Effect of Reaction Time on Modification of Multi-walled Carbon Nanotubes with HNO₃

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Abstract. The functionalization of Multi-walled Carbon Nanotubes (MWCNTs) is addressed to improve its interaction capability with other materials for further applications. In this research, MWCNTs functionalization was carried out in several steps such as oxidation, filtration, washing, and drying. The optimization of reaction time for MWCNTs functionalization was conducted to achieve the optimum condition which efficiently functionalizes MWCNTs surface. The sample characterizations were investigated by Boehm titration, Fourier Transform Infrared (FTIR) Spectroscopy, Thermo Gravimetric Analysis (TGA), and dispersion test. As a result, carboxylic groups were successfully attached onto the MWCNTs surface and stable dispersion of MWCNTs was obtained after 12 hours. Oxidation with nitric acid for 12 hours at room temperature is the optimum treatment time for surface modification.

1. Introduction
Multi-walled Carbon Nanotubes (MWCNTs) have attracted great attention because of their unique characteristics including high aspect ratio, high surface area, and stability of nanoparticles. However, MWCNTs are hydrophobic and are poorly dispersed in either water or organic solvent. Because of its fine size, high surface energy of MWCNTs and with its intrinsic Van der Waals forces, raw MWCNTs tend to aggregate and entangle [1]. These characteristics will limit their application. Covalent surface modification displays functional groups such as −COOH, −COH and −OH groups that are attached to the sidewall and side end of MWCNTs by covalent bonds [2]. Chemical oxidation is carried out for functionalization of MWCNTs. MWCNTs can be treated with strong oxidant such as HNO₃, KMNO₄, or HNO₃/H₂SO₄ to form fractional concentration of carboxyl groups and this can increase the MWCNTs solubility characteristics.

Previous studies described numerous methods for chemical functionalization of carbon nanotubes (CNTs). Shen et al. [1] reported that amino-functionalized MWCNTs can improve their dispersion in H₂O. Olugbenga et al. [3] showed that using of organic acid-inorganic acid mixture is potential for the purification of CNTs. L. Thi Mai Hoa [4] oxidized MWCNTs in a mixture of HNO₃/H₂SO₄ to study the influence of different oxidizing conditions on the morphological and chemical-physical properties of MWCNTs.
In this paper, we are concerned with optimization of reaction time for MWCNTs functionalization by oxidizing the MWCNTs with nitric acid and investigate the influence of reaction time on the amount of carboxylated groups in modified MWCNTs.

2. Experimental

2.1. Material
Multi-walled carbon nanotubes (MWCNTs with an OD 6-9 µm, length 5 µm, and carbon basis >90%) was purchased from Cheap Tubes Inc, USA. Nitric acid (HNO₃ 65% v/v), glacial acetic acid, and sodium hydroxide were purchased from Sigma Aldrich, USA. Hydrochloric acid (HCl 37% v/v) was purchased from Mallinckrodt Pharmaceuticals, UK. The solution of 0.05 N sodium hydroxide and 0.05 N hydrochloric acid for titration process are prepared.

2.2. Oxidation of the MWCNTs
Oxidation of MWCNTs was conducted according to the previous method reported by M. Habibizadeh et al. [5]. Raw MWCNTs were functionalized by adding 500 mg of MWCNTs in a round bottom flask with 100 mL of 14.4 M HNO₃. A bottom flask equipped with reflux was immersed in oil bath on the top of hot plate. This process was run by vigorously magnetic stirring. After the certain reaction time, MWCNTs were filtered and washed with aquadest to neutral pH. Functionalized MWCNTs were dried in oven at 80°C for 24 hours. For the study of effect of reaction time, the mixture was treated by magnetic stirring for 6, 9, and 12 hours at room temperature which represent as Sample A, B and C, respectively.

2.3. Characterization of MWCNTs
The functional groups of functionalized MWCNTs were analyzed using Fourier Transform Infrared Spectroscopy (FTIR) (Spectrophotometer Shimadzhu FTIR-8201 PC, Country) with KBr method. Boehm titration was used in order to calculate acidic groups in functionalized MWCNTs which represent the relative concentration of acidic groups on the surface. The oxidized MWCNTs were immersed in 0.05 N NaOH solution and stirred continuously for 24 h to reach the equilibrium state, then dropwise titrated with 0.05 N HCl solution until the neutral point in order to determine the unreacted NaOH solution. The concentration of acidic groups on the surface MWCNTs is equal to the amount of reacted NaOH. Goertzen et al. [6] has introduced the total amount of reacted surface functionality (n_{cSF}) with equation 1 as below:

\[ n_{cSF} = N_B \times V_B - N_T \times V_T \times \frac{V_B}{V_a} \]  

where \( N_B \) and \( V_B \) are the concentration and volume of the reaction base mixed with the carbon. \( n_{cSF} \) denotes the moles of carbon surface functionalities on the surface of the carbon that reacted with the base during the mixing step. \( V_a \) is the volume of the aliquot taken from \( V_B \). \( N_T \) and \( V_T \) are the concentration and volume of the acid added to the aliquot.

Thermo Gravimetric Analysis (TGA) was used to estimate the degree of functionalization and investigate the thermal stability of samples. The weight of the samples was approximately 10 mg. The test was performed under N₂ (100 mL/min). The sample was heated at 10°C min⁻¹ from 30°C to 800°C. The grafting percentage (GP) of the MWCNTs-COOH surface was determined using the following equation [4]:

\[ GP = \frac{\Delta W_{MWCNT-COOH} - \Delta W_{MWCNTs}}{\Delta W_{MWCNTs}} \times 100\% \]  

\( \Delta W_{MWCNT-COOH} \) and \( \Delta W_{MWCNTs} \) are the percentage weight loss of MWCNTs-COOH and MWCNTs, respectively.
The dispersion test was carried out to determine the improvement of MWCNTs solubility after being modified. The oxidized MWCNTs (100 mg) were dispersed in 5 mL water by vigorously shaking for 10 minutes at room temperature. The mixture was left to stand for 48 hours to observe its stability.

3. Result and Discussion
Raw MWCNTs could be functionalized with oxygen-containing groups like -COOH and -OH at the MWCNTs ends and at the outer sidewall, where the defects are introduced through oxidation [5]. These could be further used for the reaction to conjugate more functional groups as shown in Figure 1.

![Figure 1](image)

**Figure 1.** Reaction scheme for functionalization of MWCNTs.

To analyze total acidic groups in carboxylates MWCNTs, Boehm titration was performed. Figure 2 shows the total amount of -COOH groups in functionalized MWCNTs that increase along with the reaction time. The mmol of acidic functional groups (-COOH) per gram of functionalized MWCNTs materials is given in Figure 2.

![Figure 2](image)

**Figure 2.** The concentration of -COOH groups estimated by Boehm acid-base titration method.

As seen from the data, the extent of –COOH functional group of every sample gradually increase along with the treatment duration from 2.53 mmol/g on sample A to 3.08 mmol/g on sample B to 3.99 mmol/g on sample C.

The functionalization of MWCNTs was confirmed by FTIR Spectroscopy. Table 1 shows the FTIR spectra characteristics of raw and functionalized MWCNTs. As can be observed in FTIR spectra, the characteristic peaks, named X and Y band, are identified. The first peak, X band, is corresponded to the C-O stretching vibration. It is located at 1126.43; and 1111 cm\(^{-1}\) for samples B, and C,
respectively. The second peak is Y band, which is related to the stretching of C=C bonds [4]. The peak is located at 1527.62 cm\(^{-1}\) for all samples. No shifting occurs in modified MWCNTs samples, but the intensity changed along with the treatment duration. Furthermore, the peak at 3448.72 and 1635.64 cm\(^{-1}\) are corresponded to hydroxyl (O-H) and carbonyl groups (C=O), respectively [5]. It can be observed from Table 1 that the position of X and Y band are shifted for raw MWCNTs compared to functionalized MWCNTs.

| Sample | Peak, cm\(^{-1}\) | Intensity | Intensity Ratio, I\(_X\)/I\(_Y\) |
|--------|-----------------|-----------|-----------------------------|
| A      | X: -            | -         | -                           |
|        | Y: 1527.62      | 1.438     | -                           |
| B      | X: 1126.43      | 9.385     | 1.222                       |
|        | Y: 1527.62      | 7.682     |                             |
| C      | X: 1111.00      | 29.320    | 1.012                       |
|        | Y: 1527.62      | 28.960    |                             |

The shifting can be caused by treatment effect upon strong acid (HNO\(_3\)). The functionalization process of MWCNTs, especially with strong acid, will breaks some of its bonds and attaches functional groups that can be interpreted as defects on the structure. When the functionalization process is carried out, these peaks can still be identified. This proves that the modification process does not damage the structure of MWCNTs [4]. Comparing the X and Y band for functionalized MWCNTs samples, it is clear that the intensity increased. It shows that the carboxyl group was successfully attached to MWCNTs. In addition, change in intensity ratio I\(_X\)/I\(_Y\) can also further support the formation of carboxylated MWCNT.

Figure 3. FTIR spectra for functionalized MWCNT

The influence of treatment duration is showed in FTIR spectrum as shows in Figure 3. From the IR absorption spectra, it was found that the increase of treatment duration will strengthen the peak intensity of carboxyl groups. The absorption spectrum of MWCNT-COOH mainly consisted of –OH
stretch at 3448 cm\(^{-1}\) and carboxyl >C=O stretch at 1635 cm\(^{-1}\). The result was in agreement with the explanation above.

In order to confirm the grafting rate of -COOH on the surfaces of MWCNTs, the thermal gravimetric analyses (TGA) are performed. We did comparison the TGA analysis of raw material of MWCNTs and the selected functionalized MWCNT based on the result from Boehm titration (sample C). Figure 4 shows the TGA analysis of raw MWCNT, and Sample C of MWCNT-COOH that presents the curves corresponding to the weight loss as a function of temperature. We observed a weight loss of 7.51\% for raw MWCNT in TGA curves. For the MWCNTs-COOH obtained after modification, the final weight loss for Sample C is 13.45\%. As shown in TGA curve, the oxidized MWCNTs start decomposing earlier than raw MWCNTs. It can be attributed to the presence of functional groups on the nanotubes [4]. As calculated by equation (2), the grafting percentage (GP) corresponding to C is 5.93\%, which reveals that an increase of the thermal degradation is observed for functionalized MWCNTs.

Figure 5 shows the dispersion images of MWCNTs-COOH in comparison with the raw MWCNTs in water (100 mg/5 mL). Raw MWCNTs could not disperse because of the strong intrinsic Van der Waals forces between them. Raw MWCNTs was totally separated from water and form bundles. However, sample A, B, and C could only maintain its stable dispersion for 10 minutes and after 48 hours, the samples were completely precipitated. This means that the increase of reaction time in oxidation reaction has not yet effectively reduced the apparent activation energy of MWCNTs, which can prevent the aggregation phenomenon [7].

\[\text{Equation (2)}\]

\[
\text{GP} = \frac{\text{Weight loss of functionalized MWCNTs} - \text{Weight loss of raw MWCNTs}}{\text{Weight loss of raw MWCNTs}} \times 100\%
\]
4. Conclusion

The usefulness of carbon nanotubes can be limited by its hydrophobic nature. Most of the purification and functionalization methods for the improvement of the hydrophilicity as resulted to the destruction of the carbon nanotube side walls and shortening of the chain length. The purification and functionalization methods adopted in this research were able to achieve the grafting of -COOH groups into MWCNT's surface. The result shows that functional groups will increase with the rise of reaction time. The highest result of functionalization occurred under the reaction time 12 hours with the concentration of acidic groups reaches 3.99 mmol/gram and grafting percentage reaches 5.93%.

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