Synthesis and Characterizations of 3-dimensional Graphene Scaffold via Low Pressure Chemical Vapour Deposition

Norani Muti Mohamed[1,2], Mohamed Salleh Mohamed Saheed[1,2], Balbir Singh Mahinder Singh[1,2,] Mohamed Shuaib Mohamed Saheed[1,2]

[1]Centre of Innovative Nanostructures and Nanodevices (COINN), Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar, Perak Darul Ridzuan, Malaysia.

[2]Department of Fundamental and Applied Sciences, Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar, Perak Darul Ridzuan, Malaysia.

***Abstract*— The interconnected 3D graphene structure was synthesized using low pressure chemical vapour deposition (LPCVD at 3 Torr) with different level of methane concentrations on nickel foam catalyst. The grown graphene were subjected to SEM, TEM and Raman analysis at 514 nm in order to determine the quality of the structures and position of G-band and 2D-band with respect to the variation of methane concentration. Raman spectrum described the occurrence of G-band and 2D-band peaks at ~1580 cm^{-1} and 2700 cm^{-1}, respectively. The suppressed D-band peaks indicate the high crystallinity of the grown graphene. Shape of 2D-band peak shows an increase from two to five layers of graphene with an increase in CH_4 vol%. These multiple layers of graphene structure will be beneficial for improvement of transport properties in flexible perovskite solar cell (PSC).**

Keywords—3D graphene, low pressure CVD, high crystallinity.

I. INTRODUCTION

In the past years, there were many efforts to produce highly interconnected 3D graphene from sol-gel, template assisted and via chemical vapour deposition [1,2]. To preserve the intrinsic characteristic of 3D graphene, the technique of growth must be carefully considered to reduce the defects during the growth. The 3D graphene were being used to replace the conventional semiconductors in the electronic applications such as super capacitors, opto-photonics and photovoltaic. Such limitations as the scarcity and the high cost of rare metal, the stability towards acidic and alkaline environments, thermal stability and cost effectiveness and high manufacturing throughputs promotes graphene as the right replacing candidate.

II. MATERIALS AND METHODS

A. Materials

Poly methyl methacrylate (PMMA), iron (II) chloride, and nickel foam were acquired from Sigma Aldrich. All chemicals were used as received without further purification.

B. Methodology

Microporous nickel foam was chosen as the sacrificial template for the graphene growth with the intention to get the 3-dimensional graphene to emulate the porous structure of nickel foam template. The microporous nickel template was first cleaned with acetone in ultrasonic for 20 minutes followed by rinsing with isopropanol for 10 minutes, with deionized water and finally dried at room temperature. The cleaned nickel template was then loaded into the low pressure tube where constant flow of Argon and H_2 gas (ratio of 5:1) were introduced. The nickel foam template was annealed up to 1000ºC before carbon source of methane gas with flow rate of 40 sccm was flowed in. Various carbon deposition concentrations were used for the study.

The grown graphene was cooled down rapidly to room temperature for the next process to obtain free standing nanoporous graphene. PMMA is used as the support layer for graphene during the nickel etching process. The PMMA was coated on the nickel/graphene structure and baked at 80ºC for 1 hour and left to cool down at room temperature. Sacrificial nickel template was etched with 30% iron (III) chloride in DI water solution. Graphene coated PMMA with completely etched Ni foam was obtained and dried overnight at room temperature. The PMMA coating was then removed by using hot acetone at 80ºC. The outcome is a 3-dimensional standalone graphene which can then be transferred to the appropriate target substrate.

C. Characterizations

Field emission scanning electron microscope (FESEM) Zeiss Supra55 VP was used to determine the material composition and the morphology of the free standing graphene grown in atmospheric and low pressure condition. TEM analyses were recorded by High resolution transmission electron microscope (HRTEM) Zeiss Libra operating at 200 kV. Graphene samples were transferred onto Cu mesh to perform the TEM analysis. Analysis by Raman spectroscopy (Renishaw) was conducted using wavelength 514 nm provided by YAG-Nd laser with different laser power densities.

III. RESULTS AND DISCUSSION

A. SEM Analysis

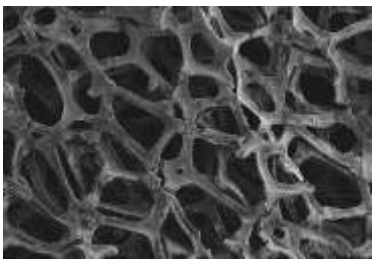

Fig. 1: SEM image of 3D graphene.

The morphology of grown 3D graphene was observed via SEM. The EDX on the multiple points of the microporous 3D graphene shows that the remaining Ni template residue is 0.09% which indicates complete etching. Figure. 2 shows the SEM view of free standing microporous 3D graphene. From the SEM image, the 3D graphene have interconnected and a continuous network of ligaments mimicking the porous structure of Ni foam.

B. TEM Analysis

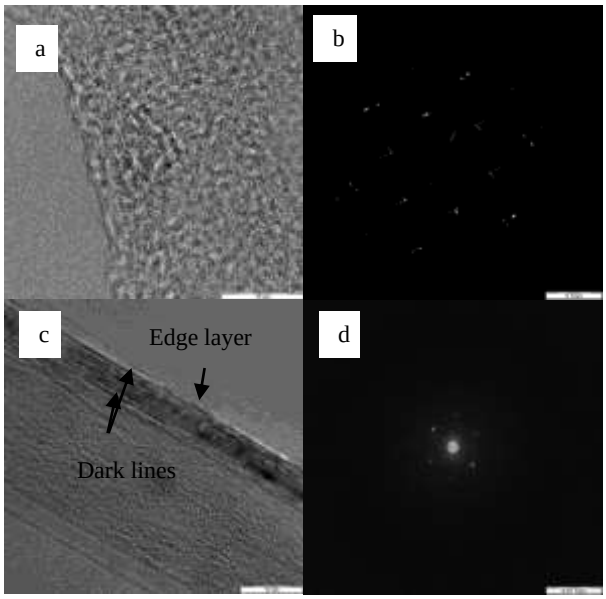

Fig. 2: a) TEM image with low-magnification at 10 nm of nanoporous graphene. The selected area (inset) shows the 'honeycomb' structure of the 3D graphene. b) Electron diffraction pattern taken from the flat region. c) TEM image at high magnification at 100 nm shows the different number of 3D graphene layers. d) Electron diffraction pattern shows the strong indication of interconnected multilayer of the graphene and the curvature of the graphene lattice.

Figure 2b consistently shows the similarity of the two layer graphene as reported in literature [3,4]. Further confirmation is provided by the folded and edge layers normally seen as dark lines in Fig 2c, which indicate the presence of multilayer that corresponds to the electron diffraction pattern in Fig 2d. The difference between the electron diffraction points was mostly due to the existence of curvatures of graphene sheet.

C. Raman Analyses

Figure 3 shows the Raman spectrum obtained for LP-3DG. The Raman spectrum for LP-3DG have the average G band peak shift ~1582.83 cm^{-1} for the normalised peaks which was obtained with 514 nm wavelength as in Fig. 3. Raman spectrum revealed that the number of layers of graphene grown increases with an increase of CH_4 concentration as indicated by the shift of G band peaks to the left.

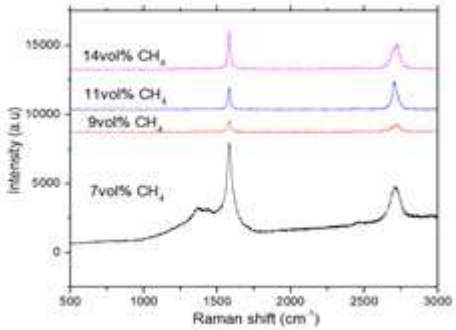

Fig 3: Raman spectrum for varying concentration of CH_4 in low pressure chamber.

The Raman spectrum for 7 vol% LP-3DG gives rise to D band at 1369 cm^{-1}. The LP-3DG FWHM(G) to be between 17.8 cm^{-1} to 18.2 cm^{-1} for Raman spectrums without D band whilst the FWHM (G) for 7 vol% LP-3DG recorded at 48 cm^{-1}. Those obtained values of FWHM (G) which were found to be slightly higher than the single crystalline graphite ~13 cm^{-1} [4,5]. The presence of structural disorder of 7 vol% LP-3DG can be observed with large FWHM (G), position of G band further away from 1580 cm^{-1} and coupled with the rise of D band. The combination of large FWHM (G), position of G peak closer to 1580 cm^{-1} and the absence of D band in all of other samples indicate the high quality of 3DG obtained.

IV. CONCLUSIONS

High quality, interconnected 3D hollow graphene were successfully grown via low pressure condition. These 3D graphene grown at low pressure exhibited almost similar characteristics with the pristine graphene quality.

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