Chemically Modified Multi-walled Carbon Nanotubes (MWCNTs) with Anchored Acidic Groups
(Pengubahsuaian Secara Kimia ke atas Nanotiub Karbon dengan Multi-berdinding Mengabungkan Kumpulan Berasid)

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ABSTRACT

Surface functionalization of multi-walled carbon nanotubes (MWCNTs) was carried out using a gas phase treatment in a Universal Temperature Program (UTP) reactor by flowing SO₃ gas onto the CNTs while being heated at different temperatures. The functionalized nanotubes were characterized using X-ray Fluorescence (XRF), Fourier Transform Infrared Spectroscopy (FT-IR) and Raman spectroscopy. The amount of oxyen and sulfur containing groups was determined by acid-base titration. The titration results were in good agreement with elemental analysis using x-ray fluorescence. FTIR analysis showed the presence of oxygen and sulfur containing groups, S=O, C-S, C=O and -COOH. Raman spectroscopy confirmed that oxygen and sulfur containing acidic groups covalently attached to the sidewall of the MWCNTs.

Keywords: Carbon nanotubes; characterization; functionalization; sulphur-based surface

ABSTRAK

Fungsionalisasi permukaan nanotiub karbon multi-berdinding (MWCNTs) dilakukan dengan menggunakan rawatan fasa gas dalam reaktor Universal Temperature Program (UTP) dengan mengalirkan gas SO₃ ke dalam MWCNT sambil dipanaskan pada suhu yang berbeza. Nanotiub karbon yang difungsikan dianalisis menggunakan pendaflour sinar-X (XRF), spektroskopi inframerah penjelmaan fourier (FT-IR) dan spektroskopi Raman. Jumlah oksigen dan kumpulan yang mengandungi sulfur ditentukan dengan titrasi asid-alkali. Keputusan titrasi berkesesuaian dengan analisis unsur menggunakan XRF. Analisis FTIR menunjukkan adanya oksigen dan kumpulan yang mengandungi sulfur, S=O, C-S, C = O dan-COOH. Spektroskopi Raman mengesahkan bahawa oksigen dan sulfur adalah kumpulan asid yang diikat secara kovalen pada dinding permukaan MWCNTs.

Kata kunci: Ciri; fungsionalisasi; permukaan asas sulfur; nanotiub karbon

INTRODUCTION

In recent years, a great deal of attention has been focused onto the application of carbon nanotubes as adsorbents to remove toxic and harmful substances from wastewater and air. The large specific surface areas, as well as the high chemical and thermal stabilities, make carbon nanotubes an attractive adsorbent for heavy metals. However, due to its low dispersibility in aqueous systems caused by high Van der Waals forces among tubes, CNTs tend to agglomerate and form bundles in composites instead of individual tubes (Ma et al. 2008; Zhang et al. 2007). Therefore, chemical modifications of CNTs surfaces have been a key research area due to their hydrophobicity properties in aqueous systems. Surface functionalization can effectively improve the dispersibility and reactivity of the CNTs for application in aqueous systems. Nitric acid is one of the most frequently used agents in the oxidation of CNTs. Initially, oxidation begins at the tubes ends, where the distribution of pentagons entails greatest lattice strain, leading to tip opened CNTs (Wang et al. 2009a). As a high curvature in the nanotubes structure is prevalent, the sidewalls are also under strain and are attacked under prolonged oxidation which leads a dramatic increase in the amount of sp³ carbon possessing phenol, lactone, quinine, carboxyl and other groups. Based on these oxygen-containing functions, the subsequent organic or inorganic modification on the CNTs surface has been reported, which demonstrated an improvement in the solubility of CNTs (Wang et al. 2009b). It is also important to develop adsorbent material that can perform the function via two mechanisms simultaneously which are chemisorptions and physisorption. Physisorption is the interaction when an atom or molecule is bound to the surface of a solid by van der Waals forces. On the other hand, chemisorption involves stronger forces and forms chemical bonds that involve the transfer or sharing of electrons. This occurs when an atom or molecule is bound to a surface through overlapping of one or more of its electron orbitals (Clark 1974).

In this study, we investigated the optimum conditions needed to functionalize MWCNTs with high

amounts of acidic sides while achieving a porous material with high surface area. The aim of modification is to introduce oxygen and sulfur containing functional groups as well as to increase its dispersibility in aqueous environment.

EXPERIMENTAL METHOD

MATERIALS

MWCNTs prepared by catalytic chemical vapor deposition (CCVD) process were supplied by Bayer MaterialScience AG, Germany. The CNTs have a purity >95% and the diameter of tubes averages 13 – 16 nm with outer mean diameter about 13 nm, inner mean diameter about 4 nm and length of $> 1\mu$m according to the supplier.

MODIFICATION OF CNTS

In this study, functionalization process was carried out by gas phase treatment in a Universal Temperature Program (UTP) reactor by flowing SO_3 gas onto the CNTs while being heated to different end temperatures, see Table 1. The gas phase reaction was carried out in a horizontal quartz tube reactor heated by a UTP reactor. A weighed sample of CNTs (~3 g) was placed in the horizontal quartz tube reactor fitted with gas inlet and the outlet was connected to trapping system. A multi-neck flask containing 20% SO_3 in concentrated H_2SO_4 fitted with gas inlet/outlet tubes was connected to reactor tubes. Argon stream was used to carry SO_3 vapor into the quartz tubes.

CHARACTERIZATION OF THE MODIFIED CNTS

Surface acidic determination. The amount of acidic sites in the treated MWCNTs was determined by direct titration with 0.01 M NaOH solution. A weighed amount of treated Baytubes (0.1 g) was transferred into 100 mL Erlenmeyer flask. Fifty milimeter of the solution of 10^{-3} M KCl was added into the flask. The flask was shaken at 400 rpm for 24 hours under vigorous magnetic stringing to ensure equilibrium was reached. The solution was then directly titrated with 0.01 M NaOH solution. The titration was carried out using Mettler DL25 Autotitrator. This equipment is equipped with titrator DL25, automatic burette 20 mL, stirrer and was connected to a computer, which controlled the equilibrium condition and titrant delivery. The dynamic dosing of the titrant in increments of 0.1 mL to the suspension samples and the pH of the solution was measured every 10 second.

ELEMENTAL AND STRUCTURAL CHARACTERIZATION

The structural defects of MWCNTs were investigated using Raman Spectroscopy, respectively. The Raman spectrograph used in this study was HORIBA Jobin Yvon spectrometer and the light source used was 632.8 nm with 10x objective. The extent of sulfonation of the MWCNTs was determined using X-ray Fluorescent (XRF) of Bruker P4 engine. The surface functional groups of sulfonated CNTs was determined using a Fourier Transforms Infrared Spectroscopy (FT-IR). The IR spectra of the functionalized samples were recorded using a Perkim Elmer Spectrum 100 series equipped with Universal ATR sampler accessories. The scanning range of the experiment was $600 – 2500$ cm^{-1} and during the test, the number of scanning with the air as background is kept constant.

TABLE 1. Chemical and structural properties of MWCNTs functionalized samples

Samples	Parameter		pKa value		Total number of surface acidic	Functional groups present	Raman Shift (cm-1)		ID/IG	No of molecules (mole) 10-5	
	Temp (°C)	Time (hr)	pKa1	pKa2			D	G		C	S
B6	100		3.50	5.98	4.36	Carboxyl and lactone	1327.94	1598.05	1.51	11249	6.841
B7	200	2	3.34	7.10	6.05	Carboxyl and phenol	1328.74	1601.81	1.59	15800	16.45
B8	300		4.02	7.00	2.70	Carboxyl and lactone	1327.15	1601.06	1.53	14500	2.618

RESULTS AND DISCUSSION

SURFACE ACIDITY

The results presented in Figure 1 and Table 1 show the titration profile of the functionalized samples. The profile of the titration curves for samples B7 and B8 are almost similar. The B6 sample, which was treated at 100ºC, clearly contains two distinctive peaks that were detected in NaOH filtrate. This implies the presence of two types of functional groups. In contrast, B7 and B8 (treated at 200 and 300ºC, respectively) show two peaks that cannot be resolved well, possibly due to degree of oxidation at high temperature which generates molecular oxidation debris on the carbon surfaces. The oxidative treatment of CNTs leads to erosion of their structure (Figure 4). It was observed that as the shortening and thinning of the CNT layer occurs, carbonaceous debris was produced (Wang et al. 2009). From the first derivative order of the titration profile, the two indistinctive peaks can also be assumed to be due to the presence of two different functional groups on the surfaces of the samples. The equivalent point was reached when the moles of base added equals the moles of acid in the samples. This point can be use to determine the number of acidic sites in the samples. As shown in Table 1, the first acid dissociation constant (pKa_1) of B6, B7 and B8 have values of 3.34, 3.50 and 4.02, respectively which can be assigned to dicarboxylic a acid group which is one of carboxylic members. These pKa values were in very good agreement with values reported by Murakami et al. (2003), where the acid dissociation constant of dicarboxylic acid was about 3.8 which were assigned as carboxyl groups. The first and second acid dissociation constants of dicarboxylic acid are 1.7 – 4.5 and 4.1 – 5.8, respectively (Murakami et al. 2003). The B6 sample showed the second acid dissociation constant (pKa_2) value of 5.98 which might be related to high numbers of lactone groups. The second acid dissociation constant (pKa_2) of 7.0 for B7 and 7.1 for B8 can be assigned as phenolic and lactone groups, respectively. The results show acidic sites created with different acid dissociation constants (Ka) values. The magnitudes of the Ka and pKa values of different acid give the comparison of their relative strength.

As reported by Barkauskas and Dervinyte (2004), the surface functional groups were divided into carboxyl (pKa = 2.0- 4.0), lactone (pKa = 4.0 – 7.0) and phenol (pKa =7.0 – 10.0). The acidic sites with pKa < 8 corresponded
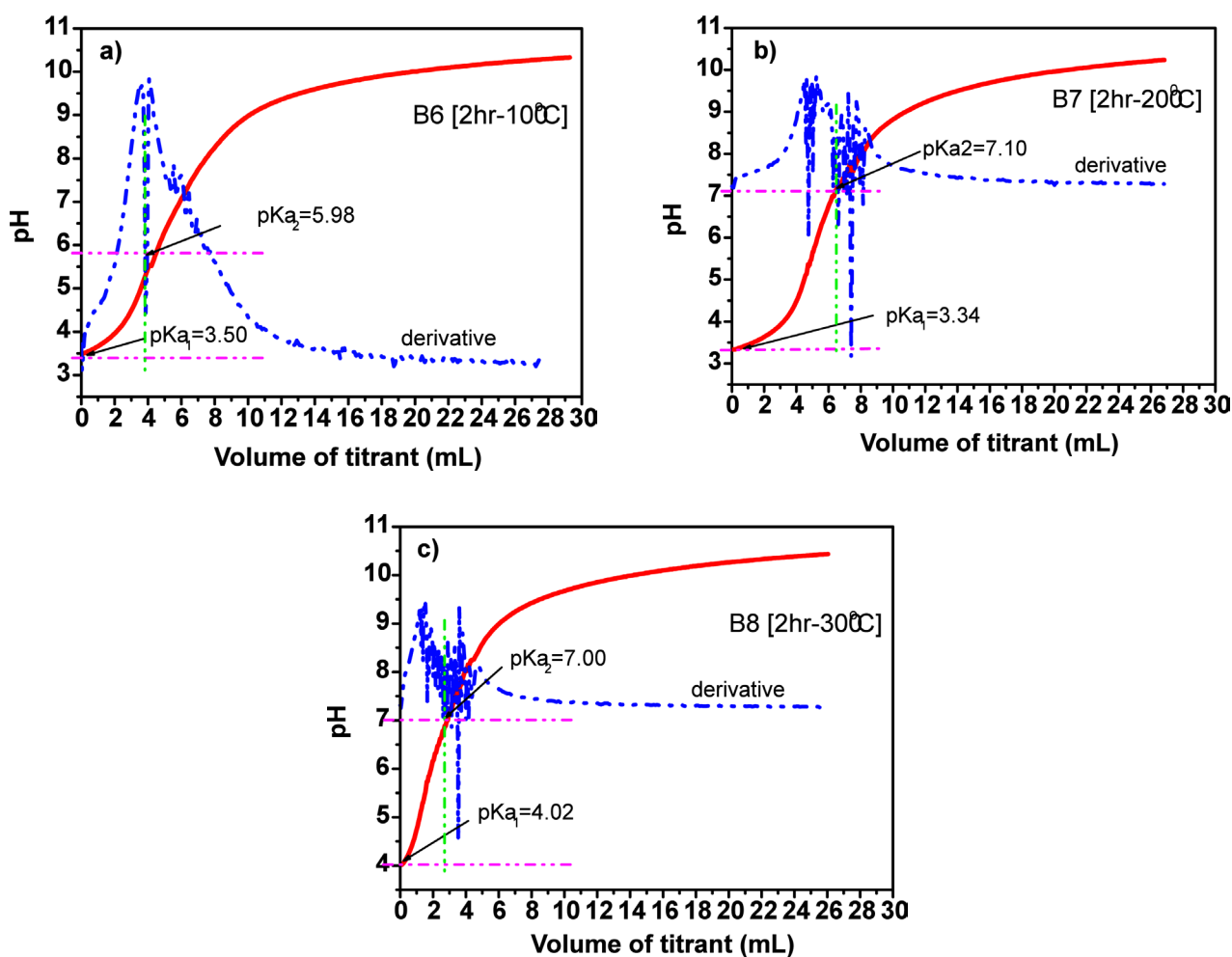
FIGURE 1. The acid base titration profile (a) B6 (b) B7 (c) B8

to carboxylic or lactone and acidic sites with pKa > 8 corresponded to phenolic groups (Puziy et al. 2001). They also reported that the acidic sites with pKa value around 3.5 – 3.9 can be assigned to carboxylic groups, the groups with pKa value around 7.7 – 8.0 can be connected to phenolic groups and the groups with pKa around 5.3 – 5.9 can be assigned to hydroxyl groups. From the results, the samples treated at 200°C (B7) showed the lowest pka_1 and highest pka_2 values as compared to B6 and B8 which been treated at 100 and 300°C. This might be due to the high degree of oxidation which created high amount of carboxylic functional group on the carbon surfaces and the high value of pka_2 results from a small amount of phenolic group which was created on the surfaces. Thus, stronger acidic groups need higher volume of NaOH to neutralize the surfaces. Since, the B7 sample consume higher volume of NaOH for neutralization, the amount of acidic sites were significantly higher than other treated samples of 6.05×10^{-4} mol g^{-1}. The amount of acidic sites for the B6 sample was 4.36×10^{-4} mol g^{-1}. This is lower than B7 due to the low treatment temperature, implying less number of functional groups created on the surfaces. Samples treated at higher temperature of 300°C showed lower number of acidic site created on the carbon surface.

FUNCTIONAL GROUP IDENTIFICATION

Attenuated Total Reflectance Infrared (ATR-IR) spectroscopy was carried out to identify the functional groups present on the sidewall of the functionalized samples. The IR transmittance bands of all functionalized samples are shown in Figure 2. Samples treated at 200°C (B7) and 100 °C (B6), 300 °C (B8) showed medium and weak line at 3720 and 3785 cm^{-1}, respectively. This indicated the presence of unbound or free hydroxyl group (–OH)

of phenol which usually adsorbs strongly in the range of 3650 – 3584 cm^{-1} region (Nyouist 2001). This is in contrast with the intermolecular hydrogen bonded OH:OH frequency which occurs at lower frequency 3200 – 3400 cm^{-1} (Naseh et al. 2009; Nyouist 2001). The broad weak line at 3175 and 3365 cm^{-1} might be due to the presence of intermolecular hydrogen bonding. The B7, B8 and B6 showed strong, medium and weak transmittance band at 2353 cm^{-1}. This indicated the presence of CO and CO_2 groups. Apparently, a CO and CO_2 group originally exhibit the spectrum in the range of 2100 to 2400 cm^{-1} (Owens & Poole 2008). The IR spectrum of B7 showed a strong peak at 1702 cm^{-1} while B6 and B8 showed a weak and medium peak, respectively. This line spectrum was assigned to the C=O stretching mode of the –COOH groups (Naseh et al. 2009). The strong transmittance band observed from the B7 sample might be due to the strong oxidation by SO_3 vapour that created more carboxylic groups on the carbon surfaces at treatment temperature of 200°C. In contrast, the weak peak was observed for the B6 sample. This is possibly due to the low number of carboxylic group created on the sidewall of functionalized sample that was treated at 100°C. At low temperature of acid treatment, the low degree of acid dissociation created low number of acidic sites on the surface of functionalized samples. It was reported that refluxing or sonicating CNTs in nitric acid and another strong oxidant such as sulfuric acid opens the ends of the CNTs and introduces carboxylic groups at the open ends and at defect sites on the CNTs. Meanwhile, the medium peak observed for B8 might be due to the decomposition of carboxylic group at higher temperature of 300°C. It is well documented that the carboxylic acids groups are least stable and typically decompose at temperatures below 600°C (Tessonnier et al. 2009). Generally, it is well
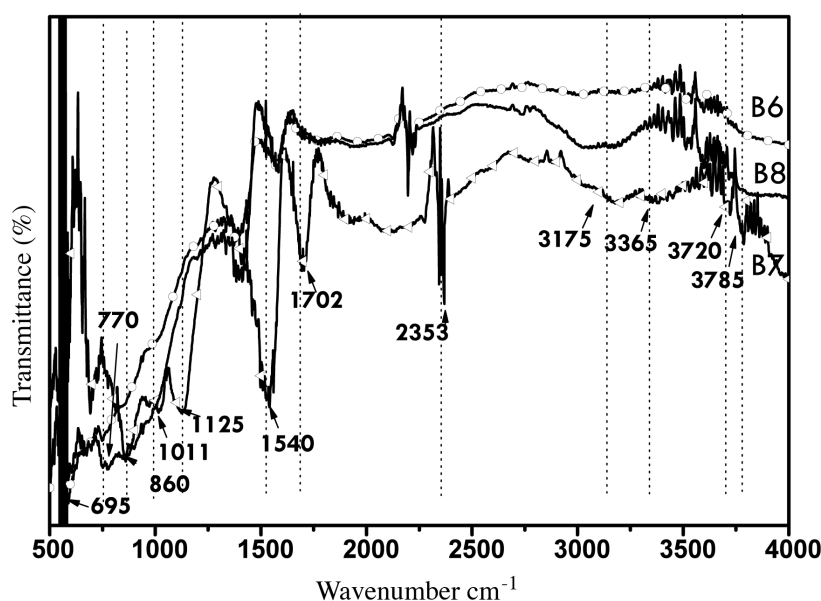

FIGURE 2. ATR-IR spectra of functionalized samples of gas phase treatment

known that the carboxylic groups with strong acidity have tendency to appear at lower wavenumbers (Murakami et al. 2003). The peak at 1540 cm^{-1} refers to the C=C stretching mode which originates from the backbone of carbon nanotubes. A similar feature of transmittance band was reported by Naseh et al. (2009) and Yu et al. (2008). The sample that has been treated at 200°C, B7, showed a strong line at 1125 cm^{-1} indicating SO$_2$OH groups representing the SO$_2$ symmetric stretching mode. This line probably results from the formation of sulfonate groups on carbon surfaces (Silverstein & Bassler 1991). There was almost no transmittance band at 1125 cm^{-1} for samples B6 and B8. This might be due the low number of acidic site and sulphur molecules created on the functionalized carbon surfaces. The weak transmittance band at 1110 cm^{-1} detected by B7 is C-O stretching mode possibly due to the presence of phenol group (Serp & Figueiredo 2009). This result is consistent with the pKa value obtained from titration method. Samples also showed a peak at 860 cm^{-1} which can be assigned to S-O-C stretching groups. In low frequency range, the peak at 770 cm^{-1} and 695 cm^{-1} were related to C-S stretching mode suggesting the existence of sulfonic acid groups. The C–S group is less polar than the C–O group and has a considerably weaker bond. Therefore, the band is not intense and reduced at lower frequencies. In fact the stretching vibration assigned to C-S linkage occur in the region of 700 – 600 cm^{-1} (Silverstein & Bassler 1991).

RAMAN SPECTROSCOPY

Raman spectra of the functionalized samples and the quantitative results are summarized in Figure 3 and Table 1. Raman spectra of functionalization samples contain two domains in the range of 1000 – 2000 cm^{-1}. The first one located at ~1340 cm^{-1} is denoted as D band, as it is related to scattering from defects and amorphous carbon impurities present in the MWCNTs samples. The second feature with a frequency range from 1550 to 1600 cm^{-1} is referred to as the graphite (G) band. In graphite, the G band exhibits a single peak at 1582 cm^{-1} related to tangential mode vibration of the carbon atoms (Haris 2009). The degree of functionalization was quantified using the D to G band intensity ratio (I$_D$/I$_G$) ratio which is the intensity of the disorder mode at 1360 cm^{-1} divided by the intensity of graphite mode at 1600 cm^{-1}. In this study, the I$_D$/I$_G$ ratio (Table 3) values is 1.51, 1.59 and 1.53 for sample B6, B7 and B8, respectively. The B7 showed the highest of I$_D$/I$_G$ ratio values of 1.59 as compared to B6 and B8 samples. Generally, an increase in the I$_D$/I$_G$ ratio indicates an increase in the number of defects on the sidewall of the MWCNTs (Jeong et al. 2010).

It is also interesting to note that the band frequency for all samples showed noticeable shifts in certain characteristic vibrational modes. All functionalized samples showed the shifted D and G band frequency of upshift and downshift about 1 to 3 cm^{-1}. The B6 and B8 had almost the same D band frequency about 1327.94 and 1327.15 cm^{-1}, respectively. The D band frequency for B7 is 1328.74 cm^{-1}. The sample B7 showed slight upshift of D band frequency as compared to B6 and B8. The shifting of the D band frequency might be due to the chemical charge transfer of the functionalized samples at different temperature treatment (Dresselhaus et al. 2004). The introduction of bulky sulfur-containing functional groups on the surface of CNTs induces the strains on the nanotubes walls and thereby results in the shifting of the peaks. This explains why the B7 was shifted than the other two samples. These results are also in good agreement with the XRF and titration data where B7 has the highest acidic functional group and sulfur molecule content. In addition, the G band frequency for all samples also shows the same features of upshifting and downshifting of peaks.
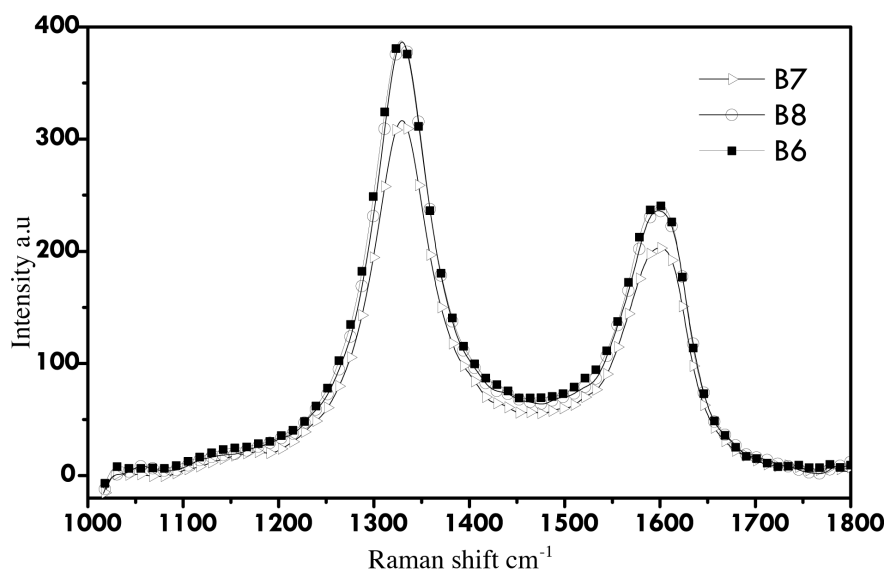

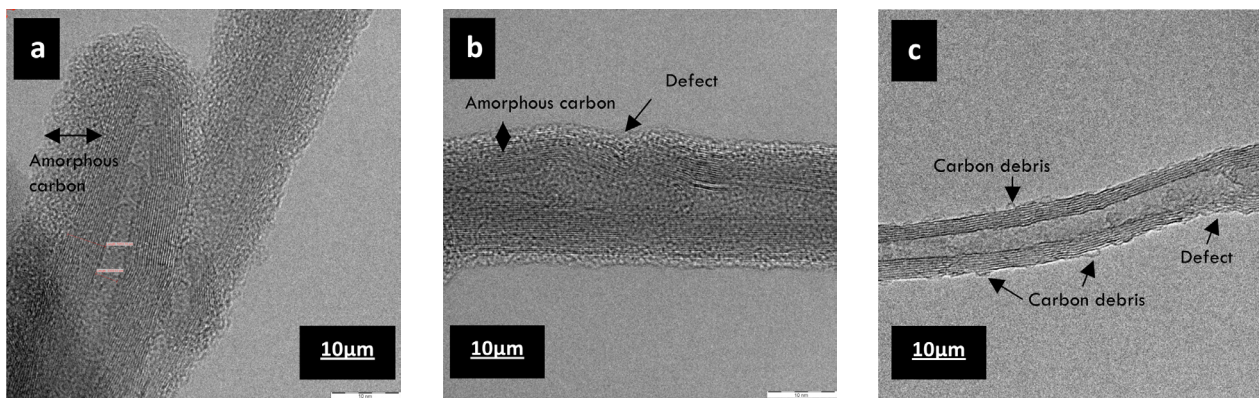FIGURE 3. Raman scattering spectra of three different functionalized sample

FIGURE 4. The TEM images of MWCNT sample (a) raw MWCNTs (b) purified MWCNTs shows reduced thickness amorphous carbon layer (c) Purified MWCNTs after Sulfonation showing carbon debris and defects due to erosion by the chemical treatment

X-RAY FLUORESCENCE

The functionalized samples were also quantified by XRF analysis to determine carbon and sulfur content. The number of molecules for carbon and sulfur was calculated to quantify the changes of sulfur loading. Compositional data in terms of changes in sulfur loading obtained using XRF are presented in Table 1. Bulk composition analysis using XRF showed that, B7 exhibit the highest sulfur loading and followed by B6 and B8. These are in agreement with the amount of acidic site given by titration technique. The high number of sulfur content for sample B7 probably results formation of S-carboxyl groups such as SO_2OH groups on functionalized sample. This has been confirmed by ATR-IR technique that showed the strong transmittance band at 1125 cm^{-1}. Sample B8 exhibitsed lowest number of sulfur content possibly due to the low thermal stability sulfur containing functional groups at high temperature of 300 ^{o}C. This result indicated that, gas phase might be a better way to introduce high amount of sulfur containing functional groups.

CONCLUSION

The amount and type of acidic functional groups were determined by acid base titration technique, ATR-IR spectroscopy and XRF measurement. The chemical treatment had successfully anchored acidic functional groups on the MWCNT samples.The optimum condition of treatment was found to be at 200°C for 2 h that created the highest number of acidic functional groups on the functionalized samples. The ATR-IR studies showed the formation of oxygen and sulphur containing functional groups. Raman spectroscopy showed B7 exhibited the highest intensity ratio I_D/I_G of 1.59 indicating the high density of structural defects created on the MWCNTs.

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