Active Phase of Cobalt Oxide (Co_3O_4) as a Promising Catalyst for Graphene Growth by Alcohol Catalytic Chemical Vapor Deposition

Mohd Asyadi Azam, Nor Najihah Zulkapli, Noraiham Mohamad, Mohd Shahadan Mohd Suan, Ghazali Omar

***Abstract*: The presence of active catalyst during graphene growth by alcohol catalytic chemical vapour deposition is a compulsory. This study is aimed to validate the effect of annealing temperature for the formation of active cobalt oxide (Co_3O_4) film on the graphene growth by alcohol catalytic chemical vapour deposition technique. Active Co_3O_4 film was prepared on silicon wafers by sol-gel process, using cobalt acetate tetrahydrate as the precursor compound and absolute ethanol as the solvent. The active Co_3O_4 phase was achieved by annealing process at 450, 500, 550 and 600 °C. The graphene is grown from active Co_3O_4 film under 900 °C of chemical vapor deposition (CVD) processing temperature for 5 minutes. The obtained Co_3O_4 was characterized by x-ray diffraction and Raman spectroscopy. The as-grown graphene from active Co_3O_4 film annealed at 450 °C was characterized by Raman spectroscopy and field emission scanning electron microscope (FESEM). The results demonstrate that spinel type cubic structure of Co_3O_4 could be produced at the varied annealing temperatures but the optimum XRD result was at 500 °C annealing temperature. The presence of active Co_3O_4 phase was supported with the exhibited peaks of four Raman-active phonon modes in the Raman spectra. The quality of as-grown graphene determined from the ratio of 2D-band over G-band intensities is 1.010; an indication of few layers of graphene. Active Co_3O_4 film is able to produce good quality of graphene comparable with Ni and Cu catalysts. And graphene can be used in many devices, including electronic device, energy storage device, power device, and others.*

***Keywords* : Active Co_3O_4, sol-gel process, graphene growth, alcohol catalytic CVD**

I. INTRODUCTION

Graphene is an extraordinary 2-dimentional material that has been attracting extensive attention in nanoscience and technology. Its distinctive properties such as theoretically high sheet resistance, 1000 Ω/sq, high surface area (2630 m^2/g) and high capacitance value (1954 F/g) have made graphene one of the leading candidates for various types of applications. The example application for such unique material is mobile electronic devices, back-up power supplies and hybrid electric vehicles [1-3].

There are many approaches to produce graphene such as mechanical cleavage [4-5], carbon precipitation from metals, epitaxial growth on SiC and chemical vapour deposition (CVD) [6-9]. Previously, several studies have claimed that alcohol catalytic CVD is one of the most assuring technique in carbon nanotube (CNT) growth due to its broad selectivity of substrates, good economic value and good catalytic reaction [10–12]. Due to less amorphous carbon formation, the CNT grown from this technique has high potential in developing electronic devices, and will produce high quality CNTs [13–14]. Since CNT and graphene are in the same group of materials, thus it is applicable to use alcohol catalytic CVD technique in producing graphene.

The presence of catalyst during the growth process is compulsory for alcohol catalytic CVD technique. Cobalt catalyst is the most appropriate catalyst for alcohol CVD technique [15]. The oxide layer that could be formed by air decomposition is the phase of Co_3O_4, while phases of Co and CoO can be found in the vacuum [16]. Crystalline Co_3O_4 is an active phase among its well-known three polymorphs [17]. Also, the thickness of catalyst may affect the growth of graphene [18]. The amount of adsorbed carbon into the small thickness of catalyst film is not enough to enhance the precipitation of all carbon elements for a film of graphene forms on the surface. By increasing the thickness of catalyst film, the number of graphene layer will be increased. Hence, this report is prepared to validate the effect of annealing temperature for the formation of active Co_3O_4 film on the graphene growth by alcohol catalytic CVD technique.

II. EXPERIMENTAL

Using sol gel spin-coating technique, active Co_3O_4 films were synthesized. The precursor solution was prepared to produce a 0.05 mol / L concentration solution by diluting 124.54 mg of Co acetate tetrahydrate ($Co(CH_3COOCH)_2.4H_2O$) into 10 mL of absolute ethanol. The solution was vigorously stirred for 10 min and kept in ultrasonic bath for 2 h, resulting in a light pink color solution. The silicon wafer P-type was cut in sizes of 15 mm or 15 mm. The substrates were washed by soaking in acetone, left in

Revised Manuscript Received on March 15, 2020.
***** Correspondence Author
Mohd Asyadi Azam*, Fakulti Kejuruteraan Pembuatan, Universiti Teknikal Malaysia Melaka, Melaka, Malaysia. Email: asyadi@utem.edu.my
Nor Najihah Zulkipli, Fakulti Kejuruteraan Pembuatan, Universiti Teknikal Malaysia Melaka, Melaka, Malaysia. Email: p051520007@student.utem.edu.my@utem.edu.my
Noraiham Mohamad, Fakulti Kejuruteraan Pembuatan, Universiti Teknikal Malaysia Melaka, Melaka, Malaysia.
Mohd Shahadan Mohd Suan, Fakulti Kejuruteraan Pembuatan, Universiti Teknikal Malaysia Melaka, Melaka, Malaysia.
Ghazali Omar, Fakulti Kejuruteraan Pembuatan, Universiti Teknikal Malaysia Melaka, Melaka, Malaysia.

ethanol for sonication for 10 min, and dried with the use of nitrogen blow. The Co acetate tetrahydrate / absolute ethanol precursor solution was spin coated for 60 s at 6000 rpm on the cleaned substrates. The spin-coated wafers were then preheated to vaporize the solvent at 80 ° C for 5 min, thereby leaving Co catalyst films on the wafer. Later, for an annealing process, the preheated wafer was placed in the 450, 500, 550 and 600 ° C vacuum furnace to obtain crystalline Co_3O_4 films.

The prepared catalyst film for the graphene growth was positioned in a horizontal quartz tube reactor (MTI-OTX 1200X). The tube was evacuated to 0.4 Pa using oil-free scroll pump. To prevent excessive oxidation of the Co catalyst, at a pressure of 400 Pa Ar gas was injected into the system simultaneously with 5 min of rapid heating and 5 min of second annealing phase. Once the annealing step completed, another Ar gas flow piping was purged into a closed-tank ethanol to vaporize the ethanol and instantly lead off at flow rates of 100–150 sccm into the system. The growth process was carried out for 5 min at an internal pressure of 4-10 kPa. The ethanol gas flow was stopped after the growth process, and the sample was left to cool to RT. The process of annealing and growth was performed at 900 ° C of CVD processing temperature.

The confirmation of the presence of active Co_3O_4 was done by PANalytical X-ray Diffraction (X'Pert Pro MPD PW3060/60). The surface morphology and the cross section of the sample were analyzed by using field emission scanning electron microscope (FESEM, Hitachi SU8100). Raman analysis for the active Co_3O_4 films and for the as-grown graphene was conducted by using Raman spectroscopy (Uni-RAM 3500) with 532 nm wavelength laser excitation (Nd: YAG).

III. RESULTS AND DISCUSSION

A. XRD Analysis

Figure 1 shows the XRD patterns of the dried Co film, the film that is prepared before annealing process and 4 samples that annealed at different annealing temperature; 450, 500, 550 and 600 ºC. Dominant diffraction peaks are detected at 36.8º and 42.4º while minor diffraction peaks are detected at 52.2º, 55.9º and 61.9º, for the Co film annealed at 450 ºC. For the film annealed at 500 ºC, the same dominant peaks at 36º and 42.4º are observed but with more minor peaks at 31.2º, 52.4º, 55.9º, 59.4º, 61.6º and 65.3º. However, only one dominant peak is observed for the sample annealed at 550 ºC with no other minor peak is presence. For Co film annealed at 600 ºC, the dominant peaks are similar with the Co films annealed at 450 ºC and 500 ºC with three minor peaks observed at 59.5º, 61.6º and 65.3º. The Co film dried at 80 ºC shows no presence of dominant peak, which indicates amorphous phase. The diffraction peaks detected at 31.2º, 36.8º, 55.9º, 59.4º, 59.5º and 65.3º could be indexed to the spinel type cubic structure of Co_3O_4 [19-20]. From the observation, Co_3O_4 cubic structure can be formed at 450, 500, 550 and 600 ºC annealing temperatures. Yet, this result cannot determine that the Co_3O_4 structure produced from this sol-gel process may produce graphene structure until it undergoes graphene growth process by alcohol catalytic CVD technique.

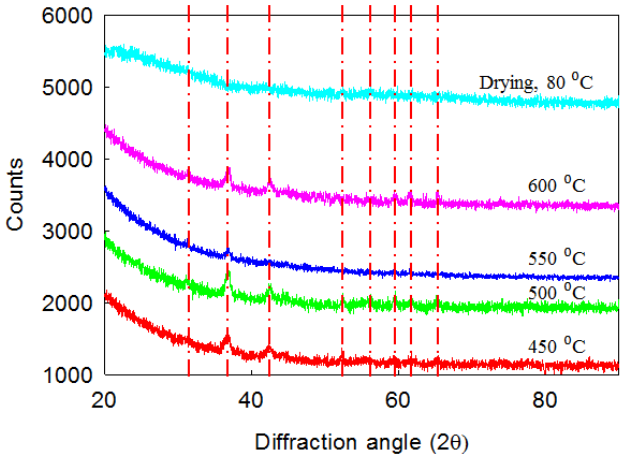

Fig. 1. XRD patterns of the Co film dried at 80 ºC and annealed Co_3O_4 films at 450, 500, 550 and 600 ºC.

B. Raman Analysis

Another analysis to confirm the formed of spinel cubic structure Co_3O_4 is an active Co_3O_4 is by Raman analysis. Theoretically, the normal spinel structure for Co_3O_4 crystal is Co^{2+} $(Co^{3+})_2$ O^2_{-4} (space group O^7_h) with Co^{2+} and Co^{3+} located at tetrahedral and octahedral sites [21]. Raman analysis is considered to be based on the interaction of molecular vibrations, phonons or other excitations in the system with laser light, resulting in the energy of the laser photons being moved up and down, thus giving information to the vibrational modes in the system [22]. Previously, it is mentioned that the reduction of the 42-dimentional representation Γ of the vibrational modes at k=0 into irreducible representations of the factor group O_h gives A_{1g}, E_g, $3F_{2g}$, $5F_{1u}$, $2A_{2u}$, $2E_u$ and $2F_{2u}$ [23]. The A_{1g}, E_g and $3F_{2g}$ is the fingerprint for Raman active of Co_3O_4. Raman spectrum of active Co_3O_4 film annealed at 450 ºC clearly displayed Raman-active phonon modes located approximately at 196, 480, 619 and 684 cm^{-1}, that correspond to the F^1_{2g}, E_g, F^2_{2g} and A_{1g} (Fig. 2). F^3_{2g} might be overlapped with Si peak. This indicates complete crystallization of the Co_3O_4 phase [19]. However, the crystallization of Co_3O_4 phase depends on the thickness of Co film spin-coated on the substrate since 1 layer spin-coated Co film shows weak intensity as compared with 5 layers of coating.

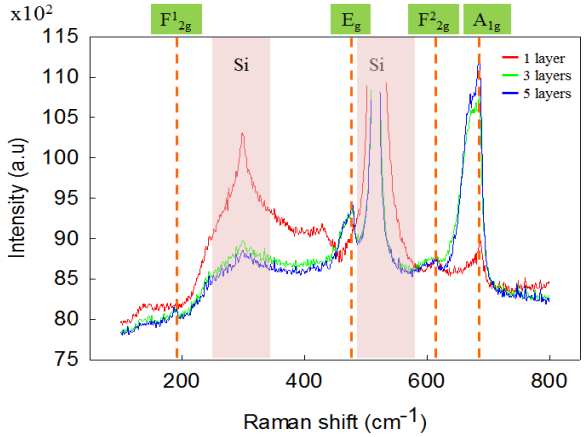

Fig. 2. Raman spectra of active Co_3O_4 films.

Further study has been conducted to confirm the spinel cubic structure of Co_3O_4 is an active catalyst for graphene growth by alcohol catalytic CVD. Since theoretically Co_3O_4 structure can be formed at 450 ºC, thus the Co film annealed at 450 ºC was used for this purpose (Fig. 3). With absolute ethanol as the carbon feedstock, graphene is indicated by the presence of G-band and 2D-band in the Raman spectrum at 1621 cm^{-1} and 2680 cm^{-1}, respectively. G-band is specified as the graphitic structure and 2D-band is secondary peak indicates the number of graphene layers [24]. These bands are the fingerprint for the existence of graphene on the sample. The intensity ratio of 2D-band over intensity of G-band was calculated in order to qualitatively ascertain the structures of the produced graphene. The I_{2D}/I_G ratio was calculated to be 1.010. This indicates the growth of a few layers of graphene. Hence, even though the existed bands are not strong enough to overcome the intensity of Si peak, it is proved that the active Co_3O_4 is able to synthesize graphene layer by alcohol catalytic CVD.

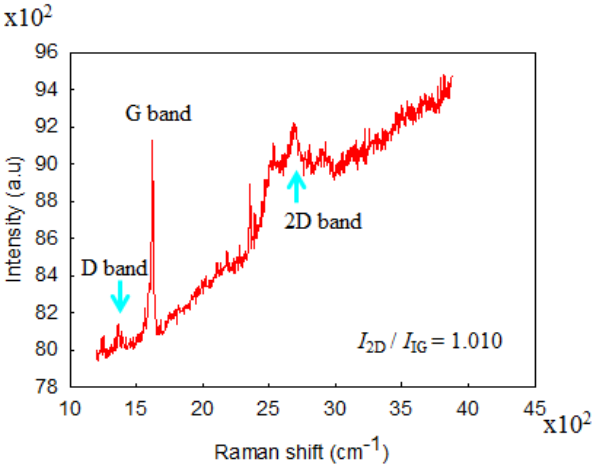

Fig. 3. Raman spectrum of graphene grown from active Co_3O_4 film annealed at 450 ºC.

C. Surface Morphological Analysis

For the morphology of the as-grown graphene from the active Co_3O_4, again, the sample that annealed at 450 ºC was used for this study. The sample was characterized by field emission scanning electron microscopy (FESEM). Fig. 4a displays the homogeneous distribution of graphene on the sample surface. Closed-image at 50k magnification shows that the graphene structure is well-formed (Fig. 4b). Along with the presence of graphene structure, CNT structure is also observed on the surface. This indicates that the CVD processing temperature at 900 ºC is not enough to eliminate the CNT growth. Higher CVD processing temperature is needed to make sure there is only graphene structure formed on the surface. Somehow, the existence of CNT might be helpful in a certain application. This is an interesting finding for those who may need both graphene and CNT in their composition. The graphene which appears to be particle-like with irregular shapes and sizes has the average diameter of graphene formed on the surface is 170.78 nm (Fig. 4c).

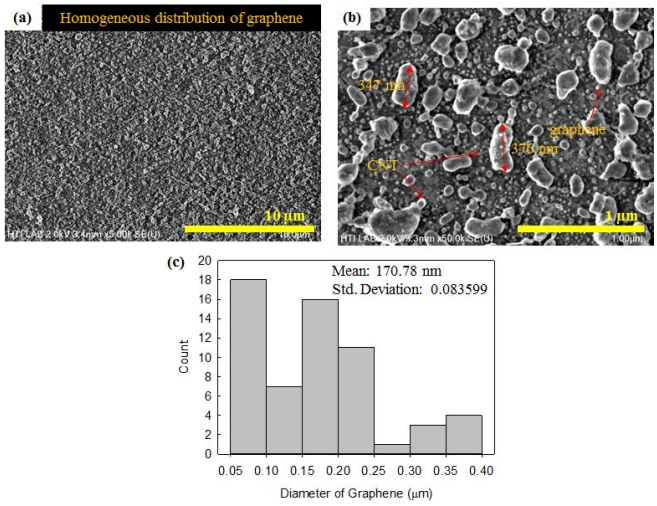

Fig. 4. (a)-(b) FESEM images of as-grown graphene from the active Co_3O_4 film. (c) Histogram of the graphene diameter distribution captured from the image.

Morphology of the cross-section of the as-grown graphene is also examined by FESEM image, as shown in **Figure 5a**. From the image, the graphene layer is grown on the rough surface of active Co_3O_4. Therefore, from this result, it can be specified that the exhibited Raman spectrum is affected by the surface roughness of the active Co_3O_4. Smooth surface with small surface roughness, may result in good formation of graphene layer. There is a claim that the thickness of catalyst film may affect the growth of graphene [5, 19]. This is because the amount of adsorbed carbon into the small thickness of catalyst film is not enough to enhance the precipitation of all carbon elements out on the surface to form graphene layer. In this study, the average thickness of active Co_3O_4 is 308.9 nm. This implies that the thickness is enough to ignite the precipitation of carbon elements onto the surface. However, it is not a conclusion to decide that the measured thickness is the optimum to ignite the precipitation of carbon elements onto the surface. Generally, higher annealing temperatures might introduce smaller thickness due to the shrinkage that happens during the process. It is much easier to ignite the precipitation of carbon elements onto the surface with smaller thickness of active Co_3O_4.

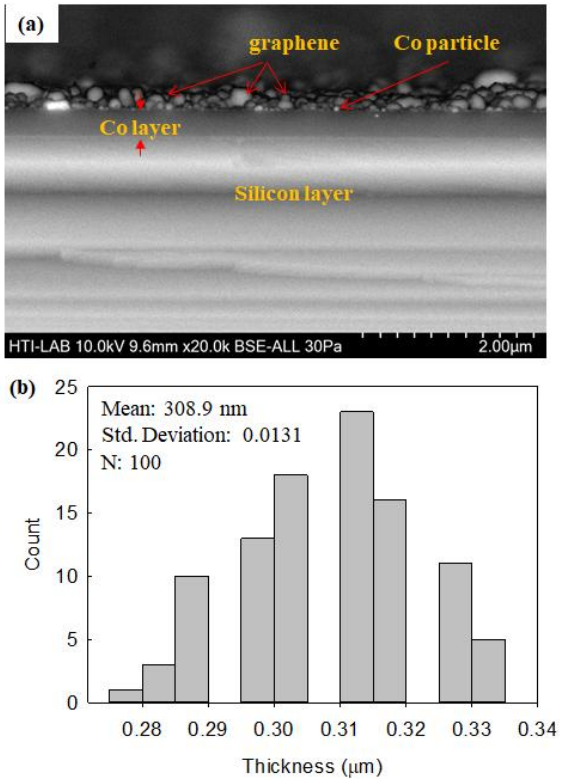

Fig. 5. (a) FESEM cross-section image of the as-grown graphene from active Co_3O_4 film. (b) Histogram of the thickness of active Co_3O_4 film distribution captured from the image.

IV. CONCLUSION

This study aims to validate the effect of annealing temperature for the formation of active Co_3O_4 film on the graphene growth by alcohol catalytic chemical vapor deposition (CVD) technique. Active Co_3O_4 film was prepared on silicon wafers by sol-gel process, using cobalt acetate tetrahydrate as the precursor compound and absolute ethanol as the solvent. The active Co_3O_4 phase was achieved by annealing process at 450, 500, 550 and 600 °C. The graphene is grown from active Co_3O_4 film under 900 °C of CVD processing temperature for 5 minutes. The obtained Co_3O_4 was characterized by X-ray diffraction and Raman spectroscopy. The as-grown graphene from active Co_3O_4 film annealed at 450 ºC was characterized by Raman spectroscopy and field emission scanning electron microscope (FESEM). The results demonstrated that spinel type cubic structure of Co_3O_4 could be produced at the varied annealing temperatures but the optimum XRD result was at 500 ºC annealing temperature. The presence of active Co_3O_4 phase was supported with the exhibited peaks of four Raman-active phonon modes in the Raman spectra. The quality of as-grown graphene determined from the ratio of 2D-band over G-band intensities is 1.010; an indication of few layers of graphene. Overall, Co_3O_4 is a promising transition metal catalyst for graphene growth.

ACKNOWLEDGMENT

Authors would like to thank Universiti Teknikal Malaysia Melaka (UTeM) for facilities and financial support for this research.

REFERENCES

1. A. Reina, X. Jia, J. Ho, D. Nezich, H. Son, V. Bulovic, M. S. Dresselhaus, and J. Kong, “Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition” Nano letters, vol. 9(1), 2009, pp. 30-35.
2. V. Subramanian, H. Zhu, R. Vajtai, P. M. Ajayan, and B. Wei, “Hydrothermal synthesis and pseudocapacitance properties of MnO2 nanostructures”, J. Phys. Chem. B, vol. 109, 2005, pp. 20207.
3. M. A. Azam, N. N. Zulkapli, N. Dorah, R. N. A. R. Seman, M. H. Ani, M. S. Sirat, et al., “Critical considerations of high quality graphene synthesized by plasma-enhanced chemical vapor deposition for electronic and energy storage devices”, ECS Journal of Solid State Science and Technology, vol. 6 (6), 2017, pp. M3035-M3048.
4. B. Padya, N. Narasaiah, P. K. Jain, and T. N. Rao, “A facile co-solvent strategy for preparation of graphene nanoplatelet powder: An industrially viable innovative approach”, Ceramics International, vol. 45(10), 2019, pp. 13409-13413.
5. X. Zang, Q. Zhou, J. Chang, Y. Liu and L. Lin, “Graphene and carbon nanotube (CNT) in MEMS/NEMS applications”, Microelectron. Eng., vol. 132, 2015, pp. 192-206.
6. J. H. Lee, E. K. Lee, W. J. Joo, Y. Yang, B. S. Kim, et al., “Wafer-scale growth of single-crystal monolayer graphene on reusable hydrogen-terminated germanium”, Science, vol. 344 (6181), 2014, pp. 286-289.
7. J. Liu, and L. Fu, “Controllable growth of graphene on liquid surfaces”, Advanced Materials, vol. 31(9), 2019, pp. 1800690.
8. D. Geng, J. Hu, W. Fu, L. K. Ang, and H. Y. Yang, “Graphene-Induced in Situ Growth of Monolayer and Bilayer 2D SiC Crystals Toward High-Temperature Electronics” ACS Applied Materials & Interfaces, vol. 11(42), 2019, pp. 39109-39115.
9. M. H. Oliveira Jr, J. M. J. Lopes, T. Schumann, L. A. Galves, M. Ramsteiner, et al., “Synthesis of quasi-free-standing bilayer graphene nanoribbons on SiC surfaces”, Nat. Commun., vol 6 (1), 2015, pp. 1-7, 2015.
10. N. N. Zulkapli, M. A. Azam, N. M. A. M. Zubir, N. A. Ithnin, and M. W. A. Rashid, “A simple and room temperature sol–gel process for the fabrication of cobalt nanoparticles as an effective catalyst for carbon nanotube growth”, RSC Advances, vol. 5, 2015, pp. 95872-95881.
11. M. S. A. Bistamam, and M. A. Azam, “Tip-growth of aligned carbon nanotubes on cobalt catalyst supported by alumina using alcohol catalytic chemical vapor deposition”, Results in Physics, vol. 4, 2014, pp. 105-106.
12. M. A. Azam, K. Isomura, A. Fujiwara, and T. Shimoda, “Direct growth of vertically aligned single-walled carbon nanotubes on conducting substrate and its electrochemical performance in ionic liquids”, Phys. Status. Solidi. A, vol. 209, 2012, pp. 2260-2266.
13. T. Izak, T. Danis, M. Vesely, M. Marton, and M. Michalka, “Influence of co-catalyst on growth of carbon nanotubes using alcohol catalytic CVD method”, Vacuum, vol. 82(2), 2007, pp. 134-137.
14. M. A. Azam, N. Dorah, R. N. A. R. Seman, N. S. A. Manaf, and T. I. T. Kudin, “Electrochemical performance of activated carbon and graphene based supercapacitor”, Materials Technology, vol. 30 (sup1), 2015, pp. A14-A17.
15. M. A. Azam, M. W. A. Rashid, K. Isomura, A. Fujiwara, and T. Shimoda, “X-Ray and Morphological Characterization of Al-O Thin Films Used for Vertically Aligned Single-Walled Carbon Nanotube Growth”, Advanced Materials Research, vol. 620, 2013, pp. 213-218.
16. J. K. Kim, J. Y. Ju, S. K. Choi, S. Unithrattil, S.S. Lee, et al., “In-situ preparation and unique electrochemical behavior of pore-embedding CoO/Co3O4 intermixed composite for Li+ rechargeable battery electrodes”, Journal of Power Sources, vol. 378, 2018, pp. 562-570.
17. P. Kannan, T. Maiyalagan, A. Pandikumar, L. Guo, P. Veerakumar, and P. Rameshkumar, “Highly sensitive enzyme-free amperometric sensing of hydrogen peroxide in real samples based on Co3O4 nanocolumn structures”, Analytical Methods, vol. 11(17), 2019, pp. 2292-2302.
18. J. Tracy, O. Zietz, S. Olson, and J. Jiao, “Plasma-Enhanced Chemical Vapor Deposition of Acetylene on Codeposited Bimetal Catalysts Increasing Graphene Sheet Continuity under Low-Temperature Growth Conditions”, Nanoscale research letters, vol. 14(1), 2019, pp. 335.
19. K. Fukui, and Y. Suzuki, “Well-facetted spinel-type Co3O4 microcrystal assembly prepared by hydrothermal synthesis and post-thermal decomposition”, Ceramics International, vol. 45(7), 2019, pp. 9288-9292.
20. R. Zhang, S. Gao, T. Zhou, J. Tu, and T. Zhang, “Facile preparation of hierarchical structure based on p-type Co3O4 as toluene detecting sensor”, Applied

Surface Science, vol. 503, 2020, pp. 144167.
21. O. M. Sousa, J. S. Lima, A. F. Lima, and M. V. Lalic, "Theoretical study of structural, electronic and magnetic properties of the spinel Co3O4 under the pressure from 0 to 30 GPa", Journal of Magnetism and Magnetic Materials, vol. 484, 2019, pp. 21-30.
22. G. S. Bumbrah, and R. M Sharma, "Raman spectroscopy–Basic principle, instrumentation and selected applications for the characterization of drugs of abuse", Egyptian Journal of Forensic Sciences, vol. 6(3), 2016, pp. 209-215.
23. I. Hurwitz, D. Raanan, L. Ren, H. Frostig, P. Oulevey, et al., "Single beam low frequency 2D Raman spectroscopy", Optics Express, vol. 28(3), 2020, pp. 3803-3810.
24. P. Zhao, B. Hou, X. Chen, S. Kim, S. Chiashi, E. Einarsson and S. Maruyama, "Investigation of non-segregation graphene growth on Ni via isotope-labeled alcohol catalytic chemical vapor deposition", Nanoscale, vol. 5 (14), 2013, pp. 6530-6537.

AUTHOR'S PROFILE

Ir. Dr. **Mohd Asyadi Azam** was born on 31st May 1979, in Johore, Malaysia. Dr. Asyadi is currently the Deputy Dean (Research and Postgraduate Study) of Faculty of Manufacturing Engineering, Universiti Teknikal Malaysia Melaka (UTeM), a position he has held since March 2018. He joined UTeM as a permanent academic staff in 2006. He also has served as Head of Department (Engineering Materials Dept) and Coordinator for Center of Excellence in UTeM. After graduating in Materials Science and Engineering from Shibaura Institute of Technology in 2003, he then completed his Master of Engineering (Materials Science and Engineering) in 2005 at the same university in Tokyo, Japan where he consecutively won award; Hisamoto Yanai Memorial Award for his excellence in academics. During his PhD, he was awarded the Japan Society for the Promotion of Science (JSPS) scholarship for his remarkable research topic; aligned carbon nanotube growth for supercapacitor application. Upon his completion of his study, he was awarded Best Student Award due to academic and research excellences. Dr. Asyadi has received several accolades for his outstanding scientific research including the UTeMEX, MTE, ITEX and SIIF innovation Gold Medal and Special Awards starting year 2014 until now. Dr. Asyadi has published over 100 technical papers, 3 book chapters, monographs and technical reports on energy storage device including supercapacitors and lithium ion batteries. He received the highest citation for journal publications based on the WOS and Scopus citation index for energy storage device and chemical vapor deposition of carbon nanomaterials including graphene and carbon nanotube.