Chapter V

Large area Single Layer Graphene by Pyrolysis of Polymer for a) Supercapacitor Application and b) Graphene-P3HT Composite for Field-Effect Transistor Application

This chapter discusses the synthesis, properties and applications of large area single layer graphene. Graphene is synthesized from pyrolysis of poly (acrylic acid) sodium salt. This method represents a facile approach to large area single layer graphene. The process is catalyst/template free. It is simple bottom-up process by which large amounts of graphene can be synthesized in single batch requiring no specialized chemicals. The method is scalable and establishes a new and easy approach to fabricate micron size sheets of graphene. The as synthesized graphene is highly conducting in nature with specific conductivity of 100 S/m and also exhibits extremely high surface area which is 350 m²/g. The as synthesized graphene shows excellent properties for supercapacitor application. The graphene synthesized by this method was also composited with P3HT and characterized for field-effect transistor application.
Section-I: Large size single layer graphene by pyrolysis of polymer for supercapacitor application

5.1 Introduction

Graphene is a one atom-thick planar sheet of sp²-bonded carbon atoms that are densely packed in a honeycomb crystal lattice. It is also the basic structural unit of some carbon allotropes including graphite, charcoal, carbon nanotubes and fullerenes. Graphene has some unique physicochemical properties such as excellent electrical, thermal conductivity, high surface area and optical transparency etc. [1-3]. The electrical conductivity of graphene is highest as compared to any other material on earth. Electrons moving in graphene behave as massless Dirac fermions which renders remarkably high electron mobility in graphene at room temperature [4, 5]. Graphene bilayer acts as field-effect transistor where the band gap of graphene can be tuned from 0 to 0.25 eV, by applying voltage to a dual-gate bilayer graphene at room temperature [6]. The single layer graphene can have very high surface area of around 2630 m² g⁻¹ [7]. These properties render graphene various functionalities which are important in several fields such as supercapacitors, Li-ion batteries, photovoltaics, sensor, nanoelectronics etc. [1, 8-17]

There are very limited methods for the synthesis of graphene which include micromechanical cleavage, sonication in various solvents, chemical reduction of graphite oxide (GO), pyrolysis of polymers or organic materials, thermal decomposition of SiC and chemical vapour deposition etc. [18-27]. In micromechanical cleavage method graphene layers are peeled off from graphite. Chemical reduction method involves the reduction of graphite oxide (GO) to graphene by suitable reducing agent such as hydrazine hydrate. Chemical vapour deposition involves epitaxial growth of graphene on suitable substrate such as silicon carbide at high temperature. Pyrolysis is also a unique method to synthesize graphene wherein the organic precursors such as sugar, sodium ethoxide, or suitable polymers such as PMMA, PAN, PS etc. are thermally decomposed in presence of catalysts at high temperature in an inert atmosphere. Out of these methods CVD is very expensive, micromechanical cleavage method is not useful for bulk production of graphene, and chemical exfoliation method involves use of toxic and hazardous chemicals. So in comparison with these methods, pyrolysis has several advantages. It is one step method where large scale production of
Single sheet graphene is possible with or without presence of catalyst (depends upon the choice of precursor). It does not involve use of toxic materials and chemicals for synthesis.

In this work the catalyst free synthesis of graphene by pyrolysis route is demonstrated. Briefly the polymer poly(acrylic acid) sodium salt (Mol Wt 5000) is pyrolyzed in argon atmosphere at 1000°C for 4 hours. This pyrolyzed product was washed for purification, filtered and dried in air. The carbon mass obtained was examined for the structural, chemical and morphological properties using various techniques. The surface area of as synthesized graphene was found to be 350 m²/g, which is significant from the application point of view. The specific conductivity of this graphene was nearly 90 S/m. The as synthesized graphene was tested for supercapacitor application and shows high capacitance value of ~130 F/g when tested in aqueous electrolyte in a typical electrochemical cell. The high surface area with conductive graphitic framework together provide a large double layer area, fast ion transport and efficient charge harvesting in aqueous electrolytes.

5.1.2 Experimental Section

The poly(acrylic acid) sodium salt was obtained from Sigma Aldrich (Mol wt 5,000). For pyrolytic decomposition, the polymer was heated in a furnace at 1000°C for 2 hours in argon atmosphere. The product formed by pyrolysis of polymer was then washed and purified carefully with D.I. water to remove the inorganic by-products. This process was repeated till the pH of carbon mass dispersed in water became neutral. This carbon mass then dried subsequently and examined for the structural, chemical and morphological properties using various techniques such as X-ray diffraction (XRD, Philips X’Pert PRO), Raman spectroscopy (Confocal micro-Raman spectrometer LabRAM ARAMIS Horiba Jobin-Yvon apparatus with laser excitation wavelength of 532 nm), high resolution transmission electron microscopy (HRTEM, FEI Tecnai 300) and field emission scanning electron microscopy (FESEM, Hitachi S-4200). The surface area and porosity study were performed by the standard nitrogen adsorption (BET method) isotherm at 77K. Electrochemical measurements were performed with Autolab PGSTAT Potentiostat. Specific capacitance of graphene was determined by cyclic voltammetry (CV) measurements in 1 M H₂SO₄.
5-1.3 Results and Discussion

Figure 5.1 shows the TEM image of as synthesized carbon mass. It shows presence of graphene sheets which has size of few microns. The graphene sheet shows a typical wrinkled morphology with presence of numerous folding. It resembles the crumpled silk veil wave structure which is characteristic of 2D geometry of graphene. High resolution TEM confirms the presence of monolayer graphene with high transparency. Inset of figure 5.1d shows the selected area electron diffraction pattern taken for graphene. The SAED pattern is relatively diffused, due to the folded structure of graphene sheet which do not hold perpendicular to the electron beam.

![TEM images of Graphene](image)

Fig. 5.1 TEM images of Graphene

Figure 5.2 shows the XRD spectrum and Raman spectrum of as synthesized graphene. The presence of characteristic graphitic peak at around 26° in the XRD spectrum confirms the presence of graphene sheets which are stacked above one another when it
is in the powder form. The peak is very broad confirming the presence of few layer graphene. It is expected to get this peak in the XRD spectrum, as pure high quality graphene sheets attract each other due to van der walls forces. graphene sheets, which can come closer due to attractive forces amongst them in order to minimize the surface energy. Hence when the bulk quantity of dispersed graphene sheets is dried by removing solvent these sheets again come closer by van der walls forces and gives characteristic peak at 26° in the XRD spectrum.

![XRD and Raman Spectra](image)

**Fig. 5.2 A) XRD spectrum and B) Raman spectrum of graphene**

Raman spectroscopy was further used to characterize the graphene sample. Raman spectroscopy is generally employed to distinguish between different forms of graphitic carbon such as graphene, CNT, graphite or non-graphitic amorphous carbon etc. It also useful for the differentiation between single, double and multiple layered graphen [28-34]. Figure 5.2B shows the Raman spectrum of as synthesized graphene. The signature peak present at 1585 cm\(^{-1}\) in the Raman spectrum of graphene corresponds to the G band. Generally this peak is present at 1580 cm\(^{-1}\) in the case of graphite, CNTs, graphene and amorphous carbon. Presence of D band peak at about 1345 cm\(^{-1}\) in case of graphene signifies disordered nature (defects) of the graphite like system. This peak is usually present in CNTs, chemically converted graphene (CCG) and amorphous carbon. Also it can be noted that the intensity ratio I_D/I_G is about 0.6 which signifies presence of fewer defect in the graphene. The high quality graphene is characterized by the presence of G’ or 2D peak which appears at 2700 cm\(^{-1}\) in the Raman spectrum.
Table 5.1 Tables of referenced Raman parameters for single layer graphene

<table>
<thead>
<tr>
<th>No.</th>
<th>Reference (data for single layer graphene with green laser (514, 538 nm) excitation for Raman spectroscopy)</th>
<th>Position of G peak (cm(^{-1}))</th>
<th>Position of 2D peak (cm(^{-1}))</th>
<th>FWHM of 2D peak (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.</td>
<td>G’ band Raman spectra of single, double and triple layer graphene by Dresselhaus <em>et. al.</em> <em>Carbon</em>, 2009, 47, 1303</td>
<td>-</td>
<td>~2700</td>
<td>18-28</td>
</tr>
<tr>
<td>5.</td>
<td>Temperature Dependence of the Raman Spectra of Graphene and Graphene Multilayers by A. A. Balandin <em>et. al.</em> <em>Nano Lett.</em>, 2007, 7, 2645</td>
<td>~1582</td>
<td>2691 (488 nm laser)</td>
<td>-</td>
</tr>
<tr>
<td>6.</td>
<td>Freestanding Graphene by Thermal Splitting of Silicon Carbide Granules by X. Bao <em>et. al.</em> <em>Adv. Mater.</em> 2010, 22, 2168</td>
<td>~1585</td>
<td>~2700</td>
<td>-</td>
</tr>
<tr>
<td>8.</td>
<td>Our work (large size single sheet graphene)</td>
<td>1585</td>
<td>2696</td>
<td>51</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No of graphene layers</th>
<th>Position of 2D peak (cm(^{-1}))</th>
<th>FWHM of 2D peak (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>~2700±5</td>
<td>20-30</td>
</tr>
<tr>
<td>2</td>
<td>~2710</td>
<td>30-55</td>
</tr>
<tr>
<td>3</td>
<td>~2715</td>
<td>more than 60</td>
</tr>
<tr>
<td>Our work (large size single sheet graphene)</td>
<td>2696</td>
<td>51</td>
</tr>
</tbody>
</table>
The 2D peak is due to the Raman vibration of second order of zone-boundary phonons which satisfy the Raman fundamental selection rules in case of single layer graphene but not in case of graphite or multi-layer graphene. So this peak is present in the Raman spectrum of single layer graphene and absent in that of graphite, multi-layer graphene and amorphous carbon. Presence of sharp signature peak corresponding to 2D band at 2700 cm\(^{-1}\) in the case of our graphene then signifies the presence of single layer graphene. Also the intensity of 2D peak is equal to or slightly more than that of D peak indicating highly crystalline nature of the as synthesized graphene.

Raman spectroscopy can also be used to distinguish between single layer, bilayer to few layer graphene. Especially careful analysis of 2D peak in Raman spectra can assure the quality of graphene. The positions of 2D peak as well as its broadening or FWHM are the important parameters that decide nature of graphene. In this regard, many authors have addressed the effect of thickness of graphene sheets on the position, FWHM and intensity of 2D band peak [28-30, 35-39]. Also it should be emphasized that the position, FWHM and intensity of the 2D band peak also depends upon the energy of laser used for excitation in Raman studies. According to these studies, single sheet graphene shows the presence of 2D band at around ~ 2700 cm\(^{-1}\) for the case of green excitation wavelength (\(\lambda =514\) nm or \(\lambda =538\) nm) and this peak shifts to higher wavenumber as the thickness of graphene increases from 1 layer to n layer graphene or graphite up to 2750 cm\(^{-1}\). For the case of red excitation wavelength (\(\lambda = 633\) nm) the position of 2D band lies at ~ 2650 cm\(^{-1}\) in the case of single sheet graphene and shifts to higher wavenumber as the thickness of graphene increases from 1 layer to n layer up to 2700 cm\(^{-1}\). In our sample, with green excitation wavelength (\(\lambda =514\) nm), the 2D peak is located around ~2696 cm\(^{-1}\), clearly indicating primarily the presence of single sheet graphene. In table 5.1 the peak position of 2D peak of our sample with the values reported in the literature on single layer graphene is compared. Notably any shift is found in the 2D peak as compared to the data from literature as shown below in table 5.1. The FWHM in our case is slightly broader (51 cm\(^{-1}\)) as compared to that for the case of single layer graphene reported by others (30 cm\(^{-1}\)). This can be attributed to the folding edge strains and related defects in the graphene. It should be emphasized that these reports are mostly for large area graphene sheets (thin films on support material like Si) while our sample represents graphene sheets without support.

The surface area and porosity of the graphene were measured by nitrogen adsorption-desorption method at 77 K. The surface area is found to be significantly high, ~350
m$^2$/g. Figure 3A shows the pore size distribution of as synthesized graphene. It indicates the average pore diameter of graphene is less than 1 nm which indicates microporous nature [40]. Figure 3B shows the Nitrogen adsorption-desorption isotherm of graphene. It exhibits type II isotherm which is characteristic of multilayer adsorption at high P/P$_0$ value [41]. Also it shows small but prominent hysteresis behavior.

![Graphene Porosity and Nitrogen Adsorption Desorption Isotherm](image)

**Fig. 5.3 A) Porosity data and B) N$_2$ isotherm of graphene at measured at 77 K.**

The resistivity of graphene is measured by two probe method. It is very difficult to make a mechanically strong pellet out of graphene powder for conductivity measurements, therefore the powder was placed in a die and a known (50 kg/m$^2$) pressure was applied. The contact was made from both the sides of the die, and the top
and bottom parts of the die were separated by a flexible insulator to avoid contact. The resistivity was calculated by knowing the dimension parameters of dye and thickness of material.

![Schematic of conductivity measurement assembly](image)

**Fig. 5.4 Schematic of conductivity measurement assembly**

The resistivity of our sample was found to be ~0.011 Ω·m. The specific conductivity calculated from this value comes around to be 90 S/m, indicating highly conducting nature of the graphene.

![CV curves of graphene at different scan rates](image)

**Fig. 5.5 CV curves of graphene at different scan rates**
Figure 5.5 shows the typical cyclic voltammetric response of graphene recorded in 1M H$_2$SO$_4$ solution. The CV curves exhibit a slightly skewed rectangular shape without any redox peaks (oxidation or reduction). The shape of curve becomes skewed but remains nearly rectangular even at high scan rate of 100 and 200 mV/s. This indicates that the graphene possesses significantly lower resistance for ion transport during high-rate charge and discharge processes. The average value of capacitance from CV curves is about 130 F/g.

5.4.4 Conclusion

This section demonstrates catalyst free synthesis of large area single layer graphene without use of any template. The as-synthesized graphene exhibits fairly high surface area of about 350 m$^2$/g and shows bulk specific conductivity of 90 S/m. This graphene also shows good CV behaviour with approximate specific capacitance of 130 F/g.
Section-II: Graphene-P3HT composite for Field-effect transistor application

5-II.1 Introduction

Graphene has some unique physicochemical properties such as excellent electrical, thermal conductivity, high surface area and optical transparency etc. as discussed in previous section. Due to these properties graphene has attracted attention of scientist for a range of applications, such as as electrode material in supercapacitors, batteries displays, solar cells, and sensors [1-17] On the other hand organic and polymeric semiconductors offer potential low-cost, high-volume manufacturing of flexible transistor-based electronics, such as display drivers, radio frequency identification tags, pressure mapping elements, and chemical sensors etc. [42-49]. Today other than silicon based transistors, organic and polymeric semiconductors based transistors exhibit high on/off ratios in organic field-effect transistors. But these OFETs suffer from low mobility’s that limit the range of possible applications [50-54]. In this case it is interesting to see that graphene is a new 2D material which posses very high electron mobility can be an ideal candidate for a transistor material with gigahertz or terahertz of working frequency. Although poor on/off ratios of graphene based devices is the major hurdle in the development of FETs made so far. Also in case of OFETs the need for higher mobility organic semiconductors is still compelling, especially for materials used in conjunction with solution processes. The new alternative to this problem involve the use of both organic semiconductor materials together with carbon-based materials such as graphene and carbon nanotubes (CNTs) etc. which exhibit very high mobility. This approach enhances the effective mobility while keeps the on/off ratio sufficiently high in the device. This strategy also significantly enhances the charge injection/extraction across the electrode/organic semiconductor interface. This is due to highly conductive charge-transporting layer between the electrode and the active semiconductor layer. [55]

In this regard there are few reports for the use of organic semiconductor/carbon nanotube hybrid field-effect transistors [56–61] where inclusion of CNT with organic semiconductor results in remarkable increase in apparent field-effect mobility. Further it is indicated that CNTs act as conducting bridges between the crystalline regions of the semiconductor film thereby increasing the mobility. However, at the same time the on/off ratio appears to decrease just as the mobility begins to increase. This is because one dimensional carbon nanotubes has a percolation threshold when mixed with
organic semiconductor. At low density of CNTs, the mobility of the organic semiconductor film increases drastically, but as the density of the CNTs appears to approach the percolation threshold, the on/off ratio is observed to decrease. With graphene, due to the single atom two-dimensional lattice, it is expected to have better electronic, mechanical and physical properties that will improve FET operation. It is expected that addition of graphene will provide good connection between the crystalline regions of the semiconductor film. Also compared to CNTs, increased area in the conduction channel of an organic semiconductor transistor can be covered by graphene before they start to percolate and reduce the on/off ratio. As a result, the mobility of organic transistors with graphene would be expected to show higher values than what can be accomplished using CNTs before device on/off ratio drops. In this regard there are very few reports for the use of organic semiconductor/graphene composite material as a channel material for FET based device applications. Hence this is very attractive area of research for the preparation of new generation devices based on graphene/organic semiconductor hybrid.

In this work, a general approach for the preparation of solution processable organic semiconductor/graphene hybrid thin film transistors is presented. In this method, graphene was synthesized by pyrolysis of poly (acrylic acid) sodium salt. The method is a catalyst free and cost effective. The as prepared organic semiconductor/graphene hybrid thin film transistor shows their efficient working. It is seen that as compared to FETs with pure organic semiconductors, hybrid FETs exhibit much higher effective mobility while keeping the on/off ratio of devices sufficiently high.

5-II.2 Experimental Section

The graphene was synthesized by pyrolysis of poly (acrylic acid) sodium salt, as explained in the previous section. In this work, poly-(3-hexylthiophene) (P3HT), an organic semiconductor was blended with this as synthesized graphene in dichlorobenzene (DCB) and spin coated on Si/SiO$_2$ substrate having gold electrodes. A 7w/w% graphene/P3HT composite was used to prepare the channel material of FET. The required graphene dispersion was made in P3HT solution of fixed molarity. This solution was then subjected to ultrasonic agitation and. This yielded a dark-purple solution with polymer nanoparticles and graphene suspended in DCB. A heavily doped silicon wafer with 300 nm thermally grown SiO$_2$ was used as a substrate material.
Wafers were cleaned by sonication in acetone, isopropanol and DI water, respectively, followed by N₂ drying. Hybrid field-effect transistors were fabricated by spin coating the P3HT/graphene composite solution onto a substrate at 1400 rpm for 60 s followed by vacuum drying to give 20–50-nm thick semiconductor layer. Control devices were fabricated with pure P3HT films using the same procedures but without the addition of graphene to the DCB solution. Gold source-drain electrodes were pre-deposited prior to spin coating with channel length $L = 20 \mu m$ and channel width $W = 1 \text{mm}$. All of the resulting devices were annealed in a vacuum oven at 1100°C for 20 min, followed by slow cooling. All the current–voltage (I–V) curves were measured at room temperature under ambient conditions using a Cascade probe station connected to two Keithley 2400 source/measure units. The effective field-effect mobility of each transistor was extracted from the transfer characteristics using a linear fit to the plot of the square root of saturation source-drain current as a function of the gate voltage $V_g$.

5-II.3 Results and discussion

All the characterization for graphene is presented in previous section of same chapter. Here the application part of graphene/P3HT composite has only discussed. Graphene has high electron mobility, hence when incorporated into an organic semiconductor film, provides “fast lanes” for charge carriers within the conduction channel. Thus it enhances the effective mobility of the entire transistor device thereby reduces the conduction channel length, which acts to enhance the output source-drain current of the field-effect transistor.

Fig. 5.6 Output characteristics of A) pure P3HT, B) 7% graphene/P3HT FET devices.
To compare the results only P3HT was also spin coated on silicon wafer having pre-deposited gold electrodes and studied for their transistor characteristic. The results are summaries in a table given in figure 5.8, which confirms the enhancement in the performance of transistors made from P3HT/graphene hybrid. The measured current–voltage characteristics for P3HT/graphene FETs show well-defined gate modulation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>On-off ratio</th>
<th>Mobility (cm²V⁻¹s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT</td>
<td>1.37E+03</td>
<td>0.002</td>
</tr>
<tr>
<td>7%-GR-P3HT</td>
<td>3.67E+03</td>
<td>0.021</td>
</tr>
</tbody>
</table>

Fig. 5.7 Transfer characteristics of pure P3HT and 7% graphene/P3HT FET devices and respective on/off ratios and mobility values.

Figure 5.6 depicts the current–voltage characteristics of pure P3HT as well as graphene/P3HT hybrid transistor, and Figure 5.7 compares the transfer characteristics of the same graphene/P3HT hybrid transistor to that of a pure P3HT transistor. It should be noted that much higher current was obtained from the device with graphene/P3HT device. In the case of 7% graphene/P3HT device the mobility is increase by one order (0.02 cm² V⁻¹s⁻¹) as compared to that from the pure P3HT FET (0.002 cm² V⁻¹s⁻¹). The on/off ratio of the 7% graphene/P3HT FET is nearly thrice that of the pure P3HT FET.

5-II.4 Conclusion

In conclusion, this section demonstrates a new way of synthesizing graphene/P3HT composite and its application for field effect transistors. It is shown that effective mobility as well as on/off ratio of polymer/graphene hybrid FETs can be significantly higher than that of a pure polymer FET. The mobility of graphene/P3HT FET device is found to be 0.02 cm² V⁻¹s⁻¹ which is one order higher as compared to only P3HT FET device. The on/off ratio of the graphene/P3HT FET device is also found to be nearly thrice that of the pure P3HT FET device.
5.2 References


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