoroughly with THF. Thus, the obtained solids were dried by vacuum for 6 h.

## RESULTS AND DISCUSSION

The Fig. 2 presents the FT-IR spectrum of Amine, Methyl 2-(2-amino-4-oxothiazol-5(4H)-ylidene) acetate, and modified-MWNTs. In 1, the peak at 1531 cm<sup>-1</sup> is assigned to the active carbon stretching mode of the MWNT-COOH<sup>14</sup> that forms the framework of the carbon nanotube sidewall. The appearance of the absorption peaks at 1722 and 1047 cm<sup>-1</sup> in the IR spectra of MWNT-COOH clearly indicates carboxylic groups on MWNTs<sup>15</sup>. The two bands at 2800-2950 cm<sup>-1</sup> which are seen in all spectra are assigned to CH stretching of MWNT-COOH defects. In the spectrum 2, the appearance of the two new peaks at 1651 cm<sup>-1</sup>(Amide A) and 1687 cm<sup>-1</sup>(Amide B) indicates that amine has been successfully anchored onto the external surface of MWNTs (in compared to spectrum of Amine and 1). In addition, the peak at 1707 cm<sup>-1</sup> can be assigned to C=O ester as compared to 1709 cm<sup>-1</sup> in Amine spectrum. In the spectra 3, the peak of Amide (B) has been disappeared and the remarkable peak at around 1661 cm<sup>-1</sup> are appeared which can be assigned to Amide (A). The peaks at around 3200-3500, 1540-1580, 1420-1530, 1200-1400 and 1000-1100 cm<sup>-1</sup> correspond to N-H and OH stretching modes, C=C stretching nanotube, aromatic ring modes, C-N and C-O stretching modes, respectively. From these results it can be deduced that the MWNT-COOH of has been successfully modified by thiazole derivative.

Further evidence for the functionalization of MWNT-COOH was obtained by Raman spectroscopy which is a powerful tool used to characterize the functionalized CNT. Generally the G lines, which is tangential-mode peak, are observed at around 1572 cm<sup>-1</sup> and D lines, attributed to the defects and disorder-induced peaks<sup>16-17</sup>, are observed at around 1347 cm<sup>-1</sup> for both MWNT-

**Table 1: Elemental analysis of modified MWNTs 1-3**

MWNT	%C	%H	%N	%S
1	96.8	0.18	0.00	0.00
2	89.24	1.69	1.85	2.13
3	88.92	2.01	3.57	2.06



Fig. 1: Synthesis route of modified MWNT-COOH

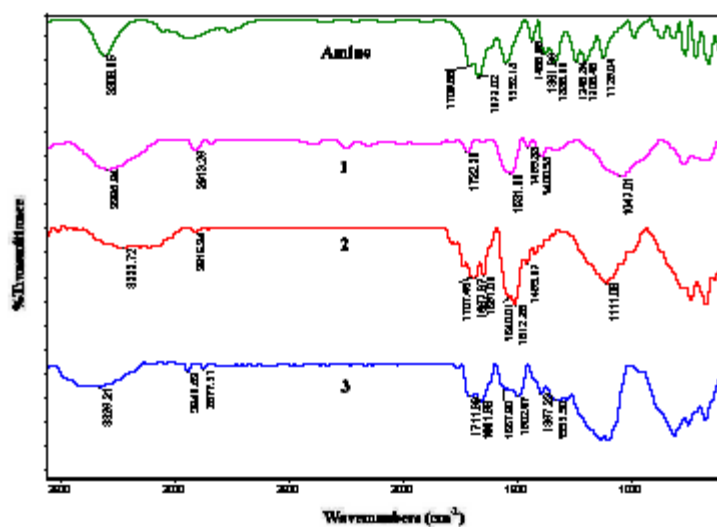


Fig. 2: FT-IR spectra (after baseline correction) of Amine, MWNT-COOH(1), MWNT-Amide(2) and MWNT-Thiazole(3)

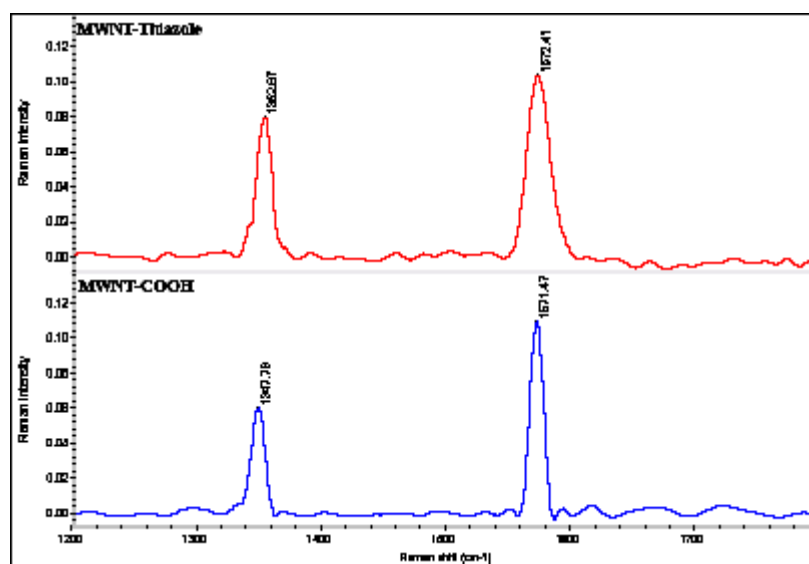


Fig. 3: The raman spectra of MWNT-COOH and MWNT-Thiazole.

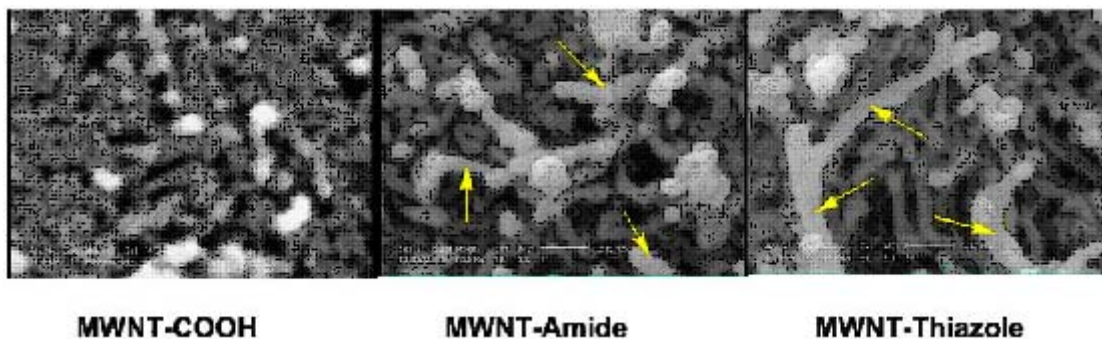
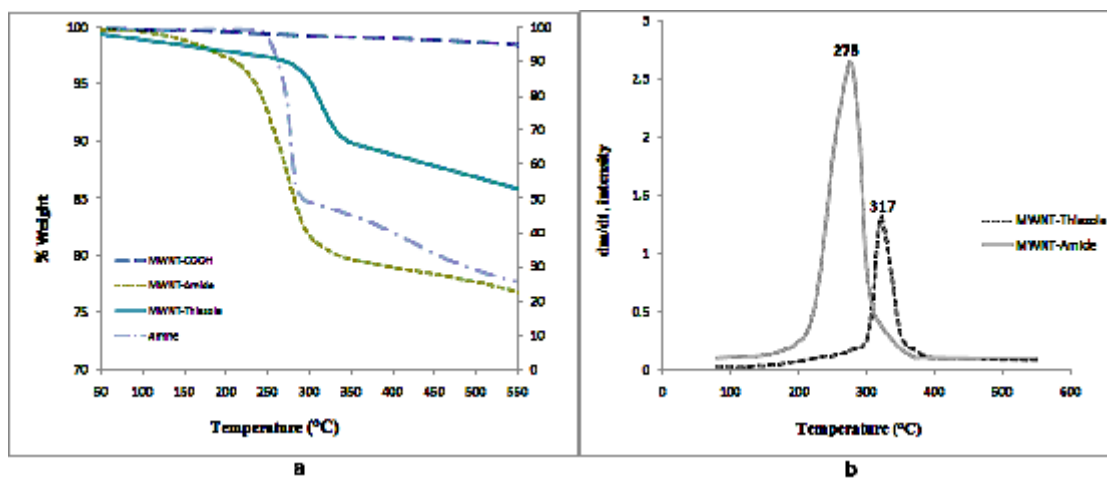


Fig. 4: The SEM images of modified MWNTs

Fig. 5: TGA (a) and DTG (b) curves of modified-MWNTs in the N<sub>2</sub> (10 °C /min)

COOH and MWNT-Thiazole as was shown in Fig. 4. It is obvious that ( $I_D/I_G$ ) ratio increases from 0.564 in 1 to 0.781 in 3 after functionalization. This increase in D band intensity is related to the  $sp^3$  hybridization of carbon and is used as an evidence of the disruption of the aromatic system of  $\pi$  electron by the attached molecules<sup>18</sup>. In other words, this indicates a partial destruction of the conjugation structure of the MWNT sidewall because of attaching thiazole derivative.

In Fig. 4, SEM images of MWNT-COOH, MWNT-Amide and MWNT-Thiazole are shown. In the SEM image of MWNT-COOH, it seems that the uniform surfaces of nanotubes are relatively smooth. By the functionalization, MWNT-Amide and MWNT-Thiazole, a tubular layer of uniform organic compounds (Amine and thiazole derivative) is clearly present on the surface of the MWNT-COOH (the

rough part) and the diameters of the modified MWNTs are slightly increased as compared to that of MWNT-COOH. The results suggest that the created organic compounds are attached on the MWNT by covalent bond.

Other evidence for modified MWNTs 1-3 was obtained by elemental analyses which are shown in Table 1. Apart from the carbon values, the changes of atomic percentages H (1.69%), N (1.85%) and S (2.13%) in 2 and H(2.01%), N(3.57%) and S (2.06%) in 3 (as compared those in 1) indicated that 1 is functionalized. On the other hand, the increase of percentage of H, N and S for 2-3 in comparing to 1 confirms the 2-3 formation. Based on these data coupled with the assumption that the atomic percentages of nitrogen, hydrogen and sulfur were originated from the employed Methyl-2-(2-amino-4-oxothiazol-5(4H)-ylidene)

acetate and phenylhydrazine, we confirmed the functionalization of MWNT-COOH.

Figure 5a provide quantitative information on the nanotube functionalization by using TGA results. Since MWNT-COOH are almost thermally stable as shown in Fig. 5a, the weight loss before MWNTs decomposition can be used to estimate the quantity of various groups attached to nanotube by TGA. In TGA graphs of MWNT-Amide and MWNT-Thiazole, one decomposition at around 200-340°C (Amine) and 260-360°C (thiazole derivative), respectively are observable as comparing with Amine thermogram. If the mass loss of the MWNT-COOH at 360 °C (%0.88) is used as the reference, the mass loss of functionalized MWNT by Amine and thiazole of MWNT-Amide and MWNT-Thiazole at 360 °C is about %17.85 and %7.6, respectively. These results indicate that there is one amide group for MWNT-Amide per 69.3 and one thiazole derivative for MWNT-Thiazole per 270 carbon atoms of MWNT, respectively.

The DTG curve provides further evidence for covalent modification. In Fig. 5b, the major peak at 275 °C for MWNT-Amide and 317 °C for MWNT-Thiazole could be attributed to the loss of the Amine and thiazole groups, respectively bonded to MWNT.

## CONCLUSION

In summary, we have introduced Methyl 2-(2-amino-4-oxothiazol-5(4H)-ylidene) acetate and thiazole derivative onto the surface of nanotubes. These modifications were demonstrated by their SEM images, FT-IR, Raman, elemental analysis, TGA and DTG. By this functionalization, active sites for further reactions are provided.

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