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Preliminary Analysis on Pore Structure of Modified Multi-Walled Carbon Nanotubes

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ABSTRACT

The modification of multi-walled carbon nanotubes (MWCNTs) via HNO_3:HCl (3:1 v/v) acid treatment was investigated. Commercial MWCNTs was refluxed in the acid mixture for 6 hours at 60°C and the final products was denoted as modified MWCNTs. The morphology and structural properties were characterized via FESEM and RAMAN spectroscopy respectively. Nitrogen adsorption isotherms were measured and the Brunauer-Emmett-Teller (BET) equation was used in determining the BET surface size. The pore size distributions (PSDs) of MWCNTs were then determined using the Barrett-Johner-Halenda (BJH) equation. From FESEM images, the modified MWCNTs are observed to be more compact than commercial MWCNTs. In parallel with the FESEM results, the porosity of modified MWCNTs from the nitrogen adsorption isotherms analysis is less than the commercial MWCNTs since their nitrogen adsorption is lower. The relative intensity, I_D/I_G of modified MWCNTs is 1.017 which is higher compared to the commercial MWCNTs with relative intensity 0.847. Most of the pore sizes of commercial and modified MWCNTs are distributed in mesopore area. However, the pore size distribution of modified MWCNTs shows tendency to macropore size area. After the acid treatment, the BET surface size of commercial MWCNTs is found to be decreased from 108.1275 m^2/g to 90.3318 m^2/g, whereas their average pore width is increased from 170.339 Å to 179.301 Å.

Keywords: acid treatment, Brunauer-Emmet-Teller, MWCNTs.

1. INTRODUCTION

Carbon nanotubes (CNTs), has emerged and gained great interest to be utilized in many applications particularly as adsorbent [1, 2] and gas sensor [3-5]. This is due to their unique specific characteristics such as having high porosity and high surface area [6]. However, the entangled form of CNTs limits their use.

Modification of CNTs using acid treatment comes as efficacious way to optimize their uniqueness. The modification of CNTs assists in improving the dispersion by reducing the attractive Van der Waals interaction among them [7]. Moreover, acid treatment helps in omitting carbonaceous particles such as amorphous carbon, fullerenes, nanoparticles and residual catalyst that usually present in the as-prepared MWCNTs [8]. It is desirable to have without impurities MWCNTs with minimum or without defects.

BET analysis provides precise specific surface area assessment of materials by nitrogen multilayer adsorption as a function of relative pressure. The nitrogen adsorption at a temperature of 77K leads to BET isotherm. BJH analysis can be employed to determine pore area and specific pore volume using adsorption and desorption techniques. This technique characterizes pore size distribution independent of external area due to particle size of the sample.

In this work, the commercial and modified MWCNTs via acid treatment are characterized by using FESEM and RAMAN spectroscopy in order to analyse their morphologies, impurities and defects presence respectively. These MWCNTs were then further characterized using Brunauer-Emmett-Teller (BET) and Barrett-Johner-

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Halenda (BJH) equation to determine their surface area and pore size distributions respectively. As we know, the study on physical characterization of MWCNTs using Brunauer-Emmett-Teller (BET) and Barrett-Johner-Halenda (BJH) equation are still very limited. Therefore, this paper present the analysis on the effects of HNO_3:HCl (3:1 v/v) acid treatment on the surface area, pore volume and pore size distribution of MWCNTs.

2. MATERIALS AND METHOD

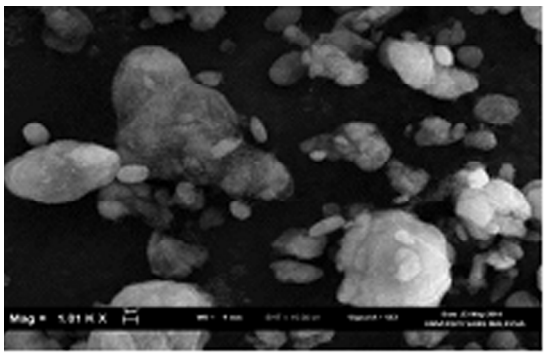
In this work, the commercial MWCNTs with a purity of > 95%, outer diameter of > 50 nm and length of 10-20 μm was purchased from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences. The HNO_3 (65 wt%) and HCl (65 wt%) were obtained from R&M marketing, United Kingdom. The commercial MWCNTs was refluxed in HNO_3: HCl (3:1 v/v) for 6 hours at 60°C. After that the mixture was allowed to cool at room temperature overnight before being filtered. The precipitate, known as modified MWCNTs was washed by distilled water until the water pH approximately at 7. The modified MWCNTs was dried overnight at 80°C to remove volatile solvents.

The morphology characterization for commercial MWCNTs and modified MWCNTs were examined by using field emission scanning electron microscope (Carl Zeiss Leo Supra 50 VP Field Emission). The physical properties for both samples were determined by N_2 adsorption-desorption at 77 K using SAP analyzer (TriStar II 3020). The N_2 isotherms were measured at a relative pressure range of 0.0004-0.99 and then were employed to determine surface area of MWCNTs using Brunauer-Emmett-Teller (BET) equation. The pore size distributions (PSDs) of both MWCNTs samples were determined using the Barrett-Johner-Halenda (BJH) equation.

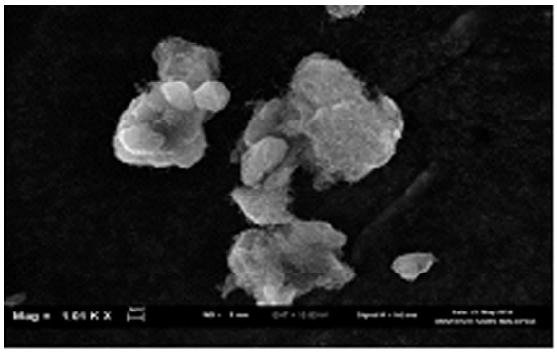
3. RESULTS AND DISCUSSION

3.1. Morphology Analysis

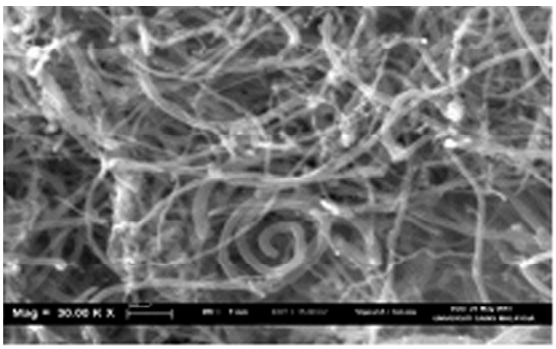
The morphologies of commercial and modified MWCNTs were probed using Field Emission Scanning Electron Microscope (FESEM).



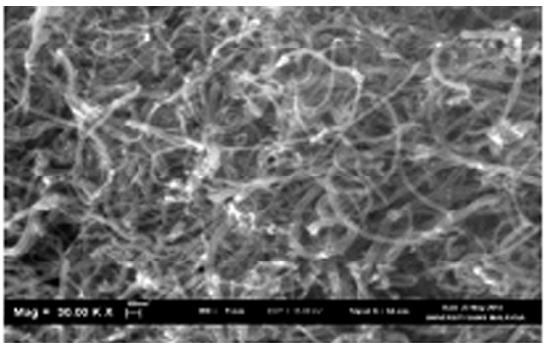
(a) Commercial MWCNTs at 1 k magnification



(b) Modified MWCNTs at 1 k magnification



(c) Commercial MWCNTs at 30 k magnification



(d) Modified MWCNTs at 30 k magnification

Figure 1: Images of commercial and modified MWCNTs at 1 k and 30 k magnification

Figure 1 depicts the indistinguishable images of commercial and modified MWCNTs. Figure 1(b) of modified MWCNTs does not show any significant changes as compared to the commercial MWCNTs, which imply that the modification using HNO_3:HCl (3:1 v/v) does not induces severe defects on the MWCNTs as the MWCNTs is still discernible as its original structure. However, it is observed in Figure 1(d) that modified MWCNTs is more compact as compared to the commercial MWCNTs. The lower porosity of modified MWCNTs is corresponding to the formation of functional groups on their surfaces [9]. The functional groups that potentially presents are hydroxyl, carbonyl and carboxyl groups [10, 11].

3.2. Raman Spectra Analysis

Raman spectroscopy is a useful tool to characterize CNTs which can provide the defects and tube alignment information of the CNTs. The characteristic bands are D band and G band at about 1350 cm^{-1} and 1580 cm^{-1} respectively [12]. The D band is associated with the existence of amorphous or disordered (sp^3 hybridized) carbon in the CNTs sample. The disorder is attributes to the finite or nanosized graphitic plain and other forms of carbon such as rings along with defects on the walls, vacancies, heptagon-pentagon pairs, kinks and heteroatoms [13]. The G band is related to the vibrations in all sp^2 carbon materials [14]. Figure 2 shows the Raman spectra of commercial and modified MWCNTs.

The two main peaks corresponding to D and G bands observed at ~1328 cm^{-1} and ~1579 cm^{-1} respectively. The fixed peaks of D band and G band imply that the graphitic structures of MWCNTs is not damaged after the acid treatment [15]. This result is parallel with the previous FESEM results which depicts the unaffected structure of modified MWCNTs. The presence of defects on the MWCNTs sidewall can be identified by the ratios of intensities of the characteristic peaks, (I_D/I_G) [12]. As shown in Table 1, the I_D/I_G ratio of MWCNTs was increased after the acid treatment. This circumstance is attributes to the sidewall sp^2 to sp^3 hybridization of MWCNTs due to the formation of covalent bond with functional groups [16, 17]. The compactness of modified MWCNTs which expected due to the functional groups emergence depicts in FESEM image is in line with this statement.

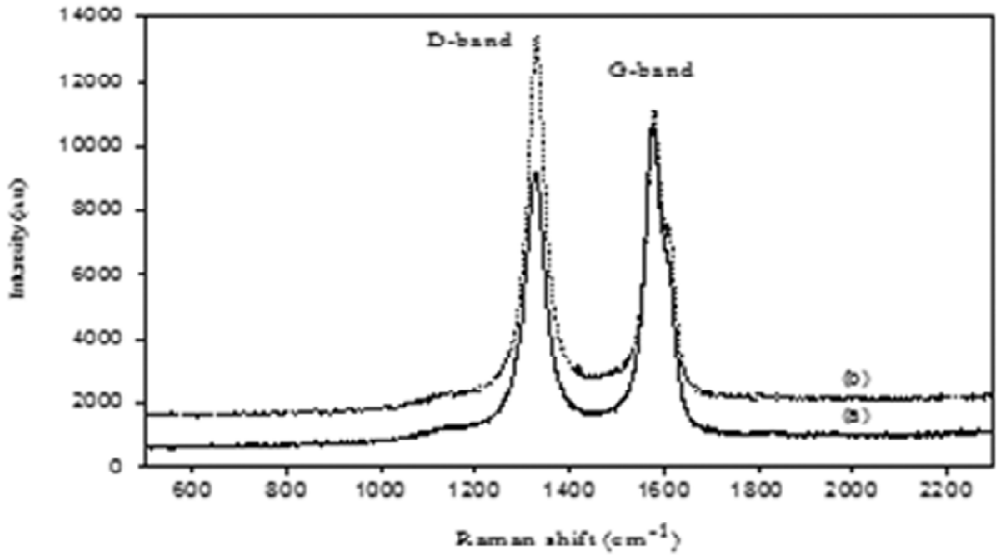


Figure 2: Raman spectra of (a) commercial and (b) modified MWCNTs

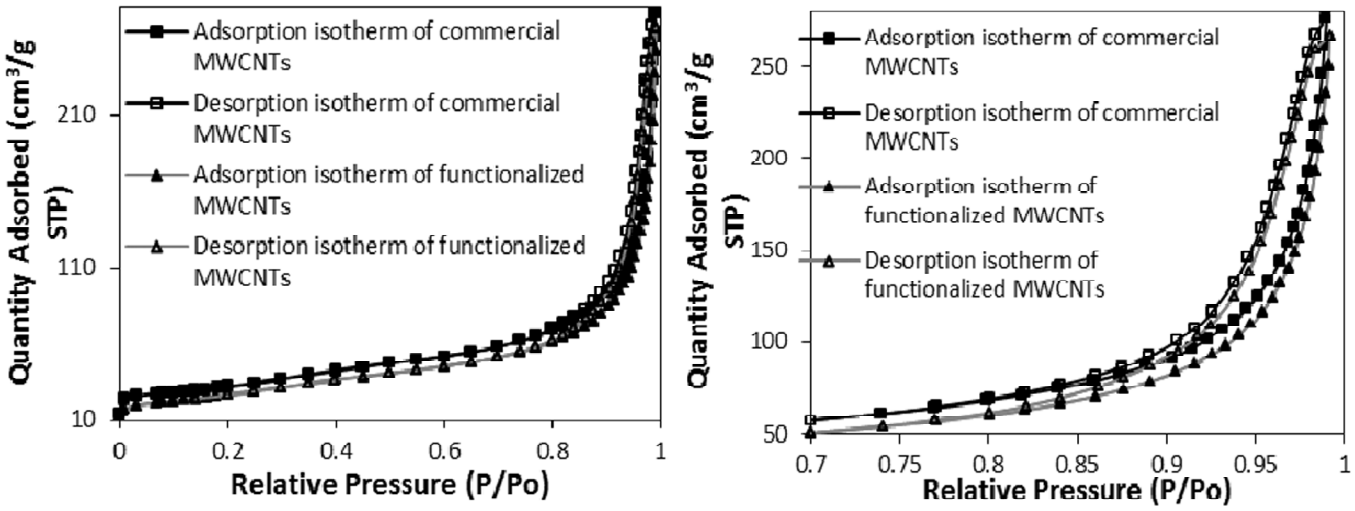
Table 1
Estimation of defect level of MWCNTs

Sample	I_D/I_G
Commercial MWCNTs	0.847
Modified MWCNTs	1.017

3.3. Nitrogen Adsorption-desorption Isotherms Analysis

In Figure 3, the nitrogen adsorption-desorption isotherms of commercial and modified MWCNTs are presented. Both MWCNTs showed Type IV physisorption isotherms with a characteristic H1 hysteresis (IUPAC classification). These results imply that most of the pores of both commercial and modified MWCNTs are in mesopore size [9]. It also can be observed that the nitrogen adsorption of modified MWCNTs is lower than commercial MWCNTs indicates the lower porosity in the modified MWCNTs compare to the commercial MWCNTs [18]. This argument is parallel with the previous FESEM results. Low nitrogen adsorption of modified MWCNTs also indicates their low specific surface area and pore volume. The adsorption and desorption trajectories diverge at the 0.75 and 0.8 relative pressure for functionalized MWCNTs and commercial MWCNTs respectively to form the characteristic hysteresis loop. The H1 hysteresis loop arises due to the capillary condensation of the gas in the mesopores, indicating the transition from the adsorption to the condensation of nitrogen near the saturation vapor pressure [19]. The modified MWCNTs exhibits a slightly larger hysteresis loop when compared to the commercial MWCNTs which indicates enhanced macroporosity in the modified MWCNTs [20].

In Figure 4, most of the pore sizes of commercial and modified MWCNTs are distributed in mesopore area which is in the range of 20 to 500 Å. This result is consistent with the previous statement which stating



(a) Full isotherm **(b) Expanded view of high relative pressure region**

Figure 3: Nitrogen adsorption-desorption isotherms of commercial and modified MWCNTs recorded at 77 K

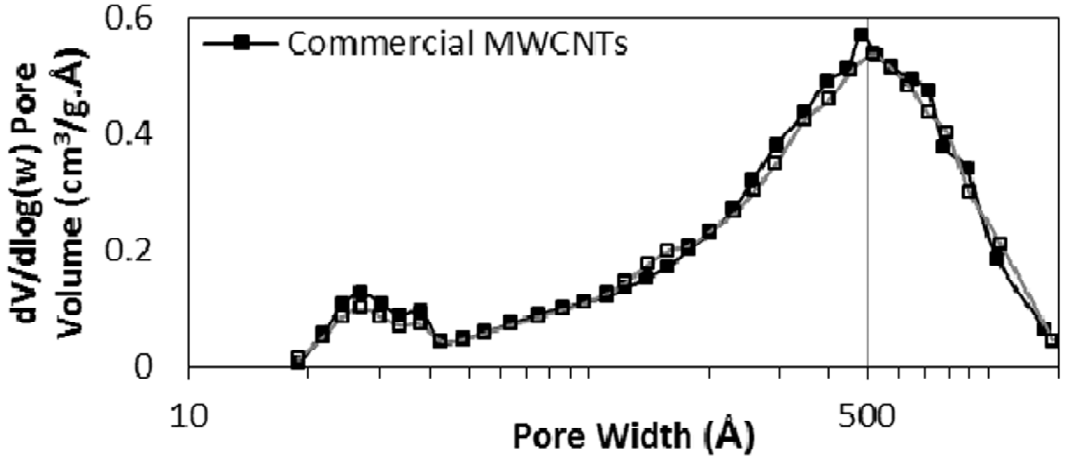


Figure 4: Pore size distribution

that type IV isotherm indicates the mesopore size of MWCNTs [9]. However, the pore size distribution of modified MWCNTs is tends to macropores size area after the acid treatment. This statement is also in line with the previous result that has confirmed the macroporosity enhancement of modified MWCNTs.

The physical properties of commercial and modified MWCNTs are shown in Table 2. The pore structure of MWCNTs changed after the acid treatment which results in the decrease of the BET surface size and the increase of the average pore width. These circumstances may attribute to the removal of amorphous carbon on the sidewall of commercial MWCNTs. The slightly decreased pore volume is probably due to the pore entrance blockage by the functional groups [21].

Table 2
Physical properties of commercial and modified MWCNTs

Sample	BET Surface Size (m^2/g)	Pore Volume (cm^3/g)	Average Pore Width (Å)
Commercial MWCNTs	108.1275	0.419249	170.339
Modified MWCNTs	90.3318	0.410755	179.301

3.4. Illustration of Pore Size and Bet Surface Area

The pore size and BET surface area of commercial MWCNTs before and after the acid treatment were illustrated in Figure 5. The area covered by the solid line is the BET surface area.

As shown in Figure 5(a), the area covered by the solid line is including the amorphous carbon on the commercial MWCNTs sidewall which gives the highest BET surface size. After the acid treatment, the area covered by the solid line is reduced due to the amorphous carbon removal which etching the sidewall and creating the new pores as shown in Figure 5(b) and Figure 5(c) respectively. The new created pores indirectly cause the increase of the average pore width, which results the modified MWCNTs pore size distribution tends to macropore size area. The functional groups attached at the pore entrance cause the pore volume to be slightly reduced as shown in Figure 5(c).

4. CONCLUSION

The modification of MWCNTs using HNO_3:HCl (3:1 v/v) acid treatment are considered successful in producing purified with remained structure of MWCNTs. FESEM images show that the modified MWCNTs does not much differ from the commercial MWCNTs which means that the structure of MWCNTs after the acid treatment are not damaged. The increased I_D/I_G ratio of modified MWCNTs indicates grafting of functional groups on the defected side wall. This RAMAN spectroscopy result is parallel with the

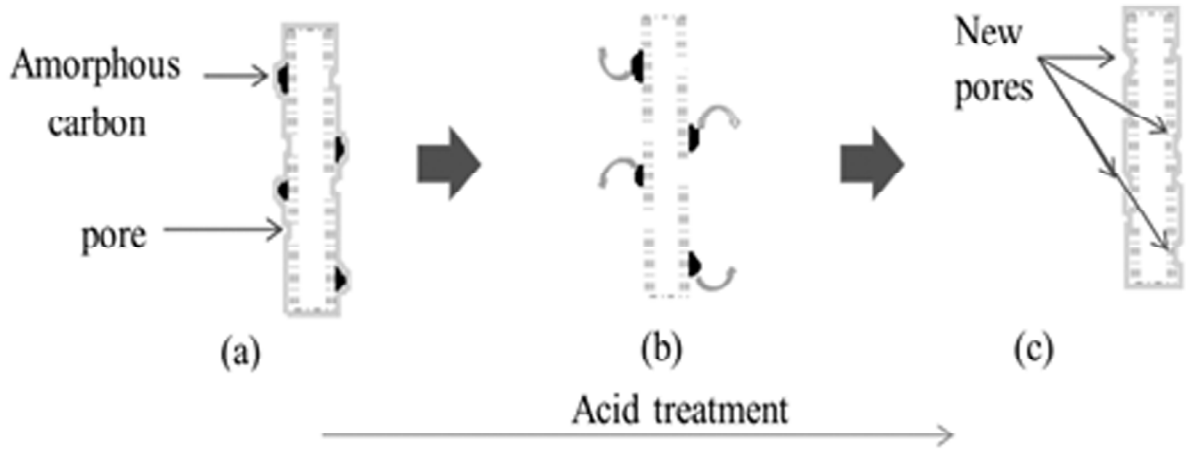


Figure 5: Illustration of pore size and BET surface area of commercial MWCNTs before and after the acid treatment

compactness of modified MWCNTs shown in FESEM image. The nitrogen adsorption isotherms show that the modified MWCNTs is more compact compared to the commercial MWCNTs which attributes to their lower nitrogen adsorption. This result strongly supports the previous argument on the porosity of both MWCNTs. The BET surface size of modified MWCNTs is less compared to the commercial MWCNTs due to the removal of amorphous carbon on the MWCNTs sidewalls. This removal also leads to the increase of modified MWCNTs average pore width. Both MWCNTs samples pore are mostly distributed in the mesopore size area. However the pore size of modified MWCNTs showing tendency to macropore size area after the acid treatment. This circumstance is probably due to the created new pore after the amorphous carbon removal.

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