Chapter 8

A green method to synthesize graphene on a large scale

Synthesis of graphene by high energy ball milling of graphene oxide in an inert atmosphere is discussed in this chapter. Characterization of the samples using i) FTIR spectroscopy, ii) TGA-DSC, iii) UV-Vis spectroscopy, iv) Raman spectrum, v) XPS spectroscopy, and vi) TEM are discussed in details. Photoluminescence property of the sample is studied briefly.

8.1 Introduction

Graphene, with its extraordinary electronic [1], mechanical [2], and thermal [3], properties has created excitement in the area of basic [4, 5] and applied research [6, 7]. Initially production of large area single layer graphene sheet with no defect was the aim and was best produced by the so called “peel off” method from highly oriented pyrolitic graphite (HOPG) [1]. As this method was not suitable for large scale production, a number of methodologies for producing graphene evolved [8-13]. Graphene produced by these techniques, however, differed in terms of defects and functional groups present from those originally prepared by mechanical peeling [14, 15].

Defects in chemically converted graphene (CCG) play different roles mainly because of two reasons. One is the establishment and continuous research to find protocols to remove them from the graphene structure [16, 17] so as to bring the resulting properties closer to those of mechanically peeled off graphene. The second one is to find important usage of
defects in further applications of graphene such as composite [18-20], graphene paper [21, 22], ferromagnetic graphene [23]. So, when a methodology of creating graphene appears in the research scenario, the main concern is to work out a procedure which is greener, easier and up scalable compared to the existing ones [24].

In this article, we report a very simple and green method for the production of graphene from graphene oxide (GO). The method is devoid of any hazardous chemicals that have been used for producing CCG.

8.2 Experimental Section

8.2.1 Method

The GO was prepared using a modified Hummers method [25]. Thus prepared GO powder was then ball-milled for different durations with zirconium oxide balls of diameter 5mm in a FRITSCH Pulverisette 7 planetary ball mill in inert (Ar) atmosphere. The ball to mass ratio (BPMR) was kept constant at 20:1 with angular speed 800 rpm. Although the range of disc and vial rotation was kept in the range of high energy ball milling, the time used for the synthesis of the final product was kept rather low deliberately. The samples were named as BM1, BM2, BM3 and BM4 for 75, 120, 180 and 240 min ball milling respectively.

8.2.2 Characterization

The synthesized samples were characterized using different techniques. FTIR and UV-Vis spectra of the samples were recorded using Shimadzu FTIR 8400S and Varian Cary 5000 UV-Vis-NIR spectrophotometers respectively. The thermal characterization of the samples was carried out using TA Instrument SDT Q600 DSC-TGA and Q2000 DSC. The photoluminescence spectrum was recorded using ELICO SL 174 Spectrofluorometer. Raman scattering study was performed with 514.5 nm excitation of continuous He/Cd laser and dispersion with 2400 gr/mm grating in the backscattering configuration using Raman spectrometer (inVia Renishaw). A thermoelectric cooled ‘back-thinned’ charged coupled detector was used for the detection of scattered intensity. The morphology of the sample was visualized using JEOL 2010 Transmission Electron Microscope.
8.3 Results and Discussion

8.3.1 FTIR Spectroscopy

The structure of GO is dependent on preparation methodology and is still under debate in the literature [26]. As we followed the modified Hummers method, the expected established structure can be described by the Lerf–Klinowski model [9, 16, 26].

![Fig. 8.1. FTIR spectrum of (a) raw GO, (b) the samples BM1, BM2, BM3, and BM4 (c) BM3 and BM4, (d) raw GO and BM3.](image)

The corresponding bending and stretching modes are identified in the FTIR spectrum (Fig. 8.1(a)). The characteristic peaks are for C=O (~1725 cm\(^{-1}\)), C=C aromatic bond (~1634 cm\(^{-1}\)) and C-O (~1065 cm\(^{-1}\)). The peaks at 3406, 1390 and 652 cm\(^{-1}\) correspond to stretching, deformation and bending modes of O-H group of adsorbed water molecules respectively. Fig. 8.1(b) shows the FTIR spectra of the samples BM1, BM2, BM3 and BM4 together and it is apparent that with increasing ball milling time the amount of the oxygen-containing
functional groups (~1725 cm\(^{-1}\)) are decreasing. However, in Fig. 8.1(c) where the FTIR spectrum of sample BM3 and GO are depicted separately, the C=C and C-C aromatic bonds (~1629 cm\(^{-1}\) and ~1500 cm\(^{-1}\)) remain the most prominent signatures in sample BM3, with most remarkable reductions being in the oxygen-containing groups. From this result it is evident that this sample is very similar to chemically reduced graphene [12]. The sample BM4 however shows break down of the aromatic C=C bonds in the FTIR spectrum (marked in Fig. 8.1(d)) indicating a loss of graphene structure with milling time higher than 180 min. Thus the optimum milling time to obtain graphene from GO is concluded to be 180 min.

### 8.3.2 Thermal characterization

Thermogravimetric analysis (TGA) of raw GO under N\(_2\) atmosphere shows (Fig. 8.2(a)) two major mass losses around 373 K (22 % mass loss) and between 423 and 523 K (33 % mass loss). The first one is ascribed to the adsorbed water loss while the second one is due to removal of oxygen-containing carboxylic groups [9, 24, 27]. The sample BM3, which has already taken the graphene structure, is also subjected to TGA analysis under same condition. The analysis shows drastically reduced amount of mass loss than GO in the same temperature range around 373 K. However, some functional group remains in the reduced GO sheets as is evident from higher mass loss in the range of 423 to 523 K, which is however much less compared to the original GO (Fig. 8.2(a)). The corresponding differential scanning calorimetry (DSC) shows (Fig. 8.2(b)) substantial heat flow in this range which is comparable to earlier reported results [27].

![Fig. 8.2. (a) TGA curves of raw GO and sample BM3. (b) DSC curve of the raw GO.](image)

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8.3.3 UV-Vis absorbance spectroscopy

The UV-visible absorbance spectra of dispersions of GO and sample BM3 in ethanol are presented in Fig. 8.3.

![Absorbance Spectrum of GO and BM3](image)

**Fig. 8.3. Optical absorbance spectra of dispersions of GO and sample BM3.**

The peak at 256.5 nm in case of GO dispersions corresponds to $\pi\rightarrow\pi^*$ transitions of aromatic C-C rings. The small shoulder around 310 nm in GO can be attributed to $n-\pi^*$ transition of C=O [28, 29]. The absorption peak for dispersion of BM3 is red shifted to 273.6 nm. This confirms that the carbon network is not disturbed upon milling for 180 min. The UV-Vis absorbance spectrum is consistent with the results of FTIR spectra and confirms the formation of graphene by 180 min milling of GO.

8.3.4 Photoluminescence Spectroscopy

Fig. 8.4 shows the room temperature photoluminescence spectra of the 180 min ball milled sample (BM3) after exciting the system with a laser of wavelength 285 nm. A single broad peak is observed around 345 nm (3.6 eV). This is very similar to that observed previously [29]. The origin of this UV blue emission could be the radiative recombination of
the electron-hole pair, which was generated in the defect sites, which served as the localized states in the system.

Fig. 8.4. Photoluminescence spectrum of BM3 for excitation at 285 nm.

8.3.5 X-Ray Photoelectron Spectroscopy

To quantify the chemical composition and investigate the surface chemistry of the ball milled sample (BM3), X-Ray photoelectron spectroscopy was employed. The C1s XPS spectrum of BM3 is presented in fig. 8.5.

Fig. 8.5. The C1s XPS spectrum of the sample BM3.
The spectrum clearly indicates the presence of C=C and C-C bond as the prominent feature of the sample with a certain degree of oxygen functionality. The intensity of the peak corresponding to C in C-O bonds (~ 286.95 eV) is much smaller compared to that of C=C and C-C bonds (~ 284.23 eV) [9]. The XPS spectrum further strengthens our argument that deoxygenation of GO is possible upon 180 min ball milling and subsequently graphene is formed.

8.3.6 Raman Spectroscopy

Fig. 8.6 shows the Raman spectrum (514.5 nm excitation) of GO and BM3. It is seen that the most intense features are G-peak (~1593 cm\(^{-1}\)) and D-peak (~1352 cm\(^{-1}\)). The less intense peaks are attributed to 2D peaks (~2700 cm\(^{-1}\)) (historically G’ peak) and D+G peak (~2938 cm\(^{-1}\)).

![Raman Spectrum](image)

**Fig. 8.6.** Raman spectrum of GO and BM3 at 514.5 nm excitation.

G-peak (band) is an intrinsic feature of carbon nanotube, graphene, and all other graphitic materials. This corresponds to the first order scattering of the doubly degenerate zone center E\(_{2g}\). The E\(_{2g}\) mode in G band involves the in plane stretching motion of pairs of sp\(^2\) hybridized carbon atoms [30]. D-peak is not however, an intrinsic property of graphitic material, as it violates the selection rule. D-peak arises in the Raman spectra, if there is a
defect or disorder in the system and also from the edge states. The prominence in D-band may also occur due to reduction in size of the in-plane sp² domains [9]. The D and G band (≈1354.7 cm⁻¹ and 1587.9 cm⁻¹) also occur in the Raman spectrum of GO (Fig. 8.6) with an intensity ratio of 0.87, which is smaller in comparison to milled GO (BM3). On ball milling, a reduction of GO occurred which resulted in a decrease in the average size of the sp² domains. The new graphitic domains that formed upon reduction in ball mill are smaller in size than that of base GO.

We observe a single sharp D peak in the Raman spectra of BM3. The peak intensity ratio of D and G band gives a good measure of the disorder in the graphene samples. In our case (BM3), we have observed that the $I_D/I_G$ comes out to be 0.97, which is significantly higher than that observed for mechanically exfoliated graphene [30], and smaller than that obtained for chemically reduced graphene [9].

The in plane crystallite size $L_a=4.4(I_G/I_D)$ signifies the measure of dislocations, vacancies and presence of other atoms which do not belong to graphitic network [31]. Being inversely proportional to the amount of crystal boundary, it gives an idea of chemical functionality and shear strength of linkages [31-33]. In fact the fraction of sp² bonds is reflected in the amount of disorder, which in turn controls the electrical, optical, mechanical and other physical properties. In our case $L_a=4.63$ nm (excellent is $L_a≈4$) which signifies improved quality of the layer and higher shear strength [34], and it is suitable for various chemical and electrochemical studies. The 2nd order Raman peak 2D appears at 2600 cm⁻¹. The 2D peak seems to be smeared, which usually is not observed in the mechanically peeled graphene [30] or graphene grown on different substrates [35]. The 2D peak is very sensitive to the stacking order of the graphene sheets along the c-axis, and the number of layers [36]. We have performed the Raman study using powder sample, having random orientation, hence this kind of smeared peak is expected to arise in our case. However, this 2D feature can be explained on the basis of two phonon 2nd order Raman scattering process.

### 8.3.7 Microstructural characterization using TEM

Fig. 8.7(a) shows a large area graphene sheet from BM3, whereas Fig. 8.7(b) presents a very thin graphene sheet from the same sample. The edges in this sample show folding, indicating the thinness of the sample. Fig. 8.7(c) shows the selected area electron diffraction pattern of the same sample, representing the hexagonal crystal structure.
In general, the actual reason of the corresponding phase transformation from GO to graphene is yet to be understood. The high energy ball milling method has been previously employed to synthesize nanoscale materials and some phase transformation has also been observed [37]. We argue in our case, that the heat generation in the ball milling process is the key reason for this phase transformation. As seen from the literature [38] and also from DTA-TGA study of both GO and BM3 (Fig. 2(a) and (b)), around 423-523 K a high mass loss due to the removal of carboxylic groups in GO is observed, which is absent in BM3. From this we conclude that the particular BPMR and time of milling in inert atmosphere subsequently generated the particular temperature inside the closed vial, which was able to reduce GO thermally to form graphene. Since the particular structural difference between GO and CCG is the presence of carboxylic groups, one can reach the graphenic structure readily from GO by the removal of the functional group. In chemically modified graphene preparation [9] this idea was employed by the workers by using hydrazine hydrate. Also thermal reduction of GO to form graphene has [38] also been observed. Our FTIR and XPS data substantiate the above arguments.

8.4 Conclusions

We have been able to synthesize graphene using a new green and scalable approach starting from GO. The method viz; high energy ball milling, has been used for synthesis,
without using any harsh chemicals. Different characterization techniques employed (FTIR, Raman, UV-Vis, XPS spectroscopy) show that the material of interest is significantly different from GO, and very much close to that of CCG. The Raman spectroscopic study shows that the system is much less disordered in comparison to chemically modified graphene, as far as the $I_D/I_G$ ratio is concerned. A photoluminescence spectrum has also been observed in the UV-blue region due to defect induced localized states between $\pi$ and $\pi^*$ levels. The photoluminescence property could be exploited by using this bio-compatible material as a marker for biological applications.
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