SCIENTIFIC RESEARCH JOURNAL,
VOL 18, No 1 (2021) 15 - 27
https://doi.org/10.24191/srj.v18i1.11386

Modifies Hummer's Method of Graphene Oxide Nanostructures for Fibre Optic Sensors Application

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Received:3 December 2020
Accepted: 8 December 2020
Online First: 28 February 2021

ABSTRACT

For optical fibre sensors applications, nanomaterials have been widely used to enhance sensor performance. Here, the fibre optic uses the transmission of light by total internal reflection along with the fibre and depending on the diameter of the fibre and the wavelength of the light used. Among others, graphene oxide nanostructures (GO) would offer exceptional advantages on the sensing mechanism due to the 2D properties of the monocellular layer originally from graphite. The main objectives of this research are to successfully synthesis GO using a chemical reduction method known as modifies Hummer's method and later, deposited the GO onto the modified fibre optic layer to create a sensing platform. Before that, the standard plastic of fibre optic (POF) was modified by removing the cladding layer (1 cm) using a mechanical etching technique, thus the sensing platform can be created. The morphology and optical properties of the system were characterised using scanning electron microscopy (SEM) and ultraviolet-visible (UV-Vis) spectroscopy. The result of the preparation and characterisation of GO-optical fibre coatings was presented, considering its potential use for sensing applications. The stable GO was prepared by three hours of stirring time during the synthesis and a longer dipping time was preferred to fully coat the core of the exposed POF. Aiming to explore this scheme for sensing applications, GO-coated tilted fibre will be later measuring via refractive index variations. An improvement on the sensitivity should be obtained and thus become a promising sensing platform for the development of a new line of sensors.

Keywords: *graphene oxide, plastic core, fibre optic sensors, nanostructures*

INTRODUCTION

Nanotechnology has turned into a fundamental and significant field device to create different sorts of nanoparticles with high surface zone to volume proportions and remarkable properties. In this manner, nanoparticles have been used for a few biomedical applications; including diagnostics, sedate conveyance, biomarkers, and unmistakable antibacterial, antifungal, and hostile to biofilm operators. Since the beginning, nobody ever thought that the mere tip of a pencil would be the most talked about material among the researchers over a decade. In the year 2004, [1] have successfully exfoliated a single layer of carbon from the graphite from the tip of the pencil and called it 'graphene' by the IUPAC commission.

Graphene has great optical, thermal, and mechanical properties. Single sheet graphene is a highly transparent material but each layer in thickness absorbs up to 2.3% of white light, with less than 0.1% reflectance. Graphene is also known to be one of the strongest materials ever made and a single-layer graphene sheet can withstand up to 42 $N.m^{-1}$ of stress, with Young's modulus of 1.0 TPa [2]. On the other hand, the oxidation of graphite crystals will generate a new structure known as graphene oxide (GO). GO specifically known for a honeycomb structure, which is a 2-dimensional nanomaterial of *sp2* and *sp3* with single-atomic-layered consist of carbon, hydrogen, and oxygen [3]. These functional groups include hydroxyl, epoxy, and carboxylic acid moieties that allow GO to experience various kinds of chemical and biochemical interactions with other biological molecules leading to a very rich surface chemistry diversity which making GO soluble in many solvents, both aqueous and organic. Thus, GO has been used widely in nanocomposite materials, polymer composite materials, energy storage, biomedical applications, and catalysis, and as a surfactant with some overlaps between these fields [4].

Although with all the advantages of the GO, it does, however, suffer from a low electrical conductivity and is an electrical insulator. To gain the benefits of GO, it is typically dispersed, added into a formulation, made into a film or other nano-enabled product, or then reduced to restore the

graphene structure, which is known as reduced graphene oxide (rGO). Until now, many techniques have been performed to synthesize GO. But with all methods that have been explored, the yield of produced GO was very low and cannot achieve high-quality industrial production. In contrast, among all, the chemical reduction of GO is reported to be the most promising method concerning large-scale productivity at a low cost in a short time [1, 3]. The demand for optical with the characteristics of GO which inherent electrical and mechanical properties, holding great potential for ultrasensitive sensor application [2].

An optical fibre or also known as the fibre optic is referred to the technology that is related to the transmission of information as light pulses along with a plastic or glass strand or fibre. This fibre optic medium is using long-distance high-performance data networking, thus allowing several high-out telecommunication services including internet, telephones, and television. From that point forward, the lines for the web have been moved up to fibre optic links, and those equivalent links are utilised straightforwardly with gadgets. In another view, the standard fibre optic configuration (see Figure 1) can be decorated to the application of the sensors by some modifying into its structure. The fibre optic sensors can be constructed by integrating the optical fibre with any advanced materials such as graphene-based, which will, at last, disrupt the light propagation signal, hence, allowing the interaction of the light with surroundings, which to be measure as a detection signal. Moreover, the use of graphene-based elements can enable the use of distributed sending in harsh environments without the use of an armature.

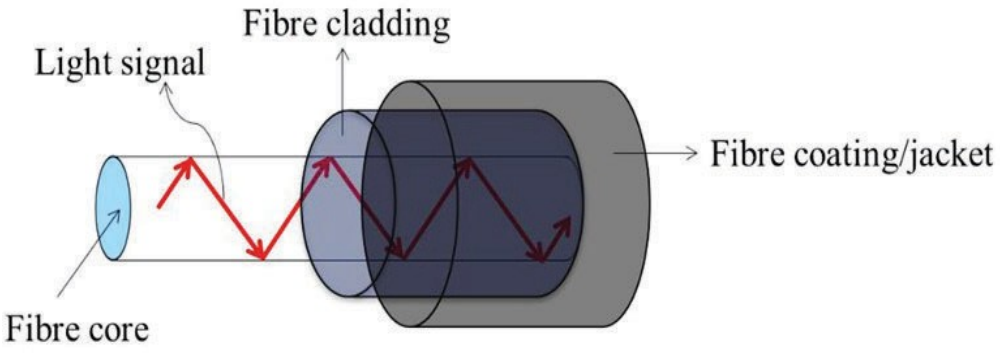

Figure 1: Schematic Drawing of the Core and Cladding Structure of a Standard Fibre Optic Probe

To keep the optical sign in the centre, the refractive record of the centre must be more prominent than that of the cladding. The difference in densities between these two components permits the cables to act following the principle of total internal reflection (TIR). Likewise, the fibre centre has a higher refractive index (RI) than the cladding which enables the light to be deeply kept with negligible loses over long separations [5]. That is why if the core is bent or strained, it can cause of change in reflected wavelength which could not get the maximum data transfer due to unexpected change in the measured strain. Thus, as the GO coated around the core layer of the fibre optic, the light propagates in the core modes (see Figure 1) will be affected, caused the RI modulation between the core and the cladding, which creates a sensors signal [6].

The main purposes of this project were to synthesize the GO nanostructures with a simple environmentally friendly chemical route and later focused on creating a sensing platform on the fibre optic probe. The fabrication of the sensing platform included the modification of the core structure of the fibre optic by removing the outer layers including coating/ jacket and cladding layer of the probe and later proceed to its suitability to be coat with GO. The work also included the optical and morphology characterisations using ultraviolet-visible (UV-Vis) spectroscopy and scanning electron microscopy (SEM); respectively. In summary, fibre optic sensor innovation, thusly, has regularly been encouraged by the improvement and resulting large scale production of component to help these industries. Even though the technology is relatively new and highly in start-up cost, this work is driven by the advantages of fibre optic-based sensors including the capacity to be light-weight with extremely little size, passive towards electromagnetic interference (EMI), high sensitivity, wide transfer speed, and robust towards the harsh and extreme environments.

MATERIALS AND METHODS

Materials and Chemicals Required

Graphite powder (<20 μm, Aldrich Chemistry), potassium permanganate; $KMnO_4$ (99%, R&M Chemicals), hydrogen peroxide; H_2O_2

(40% wt, Sigma), sulfuric acid; H_2SO_4 (98%, Sigma). Plastic of fibre; POF (Cable MIKROE-1473) was brought from MikroElektronika, USA.

Synthesis of GO using Modifies Hummer's Method

In this method, 25 ml of H2SO4 and 1 g of graphite powder were mixed and stirred for several minutes in a volumetric flask in an ice bath setup (0°C – 4°C). Then, 3 g of $KMnO_4$ was slowly added into the solution so that the temperature was carefully keeping less than 20°C. Here, the mixing time was studied by varying the stirring time for one hour 30 minutes, and three hours; respectively. Later, 50 ml of deionised (DI) water was drop-by-drop added for 20 minutes with a rate of 2.5 ml/min into the mixture to control the temperature less than 50°C to start the oxidising process. After some time, the colour changed to dark brown (see Figure 2, a) and later 100 ml of DI water was added to complete the oxidation process of the remaining graphite that has left.

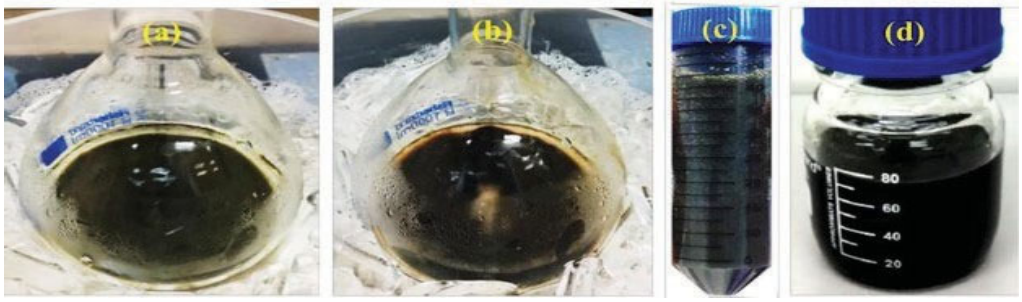

Figure 2: Mixture of GO Solution using Modifies Hummer's Method After (a) Added 50 ml of DI and (b) Added 100 ml of DI Water for the Three Hours of Stirring Under an Ice Bath Setup. GO Solution Produced After Sited-Down Overnight and Discard the Excess Water with Reaction Stirring Time of (c) One Hours 30 Minutes and (d) Three Hours

In the final step, 5 ml of H_2O_2 was added to remove the excessive amount of $KMnO_4$ or in a simple word is to stop the reaction (see Figure 2, b). The produced GO solution was left overnight and later the excess water around 30 ml was discarded. The concentrated GO was diluted with DI water to the final volume required (see Figure 2 c, d) and ready to be used for the fabrication of the fibre optic probe.

Fabrication of Sensor Probe

The POF that has been used for this project was made of 0.5 mm polymethylmethacrylate (PMMA) core diameter and length of 1 cm were chosen to be uncladded. The opened region was stripped to remove the jacket/coating layer (black cable, see Figure 3) and then uncladded by chemical etching using DI water and acetone solution and washed with DI water again before been used for coating with GO [3]. The bare probe was coated with GO (prepared from three hours stirring time) by dip-coating technique with a dipping time of two hours.

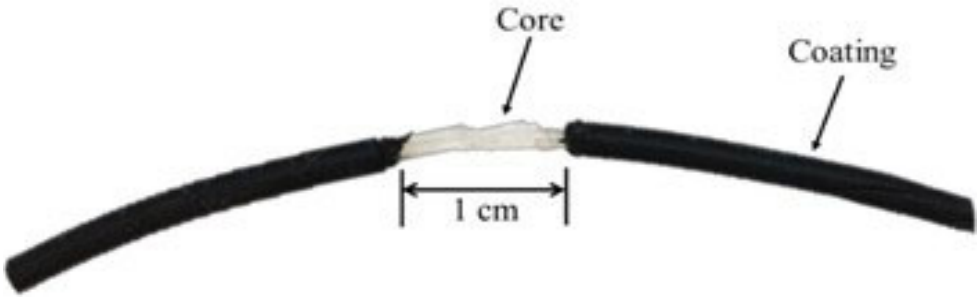

Figure 3: Image of Plastic of Fibre After Mechanical Stripping and Chemical Etching using Acetone Applied to Remove the Coating Layer

Characterisation of GO and Optical Fibre

To confirm that the prepared GO solution contained a high number of single-layered GO sheets, the Ultraviolet-visible (UV-Vis) spectrum of the GO aqueous dispersion (prepared from various stirring time of one hour 30 minutes and three hours) was measured using UV-Vis spectroscopy (Jasco model V-670) scanned from the wavelength of 200 nm to 900 nm using plastic cuvette. This technique is proven to be simple and easy on measuring the quality of synthesised GO aqueous dispersions [7]. The morphologies of the fibre optic probe before and after coated with GO was observed under a scanning electron microscope (SEM) (HITACHI SU3500) with magnifications starting from 15.0kV with 35X magnification until 1000X magnification with the same amount of voltage.

RESULTS AND DISCUSSION

The UV-Vis spectroscopy was used to measure the intensity of light and it is

proportional to the wavelength of the prepared GO samples as presented by Figure 4. The absorbance of GO has typically measured at the wavelength range of 220 nm to 300 nm [8]. Based on the UV-Vis spectrum obtained at ~230 nm indicate that the GO was successfully formed from both samples (see Figure 4, a). The plasmon peak at ~230 nm is due to the transition of n to n* of the aromatic C–C bonds. This respective peak is related to the number of nanoscale sp2 clusters that appeared on the GO sheets, which correlated to the amount of single-layered GO sheets present in the aqueous dispersion as in agreement with [7-10]. This result suggested that the samples produced a higher number of GO sheets in single-layered with three hours reaction time is produced sharp peak compared to one hours 30 minutes GO solution. The wavelength (shoulder) measured at ~280 nm to 300 nm is corresponding to the n – n* transitions of the oxygen functional group (C=O) as observed on spectra of Figure 4 (d) and (e). No peak was measured at 265 nm indicated that the oxidation process of graphene into GO was completed for both samples [8].

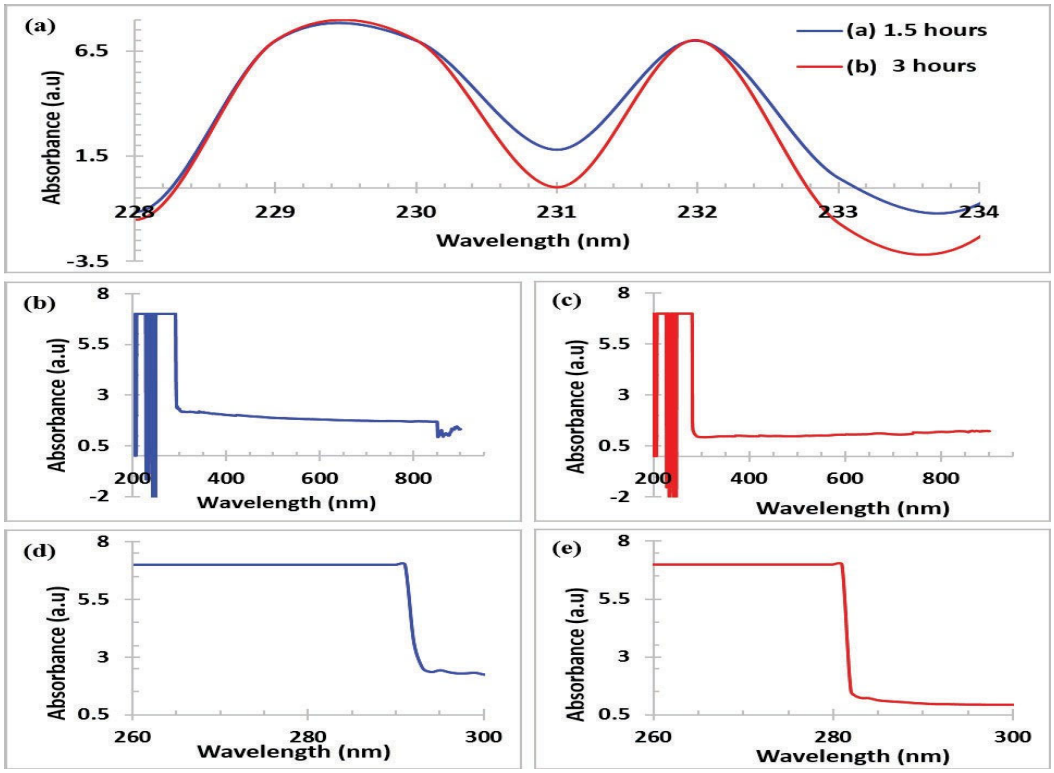

Figure 4: (a) UV-Vis Spectra of 5% v\v GO Samples Diluted with DI Water Zoom in a Range of 228 nm to 243 nm Which the GO Sample was Prepared with a DiGerent Stirring Time of One hours 30 Minutes (Blue) and Three hours (Red). (b) and (c) Shows the Whole Scanning Spectrum of GO Sample. (d) and (e) Show the GO Spectrum Zoom in a Range of 260 nm to 300 nm

However, the sample preparation of the UV-Vis measurement should be further diluted so that the disturbance caused by the noise signal can be minimised. Moreover, the spectrum of sample GO prepared with one hour 30 minutes stirring reaction (see Figure 4, b) shows that it has a small disturbance in the 850-900 nm region to be compared with GO samples stirred for three hours (see Figure 4, c). This shows that the wavelength of the sample that has been stirred for three hours is more stable than half of the time taken, thus proved that modifies Hummer's method is successfully establish to synthesis GO.

The morphology of the fibre optic probe before and after coated with GO was observed using SEM. The core structure of POF after the etching process at the middle part and the tip was observed in Figure 5 (a) and (b); respectively. Figure 5 (b) shows clearly that the tip of the core was shrinking a little bit due to the eRect of the charging process during sample preparation for the SEM imaging. This indicates that removing part of the cladding layer must be performed carefully so that the layer still protected the structure from being shrunk. At the uncladded region (see Figure 5, c), the smooth surface was obtained after the etching process indicated that the obtained surface structure was ready to be embedded with the GO in the next step. From this image, it can be said that the clad done a good job on keeping the POF in its original shape while been heated for the coating process before undergoes into the SEM to prevent from overcharged during this process. However, the morphology of the POF can be damaged during the stripping process if not being careful using the mechanical stripper. It is shown that the process itself may result by stripped oR some of the core surfaces and resulted as a scratched surface as evidence in Figure 5 (d).

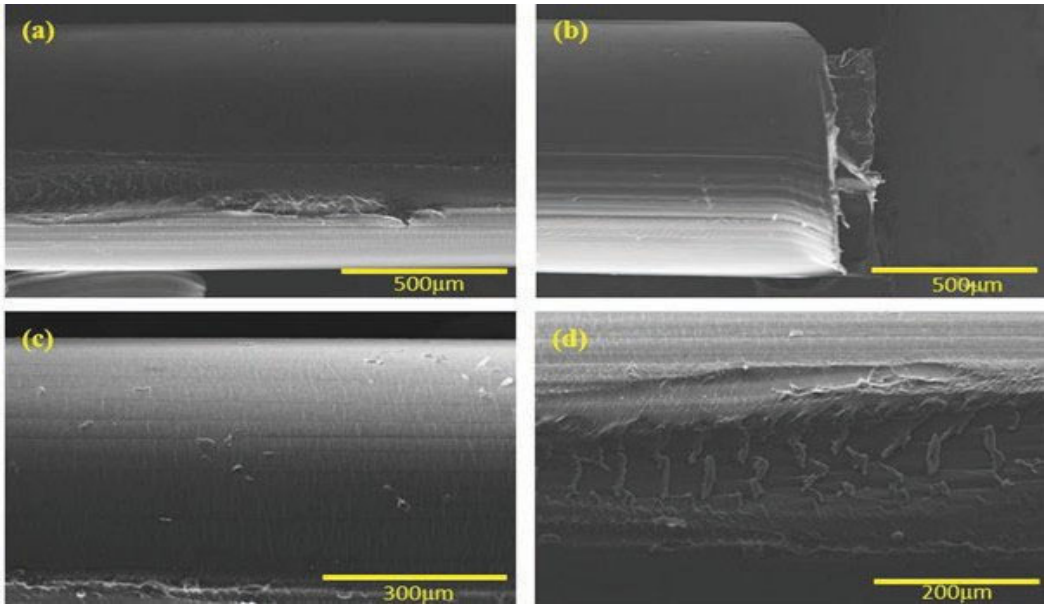

Figure 5: SEM Images of the POF After Stripping Occurred (a) at the Middle; (b) at the Tip; (c) at the Clear Middle; (d) Scratched Observed at the Middle Part of the Unclad Probe

Figure 6 (a) shows the uncladded POF probe that coated with GO samples with dipping time for two hours. From the image, it is shown that the GO was held steadily and deposited on the entire surface of the core of the fibre optic, this phenomenon might due to GO was fully dissolved on the probe after the chemical etching using the acetone to clear the clad carefully. Yet, the GO seems not fully covered the unclad region as some of the unclad areas are still exposed after the coating process, which may interrupt the sensor signal in the future. Hence, this result indicates that the dipping time needs to be further study in the future so that the unclad area of the probe will be fully coated with GO. The morphology of GO structure appeared in two-dimensional sheet-like and appeared stacked one above the other which looks deposited in clustered as evidence at higher magnification (150 X magnification) as shown in Figure 6 (b). The same characteristic of GO images was observed by [11].

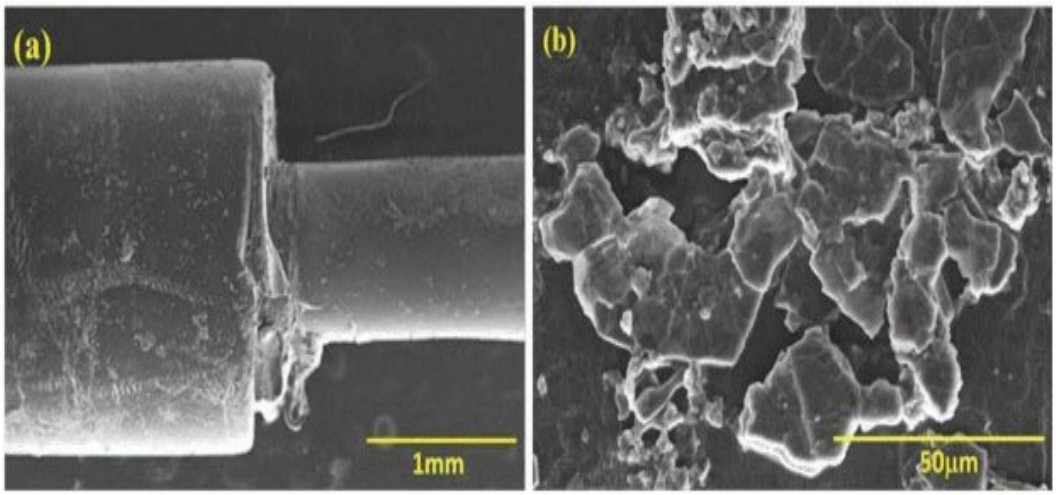

Figure 6: (a) SEM Image of the POF Probe that Coated with GO with Two Hours Dipping Time with (b) at Higher Magnification of the Coated Area on the Unclad Area of (a)

From these finding, it is confirmed that the GO can be synthesized using modifies Hummer's method even no sodium nitrate ($NaNO_3$) has been used during the reaction as compared to the work developed by [11, 12] which no toxic gasses such as N_2O_4 and NO_2 were released during the oxidation procedures. This also means no residues including 3NO- and Na+ presented on the synthesized sample, hence simplified the washing process of purifying GO. This result also proved that the GO sheets were successfully embedded on the core of the POF, and subsequently ready to be a sensing platform for the application of the sensors. Moreover, the sensing platform can further be integrated with other novel materials such as hydrogels [13], thus opening a unique and more versatile optical-based sensing mechanism, especially for biosensors application.

CONCLUSIONS

In summary, GO was successfully synthesized using modifies Hummer's method which needed three hours of stirring time to produce a stable GO in an aqueous solution. The measurement UV-Vis spectroscopy is proven to be useful to study the intensity change of the peaks that refers to the GO layer number change. Besides, the intensity ratios of these peaks can further give information about the concentration of the GO produced. The morphology of GO was further confirmed from SEM images and the POF

was proved to be successfully embedded with GO. For the preparation of the GO using modifies Hummer's method, it is recommended to further study the effect of other parameters such as the concentration of oxidation agent, and the oxidation reaction rate and time so that better morphology of the GO can be obtained. For the sensor probe fabrication, the preparation of 5% v/v of acetone and 95% v/v of DI water used to unclad the exposed core is needed for the core so that when the process of dipping or coating the core using the GO, it will allow it to sit steadily at the core due to the GO fully dissolve on the core. For the POF, after undergoes coating, the core will eventually become fragile to heat as shown in previous images from SEM that the core tends to change in shape at the tip of the POF, thus careful handling must be performed.

ACKNOWLEDGEMENT

The authors greatly appreciate the technical supports from Faculty of Mechanical Engineering, NANO-Electronic Research Group, Faculty of Electrical Engineering and Photonics Research Centre of Universiti Teknologi MARA, Shah Alam, Selangor. This research was funded by the fundamental research grant scheme (FRGS): 600-IRMI/FRGS 5/3(341/2019) and FRGS-Racer grant: 600-IRMI/FRGS-RACER5/3 (011/2019).

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