Identification of surfactants aggregates on graphitic surface of carbon nanotubes

Fatirah Fadil, Nor Dalila Nor Affandi and Mohd Iqbal Misnon

Textile Research Group, Faculty of Applied Sciences, Universiti Teknologi MARA, Shah Alam, Selangor, 40450, Malaysia

ABSTRACT
There are a relatively large number of studies on surfactants facilitates the dispersion of multi-walled carbon nanotubes (MWCNTs), however reports for both orientation and size aggregation of surfactants on MWCNTs are scarcely described. In this study, we demonstrate the visualization of the surfactants aggregates onto MWCNTs using atomic force microscopic (AFM) and field emission electron scanning microscopy (FESEM) to provide information on the orientation and the grains size of surfactants-MWCNTs aggregates. MWCNTs treated with surfactants of different charges, namely sodium dodecyl sulphate (SDS), the anionic, cetyltrimethyl ammonium bromide (CTAB), the cationic and polysorbate 80 (Tween-80), the non-ionic, displayed substantial pattern of surfactant-MWCNTs surface contours. Raman spectroscopy analysis has been presented in order to report the characteristic of defective MWCNTs graphitize structure upon non-covalent adsorption of respective surfactants.

1. Introduction
The curiosity of the scientific community on carbon nanotubes (CNTs) started soon after the successful laboratory synthesis of fullerenes in the early 90’s [1]. CNTs possess an exceptional properties of good electrical conductivity, outstanding mechanical properties of strength and toughness, high chemical resistance and great thermal stability, owing to their strong in-plane graphitic C-C bonds [2–4]. However, CNTs are certainly hydrophobic, due to the absence of such surface functions, resulted to a poor interaction with extremely polar molecules such as water [5, 6]. Undeniably, the hydrophobicity of CNTs is the biggest concerns that hinders the integration of CNTs in industrial processes. In this work, a non-destructive method known as physical adsorption using surfactants to activate the surface of multi-walled carbon nanotubes (MWCNTs) was studied as the second option. Unlike previous harsh treatment experienced due to chemical oxidants, the surface activation by surfactants assisted is relatively mild and is involves of non-covalent bonding without disturbing the graphitic structure of CNTs [7–9]. The adsorption of surfactants on graphitic surface of
carbon nanotubes is expected to promote stable dispersion of carbon nanotubes for the feasibility in technical application and industrial processes.

The conventional technique of determining the surfactants adsorption has been studied by computer simulation, mathematical and kinetic analysis as such [10–12]. None of these techniques, however, provide sufficient understanding in visualizing the adsorption of surfactants on carbon nanotubes at the molecular level. The core of using atomic force microscopy (AFM) technique is to analyse a material’s surface in its full, three-dimensional topography, down to the nanometer scale [13]. Herein, the study aim to offer the accurate characterization of surfactant-carbon nanotubes aggregates deposition on substrate as a test sample by AFM and to determine the aggregation morphology of surfactants onto the CNTs surface. Details observation on the adsorption of various charged surfactants on CNTs were further investigated with FESEM and Raman analysis. The chemistry understanding associated to the surfactant-MWCNTs interaction, size of surfactant-MWCNTs aggregates and preferred orientation of respected surfactants were the objectives determined throughout the study.

2. Experimental

2.1. Materials

Multi-walled carbon nanotubes (MWCNTs) used were synthesized using an in-house built Catalytic Chemical Vapor Deposition (CCVD) reactor system and treated with 5 M of hydrochloric acid (HCl) for the removal of residual metallic catalyst [14]. Three commercial surfactants were used for the surface activation process, namely sodium dodecyl sulphate (SDS), cetyltrimethyl ammonium bromide (CTAB) and Tween-80, purchased from Sigma Aldrich and used as received. Distilled water was used for all the experiments.

2.2. MWCNTs surface activation

Each respective surfactant solutions were prepared in a concentration of 1.0% (w/v). 1 mg of purified MWCNTs were then added into 100 mL of each surfactant solutions, above of their critical micelle concentration (CMC) values. The solution of surfactant-MWCNTs mixtures were sonicated for 30 minutes in a water bath sonicator (Branson, 750 W, 20 kHz) and were left to stand overnight, to allow the sedimentation of the secondary agglomeration of the unstable MWCNTs bundles. The supernatant of MWCNTs were then isolated from the sediment of MWCNTs bundles using plate centrifuge machine (PlateSpinII, Kubota) and air dried for 24 hours near room temperature (25°C–27°C). Surface morphologies study of surfactant-MWCNTs aggregates were examined through Atomic Force Microscopy (AFM) (SII Nanotechnology Inc) and Field Emission Scanning Electron Microscopy (FESEM) (JSM-6701, Jeol). The size of MWCNTs aggregates from FESEM micrographs were measured using the Image J software (version 1.48). Raman analysis was performed using Renishaw-1000 Laser Raman Spectroscopy instrument with laser excitation source is 512 nm and laser line frequency range of 400-1800 cm⁻¹.

3. Results and discussion

3.1. Surface contours of surfactants-MWCNTs aggregates

AFM 3D profiles in Figure 1(a) displays surface contour of purified MWCNTs aggregates and its distribution which were portrayed in coarse surface and outsized scattered grains.
Figure 1. AFM top view and 3D view of (a) purified MWCNTs, (b) SDS-MWCNTs, (c) Tween-80-MWCNTs and (d) CTAB-MWCNTs aggregates.
The surface roughness indicates the intactness of MWCNTs agglomeration, signifying of the strong Van der Waals forces interaction between the MWCNTs tubules, affects from the purification process. The actual grain size of purified MWCNTs aggregates could not be precisely determined due to the complex surface roughness.

Figure 1(b-d) conversely revealed the grains cluster of surfactants-MWCNTs aggregates, respectively. The distribution of SDS-MWCNTs aggregates were depicted in an irregular grains shape as described from the randomized surface roughness in Figure 1(b). It is clearly showed that the surface roughness is reduced with the decreasing of grain size compared to the purified MWCNTs in Figure 1(a). The AFM surface contour of Tween-80-MWCNTs in Figure 1(c) also displayed a similar pattern to the grains distribution of SDS-MWCNTs aggregates. However, the grains size of Tween-80-MWCNTs is smaller than the SDS-MWCNTs. On the contrary, the AFM surface contour of CTAB-MWCNTs aggregates in Figure 1(d) shows an ordered grains distribution, in a dome grain shape.

3.2. Surface morphology of surfactants-MWCNTs aggregates

FESEM micrographs in Figure 2(a) displays the surface morphology of purified MWCNTs, in a long, continuous and agglomerated form. Meanwhile, varied surface morphologies of respected surfactant-MWCNTs aggregates were displayed in Figure 2(b-d).
Upon surface activation, the MWCNTs structure were confirmed are defect-free from any physical damages such as tubes shortening, based on observed respective FESEM micrographs. Thus, the surface treatment using surfactants is considered mild and did not caused to structural imperfections to the MWCNTs. The physical interaction between surfactants and MWCNTs not only has protected the MWCNTs tubular structure, but has facilitated the process of de-agglomeration of MWCNTs in a moderate de-bundling state. The morphology of surfactant-MWCNTs aggregates were distinct as designated from their individual FESEM micrographs. Figure 2(b) depicts a complete coverage of individual MWCNTs tubules, coated with the adsorbed Tween-80 molecules. The identification of the surfactant coverage were obviously seen through the thickening of the individual MWCNTs graphitic walls. Diameters of the individual tube of MWCNTs increased to threefold the size of its original diameter as coated with Tween-80. In contrast, the FESEM micrograph of CTAB-MWCNTs aggregates in Figure 2(c) indicated the encapsulation of MWCNTs floss by CTAB. The surfactant CTAB were appeared to have formed a bilayer on the surface of MWCNTs and gradually wrapped up the entire MWCNTs floss. The size of MWCNTs-CTAB aggregates were approximately 300 to 350 nm. Whereas, Figure 2(d) depicts the morphology of SDS-MWCNTs aggregates, with the most of MWCNTs surface has been partially coated with the adsorbed SDS molecules. A complete coated MWCNTs were observed at certain areas, as indicated by the presence of larger diameter of MWCNTs tubules in the respective FESEM micrograph. The increment of MWCNTs diameter from the initial measurement of 30 nm up to 60 nm designated to the SDS coverage on the MWCNTs surface. Whereas, the smaller diameter of MWCNTs floss were measured to be approximately 30 nm to 40 nm. Pieces of the SDS flakes were clearly observed in the FESEM micrograph, in which represented of the unattached surfactants.

FESEM characterization has confirmed that the aggregates morphology of the respected surfactants on the MWCNTs surface is complemented with the configuration assessment in AFM analysis. The encapsulation of MWCNTs by CTAB were occurred in bundles, instead of being individually coated. The attachment of CTAB bilayer onto the MWCNTs surface as observed through FESEM micrograph, explaining the appearance of dome grain shape in the respective AFM 3D profile. Tween-80 on the other hand provided a consistent surfactant coverage on the surface of the MWCNTs tubular as compared to SDS. The MWCNTs surface activation using Tween-80 give the smallest size of surfactant-MWCNTs aggregates of 251 nm. In contrast, the usage of SDS and CTAB resulted to a medium aggregates size of 435 nm and 319 nm, respectively. The aggregates size of single grain and the illustration of the possible positioning of each respective surfactant in accordance to the AFM surface contours were presented in Figure 3. From this analysis, it is shown that both of the size and shape of the grains are vary for each individual surfactant-MWCNTs aggregates, respectively.

3.3. MWCNTs graphitize structure upon surface activation

The characteristic of the defective graphitize structure of MWCNTs was further analysed using Raman Spectroscopy. Figure 4 shows Raman spectra of purified MWCNTs and surfactant-MWCNTs. The frequency mode in Raman spectra has been ascribed to phonon density of state introduced by the defects created. The G-band indicates the ordered graphitized carbon, while the D-band indicates the disordered carbon in MWCNTs. Theoretically, the G-band (1596 cm$^{-1}$), the first-order Raman scattering process is not affected by defects. In contrast, the D-band (1352 cm$^{-1}$) is a second-order Raman scattering process that is enhanced by the presence of defects or irregularities. The I$_{D}$/I$_{G}$ ratio is
the most prominent indicator to determine the purity of carbon nanotubes [15]. In this study, the ID/IG ratio is taken as a responsive to the defect formation caused by the surfactant attachment. The coverage of the adsorbed surfactants on the outer surface of MWCNTs were recognized as a defective site which was introduced upon surface activation process. In this study, the signature of MWCNTs structural defect were confirmed with the increasing intensity of D-band in the Raman spectra of both CTAB-MWCNTs and Tween-80-MWCNTs. The ID/IG intensity ratio showed that CTAB has the highest value with a reading of 1.15, followed with Tween-80 with a value of 1.06. The value of ID/IG ratio of SDS-MWCNTs was only at 0.95, a slightly higher than ID/IG ratio of purified MWCNTs which was at 0.82.

The increasing intensity of D-band indicated the presence of the adsorbed surfactant’s coverage onto the surface of MWCNTs. The increase of D-band intensity was significant to the high detection of the sp$^3$ C-C stretching mode, due to the attachment of the surfactant. The Raman spectrum of SDS-MWCNTs does not show much difference from the purified MWCNTs in their D-band and G-band intensities. This finding strongly suggesting that the SDS have the least efficiency in adsorbing onto the MWCNTs surface compared to Tween-80 and CTAB.

3.4. The influence of surfactant affinity

The preferential orientation of the adsorbed surfactant on the surface of MWCNTs has to be related with the molecular structure of surfactant. Therefore, the molecular structure
of each surfactant must be fundamentally considered in order to understand the orientation pattern of the surfactant molecules onto the MWCNTs surface. Surfactant molecule consists of two parts, the polar head group and the non-polar tail group which are associated to the hydrophilic and hydrophobic properties, respectively. The relative size and shape of the hydrophobic and hydrophilic parts of the surfactant molecule determines their affinity in aqueous, and also the possible orientation of the adsorbed surfactant onto the liquid-solid interface. Figure 5 shows the molecular structure of surfactants used in this study. Theoretically, the ionic surfactants of SDS and CTAB molecules were adsorbed onto the MWCNTs surface by the dispersion forces [16]. The hydrophobic tails of the ionic surfactant might be found in a flat or L-shape position on the hydrophobic surface of MWCNTs, while the hydrophilic head may orient itself more towards the polar surrounding of water molecules [17]. The charged heads of the SDS and CTAB were dissociated in water in order to minimize the developed charge repulsion between neighboring adsorbed surfactant molecules. However, the degree of dissociation of the charged heads of SDS and CTAB in water was relatively different due to their own polarity. The polarity
of SDS head group, $\text{SO}_4^{2-}$ in water is higher than CTAB head group, $\text{Me}_3\text{N}^+$. Consequently, the SDS molecules become more attracted to water phase and tend to form micelles despite of being adsorbed onto the hydrophobic surface of MWCNTs. As a result, fewer accumulation of SDS molecules were observed, forming an irregular pattern with random positioning and least surfactant deposition compared to the other surfactants.

In agreement with previous molecular simulation modeling studies [15], the attachment of surfactant on the MWCNTs surface showed similarity in the arrangement, of such the upward positioning (pointy shape grain) and horizontal positioning (dome shape grain). We suggested that the generated AFM surface contour is directly resulted from the orientation of the surfactant onto the MWCNTs surface. Among the surfactant used, only CTAB-MWCNTs aggregates were depicted in a dome grain shape, while SDS-MWCNTs and Tween-80 aggregates were depicted in a pointy grain shape. The previous simulation studies presented of a low SDS coverage, which is been influenced by the stiffness and the strong hydrophilic properties of SDS molecular structure [16]. Consequently, the orientation of SDS on MWCNTs surface has not followed the ideal type of surfactant orientation. Instead, the adsorbed SDS molecules onto the hydrophobic surface appear to have random orientation [17]. This possible interaction was supported by the AFM surface contour of SDS-MWCNTs aggregates in this study. Therefore, it is suggested that SDS could not be oriented in an orderly configuration due to the strong developed charge of the head group. The head group of the adsorbed SDS molecules would be certainly repelled in order to stabilize their attraction on the MWCNTs surface. On the other hand, the AFM surface contour of CTAB-MWCNTs aggregates was obviously different from the SDS-MWCNTs aggregates even though both of the surfactants shared similar ionic characteristics. Based on the AFM image, the adsorbed CTAB molecules on the MWCNTs surface were observed to be attached in a well ordered configuration. However, the size of the CTAB-MWCNTs aggregates appeared to be relatively large. The ordered positioning of CTAB could be due to the intermediate charged of the head group. As CTAB is an ionic type of surfactant with a long aliphatic chain structure, the adsorbed CTAB molecules on the MWCNTs surface follows a certain arrangement in order to minimize the intermediate charged head repulsion.
In contrast, the aggregates of Tween-80-MWCNTs exhibited random positioning on the MWCNTs surface due to uncharged hydrophilic head group of Tween-80. The accumulation of Tween-80 could possibly be driven by the hydrophobic interaction, between the hydrophobic tail of the surfactant and the hydrophobic surface of the MWCNTs. The hydrophilic head group of Tween-80 is completely soluble in water due to the fat splitting where triglyceride reacts with water to form glycerol, a soluble type of fat. Alternatively, the long and bulky hydrophobic part of Tween-80 is attracted to the MWCNTs surface, thus favored to be adsorbed onto MWCNTs [18]. The strict hindrance of the bulky molecular structure of Tween-80 has contributed another advantage in which has enabled minimization of MWCNTs coalition and prevented tube-tube interaction, thus reducing the Van der Waals interaction within the MWCNTs [19–21]. This finding suggested that the charges affinity of surfactant head group were found to determine their preferred orientation onto MWCNTs. Ionic surfactant which possess high polarity of head group has limited electrostatic interactions with MWCNTs due to high affinity in polar phase surrounding. Due to this factor, the ionic surfactant become less attracted to accumulate on the MWCNTs surface compared to the non-ionic surfactants.

**Conclusion**

In summary, the identification of surfactants aggregation on carbon nanotubes surface were facilitated by AFM, FESEM and Raman analysis. The distinctive AFM surface contours and FESEM micrographs visualized the different orientation of respected adsorbed surfactants and as well as providing size estimation of each surfactant-MWCNTs aggregates, respectively. The lowest value of $I_D/I_G$ ratio in Raman spectrum indicated of least surfactants adsorption onto the MWCNTs surface. It is suggests that an appropriate choice of a suitable surfactants needs consideration of its structure and charges affinity.

**Acknowledgement**

Special thanks are due to Assoc. Prof Dr. Nor Aziah Buang from Universiti Teknologi Malaysia for providing carbon nanotubes samples.

**References**

[1] Rao CNR, Satishkumar BC, Govindaraj A, et al. Nanotubes. Chemphyschem. 2001;2:78–105.
[2] Shah KA, Tali BA. Synthesis of carbon nanotubes by catalytic chemical vapour deposition: A review on carbon sources, catalysts and substrates. Mat Sci Semicon Proc. 2016;41:67–82.
[3] Eatemadi A, Daraee H, Karimkhanloo H, et al. Carbon nanotubes: properties, synthesis, purification, and medical applications. Nanoscale Res Lett. 2014;9:393.
[4] Blond D, Barron V, Ruether M, et al. Enhancement of modulus, strength, and toughness in poly (methyl methacrylate)-based composites by the incorporation of poly (methyl methacrylate)-functionalized nanotubes. Adv Funct Mater. 2006;16:1608–1614.
[5] Kharissova OV, Kharisov BI, de Casas Ortiz EG. Dispersion of carbon nanotubes in water and non-aqueous solvents. RSC Adv. 2013;3:24812–24852.
[6] Premkumar T, Mezzenga R, Geckeler KE. Carbon nanotubes in the liquid phase: addressing the issue of dispersion. Small. 2012;8:1299–1313.
[7] Cui H, Yan X, Monasterio M, et al. Effects of Various Surfactants on the Dispersion of MWCNTs–OH in Aqueous Solution. Nanomaterials. 2017;7:262.
[8] Alsharefa JM, Tahaa MR, Khan TA. Physical dispersion of nanocarbons in composites—a review. J Teknol. 2017;79:69–81.
[9] Ramos E, Pardo WA, Mir M, et al. Dependence of carbon nanotubes dispersion kinetics on surfactants. Nanotechnology. 2017;28:135702.
[10] Zhang X, Chen B, Wang Z. Computer simulation of adsorption kinetics of surfactants on solid surfaces. J Colloid Interface Sci. 2007;313:414–422.

[11] Chang CH, Franses EI. Adsorption dynamics of surfactants at the air/water interface: a critical review of mathematical models, data, and mechanisms. Colloids Surf A. 1995;100:1–45.

[12] Miller R, Aksenenko EV, Fainerman VB. Dynamic interfacial tension of surfactant solutions. Adv Colloid Interface Sci. 2017;247:115–129.

[13] Haugstad G. Overview of Atomic Force Microscopy. 2015. Available from http://thankuscience.com/wp-content/uploads/2019/01/afm_introduction.pdf.

[14] Buang NA, Ismail F, Othman MZ. Synthesis of Carbon Nanotube Heterojunctions from the Decomposition of Ethanol. Fuller Nanotub Car N. 2014;22:307–315.

[15] Miyata Y, Mizuno K, Kataura H. Purity and defect characterization of single-wall carbon nanotubes using Raman spectroscopy. J Nanomater. 2011;2011:1.

[16] Vaisman L, Wagner HD, Marom G. (2006). The role of surfactants in dispersion of carbon nanotubes. Adv Colloid Interface Sci. 2006;128:37–46.

[17] Jung WR, Choi JH, Lee N, et al. Reduced damage to carbon nanotubes during ultrasound-assisted dispersion as a result of supercritical-fluid treatment. Carbon. 2012;50:633–636.

[18] Moore VC, Strano MS, Haroz EH, et al. Individually suspended single-walled carbon nanotubes in various surfactants. Nano Lett. 2003;3:1379–1382.

[19] Szleifer I, Yerushalmi-Rozen R. Polymers and carbon nanotubes-dimensionality, interactions and nanotechnology. Polymer. 2005;46:7803–7818.

[20] Matarredona O, Rhoads H, Li Z, et al. Dispersion of single-walled carbon nanotubes in aqueous solutions of the anionic surfactant NaDDBS. J Phys Chem B. 2003;107:13357–13367.

[21] Yu J, Grossiord N, Koning CE, et al. Controlling the dispersion of multi-wall carbon nanotubes in aqueous surfactant solution. Carbon. 2007;45:618–623.