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Role of Defects in the Band Gap Tailoring of Carbon Black

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Abstract

With the rise in the need for cost-effective production of graphene-like systems, Carbon Black (CB) is found to be a potential candidate. This report presents the structural modification of Carbon Black (CB) subjected to hydrothermal exfoliation at various temperatures. X-ray diffraction (XRD) revealed the graphitic structure with a broad peak, indicating the amorphous nature regardless of the variation in temperatures. Raman spectroscopy revealed that defect intensity increased with the increase in temperature. The band-gaps are found to be 4eV, 2.95eV, 2.86eV and 2.21eV at the exfoliation temperatures 160ºC, 180ºC, 200ºC, and 220ºC respectively exhibiting a lowering with rise in temperature.

Keywords: Carbon Black, Band-gap, defects, amorphous

1. Introduction

Carbon Black is a form of elemental carbon obtained by the partial combustion of gaseous or liquid hydrocarbons [1]. It is generally used as a filler for rubber compounds in order to enhance its physical properties [2]. It is amorphous in nature with a lower level of crystallinity compared to graphite. It has a highly complex

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structure and its particles exhibit agglomerated spherical shape, due to the strong Vander Waals forces between the layers of the CB nanoparticles and the spacing between the layers is different from that of a pure graphite. The flat graphitic layers are curved due to these forces and hence assumes the spherical shape [3, 4, 5]. It is known to exhibit great catalytic properties [6], a conductive material [7], an adsorbent [8] and a supporting filler material.

There are numerous studies on the optical band-gap tailoring of graphene by chemical methods [9] or by various reducing agents [10, 11, 12]. Due to the difficulty in the bulk production of graphene, it is the need of the hour to investigate the properties of other graphene-like systems. Carbon Black, a potential candidate for the optical studies is reported to have the presence of graphite-like structures [13]. However, studies on the graphene-like CB system which is highly agglomerated and consisting of spherical particles is limited. In this report, we present the band-gap tailoring via the hydrothermal exfoliation method at different temperatures. The variation in the defect density at these temperatures were elucidated via Raman spectroscopy. The structural analysis and optical studies were conducted by XRD and UV-vis spectroscopy respectively.

2. Experimental Procedure

2.1. Preparation of oCB

Carbon Black (CB) was subjected to Modified Hummer's method [14]. In a typical synthesis process, 4g CB was added to cold concentrated H_2SO_4 (200 ml) solution containing $NaNO_3$ (8g) in a 500ml beaker. Now, 20g of $KMnO_4$ was added gradually under vigorous stirring while maintaining the temperature of the system below 10°C. This mixture was stirred at 35°C for 2 hours. It was then diluted with 200ml of de-ionized water. The addition of water results in excessive fuming due to the release of large amount of heat. The mixture was then stirred for 30 min and 40 ml of 30% wt H_2O_2 was slowly added to the mixture. The color of the mixture was pitch black. The mixture was then filtered and washed with 1600 ml of 5 wt% HCl aqueous solution to remove the metal ions followed by washing with ample amount of de-ionised water until the pH of the solution was neutral. Since the density of the particles is extremely low, the particles took days to settle down for further washing and centrifugation. The solution was centrifuged and dried at 70°C for 44 hours. About 1.81g of the resultant sample was obtained and was named Oxidized Carbon Black (oCB).

2.2. Hydrothermal Exfoliation:

110mg of oCB was dispersed in 55mg of DI water (2mg/ml), sonicated for 30 mins. The solution was sealed in a 55ml Teflon-lined autoclave and maintained at different temperatures 160°C, 180°C, 200°C and 220°C for 5 hours. The samples were vacuum filtered with a filter paper of pore size 0.2mm to obtain the exfoliated Carbon Black -eCB -160°C, eCB -180°C, eCB -200°C and eCB -220°C.

3. Results & discussion

3.1. XRD Analysis

X-Ray Diffraction (XRD) technique is used to investigate the structural changes in oCB. The XRD of untreated CB reveals additional peaks of (220), (311), (400) and (422) along with a broad peak at $2\theta=24.45^0$ and $2\theta=43.16^0$ corresponding to the (002) and (100) diffraction peak of graphite. The additional peaks reveal the presence of $MgAl_2O_4$ [15]. The broad peak at (002) reveals the amorphous carbon structure and the peak at (100) reveals the turbostatic graphite. After subjecting to oxidation, the peaks of $MgAl_2O_4$ disappeared in the XRD of oCB (Fig 1). This shows the demineralization of CB after the synthesis procedure. The d_{002} – spacing of the eCB at different temperatures were calculated according to the Bragg's equation. The crystalline size (L_a) and the stacking height (L_c) were calculated using the Scherrer's equation

$$D = K\lambda/\beta\sin\theta$$

Where $K = 1.84$ for L_a corresponding to θ at (100) peak and 0.89 for L_c corresponding to θ at the (002) peak respectively [16].

There is an increase in the L_a and L_c values for increasing temperatures as shown in Table 1.

When subjected to hydrothermal method at different temperatures 160ºC, 180ºC, 200ºC and 220ºC, the FWHM of the peaks corresponding to (002) lattice structure decreased with increase in

Temperature (Fig 2). This reveals the increase in the crystalline order with increase in temperature.

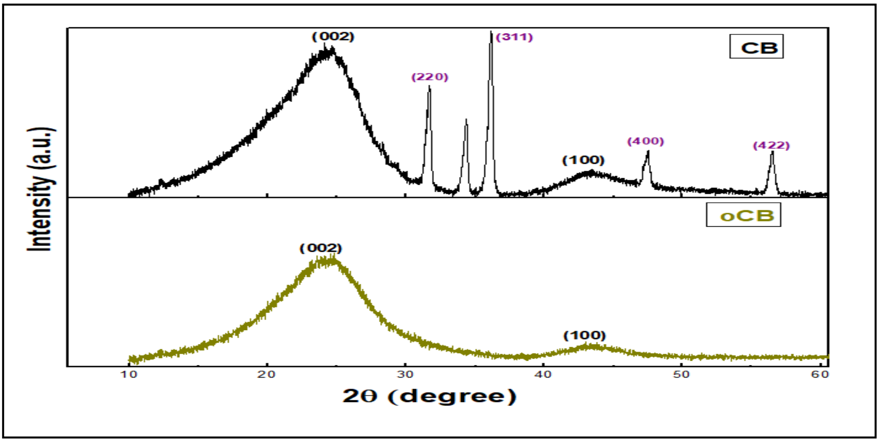

Fig 1: Demineralisation of CB post oxidation

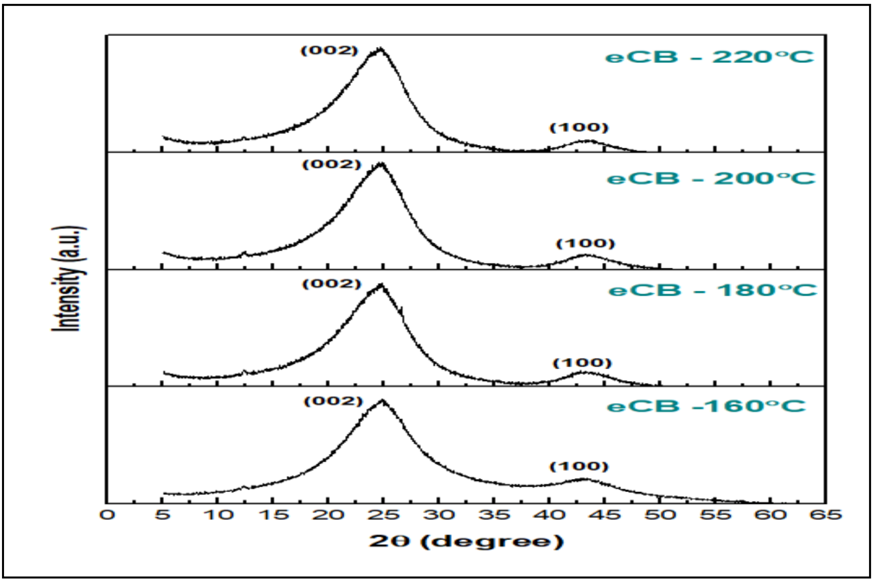

Fig 2: XRD Peaks of exfoliated Carbon Black (eCB) at different hydrothermal temperatures

3.2. Raman Analysis

The structural changes during the oxidation and reduction process is further analysed by Raman spectroscopy [17]. Typically, the Raman spectra of the untreated CB showed a sharp G band at 1584cm^{-1} and a D band at 1345cm^{-1}. The I_D/I_G value of this sample is 0.76. After subjecting it to the oxidation, the G peak has slightly been blue-shifted to 1589cm^{-1} with a reduction in its intensity with broadening of the peak. The intensity of the D-band post oxidation is seen to increase with its peak position at 1345cm^{-1}, giving rise to the I_D/I_G value to be 0.87.

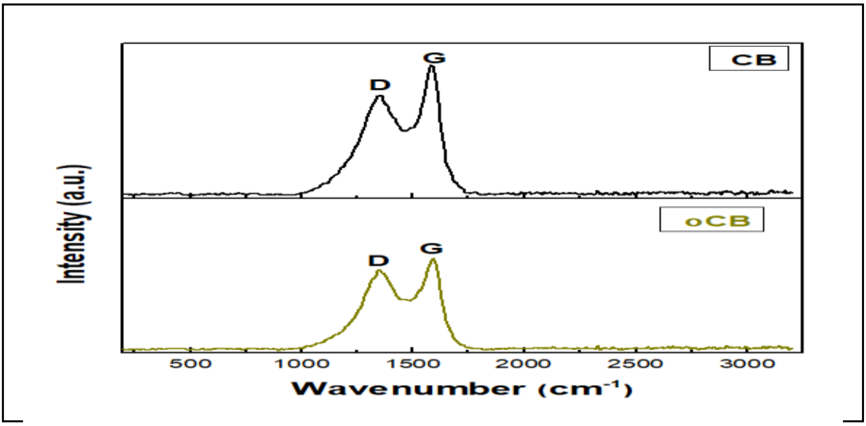

Fig 3: a. Raman Spectra of CB and oCB; b&c. deconvoluted spectra of CB and oCB

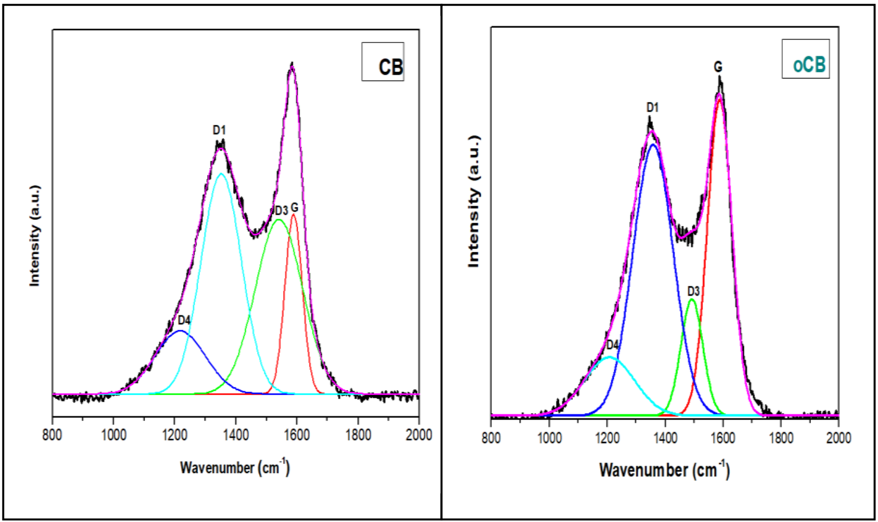

Fig 3: b & c. deconvoluted spectra of CB and oCB

The deconvoluted spectra gives an in-depth analysis of the nature of defects present in the sample. The spectra of untreated CB have peaks at D1 (1351cm^{-1}) which indicates the structural disorder, D3 (1539 cm^{-1}) indicating the amorphous carbon and D4 (1219 cm^{-1}) indicating the defects due to the sp^2-sp^3 hybridisation [18, 19]. After the oxidation process, there is a prominent increase in the intensity of D1 and a decrease in the intensity of D3. Thus, there is an increase in the crystallinity of CB post-oxidation (Fig 3).

The value of I_D/I_G increased with the increase in temperature during the hydrothermal synthesis. The D4 peak vanished with the increase in temperature (Fig 4). In CB, the graphite layers are stacked roughly but in random orientation [20]. The heat treatment would have disturbed this orientation to create more disorders. The I_D/I_G is inversely proportional to the grain size of the material for grain sizes more than 2 nm [21].

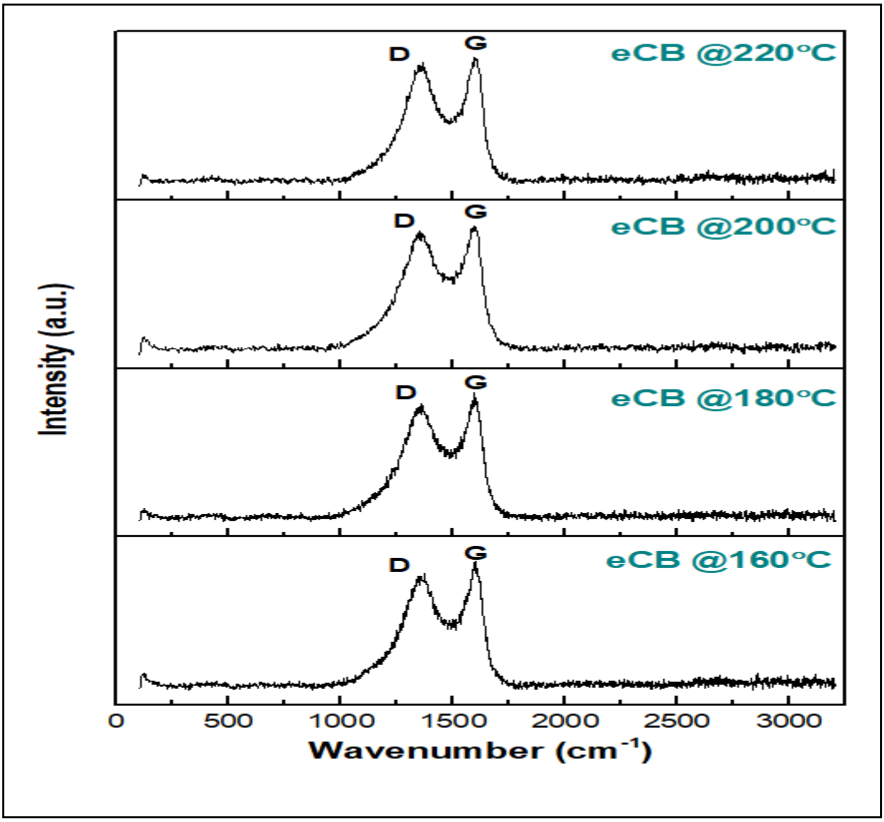

Fig 4: a. Raman spectra of eCB at temperatures 16°C, 180°C, 200°C & 220°C

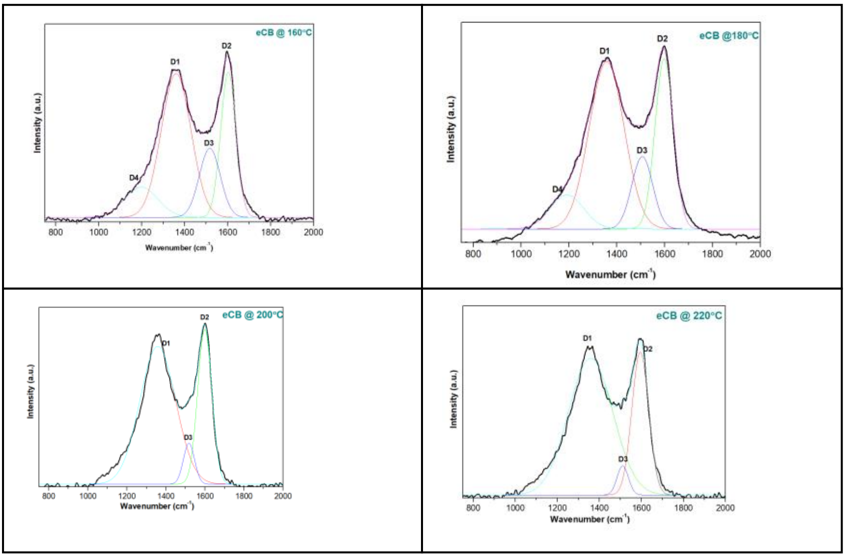

Fig 4: b,c,d & e: Deconvoluted Raman spectra for all temperatures

3.3. UV-vis Spectra

The UV-vis absorbance spectrum of CB shows a peak at 275nm indicating the π-π* transitions of the C=C networks. The calculated band gap by Tauc-plot is found to be 2.66eV (Fig 5). Post oxidation, the absorbance peak shifted to 239nm indicating the n-π* transition of C=O with a broad extension upto 900nm indicating the π-π* transition of the C=C conjugated networks [8]. The band-gap increased drastically to 4.48eV upon oxidation (Fig 6). Further, with the increase in temperature during exfoliation, the band- gap is observed to decrease (Fig 7). This could be due to the increase in the structural disorders in the system.

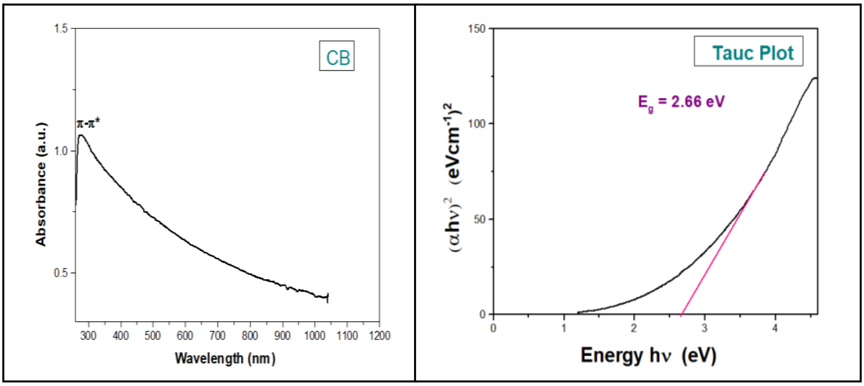

Fig 5: a. UV-vis absorbance spectrum of CB; b. Tauc-Plot analysis of CB

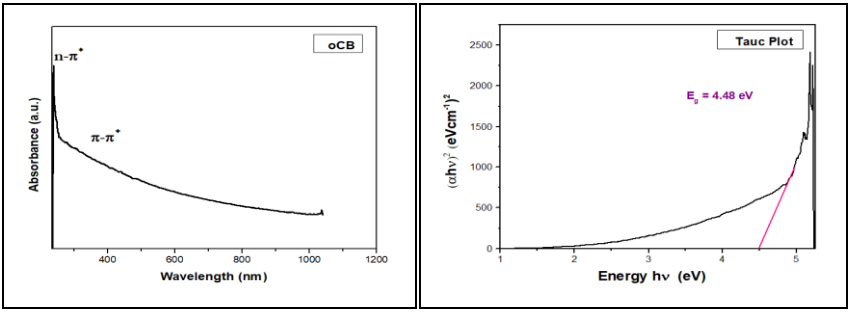

Fig 6: a. UV-vis absorbance spectrum of oCB b. Tauc-Plot analysis of oCB

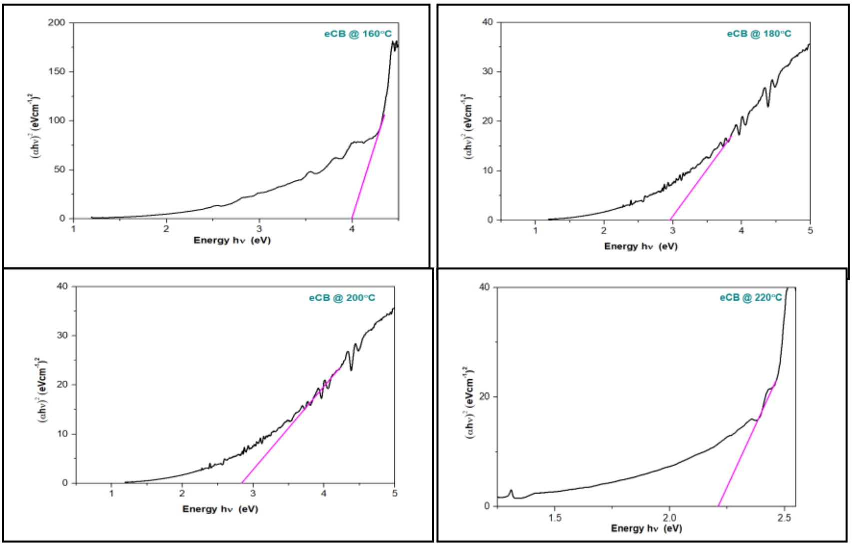

Fig 7: Tauc Plots of exfoliated Carbon Black (eCB) at temperatures 160°C, 180°C, 200°C and 220°C

Table 1: Crystalline size (La), lateral height (Lc), d-spacing, defect ratio and Band-gap at different temperatures

Material	**Temperature (°C)**	**L_a (nm)**	**L_c (nm)**	**d-spacing (nm)**	**I_D/I_G**	**Band -Gap (eV)**
CB		3.62	0.93	0.36	0.76	2.66
oCB	-	3.62	0.93	0.36	0.87	4.48
eCB	160	3.92	1.02	0.363	0.89	4.00
	180	4.75	1.05	0.37	0.92	2.95
	200	4.16	1.07	0.369	0.94	2.86
	220	4.59	1.09	0.368	0.98	2.21

4. Conclusion

The structural modification of the graphene like system derived from Carbon Black with synthesis temperature is studied. The d_{002} spacing of the system remained almost the same throughout the oxidation and exfoliation processes. Although there is no inclusion of the oxygen functional groups into the CB structure post-oxidation and exfoliation, there is an increase in the defect ratio, the crystalline size, degree of crystallinity and the band-gap of the system. The increase in the defect ratio is due to the structural disorder in the system. Therefore, the band-gap of CB can be successfully tuned by changing the degree of defects in the system.

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