Structural and Morphological Investigation for Water-Processed Graphene Oxide/Single-Walled Carbon Nanotubes Hybrids

M R Muda¹, M M Ramli¹,²*, S S Mat Isa¹,², D S C Halin², L F A Talip¹,², N S Mazelan¹,², N A M Anhar¹ and N A Danial¹,²
¹ School of Microelectronic Engineering, University Malaysia Perlis, 01000 Malaysia
² Center of Excellence Geopolymer and Green Technology, School of Materials Engineering, Universiti Malaysia Perlis (UniMAP), Perlis, Malaysia
E-mail: mmahyiddin@unimap.edu.my

Abstract. New group of materials derived from hybridization of single walled carbon nanotubes (SWCNTs) and graphene oxide (GO) which resulting novel three dimensional (3D) materials generates an outstanding properties compared to corresponding SWCNTs and GO/Graphene. In this paper, we describe a simple approach using water processing method to develop integrated rGO/GO-SWCNT hybrids with different hybrid ratios. The hybrid ratios were varied into three divided ratio and the results were compared between pristine SWCNTs and GO in order to investigate the structural density and morphology of these carbonaceous materials. With an optimized ratio of rGO/GO-SWCNT, the hybrid shows a well-organized hybrid film structures with less defects density sites. The optimized mixture ratio emphasized the important of both rGO and SWCNTs in the hybrid structures. Morphological structural and defects density degrees were examined by Field Emission Scanning Electron Microscopy (FESEM) and Raman spectroscopy.

1. Introduction
Carbon is the one of the most abundant elements found in nature which exists in various allotropic forms.

Recently, CNTs and graphene which representative of 1D and 2D carbon nanomaterials has attracting worldwide attentions during last decades due to their remarkable physical, electrical, and chemical properties [1,2].

Besides that, integrating CNTs and graphene into hybrid structures provide a novel approach to new 3D materials with advantageous properties.

Therefore, a unique and intelligent graphene-CNTs hybrid films could overcome some of the limitations and shortcomings of individual components [3–5].

Owing to the its vast properties, these materials had shown the great potential to be applied in various areas of nano-technology research such as super capacitors, batteries, biosensors, and especially for optical devices.

In this study, we reported a simple approach for preparing hybrid G-SWCNT materials using water-processed method and the carbonaceous materials were characterized using FESEM and Raman Spectroscopy.
2. Materials and methods

2.1. Materials
SWCNTs was purchased from NanoLab, US (initial purity > 95%) and functionalized using acid treatment. Fine graphite powder purchased from NE Scientific (initial purity > 90%) was pre-treated before being oxidized as reported by Muda et. al [6]. Sulphuric acid 98%, nitric acid 70%, KMnO₄ powders, HCl acid 30% and H₂O₂ 30% were purchased from Sigma–Aldrich.

2.2. GO-SWCNT mixture preparation
First, GO was synthesized by a modified hummers method as described in our previous study [6]. Pre-oxidized graphite flakes and 15 g of potassium permanganate (KMnO₄) were stirred in a solution containing concentrated sulphuric (H₂SO₄) acid for several hours. The solution reaction was then terminated by the addition of hydrogen peroxide (H₂O₂) and subsequently washed with hydrochloric (HCl) acid in order to remove the sulfate ions. The final product was washed with deionized (DI) water and dried in vacuum. The acid treatment of SWCNTs was performed using a mixture of H₂SO₄ and nitric (HNO₃) in the volume ratio (3:1). The mixture was refluxed for several hours, after which time the acid mixture was decanted. At the end of this process, the mixture was repeated washed with DI water until the pH of the solution become neutral. In order to obtain the GO/rGO-SWCNT mixture, GO powder and acid treated SWCNT were mixed thoroughly with different ratios in DI water before subjected to sonication process for well dispersion.

2.3. Film Preparation and Thermal Reduction Process
Carbonaceous films were prepared by spray pyrolysis method using a specific volume of centrifuged solution on a silicon dioxide (SiO₂) substrate. After the coating process, the samples were immediately annealed at 300°C for 3 hours in a vacuum furnace. Then the samples were characterized by field emission scanning microscopy (FESEM) and Raman spectroscopy.

3. Results and discussions

3.1. FESEM Analysis
3.1.1. GO. Figure 1 shows the surface morphology of GO sheets which produced by modified Hummer’s method with an accelerating voltage of 3kV and 150kX magnification. Based on FESEM micrograph, it can be seen obviously that the aggregated GO sheets are closely associated with another sheets.

This means that Van der Waals forces between GO sheets stack them tightly during spray deposition process. On the other hand, the GO sheets exhibit a rather wavy and crumpled structure on
the basal plane. As reported by Schniepp [7], crumpled and wrinkles formation might be attributed
to hydroxyl and epoxy group that located on basal plane which tend to form chains on the
graphitic surface, leading to the generation of topological defects along GO sheets.

3.1.2. SWCNT. Figure 2 shows the morphology of raw single-walled carbon nanotubes (SWCNTs) and
acid functionalized SWCNT (f-SWCNTs).

Generally, the raw SWCNTs contain a large quantity of impurities such as amorphous carbon
and catalytic particles. Besides, the hydrophobic nature makes SWCNTs are tends to agglomerates which
hindering it to be dispersed in various solution. Thus, acid functionalization SWCNTs is the one of the
established method that was carried out to increase solubility and purity of SWCNTs.

Figure 2. The micrograph of FESEM of (a) raw SWCNT and (b) acid treated SWCNT.

According to the figure 2, it can be clearly seen the differences of before and after acid
functionalization process where, the raw SWCNTs are agglomerated with the metal catalyst particles.
However, after functionalization process, the metal particles were totally removed.

As been discussed by Goyanes et. al [8], during acid functionalization process, the raw SWCNTs
were purified and a part of catalyst particles were possibly eliminated. They also reported that, the
functional groups were attached on the sidewall tubes during oxidation which resulting improvement
in its hydrophilicity and dispersibility.

3.1.3. GO-SWCNT Hybrid. The microstructures of the as-prepared rGO-SWCNT hybrid films with
different ratios were shown in figure 3. The nano-composite of hybrid rGO-SWCNT is a well-defined
3D structure which contains fragmented rGO flakes connected with entangled of SWCNTs.

As seen in figure 3, it can be clearly observed that, the rGO-SWCNT hybrid films with different
ratio provides a better mixture for rGO and SWCNT, in which SWCNTs randomly bridge between
graphene sheets and tend to form a well-organized hybrid structure.

From figure 3(a), the ratio 9:1 shows that the individual SWCNTs appeared to be separated on the
surface of rGO sheets. In the meantime, this result proved that the interaction between rGO and
SWCNTs tubes caused by the π-π conjugated aromatic domain [9].

In contrast, the SWCNTs that attached to the rGO sheets in ratio 5:5 showed a high degree of
dispersion as shown in figure 3 (b). It can be deduced that the dispersion between these two materials resulted homogeneously and
well-uniformed hybrid thin films. However, by increased the ratio SWCNTs as seen in figure 3(c), the
SWCNTs tubes are not individually stacked on rGO surface, but rather formed a clusters or bundles with minor aggregated morphology.

Based on observation with all these results, it can be conclude that rGO sheets were covered and connected with SWCNTs, and form a network structure.

![Image](image_url)

**Figure 3.** The micrograph of FESEM of G-SWCNT with different ratios of (a) 9:1, (b) 5:5, and (c) 1:9 ratios.

These results proved that SWCNTs were well intercalated onto rGO layer, which prevented the rGO from self-assembly restacking during thermal reduction process. On the other hand, these results also meet the agreement with previous research that was done by Chang et. al [9], which state that, the rGO-SWCNTs hybrid composite might constitute a more efficient conductive path for electrons, thereby improving the electrons transfer rate [9]. In addition, the presence of charging during the FESEM imaging suggested that the rGO-SWCNTs hybrid films were electrically conductive [10].

3.2. Raman Analysis

3.2.1. GO. Figure 4 shows the Raman spectra for GO. The formation of GO was further characterized by Raman spectroscopy in order to determine the well-ordered and disordered GO structures by evaluating the quantitative index of intensity D to G (I_D/I_G) ratio.
In general the spectra of GO consist of three peaks, namely, D mode $\approx 1350 \text{ cm}^{-1}$, G mode $\approx 1590 \text{ cm}^{-1}$, and 2D mode $\approx 2698 \text{ cm}^{-1}$. In particular, D mode corresponding to the defects in hexagonal carbon network and G mode arises due to the vibration of carbon-carbon bonds in basal plane [11].

![Raman spectra for GO.](image)

Figure 4. Raman spectra for GO.

Based on figure 4, it can be observed that D and G peak have a sharp peak, where indicates the presence of functional groups at the basal plane and edge of graphene sheets produced during the oxidation of graphite. However, the 2D peak was not reflected with the micrographs of FESEM since, the FESEM imaging and Raman spectroscopy does not directly correlate Raman peaks with monolayer GO topography. Thus, 2D peak resulted substantially lower and wider than G band, suggesting that the presence of multilayered graphene derivatives.

The intensity of $I_D/I_G$ of GO is 0.994, which regarding to the defects site graphitic structural and distortion of carbon bonds due to reduction in the in-plane sp$^2$ carbon atoms caused by oxidation. These result also consistent with previous research by Feng et. al [12] which reported that the carbon lattice in GO has developed some degree of amorphous character due to oxidation process itself.

3.2.2. SWCNT. The Raman spectra of SWCNTs exhibits a few characteristic modes that can be used to determine the diameter of nanotubes, structural defects of SWCNTs and also vibration characteristics which called as radial breathing mode (RBM). The RBM band is originated from the out-of-plane tangential acoustic modes of monolayer graphene sheet and all carbon atoms vibrate in phase along the radial direction [13]. Figure 5 shows the Raman spectra for SWCNT-COOH. On the other hand, the Radial Breathing Mode (RBM) also gives precise information about the nanotube diameter which can be measure by equation:

$$d = \frac{223.75}{\omega_{\text{RBM}}}$$

Figure 5 shows the Raman spectra of SWCNT-COOH. The RBM band located at low Raman shifts in range 158 cm$^{-1}$ ~ 269 cm$^{-1}$ show the calculated diameter of SWCNT-COOH range from 0.87 nm to 1.47 nm. These results give significant evidence regarding to the theoretical and actual diameter of SWCNT. In addition, 2D band with sharp intensity peak located at 2689 cm$^{-1}$ show the presence of
single layer graphene sheet which roll and folded into a 1D structure. The G band had shown a highest intensity peak which located at range 1496 cm\(^{-1}\) ~ 1665 cm\(^{-1}\) while, the D band was appeared as small intensity peak at range 1227 cm\(^{-1}\) ~ 1425 cm\(^{-1}\). The quality of the nanotubes was established by determining the ratio of I\(_D\)/I\(_G\).

3.2.3. GO/rGO-SWCNT Hybrid. The intensity of I\(_D\)/I\(_G\) ratio also was measured in order to determine the density of structural defects hybrid material.

Figure 6 shows the Raman spectra of (a) GO-SWCNT and (b) rGO-SWCNT with different hybrid ratio which obtained at 514 nm laser excitation wavelength. According to figure 6(a) and figure 6(b), the intense band of D, G, and 2D peak can be observed at range 1183-1452 cm\(^{-1}\), 1515-1667 cm\(^{-1}\), and 2700-2900 cm\(^{-1}\), respectively.

Based on calculated I\(_D\)/I\(_G\) ratio from both spectra, it can be clearly observed that the intensity of I\(_D\)/I\(_G\) ratio shows the same pattern, which decreased from 0.88 to 0.77, from 0.76 to 0.75, and from 0.68 to 0.64 for hybrid material with ratio of 9:1, 5:5, and 1:9, respectively. As been discussed previously, oxidation from synthesizing and functionalization process will introduce functional groups where the disrupting of sp\(^2\) bonding network as well as break the π-conjugated structure in the original hexagonal carbon structure.

However, after thermal reduction process, the functional groups that attached on the hybrid materials were majority removed thus, restoration from sp\(^3\) to sp\(^2\) bonding networks resulting from less defective site on carbon structure. According to both spectra, the ratio of 1:9 peak show the lowest I\(_D\)/I\(_G\) ratio compared to other peaks, which attributed from minimal defects at high SWCNTs loading.

The low structural defects and cluster forms of SWCNTs tubes on rGO sheets contribute to the uniform connection paths between SWCNTs and rGO sheets.
These results were consistent and well agreed with Shahriary et.al [15], which reported that the hybrid materials composed to the low D to G ratio emanated from influence of the incorporation SWCNTs on the rGO sheets.

**Figure 6.** Raman spectra of (a) GO-SWCNT and (b) rGO-SWCNT with different hybrid ratio.
Due to connection between the rGO and SWCNT, the isolated aromatic domain on the surface rGO might cause a higher extension of the delocalized π-electrons.

4. Conclusions
In summary, graphene oxide nanosheets were successfully hybridized with functionalized single walled carbon nanotubes in deionized (DI) water dispersion and then thermally reduced to form the rGO-SWCNT composite. It was found that, the incorporation SWCNT into rGO sheets not only increased the electrochemically effective surface area, but also forms a better network structure with minimal agglomeration and restacking effects. On the other hands, rGO-SWCNT with mass ratio 1:9 shows the lowest defect rates which attributed from high loading of low defects density SWCNT. This finding also proved that, the rGO-SWCNT hybrid materials have a better structural morphology and less structural defects density compared to pristine rGO and SWCNT.

References
[1] Baughman R H, Zakhidov A A and De Heer W A 2002 Science (80 ) 297 787–92
[2] Geim A K and Novoselov K S 2007 Nat. Mater. 6 183–91
[3] Yen M-Y, Hsiao M-C, Liao S-H, Liu P-I, Tsai H-M, Ma C-C M, Pu N-W and Ger M-D 2011 Carbon N. Y. 49 3597–606
[4] Fan Z, Yan J, Zhi L, Zhang Q, Wei T, Feng J, Zhang M, Qian W and Wei F 2010 Adv. Mater. 22 3723–8
[5] Kim Y-S, Kumar K, Fisher F T and Yang E-H 2011 Nanotechnology 23 15301
[6] Muda M R, Hanim K N, Isa S S M, Ramli M M and Jamlos M F 2015 High Throughput Graphene Oxide in Modified Hummers Method and Annealing Effect on Different Deposition Method Applied Mechanics and Materials vol 815(Trans Tech Publications)pp 141–7
[7] Schniepp H C, Li J-L, McAllister M J, Sai H, Herrera-Alonso M, Adamson D H, Prud’homme R K, Car R, Saville D A and Aksay I A 2006 J. Phys. Chem. B 110 8535–9
[8] Goyanes S, Rubiolo G R, Salazar A, Jimeno A, Corcuera M A and Mondragon I 2007 Diam. Relat. Mater. 16 412–7
[9] Chang L-H, Hsieh C-K, Hsiao M-C, Chiang J-C, Liu P-I, Ho K-K, Ma C-C M, Yen M-Y, Tsai M-C and Tsai C-H 2013 J. Power Sources 222 518–25
[10] Wimalasiri Y and Zou L 2013 Carbon N. Y. 59 464–71
[11] Kondratowicz I, Zelechowska K, Majdecka D and Bilewicz R 2015 Mater. Sci. 33 292–300
[12] Feng H, Wang X and Wu D 2013 Ind. Eng. Chem. Res. 52 10160–71
[13] Liu Z, Zhang J and Gao B 2009 Chem. Commun. 6902 18
[14] Kim U J, Furtado C A, Liu X, Chen G and Eklund P C 2005 J. Am. Chem. Soc. 127 15437–45
[15] Shahriary L and Athawale A A 2014 Int J Renew Energy Env. Eng 2 58–63

Acknowledgments
This work was partially supported by Fundamental Research Grant (FRGS) and Research Acculturation Grant Scheme (RAGS) funded by Ministry of Education Malaysia. Authors would also want to thank School of Bioprocess, UNIMAP and Nanotechnology Research Centre, Faculty of Science and Mathematics, UPSI.