CHAPTER VI

Investigations of Graphene like Nanocarbon Using Scanning Tunneling Microscopy/Spectroscopy

In the present chapter disorder in the GNC lattice has been extensively studied for its electronic and field emission properties. Morphological investigations are then performed using SEM which depicted microstructures comprising of atomically flat terraces (c-planes) with abundance of edges (ab planes which are orthogonal to c-planes). STM is used to observe the atomic structure of basal planes whereas FEM is found to be suitable for resolving the nanotopography of edges. Investigations suggest potential application in the flat panel display screens.
6.1 Introduction

One atom thick regular hexagonal arrangement of pure carbon atoms, popularly known as graphene [1], has drawn the immense interest of research community [2]. The unique combination of electrical [3], mechanical [4] as well as electronic [2] properties has opened up wide spectrum of applications of this first free-standing 2D crystal in solid state physics and nanoelectronics. Despite of interesting properties, large scale synthesis of graphene is still a challenge so that the dream of next generation graphene devices would come in reality. Mechanical cleavage [5], chemical vapor deposition [6], epitaxial [7], chemical exfoliation [8] are the few well known synthesis techniques. Several efforts have been made towards the production of highly crystalline graphene. As the scalability of graphene increases, probability of defect formation also gets boosted. Thus a detailed investigation of various defects present in graphene is important from fundamental sciences and technological point of view. As it is predicted that the presence of defects could modify the mechanical [9] and electronic [10-11] properties of material, several efforts are made to understand variation in graphene properties in presence of defects [12-13]. In graphene, disorder could broadly be classified as extrinsic defects in the form of adatoms, vacancies, in plane space charge, cracks, edges, and intrinsic defects like surface ripples and topological disorders. Extensive use of several characterization techniques like Raman spectroscopy [14], STEM [15] has been made to investigate these defects in the structure. In case of Raman, 1350 cm\(^{-1}\) peak named as D band is observed in the presence of defects (D for defect or disorder) [16]. Its intensity is proportional to the amount of disorder in the sample, and the ratio between the intensities of the disorder-induced D band and the first-order graphite G band (ID/IG) provides a parameter that can be used for quantifying disorder. Whereas STEM has given direct evidences of vacancy-type defects due to electron beam damage, as well as a ring-type defect, resulting from the glide movement of reconstructed atom arrangements at the edges of graphene sheets [15]. In a way these techniques have either predicted or shown the actual presence of defect sites but not given their effects on the inherent properties of pristine graphene. At what extent there could be variation in the properties due to presence of such various defects is not predicted with the help of these techniques.
Atamny et al. [17] is among the first ones to report detailed investigation of different kinds of defects in graphite using STM. They could also observe mono-layer loops and graphite ribbons with a height of only two mono-layers. Their report is first to observe defect lines with atomic resolution in case of graphite. Atomic level resolution is one of the most important advantages of STM. Graphene being a single atomic layer of graphite also possess similar structure properties. Thus STM is one of the best available tools to investigate atomic level defects in graphene due to high special resolution capability. Along with topology STM is meant to give local electronic properties of sample at subatomic level. Thus use of this unique combination of having high special resolution and direct measurement of local electronic properties is beneficial for not only detecting the presence of various defects but also looking at the variation in the electronic properties in their presence.

In this chapter this unique combination of STM is used extensively to understand the effect of defects on its electronic properties. Microscopic, electronic and structural properties of disordered GNC are analyzed with the help of STM.

6.2 Experimental Details

Synthesis details

GNC is synthesized following the method reported in Arvind et al. [18]. The precursor of soft wood charcoal powder mixed with KNO₃ and S (stoichiometric ratio ~ 85: 10:05, C: KNO₃: S) is used. Initially, precursor along with KNO₃ and S are admixed in the powder form and large number of pellets of dimension ~15 mm (diameter) and ~5 mm (thickness) are prepared. The pellets are prepared by loading 1 gm mixture into a mechanical press machine and applying a load of ~10 kPa. The prepared pellets are dried in a vacuum oven at ~80 °C for 6 h to remove residual moisture. These pellets are then stored in the dry atmosphere for further processing. One pellet at a time is taken in a glass plate, detonated under the atmospheric conditions and onset allowed for the flame assisted combustion. The complete combustion of the denoted pellet took place in about 20–30 s leading to the formation of carbon-like ash column along with smoke. The
column is crushed and the weight of the obtained powder is measured. The weight of the powder is found to be decreased down to ~35 mg with respect to its original weight value ~1 gm. The obtained powder is immersed in a mixture of DI/acetone (8:2, v/v) and sonicated for a period of 1 h followed by the vacuum filtration using PTFE filter (pore size ~1.2 µm). The process is repeated for about three to four times in order to remove the impurities such as potassium, S, and other oxide elements. Thus the powder obtained by such method is termed as as-synthesized samples. The as-synthesized samples are then subjected to intercalation followed by annealing process. The intercalation of as-synthesized samples is adopted for etching the a–C and to separate the conjugated GNC layers. The intercalation process is carried out at room temperature using mixture of H$_2$SO$_4$ (98%): HNO$_3$ (60%), (4:1, v/v) for 48 h with continuous stirring. It is previously reported that, during intercalation, nitronium ion (NO$_2^+$) is formed due to the dissociation of HNO$_3$ which could act as a weak etchant for a–C as well as oxidizing agent [19]. This process leads to evolution of CO$_2$ gas along with the liberation of N$_2$. Although, NO$_2^+$ selectively attack sp3 sites, the presence of H$_2$SO$_4$ is necessary for the intercalation to form transient species such as C-S-On and C-N-On. And this process leads to the formation of sp2 chains and the enhancement of overall sp2 content in the obtained samples. The samples processed in this way are then continuously washed using 5 mM NaOH solution. These samples are later washed in DI water until the pH of the wash water reached ~7. The obtained samples are dried in a vacuum oven for 12 h at 100 ºC. These intercalated samples are subjected to the annealing process at 1000 ºC for a period of 60 s. The annealing is carried out in a force convection oven, under the inert atmosphere conditions. The obtained GNC samples are used for further characterization.

**Experimental details**

GNC in IPA solution is sonicated until uniform dispersion is obtained. A few drops of the finely dispersed solution are collected using a micropipette and released on Si, HOPG and MoS$_2$ substrates. Sample is allowed to dry under ambient conditions, at room temperature. These samples are subjected to SEM, AFM and STM / STS. In the present work STM / STS have been used to obtain images of disordered GNC with
atomic resolution at room temperature and ambient conditions. 200μl GNC dispersed in IPA is drop coated on the substrate using micropipette. These substrates are examined under SEM and AFM. SEM analysis has been carried out, extensively on on JSM-6360A (JEOL) system operating at 20 kV. Large number of samples are chosen and employed to SEM. Similarly AFM experiments are performed in non contact mode of operation on an in-house modified Burleigh AFM head (Metris 2000) in entirely ambient condition. For performing AFM measurements a stylus cantilever made up of heavily doped Si cantilever (from Mikromasch) having radius of curvature < 50nm. (NSC35/Cr-Au, resonance frequency 210 KHz, force constant 7.5Nm\(^{-1}\)) is used. After confirming morphology under SEM and AFM the same sample is further subjected for STM/STS investigations. Freshly cut Pt/Ir tips are used for the measurements. Nanosurf STM is used to image the samples. Atomic resolution images are obtained on substrates like HOPG, MoS\(_2\). To avoid substrate effect on the observed tunneling spectra HOPG is used which is known to have metallic electronic states. The data is obtained in constant current mode with tunnel current and bias voltage applied to the tip with respect to the sample. \(I–V\) curves are obtained during imaging using sample and hold circuit. 10 \(I–V\) curves are averaged and 20 averages at each point in the \(I–V\) curves are taken. \(I–V\) curves are obtained from different spots on a particular sample. Spectroscopy is carried out at several defect sites of each sample and data is compared with respect to variation in disorder. Tunneling Spectra are obtained by plotting \(dI/dV\) as a function of bias voltage V. Same sample whose SEM and STM/STS is carried out is further analyzed for field emission property. The field emission experimental setup consists of simple anode cathode geometry, cathode is tungsten foil connected to ground and ITO (Indium Tin Oxide) coated glass screen to highly stabilized power supply (SPELLMAN Model SL10). The distance between anode and cathode is kept constant \(~3\)mm. The measurement of emission current is carried out using HP multimeter (Model 5015) capable of measuring current with accuracy of 0.1% and the recorded field emission patterns are recorded using CCD camera. Obtained results are presented.
6.3 Results and Discussion

Since graphene is exactly a single layer of atoms and each carbon atom is on the surface, thus atomic scale defects could be very important for transport properties of graphene. Absence of one or many atoms in the honeycomb lattice could significantly deviate its properties from pristine graphene. Detailed investigation of such transport properties in presence of verity of defects via STM/STS in case of GNC is presented.

Synthesized GNC is observed under SEM for morphological investigations. SEM analysis has been carried out, extensively, on large number of samples. Figure 6.1 shows the SEM micrographs of the GNC, which depicts microstructures comprising of atomically flat terraces (c-planes) with abundance of edges (ab planes which are orthogonal to c-planes). One can see from figure that, obtained GNC is of various shapes and area. Interestingly images also show sample of single, double, triple, layers at several places. The area of GNC has been measured from each sample. The magnitude of area, has found to be varied in the range from few μm$^2$ to few hundred μm$^2$. Comparatively larger sample coverage is observed in case of Figure 6.1E and Figure 6.1F samples. Samples with such large coverage are then used for further measurements.

After performing SEM measurements, same sample is subjected for AFM measurement; Figure 6.2 gives the data obtained in the AFM study. It can be seen that along with the long flakes small flakes are also seen. The height profile of the flake depicts the folding of layer at the edge as height profile shows exact multiple heights. After confirming the morphology of these GNC, the sample is further investigated for its transport properties.

Understanding the atomic structure of GNC in the configuration in which it is prepared is crucial to understand the transport properties. Along with STM image, one can obtain valuable information about the LDOS using $dI / dV$ curves from STS. First we present the large area STM image of GNC, Figure 6.3 represent the image obtained on the 100nm × 100nm sample area. Small GNC flakes can be seen on this area, which confirms that large size distribution is obtained for the prepared GNC sample from μm to nm scale.
Figure 6.1 SEM images of GNC sample which depicts microstructures comprising of atomically flat terraces (c-planes) with abundance of edges (ab planes which are orthogonal to c-planes).

After performing a larger area scan we further tried to reduce the scanning area so as to obtain atomic resolution. Variation in imaging parameters is required to get clear atomic resolution image. We present the atomic resolution images of atomically flat terraces (c-planes) of GNC along with its tunneling spectroscopy. Figure 6.4A show atomic level resolution image of 1 x 1 nm area of GNC deposited on HOPG substrate with set current 2.5nA and bias voltage 51mV. Slightly distorted honeycomb lattice could be observed. Corresponding I-V spectra along with conductance plot (inset) is shown in Figure 6.4B. It
is well proven that graphene LDOS on single layer is linear in energy and vanishes at Dirac point.

![Graphene LDOS Image](image)

**Figure 6.2 AFM images of GNC sample.**

Therefore a linear LDOS that vanishes at Dirac Point can be used to identify the signature of graphene decoupled from the substrate [20-21]. The inset of Figure 6.4B is V shaped but does not vanish at Dirac point. This leads to the conclusion that, GNC layers are more coupled to the substrate.

Figure 6.5A shows another atomic resolution images taken on 5 × 5 nm area of GNC deposited on HOPG under the same current and bias conditions. Zoomed region of above image shown in Figure 6.5B clearly depicts the presence of only three atoms out of six in the honeycomb, showing the triangular lattice. Such triangular lattice is observed in case of graphite [22-23]. Such kind of effect is referred as the carbon site asymmetry and is explained by the electronic origin [24-25]. It is well know that the surface of graphite consists of two types of non-equivalent carbon atom sites, namely A and B.
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Figure 6.3 STM image obtained on 100nm × 100nm sample area at 100mV bias voltage and 1nA current.

A-site carbon atom sits directly above a carbon atom of the underlying layer, whereas a B-site carbon atom is located above the center of a carbon hexagon of the layer underneath.

Figure 6.4 A) STM image of 1 × 1 nm area of GNC deposited on HOPG substrate with set current 2.5nA and bias voltage 51mV B) Corresponding I-V spectra along with conductance plot (inset).

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Result of the interlayer interactions is that, the p electronic levels around the Fermi energy, detected by STM, have a higher density on the B-site carbon atoms over the A-site atoms, so B-site atoms have more contribution to the tunneling current than A-site atoms and hence the carbon site asymmetry.

Figure 6.5 A) STM images taken on 5 x 5 nm area of GNC deposited on HOPG (I = 2.5 nA and V= 51mV) depicting triangular lattice. B) Zoomed area giving clear evidence of triangular lattice and C) line scale showing inter atomic distance in this triangular lattice of the order of 0.25 nm.

Though this is not the only factor contribution for the contrast in the atomic scale image formed by STM, but it does play a crucial role in the observation of such triangular lattice structures. It is found that inter atomic distance in this triangular lattice comes out to be of the order of 0.25 nm (Figure 6.5C) and matches well with the earlier reported value [23]. Along with the triangular lattice few distorted honeycomb structures could also be observed in the same image. The surprising fact is when one keeps on scanning the same region several times instead of the triangular lattice structure one could also get...
distorted atomic structure of GNC over the total scan area. People have observed such images with slight variation in scanning parameter [23].

![Figure 6.6 A) Image reveling partly triangular and partly hexagonal atomic arrangement of GNC on HOPG (I = 2.5nA and V= 51mV) B) Hexagonal atomic packing of GNC on MoS₂ substrate with set current 3.5nA and bias voltage 96mV.](image)

Figure 6.6A shows the STM image of same region after performing few repetitive scans keeping all other imaging parameter constant. No need is found to vary the imaging parameters. It can be clearly seen that only very small part of image revealed the triangular lattice structure whereas rest of the image clearly shows presence of defect sites in the atomic structure. This situation of obtaining triangular lattice and distorted honeycomb structure, one after other, gets repeated sometimes but only on few areas of the total sample. All above reported images are taken with HOPG as substrate. Few reports also count the role of tip-sample mechanical interactions in the formation of such distinct images over the same area. To ensure if this effect also dependents on the substrate beneath, images are recorded on GNC over MoS₂ substrate. Surprisingly no such observation is made on this substrate; Figure 6.6B gives the atomic resolution image of GNC on MoS₂ substrate with set current 3.5 nA and bias voltage 96 mV. Thus these measurements support the role played by substrate in image formation.
After observing atomic resolution with defect sites, effect of lattice distortion on the LDOS of disordered GNC is investigated extensively. We compared the typical tunneling spectroscopy data obtained from different regions of atomic arrangements. It is observed that when thicker sample is prepared on HOPG, by drop casting many layers of IPA in which GNC is dispersed, it is seen that though atomic resolution is obtained for the sample, $I$-$V$ tends to show similar nature irrespective of defect site.

Figure 6.7 A) STM images taken on $5 \times 5$ nm area of thick layered GNC deposited on HOPG ($I = 2.5$ nA and $V = 51$ mV), numbers represents sites where spectroscopy is performed. B) and C) Corresponding $I$-$V$ and conductance plots respectively.

Figure 6.7 represents the corresponding image (A) and spectroscopic measurements (B, C) performed on such thick sample.

Since it has been found that, the distortions in the lattice are of electronic origin and are accompanied by large increase in the LDOS at the defect site for different spatial locations. Similar measurements are performed on a thin sample to confirm whether $I$-$V$
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varies with variation in defect. Figure 6.8A shows another region of 5 × 5 nm area having set current 3.5 nA and bias voltage 240 mV of GNC deposited on HOPG substrate. Numeric in the image shows the positions where spectroscopy is performed and data is compared. The exact atomic arrangements at these different locations is zoomed and shown in the Figure 6.8B.

Figure 6.8 A) STM image on 5 × 5 nm area having set current 3.5nA and bias voltage 240mV of GNC deposited on HOPG substrate. Numeric in the image shows the positions where spectroscopy is performed. B) The exact atomic arrangements at these different locations is zoomed and shown.

First location resembles well to that of proper hexagonal packaging of atoms whereas in second location absence of inner atoms in all three hexagons can be seen. For the third location excess atoms instead of six, is observed. Due to the absence of one of the atom in hexagon distorted structure is seen on the fourth location. Central as well as peripheral atoms are mission from the two hexagons at the fifth position. Totally distorted structure is present on the area of sixth position. Thus locations with variation in defect structures are selected for performing spectroscopy. Figure 6.9A gives the respective tunneling spectra obtained at all above six locations. It can be clearly seen from the graph, one who resembles well with perfect honeycomb shows linear behavior in $I\cdot V$, $131$
whereas for all others nature is deviated from linearity. Distinct difference is seen depending upon the kind of disorder in lattice along c-planes of GNC. Thus this gives the direct evidence of variable conductivity with respect to different defect structures of the c-plane of GNC.

Figure 6.9 A) Obtained tunneling and B) conducting spectra at different defect sites located in Figure 6.8 A.

Along with atomically flat terraces (c-planes), abundance of edges (ab planes which are orthogonal to c-planes) is observed in the as synthesized sample. These sharp edges of GNC are expected to be excellent field emitters because of low work function and high electric field enhancement particularly when the applied electric field is along the basal planes. It is therefore thought it is worthwhile to investigate field emission from these samples. Field emission measurements performed on these samples reveled nanomorphology of the edges of GNC flakes. Figure 6.10A, B shows FEM images recorded at 1800 and 2300V along with their respective 3D plot. Initially FEM images showed cluster of bright spots at low voltages which later transformed into an array resembling ledges of ab planes with the increase of voltage. This can be clearly seen in Figure 6.10.
Figure 6.10 A), B) shows FEM images recorded at 1800 and 2300V along with their respective 3D plot.

$I$-$V$ characteristics recorded during these experiments are shown in Figure 6.11A. The reproducible $I$-$V$ curves yielded linear F-N plots supporting field emission as a dominant mechanism of electron emission. Figure 6.11B shows Fowler-Nordheim plot derived from $I$-$V$ curve. The turn-on voltage is found to be 2150V. The maximum current measured is 14 $\mu$A at voltage of 2300V.
Figure 6.11 A) $I-V$ characteristics recorded during FEM experiment. B) F-N plot derived from $I-V$ curve. The turn-on voltage is found to be 2150V and maximum current measured is 14 $\mu$A at voltage of 2300V.

6.4 Conclusion

In conclusion, the analysis of STM/STS of synthesized GNC revealed the importance of carbon atomic arrangements which critically influence the transport properties of the sample. Strong effect on the density of states is observed on the type of defect. Thus, such disordered GNC is well suited candidate for composite applications. The findings related to electronic and structural properties of disordered GNC are important to the development of GNC based electronics. Strong field emission pattern suggests the application of this sample in display devises.
6.5 References


