Graphene to Graphane and its Effect on Band Gap

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ABSTRACT   *Studies were made to convert graphene (a zero band gap semiconductor material) to Graphane, a non-zero band gap material. Band gap was determined by Tauc plotting. It was observed that graphane possess both indirect band gap (1.26, 1.37 and 1.68eV) and direct band gap (4.0, 415 and 5.25 eV). The magnitude of these band gaps can be controlled by hydrogenation. It was found that band gap of graphene (C=C carbon) increased to higher value by controlled conversion of C=C to C-C carbon. Graphane was characterised by Raman spectroscopy and UV-Vis spectroscopy.*

KEYWORDS :Graphene, Graphane, Band gap, Hydrogenation,
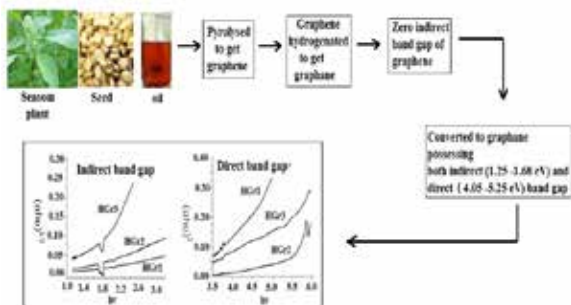
Highlight

1. Synthesis of graphane from graphene yields 3-7 layers at 800ºC and 10-15 layers at 600ºC.
2. Graphane possess indirect & direct band gap of 1.25 to 1.68 & 1.405 to 5.25 eV respectively.
3. Seasom oil used to synthesize graphene
4. Graphene converted to graphane by controlled hydrogenation at specific temperature
5. Zero indirect band gap of graphene is increased to 1.25-1.68 eV by hydrogenation

1.0 Introduction

Graphitic carbon consists of 100% sp^2 carbon with a band gap of 0.25eV, whereas diamond consists of 100% sp^3 carbon with a band gap of 5.5eV. This has opened a possibility of synthesizing carbon film with a desired band gap by controlling the sp^2/sp^3 ratio. Sharon et al [1-2] were able to experimentally show the production of carbon film with band gap of 1.4eV. It was thought that such carbon film can be used for making carbon solar cell. But it was soon realised by them that though carbon film possessed 1.4eV; its carrier concentration was very high to the tune of $10^{22}/cm^3$, which made

carbon film unsuitable for solar cell. Further investigation suggested that band gap of 1.4eV of carbon was due to its direct band gap. This suggested that while carbon film possessed direct band, it also possessed a zero indirect band gap [3] Hence, unless its zero band gap is increased to some higher value, carbon film cannot be used for making solar cell.

Discovery of graphene and effect of hydrogenation of graphene on its band gap brought some hope to utilise graphene for solar cell application. It has been observed by Jaing et al (2009) [4] that hydrogenation of graphene can alter its band gap. If hydrogenation of graphene is done such a way that its one side of carbon is converted to sp^3 carbon then its band gap becomes around 0.5eV and such graphene is named as graphone. If alternate carbon of graphene is hydrogenated then its band gap becomes 1.6eV and such graphene is called hydrogenated graphene [5-7]. However, Xiang et al.(2010) [8] proposed that if hydrogenation is done on both the sides of graphene an insulating material named graphane is formed having energy gap of 5.4eV [9-10] **.** But it is not yet established whether these band gaps are direct or indirect. Hence, it is necessary to establish whether graphane/graphone or hydrogenated graphene possesses direct or indirect band gap or both; as found in carbon film. Intrigued with such interesting possibilities, present work was undertaken to find out whether these band gaps are due to direct or indirect band gap. This communication discusses the results of hydrogenation of graphene thin film synthesized from sesame oil by CVD process and confirmation whether the band gap of hydrogenated graphene is due to direct or indirect band gap or both.

2.0 Materials and Methods
2.1 Cleaning of Copper Substrate:

A thin plate (1cm²) of copper was used as substrate for synthesis of graphene. Copper substrate was cleaned [11-12] by sonication using acetic acid, ethanol and finally isopropyl alcohol. Copper plate was further thermally cleaned using a CVD furnace having two heating

zones.. A long quartz tube of 2cm diameter was inserted through both the heating zones of furnace. Copper plate was placed at 1000⁰C under hydrogen atmosphere. Hydrogen gas was allowed to flow through the quartz tube at the rate of 100ml min^{-1} for 1.5h. This helped in reducing any copper oxide formed on the surface of the thin copper plate.

2.2 Synthesis of graphene:
Sesame oil (hydrocarbon) was used as a precursor for graphene. Sesame oil was kept in a quartz boat and placed at lower temperature zone (400ᵒC) and copper plate on a quartz plate was kept in high temperature zone (>800ᵒC). Before switching on the furnace, quartz tube was flushed with Argon gas to remove traces of oxygen and then Argon gas was continued to flow during synthesis of graphene.

Vapor of Sesame oil flowed along with argon gas to the hotter zone of furnace where it got decomposed and deposited on the copper plate forming thin film of graphene. The synthesis process of graphene took 140 min and then the furnace was switched off allowed to cool rapidly using cooling fan. The Furnace was not opened as further conversion of graphene to graphane was to be done.

2.3 Conversion of graphene to graphane by hydrogenation
The high temperature zone having graphene deposited on copper plate was heated at different trial temperatures so as to convert graphene to graphane. Quartz tube was connected with hydrogen gas and its flow rate was maintained at 20ml/min during conversion. For hydrogenation three temperatures were tried (i) 600°C for 60 min (HGr1); (ii) 800°C for 30 min (HGr2) and (iii) 800°C for 60min (HGr3).

2.4 Transfer of Graphane from Copper plate to Quartz Plate
PMMA was coated over hydrogenated graphene film deposited over copper plate so as to provide bonding strength. To etch away the copper, PMAA coated graphene/Cu was dipped in 10% ferric nitrate solution for 8hr. The PMAA coated hydrogenated Graphene floated on top of the ferric nitrate solution and was taken up on a quartz plate for further characterisation.

In order to compare properties of pure graphene (i.e. which was not grown under hydrogen atmosphere) was also likewise collected over quartz plate and referred as Gr. Any remaining PMMA along with Graphene was removed by washing with pure water and then kept for drying at 100°C. Graphene film was characterised by Raman spectroscopy and UV-Vis absorbance spectroscopy.

3.0 Results and Discussions
The–Raman spectra of all graphene films are shown in Figure-1. Pure graphene (Gr) shows a G peak at 1562 cm^{-1} and 2D peak at 2704 cm^{-1}. Absence of D peak at around 1330 cm^{-1} suggests film is graphitic and has no defects [13-14]. With increase in hydrogenation temperature (600 °C to 800°C) and duration of hydrogenation (30min to 60 min), intensity of D-peak around 1333-1355 cm^{-1} increases, conforming the increase in conversion of sp² carbon to sp³ carbon (Figure 1).It is interesting to observe that the ratio of peak height of G-band to peak height of 2D also decreases with increase of temperature and duration of hydrogenation. It has been suggested that if this ratio is <1.5 the graphene possess less than 2-3layers and if it is >1.5 the grapheme layer is expected to 10-15 layers [15]. From the Figure-1, it is noticed that ratio of G-peak to 2D peak follows: HGr3 = 1.035, HGr2 = 1.827, HGr1 = 1.829, Gr = 1.741. This suggests that number of graphene layers with HGr3 is about 2-3 layers whereas with other graphene (i.e. HGr2, HGr1 and Gr) it is more than 10-15 layers. If this be so, it would mean that with increase in temperature, graphene layers gets decomposed. Wang et al [16] studied the TGA of graphene and observed that graphene starts decomposing around 700ᵒC and at 800ᵒC about 10% of graphene remains unburnt in air. Perhaps because of this decomposition process HGr3 contains less number of layers as compared to other treatments (i.e HGr2, HGr1 and G).
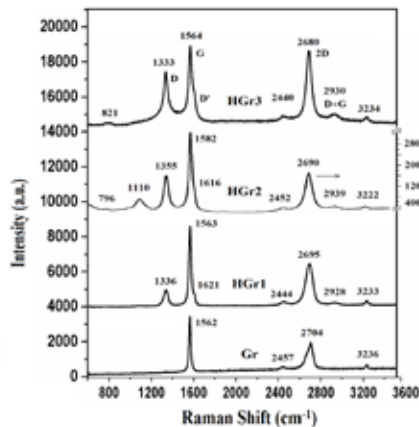

Figure 1: Raman Spectra of three differently synthesized Hydrogenated Graphene
HGr1 **at 600˚C for 60min;** *HGr2* **at 800˚C for 30 min and** *HGR3* **at 800˚C for 60 min**

3.1 Optical Absorption measurement and Band gap calculation:
Graphene produced at the three conditions i.e. 600ᵒC for 60 min (HGr1), 800ᵒC for 30 min (HGr2) and 800ᵒC for 60 min (HGr3) were used for measuring the optical absorption in the range of 200nm to 1000nm. The absorption graphs are shown in Figure2.
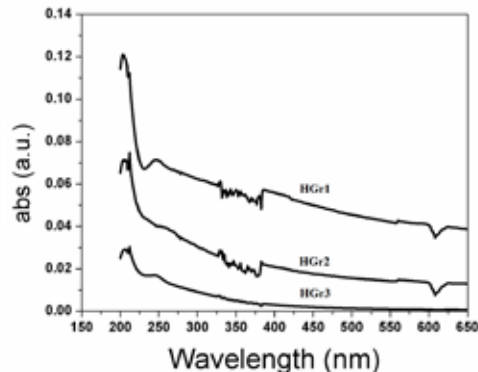

Figure 2: UV-Vis Absorption Spectra of Hydrogenated Graphene i.e. HGr1, HGr2 & HGr3

The absorption coefficient is calculated using the Tauc Law. $(\alpha h u) = \beta(h u - Eg)^{2/n}$, here Eg is optical band gap, $\alpha = A/d$, here A is the optical density and d is the thickness of sample, n= 1 for direct band gap and n=4 for indirect band gap and β is a constant that depends upon the width of the localised states in the band gap. Plot for $(\alpha h u)^{n/2}$ vs. hu gives a straight line. The intersection of the straight line at x-axis when $(\alpha h u)^{n/2}$ is zero gives the value of the band gap. Graphs of $(\alpha h u)^{1/2}$ vs (hu) and $(\alpha h u)^2$ vs (hu) from the absorption graphs (Figure 2) are plotted and graphs are shown in Figure 3A and 3B respectively.

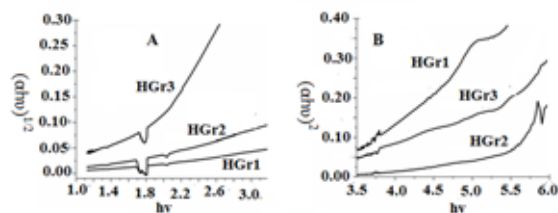**Figure 3: (A) graphs for indirect band gap i.e. when n=4 plot of $(\alpha h u)^{1/2}$ vs (hu) are made for HGr1,HGr2 and HGr3 and similarly (B) graphs for direct band gap i.e. when n=1 plot of $(\alpha h u)^2$ vs (hu) are made for HGr1,HGr2 and HGr3.**

It is observed from these graphs that the intersects of $(\alpha h\upsilon)^{n/2} = 0$ is difficult to find out because of the exponential nature of graphs. Hence a second differential of the equation i.e. $d\{(\alpha h\upsilon)^{n/2}\} / d(h\upsilon)$ is plotted vs $h\upsilon$ (Figure 4) which gives a sharp change at some particular $h\upsilon$ value. The value of $h\upsilon$ corresponding to this sharp peak is taken as the best slope of the original graph and is taken as the band gap of the material [17]..

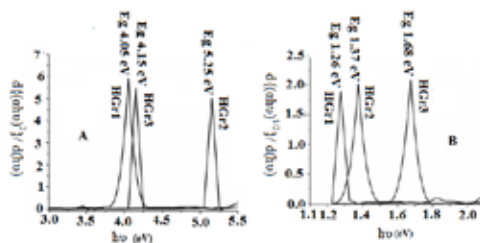**Figure 4: Plotts of (A) second differential i.e d{(αhυ)²}/d (hυ) Vs hυ for direct band gap and (B) second differential i.e. d{(αhυ)^(1/2)}/d (hυ) Vs hυ for indirect band gap for HGr1, HGr2 and HG3 graphene sheet.**

Graphs presented in Figure 4 shows very interesting result. Hydrogenation of graphene increases its zero band gap (indirect band gap) to 1.2eV to 1.68eV depending upon the temperature and duration of hydrogenation. In addition, hydrogenated graphene also posses direct band gap in the range of 4.05eV to 5.25eV.

Graphene is known to possess zero band gap and recently Sharon *et al* [3] have shown that zero band gap of graphene is due to indirect band gap. Sofo et al. (2007) [5] have reported that if hydrogenation is done such that alternate carbon of graphene is hydrogenated then its band gap is 1.6eV. This means that hydrogenation of graphene converts alternate carbon of sp^2 configuration to sp^3 configuration. Perhaps because of this, hydrogenated graphene films of HGr1, HGr2 and HGr3 show an indirect band gap in the range of 1.2eV to 1.68eV. Xiang et al (2010) [8] proposed that if hydrogenation is done on both side of graphene an insulating material graphane is formed having energy gap of 5.4eV. Interestingly the direct band gap of HGr1, HG2 and HGr3 possesses the band gap in the range of 4.05eV to 5.25eV which suggests that direct band gaps are due to hydrogenation of graphene on both side of graphene.

Sharon *et al* [1] observed that band gap of graphene is controlled by ratio of sp^2/sp^3 carbon. As the concentration of sp^3 increase (or % of sp^3) the band gap of graphene also increases. Considering the variation of sp^2 with band gap as reported by Sharon *et al* [1-2] the indirect band gap of HGr1, HGr2 and HGr3 are found to contain sp^3 carbon of 73%, 73.75% and 76.75% respectively for an indirect band gap. It was not possible to calculate for band gap higher than 1.6 eV as results shown by Sharon et al [1-2] covers the range lower than 1.6eV. From these result perhaps it can be concluded that optical absorption of these films show specific absorption of higher wavelength with graphene containing sp^3 configuration on top side of graphene, whereas its sp^3 configured carbon of both side of graphene show absorption of longer wave length.

It has been reported that graphene starts decomposing from 600°C to 800°C[16]. In addition, Raman studies have shown that if ratio of peaks of G-band to 2D band is < 1.5 then graphene sheet is expected to have 2-3 layers while if it is >1.5 then graphane sheet will contain 10-15 layers. Raman studies show that ratio of peak of G-band to 2D band is HGr3 =1.035, HGr2 = 1.827, HGr1 = 1.82 and G =1.74 (Figure 1). These studies show that except HGr3 (which has 3 layers of graphene) all other graphene sheets i.e. HGr1, HGr2 and Graphene have 10-15 layers. This suggests that hydrogenation has taken place upto about 7-12 layers, because hydrogenation of HGr3 is maximum which contains only 3 layers and as such its band gap has increased to 1.68eV due to increase in sp^3 carbon to 76.75%. Since graphene is supposed to have zero band gap and hydrogenation of graphene has increased the band gap, it may not be incorrect to classify HGr1, HGr2 and HGr3 graphene as a graphane(table-1).

Table 1: Impact of different parameters of hydrogenation of graphene on the band gap

| Sample | Hydrogenation | | Band Gap (eV) | |
	Temperature (°C)	Duration (min.)	In-Direct (bracket gives % sp³)	Direct
HGr1	600	60	1.2 [27%]	4.05
HGr2	800	30	1.3 [26.75%]	5.25
HGr3	800	60	1.68 [23.25%]	4.15

4.0 Conclusion

Graphene thin films were synthesized from sesame oil by CVD process over carefully cleaned copper substrate. These films were hydrogenated at three different conditions 600°C for 30 min, 800 °C for 30min and 800°C for 60 min. These films are designated respectively as GHr1, HGr2 and HGr3, Unhydrogenated graphene is designated as Gr. It is observed that all these three graphene films (HGr1,HGr2 and HGr3) possesses indirect band gap in the range of 1.2eV to1.68eV as well as direct band gap in the range of 4.05eV to 5.25eV. It is concluded that these hydrogenated graphene films have the characteristic properties of graphane.

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