The effect of using poly (methyl methacrylate) (PMMA) in the preparation of free standing 3D graphene

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Abstract. In order to get a free standing 3D graphene during the synthesis process, poly (methyl methacrylate) (PMMA) is often used to dissolve Ni agent. However, the use of this polymer is giving defect on structural and chemical composition of 3D graphene. The aim of this article is to study the effect of using PMMA in removing Ni agent on 3D graphene synthesis process. The 3D graphene was successfully synthesized through low pressure chemical vapor deposition (LPCVD) system. The structural defect and chemical composition study was examined using field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD) and Raman spectroscopy. Based on the findings, the use of PMMA and hot acetone was not really recommended method. The result was confirm that Ni element and oxide are still presence after the treatment process, and these structural and chemical defect might be effect to the properties of the free standing 3D graphene.

1. Introduction

3D Graphene is a multilayer of carbon atoms in honeycomb shape. 3D Graphene has attracted great attention due to its unique structure, graphene possess, extraordinary physicochemical properties, such as high carrier mobility, high thermal conductivity, promising elasticity, stiffness and high surface area. However, these promising properties will not completely utilize if the free standing 3D graphene is not properly prepared. Structural and chemical defect on 3D graphene would give very significant effect to its properties. In several nanomaterial researches, the treatment process to the material such as high annealing temperature will result high significant changes on quality of the material such as big grain size [1, 2]. The other case, treatment to the material by applying certain chemical is also affecting the properties of the material [3, 4]. Therefore, the right method is really needed to prepare particular material, in order to have high quality of the material. There are various methods have been developed in preparation of 3D graphene such as: low pressure (LP) and atmospheric pressure (AP) chemical vapor deposition [5]. These 2 methods were developed to increase the quality of 3D graphene and decreasing malformation of layers in 3D graphene [6]. These methods usually using Ni foam as the substrate to grow a free standing 3D graphene [7]. In the process of Ni removal as a substrate, poly (methyl methacrylate) (PMMA) and hot acetone are often used to make the 3D graphene remain together. However, the use of this polymer could affect the properties of 3D graphene.

This article aims to study the effect of PMMA and hot acetone in the process of synthesizing 3D graphene to get high quality of free standing 3D graphene. FESEM, XRD and Raman spectra were used to characterize the 3D graphene. According to our findings, it was confirmed that the Ni element and oxide was presence in the 3D graphene. Through these findings, we can conclude that the use of PMMA and hot acetone in the process of getting 3D graphene process is not really recommended due to its lack on structural and chemical defects.
2. Methodology
The preparation of 3D graphene was done out by using low pressure chemical vapor deposition (LPCVD) method. The pressure of LPCVD system was maintained by using vacuum pump at 3.3 mTorr and 3 mTorr for mixture of Ar and H2 at constant flow. Ni foam was used as a substrate in order to have a free standing 3D graphene. The 2 x 4 cm2 Ni foam was cleaned up before it used as a substrate using deionized (DI) water and ethanol and afterwards it dried at room temperature. The cleaned and dried microporous nickel foam placed in the quartz tube of CVD system and heat up at 1023 °C for 80 minutes. The temperature was maintained at 1023 °C for 20 minutes under Ar gas (100 sccm). H2 and CH4 gas flowed into the tubes around 90 minutes to grow 3D graphene on nickel foam.

In the process of removal Ni element, poly methyl methacrylate (PMMA) was used as the support layer to keep the 3D graphene attached. The PMMA was coated on the surface of 3D graphene and heat up at 80 °C for an hour and cooled down at room temperature. The solution of hydro chloride and distilled water was used as etching solution and afterwards nickel foam/3D graphene/PMMA template was immerged into the solution. The template edges were cut to allow etching solution to penetrate and after that the sample was put in the room temperature until it dried. The hot acetone at 55 °C was used for a couple of times in order to complete PMMA removal.

After the free standing 3D graphene was obtained, some characterizations were used to examine this 3D graphene. FESEM was used to investigate the microstructure of surface of the material and its element through EDX analysis. The phase of 3D graphene was determined by using XRD and the last of characterization was using Raman spectroscopy analysis to study its chemical analysis.

![Figure 1. Schematic of free standing 3D Graphene preparation](image)

3. Results and Discussions
3.1. Field Emission Scanning Electron Microscopy (FESEM) Analysis
3.1.1 Microstructure Analysis
Figure 2. FESEM images of 3D graphene growth on Ni foam (a) Magnification 200 µm and (b) 20 µm

The honeycomb sheet of 3D graphene on the top of Ni foam is shown in Figure 2. At the magnification 20 micro meter (b), we can see that 3D graphene (black color) was scattered on the top of the Ni foam (white color). Before the treatment using PMMA, the Ni foam seen very thick and very sharp. The 3D graphene looks having very high in porosity and very thin which consist of layers.

Figure 3. FESEM images of 3D graphene after treatment, (a) Magnification 100 µm and (b) 10 µm

As compared to microstructure of 3D graphene before treatment, after the PMMA was applied in order to support the free standing 3D graphene, the 3D graphene seems to be very thin as can see in Figure 3b. The thin layer of 3D graphene sheet was obtained after the Ni element was dissolve in the hydro chloride + deionize water solution and further treatment with hot acetone to remove the PMMA. However, it seems like the layer of Ni foam is actually not completely removed. The 3D graphene is not really free standing, it was still sticking on the Ni foam event though the amount of it was not much as compared before it treated.
3.1.2 Element Analysis

![Figure 4. EDX spectrum of 3D graphene growth on Ni foam](image)

The highest atomic percentage of the elements is carbon, this is because the 3D graphene is actually consisting of multi-layer carbon atom and it is confirmed in the Figure 4. Another element is Ni with amount 30.14%, this high percentage value also confirmed through FESEM result, where the 3D graphene was seems having very thick substrate which is the Ni foam.

| Element | Weight (%) | Atomic (%) |
|---------|------------|------------|
| C       | 69.86      | 91.89      |
| Ni      | 30.14      | 8.11       |
| Totals  | 100%       |            |

![Figure 5. EDX spectrum of 3D graphene after treatment](image)

After the treatment on 3D graphene with Ni foam by applying PMMA and hot acetone, it is confirm through EDX that the Ni element in Figure 5 is not completely removed and the percentage also still high. It is even produce a new element which is oxide, the presence of this element might be due to the sample of 3D graphene was not keep in vacuum environment.

| Element | Weight (%) | Atomic (%) |
|---------|------------|------------|
| C       | 58.54      | 81.95      |
| Ni      | 33.39      | 9.56       |
| O       | 8.07       | 8.49       |
| Totals  | 100%       |            |
3.2 X-Ray Diffraction (XRD) Analysis

The single phase of 3D graphene was obtained and it is confirmed through XRD patterns as shown in Figure 6. As shown on the XRD patterns, the intensity each of major peaks were decreasing after the 3D graphene was treated with PMMA and hot acetone. According to [8], the highest intensity is belongs to Ni element. Through XRD and EDX we can conclude that the element of Ni is not completely removed even after treated with PMMA and hot acetone.

3.3 Raman Spectroscopy Analysis

The Raman spectrum of 3D graphene as shown in Figure 7, the peaks of Ni atom is clearly observed at 4047.88 cm\(^{-1}\) and 2072.31 cm\(^{-1}\). The peaks at 1066.58 and 911.614 cm\(^{-1}\) are belongs to atom carbon and the rest which is band 954.345 is for oxide element.

![XRD patterns](image-url)  
**Figure 6.** XRD patterns of 3D graphene (a) With Ni foam, (b) After treatment

![Raman spectrum](image-url)  
**Figure 7.** Raman spectrum of 3D graphene
4. Conclusion
In summary, we have demonstrated that the 3D graphene was successfully made through LPCVD. However, in order to get the free standing 3D graphene by applying PMMA and hot acetone to the material was not really right method. Based on our findings through FESEM, XRD and Raman spectra, it was confirm that Ni element and oxide element was presence in the material. For further study, it is really important to observe a new method in preparation of free standing 3D graphene.

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References
[1] Prengki Pransisco et al, Effect of Calcination Temperature on Microstructure and Magnetic Properties of Ni\textsubscript{0.5}Zn\textsubscript{0.25}Cu\textsubscript{0.25}Fe\textsubscript{2}O\textsubscript{4} Nanoparticles Synthesized by Sol-Gel Method. American Institute of physics, 1621, 619(2014).
[2] Prengki Pransisco et al, Investigation of Nanostructure and Magnetic Properties of Nanocrystalline NiZnCu Ferrite synthesized by Sol-Gel Method, Journal of Applied Mechanic and material, 754-755 pp 1169-1174 (2015).
[3] Xiaogung Li et al, 3D graphene/ZnO nanorods composite networks as supercapacitor electrodes, Journal of Alloys and Compounds, 620, 31-37 (2015).
[4] S. Khamlich et al, Rapid microwave-assisted growth of silver nanoparticles on 3D graphene networks for supercapacitor application, 493, 130-137 (2017).
[5] Bei bei zan et al, Free- standing electrochemical electrode based on Ni(OH)\textsubscript{2}/3D graphene foam for nonenzymatic glucose detection. Nanoscale royal society of chemistry, (2014).
[6] Peng Wu et al, Novel 3D porous graphene /Ni\textsubscript{3}S\textsubscript{2} nanostructures for high performance supercapacitor Electrodes, Journal of Alloys and Compounds, 731 (2018)
[7] Beibei zan et al, Free- standing electrochemical electrode basd on Ni(OH)\textsubscript{2}/3D graphene foam for nonenzymaticglucose detection, Nanoscale, (2014)
[8] Delong li et al, Preparation of sandwich-like NiCo\textsubscript{2}O\textsubscript{4}/rGO/NiO heterostructure on Ni foam for high performance supercapacitor electrodes, Nano-Micro letter springer, 9-16 (2017).