Graphene Oxide (GO) was reduced by low energy ions via 100 keV H\(^+\), 350 keV N\(^+\) and 200 keV Ar\(^+\) ions. XRD results showed the reduction of GO and formation of rGO. FTIR and XPS analysis revealed the removal of oxygen functional groups from GO after low energy ion beam irradiation. Raman spectroscopic results showed the increase in I\(_D\)/I\(_G\) ratio with increase in fluences indicating decrease in the crystallite size of sp\(^2\) domains. The specific capacitance has increased for irradiated GO corroborating the increased work function for irradiated GO. Also, 200 keV Ar\(^+\) ions irradiated GO showed more specific capacitance compared to 100 keV H\(^+\) and 350 keV N\(^+\) ions irradiated GO due to its more electronic energy loss in it than of other ions. The reduction of graphene oxide by low energy ion irradiation is confirmed as a reliable method by which graphene based materials can be produced.
6.1 Introduction

Work of the isolation of graphene by Novoselov and co-workers in 2004, attracted considerable attention towards graphene. Graphene is a zero-gap two dimensional (2D) hexagonal pack layered structure consisting of sp$^2$ bonded carbon atoms with its excellent electrical, mechanical and electrochemical properties [1-4]. Graphene oxide (GO) and its reduced form i.e. reduced graphene oxide (rGO) are considered as variants of graphene [5,6]. GO possesses a large number of oxygen functional groups (e.g. hydroxyl and epoxy groups) on its basal plane, and lesser amounts of carboxyl, carbonyl, phenol, lactone and quinone groups at the edges depending on the oxidation of graphite during the GO synthesis [5]. The presence of these oxygenated groups converts the planar sp$^2$ carbons of graphite to sp$^3$ carbons which changes the π-π electronic conjugation and causes significant decrease in electrical conductivity [6]. The approaches to reduce the GO includes chemical [7], electrochemical [8], hydrazine [9], thermal [10] and ion beam irradiation techniques [11]. The reduced graphene oxide possesses properties similar to graphene such as high surface area, good mechanical, electrical and electrochemical properties [6]. These excellent properties make rGO useful in many applications viz. solar cells, photocatalysis, water splitting, H$_2$ production, Li ion batteries and supercapacitors [6]. In conventional chemical methods, some impurity atom/groups may attach to rGO sheets that may reduce the electrical conductivity or otherwise harsh reducing agent/high temperature is needed. Compared to other conventional methods, ion beam irradiation method is clean, doesn’t require harsh reducing agent/high temperature and there will be no impurity atoms/groups. Even the properties of rGO can be tuned just by varying the fluence/dose (by varying the time) or by varying the energy of ion beam.

Ion beam irradiation has been used intensively to modify the surface of materials because of the precise control of the process parameters and, the many effects of ions and their consequences of modifying or removing atoms/groups [11]. The energetic ions penetrate the surface of materials and deposit their energy through electronic and nuclear stopping power which leads to phenomena such as bond breaking, carbonization and cross linking [12].
The ion beam irradiation has been used to tune the electrical/electrochemical properties of graphene/GO/rGO. The mechanism of defect formation in graphene by energetic heavy ion irradiation was demonstrated by Li et al., [13]. The graphene layer showed defect creations after heavy ion irradiation, and it was split and folded along the ion track yielding double layer nanoribbons [14]. Compagnini et al., [15] irradiated graphene by 500 keV C\(^+\) ions and observed point defects as well as defects originating from direct C\(^+\)-C collisions. Recently, Bai et al., [16] reported the geometry, quality and efficiency of nanopores creation in graphene by ion beam irradiation. Willke et al., [17] doped graphene with the B, N, and C using ultra low energy ion implantation and observed variation in electronic and transport properties. Lobo et al., [18] produced rGO patterns by exposing GO to focused Ga ions having energy from 1 to 60 keV and observed deoxygenation from GO. The same research groups also produced rGO regions by exposing GO to ions from FEI Helios Nanolab 600 FIB-SEM and CO\(_2\) laser raster [19]. The H\(_2\)/Ar plasma was used to reduce the graphene oxide which showed the deoxygenation of the graphene oxide results in enhancement in the specific capacitance [20]. They have observed the increase in electrical conductivity of rGO regions [19,20]. Earlier, Hareesh et al., have irradiated graphene oxide by 100 MeV Au ion for reduction and reported the enhancement in electrochemical sensing properties of H\(_2\)O\(_2\) by the Au ion irradiated GO [11].

Generally, many reports concern the reduction of graphene oxide by ultra low energy ions or plasma or swift heavy ions. Here, we study the effect of different ion beams (energy of few hundreds of keV) having different electronic energy loss and nuclear energy loss on the reduction/deoxygenation of graphene oxide. The deoxygenation of graphene oxide by ion beams is expected [19] to increase the electrochemical properties of graphene oxide. Our study concerns the variation in supercapacitance performance of GO and ion beam irradiated GO, and also it is correlated to the work function and Raman spectroscopic results.

We chose to irradiate graphene oxide by 100 keV H\(^+\), 350 keV N\(^+\) and 200 keV Ar\(^+\) ion beams at different fluences ranging from \(5 \times 10^{13}\) ions cm\(^{-2}\) to \(1 \times 10^{15}\) ions cm\(^{-2}\). The structural properties of GO and irradiated GO have been studied using X-ray Diffractogram (XRD). The surface morphology is established using Atomic force microscopy (AFM). Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy have been used to find
the changes in chemical properties of GO after irradiation. The variation in work function is measured using the Kelvin four probe method. The supercapacitance performance of GO and irradiated GO are studied by cyclic voltammetry, galvanostatic charge-discharge cycling and electrochemical impedance spectroscopy in 3 M KOH electrolyte.

6.2 Experimental details

GO was synthesized by modified Hummers’ method and the procedure is explained in detail elsewhere [11]. The synthesized GO was dispersed in MQ water (2 mg mL\(^{-1}\)) and sonicated for 1 h. The dispersed GO was drop casted on Indium Tin Oxide (ITO) glass substrate (Resistivity \(\sim 10\) ohm/cm\(^2\)). The sample had a geometrical surface area of \((1 \times 1)\) cm\(^2\) and thickness \(\sim 750\) nm. The samples were irradiated by 100 keV H\(^+\), 350 keV N\(^+\) and 200 keV Ar\(^+\) ions at different fluences from \(5 \times 10^{13}\) to \(1 \times 10^{15}\) ions cm\(^{-2}\) at a beam current 500 nA in a vacuum \(1 \times 10^{-6}\) Torr. The electronic energy loss, nuclear energy loss and range of 100 keV H\(^+\), 350 keV N\(^+\) and 200 keV Ar\(^+\) ions in graphite were calculated using SRIM 2008 and are listed in Table 6.1.

Table 6.1: The electronic energy loss (\(S_e\)), nuclear energy loss (\(S_n\)) and Range (R) of different ion species in graphite calculated using SRIM 2008.

<table>
<thead>
<tr>
<th>Ion beam</th>
<th>Energy</th>
<th>(S_e) (eV/Å)</th>
<th>(S_n) (eV/Å)</th>
<th>R (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(^+)</td>
<td>100 keV</td>
<td>16.54</td>
<td>0.024</td>
<td>703.9</td>
</tr>
<tr>
<td>N(^+)</td>
<td>350 keV</td>
<td>78.78</td>
<td>3.235</td>
<td>525.5</td>
</tr>
<tr>
<td>Ar(^+)</td>
<td>200 keV</td>
<td>81.39</td>
<td>44.60</td>
<td>158.1</td>
</tr>
</tbody>
</table>

The irradiated samples along with pristine GO were characterized using various techniques. XRD of model BrukerAXS D8 Advance X-ray diffractometer with CuK\(\alpha\) radiation was used to study the structural properties. Surface morphological features were studied by atomic force microscope (AFM), Agilent 5500. The images were acquired at ambient conditions using intermittent contact mode employing a rectangular shaped silicon probe (NSC-15, MikroMasch, USA) having a resonance frequency and force constant of 325 kHz and 45 N/m respectively. Chemical properties for all the samples were studied using JASCO
1600, FTIR spectrometer and Omricon XPS spectrometer. Renishaw Invia laser Raman microscope was used to measure Raman spectrum with laser excitation wavelength of 532 nm. The work function of all the samples was measured using Kelvin probe digital control unit and a dual-channel colour digital storage oscilloscope.

The electrochemical performance for all the samples was measured using BioLogic potentiostat (model: SP 300) workstation with three electrode system at room temperature. Platinum wire and Hg/HgO was used as counter and reference electrode respectively. GO and ion beam irradiated GO on ITO substrate served as working electrode. The cyclic voltamgrams were recorded in an electrolyte containing 5 mM potassium ferricyanide and 5 mM potassium ferrocyanide in 0.01 M KCl which was degassed by N₂ gas. Supercapacitance performance such as cyclic voltamgrams (CV), charge-discharge (CD) and impedance analysis was carried out in 3 M KOH. The specific capacitance ($C_s$) was calculated using the equation 6.1 [20],

$$C_s = \int IdV / (\Delta V \times m \times \nu)$$  \hspace{1cm} (6.1)

Where $\Delta V$ is voltage range of one sweep segment, $m$ is active mass of material, $\nu$ is scan rate and $\int IdV$ area under CV curve. We could have also calculated specific capacitance using below equation 6.2  [20],

$$C_s = (I \Delta t) / (\Delta V m)$$  \hspace{1cm} (6.2)

where $I$ is current density, $\Delta t$ is discharge time after IR drop, $\Delta V$ is applied voltage and $m$ is active mass of material. Electrochemical impedance spectroscopy (EIS) measurement were made by obtaining Nyquist plot in the frequency range from 100 kHz to 100 mHz.

6.3 Results and discussion

6.3.1 Structure and surface morphological studies

XRD of low energy ion beam irradiated GO at a fluence $1 \times 10^{15}$ ions cm$^{-2}$ along with pristine GO is shown in figure 6.1. XRD of H$^+$, N$^+$ and Ar$^+$ ion beam irradiated GO at different fluences from $5 \times 10^{13}$ ions cm$^{-2}$ to $1 \times 10^{15}$ ions cm$^{-2}$ is shown in figure 6.2 (a), (b) and (c) respectively. The characteristic peak of GO was found to be around 10.65° corresponding to (001) plane with d-spacing 0.83 nm [20]. The intensity of this peak decreased with increase in fluence. Also a broad peak
around 25° appears for ion beam irradiated GO with d-spacing 0.35 nm corresponding to (002) plane of rGO [11]. It was observed that the intensity of the (002) plane increased with increase in ion fluence suggesting the formation of more rGO. The intensity of this plane was higher for 200 keV Ar$^+$ ion irradiated GO at a fluence of $1 \times 10^{15}$ ions cm$^{-2}$ compared to 100 keV H$^+$ and 350 keV N$^+$ ions because the Ar$^+$ ion lose more electronic energy in GO than the H$^+$ and N$^+$ ions.

Figure 6.1: XRD of GO and low energy ion beam irradiated GO at a fluence $1 \times 10^{15}$ ions cm$^{-2}$.

Figure 6.2: XRD of (a) H$^+$, (b) N$^+$ and (c) Ar$^+$ ion beam irradiated GO at different fluences along with pristine GO.
The AFM images of pristine, $\text{H}^+$, $\text{N}^+$ and $\text{Ar}^+$ ion beam irradiated GO at a fluence, $1 \times 10^{15}$ ions cm$^{-2}$ are shown in figure 6.3 (a), (b), (c) and (d) respectively. Images reveal the varying surface structures among the samples exposed to different ion beams. The morphology of GO is found to consist of larger flakes with lesser roughness when compared to the ion beam treated flakes. After ion beam irradiation, the change in morphology is seen as smaller flakes with increased roughness of the film. This indicates the formation of exfoliated flakes possessing larger surface area during irradiation induced reduction of GO. The ion beam might have created pores in GO by transferring energy in the form of electronic energy loss [16].

Figure 6.3: AFM images of (a) pristine GO and (b) $\text{H}^+$, (c) $\text{N}^+$, (d) $\text{Ar}^+$ ion irradiated GO at a fluence of $1 \times 10^{15}$ ions cm$^{-2}$. 
6.3.2 FTIR and XPS analysis

The FTIR spectra of H\(^+\), N\(^+\) and Ar\(^+\) ion irradiated GO at a fluence 1 \times 10^{15} ions cm\(^{-2}\) with pristine GO is shown in figure 6.4. The FTIR spectra of H\(^+\), N\(^+\) and Ar\(^+\) ion beam irradiated GO at different fluences in the range from 5 \times 10^{13} ions cm\(^{-2}\) to 1 \times 10^{15} ions cm\(^{-2}\) is shown in figure 6.5 (a), (b) and (c) respectively. GO showed its characteristics peaks around 1059 cm\(^{-1}\), 1410 cm\(^{-1}\), 1608 cm\(^{-1}\) and 1728 cm\(^{-1}\) corresponding to C-O alkoxy stretching, C–O carboxy stretching, aromatic C–C and C=O carbonyl stretching vibrations respectively [11]. The broad absorption band around 3250 cm\(^{-1}\) represents the –OH stretching. As can be seen from figure 6.4, the intensity of C-O alkoxy stretching, C-O carboxy stretching and C=O carbonyl stretching vibrations groups decreased with increase in fluence for all the ion beam irradiated GO. The ion beam may have lost its energy in GO via electronic energy loss results in the chain scission mainly at carbon-oxygen functional groups. It can also be seen from figure 6.4 that the intensity of the peak around 1608 cm\(^{-1}\) corresponding to C-C was not much affected after ion beam irradiation. Further to support this, XPS analysis was carried out for ion beam irradiated GO along with pristine GO and is explained in next paragraph.

![Figure 6.4: FTIR spectrum of pristine, H\(^+\), N\(^+\) and Ar\(^+\) ion beam irradiated GO at a fluence of 1 \times 10^{15} ions cm\(^{-2}\).](image-url)
Figure 6.5: FTIR of (a) H\(^+\), (b) N\(^+\) and (c) Ar\(^+\) ion beam irradiated GO at different fluences along with pristine GO.

The survey scan XPS spectra for GO and low energy ion beam irradiated GO at a fluence of $1 \times 10^{15}$ ions cm\(^{-2}\) is shown in figure 6.6. As can be seen from survey scan XPS spectra, GO showed C/O ratio as 0.71 while H\(^+\), N\(^+\) and Ar\(^+\) ion beam irradiated GO showed C/O ratio as 1.03, 1.19 and 1.87 respectively. The increased
C/O ratio suggests the decrease in oxygen functional groups in ion beam irradiated GO.

Figure 6.6: XPS survey scan of H\(^+\), N\(^+\) and Ar\(^+\) ion beam irradiated GO at a fluence of \(1 \times 10^{15}\) ions cm\(^{-2}\) along with pristine GO.

Figure 6.7: High resolution XPS of C1s for (a) pristine, (b) H\(^+\) irradiated, (c) N\(^+\) irradiated and (d) Ar\(^+\) irradiated GO at a fluence \(1 \times 10^{15}\) ions cm\(^{-2}\).
Figure 6.7 (a), (b), (c) and (d) shows the high resolution XPS of C1s for pristine, H\(^+\), N\(^+\) and Ar\(^+\) ion beam irradiated GO at a fluence 1 \times 10^{15} \text{ ions cm}^{-2} respectively. High resolution XPS of C1s for pristine GO showed peaks around 288.9 eV, 286.9 eV and 284.8 eV corresponding to C=O, C-O and C-C groups respectively. The intensity of these oxygen functional groups viz. C=O and C-O decreased for ion beam irradiated GO indicating the removal of oxygen functional groups from GO. As these oxygen functional groups are radiation sensitive [11], they may have absorbed the energy deposited by ion beam in terms of electronic energy loss results in the breakage of bonds. Similar kind of variation in the oxygen functional groups of GO was observed in our previous study when GO was irradiated by 100 MeV Au ions [11]. Also, Li et al., [20] have also observed the decrease in the intensity of oxygen functional groups of GO when exposed to H\(_2\)/Ar plasma.

6.3.3 Raman spectroscopic analysis

![Raman spectra for (a) H\(^+\), (b) N\(^+\) and (c) Ar\(^+\) ion beam irradiated GO along with pristine GO; (d) plot of I\(_D\)/I\(_G\) ratio versus fluence for different ion beams irradiated GO.](image)

Figure 6.8: Raman spectra for (a) H\(^+\), (b) N\(^+\) and (c) Ar\(^+\) ion beam irradiated GO along with pristine GO; (d) plot of I\(_D\)/I\(_G\) ratio versus fluence for different ion beams irradiated GO.
Figure 6.8 (a), (b) and (c) shows the Raman spectrum of 100 keV H\(^+\), 350 keV N\(^+\) and 200 keV Ar\(^+\) ions irradiated GO respectively along with pristine GO. Pristine GO showed its characteristics D and G bands around 1360 and 1597 cm\(^{-1}\) respectively [21]. The D band corresponds to vacancies, edge defects, grain boundaries, disordered carbon species in graphite layers and G band corresponds to in-plane bond stretching motion of C sp\(^2\) atoms [21]. After irradiation the intensity of both the bands increased with increase in fluence for all the ion species suggesting enhancement in the defects, vacancies, disorder carbon and isolated double bonds. In addition to this, the irradiated GO also showed a broad peak around 2850 cm\(^{-1}\) corresponding to 2D graphene [11]. The intensity of this peak also increased with increase in ion fluence confirming more reduction of GO. The intensity ratio of D to G band (I\(_D\)/I\(_G\)), which is a measure of disorder parameter, were calculated for all the samples and are tabulated in Table 6.2. The crystallite size (L\(_a\)) of graphene flakes in low energy ion irradiated GO can then be calculated from I\(_D\)/I\(_G\) ratio using Tuinstra-Koenig relation i.e. equation 6.3 [22],

\[
\frac{I_D}{I_G} = \frac{C(\lambda)}{L_a}
\]

where \(C(\lambda) = (2.4 \times 10^{-10} \text{ nm}^3)\lambda^4\), \(\lambda = 532\) nm. The calculated values of L\(_a\) for irradiated GO along with pristine GO are tabulated in Table 6.2 from which it is seen that the I\(_D\)/I\(_G\) ratio is more for 200 keV Ar\(^+\) ion and indicates the maximum damage in GO can be achieved by the ions which is having more electronic energy loss. Figure 6.8 (d) shows plot of I\(_D\)/I\(_G\) ratio versus fluence for different ions. It is observed from figure 6.8 (d) that I\(_D\)/I\(_G\) ratio increases nearly exponentially with fluence which is consistent with pertinent literature [23]. In all the cases, the I\(_D\)/I\(_G\) ratio reached saturation because of the effective annihilation of defects as the disordered ion-track regions begin to overlap. This increases in the I\(_D\)/I\(_G\) ratio suggests the decrease in crystallite size of sp\(^2\) domains of GO. Table 6.2 indicates that the crystallite size value decreased from 23.44 nm to 17.32 nm, 17.8 nm and 19.42 nm for 200 keV Ar\(^+\), 350 keV N\(^+\) and 100 keV H\(^+\) respectively. This decrease in the crystallite size suggests the formation of large of small sp\(^2\) domains. Mishra et al., [23] have reported that the decrease in crystallite size is attributed to irradiation induced fragmentation and is more efficient at the boundary or edges of the flakes.
Table 6.2: I_D/I_G ratio and crystallite size (L_a) values of GO and low energy ion beam irradiated GO.

<table>
<thead>
<tr>
<th>Fluence (ions cm⁻²)</th>
<th>I_D/I_G</th>
<th>L_a (nm)</th>
<th>I_D/I_G</th>
<th>L_a (nm)</th>
<th>I_D/I_G</th>
<th>L_a (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pristine</td>
<td>0.82</td>
<td>23.44</td>
<td>0.82</td>
<td>23.44</td>
<td>0.82</td>
<td>23.44</td>
</tr>
<tr>
<td>5 × 10¹³</td>
<td>0.96</td>
<td>20.02</td>
<td>0.92</td>
<td>20.89</td>
<td>0.85</td>
<td>22.62</td>
</tr>
<tr>
<td>1 × 10¹⁴</td>
<td>1.05</td>
<td>18.31</td>
<td>1.02</td>
<td>18.48</td>
<td>0.93</td>
<td>20.67</td>
</tr>
<tr>
<td>5 × 10¹⁴</td>
<td>1.09</td>
<td>17.63</td>
<td>1.07</td>
<td>17.96</td>
<td>0.99</td>
<td>19.42</td>
</tr>
<tr>
<td>1 × 10¹⁵</td>
<td>1.11</td>
<td>17.32</td>
<td>1.08</td>
<td>17.80</td>
<td>0.99</td>
<td>19.42</td>
</tr>
</tbody>
</table>

6.3.4 Work function of low energy ion irradiated GO

![Figure 6.9: Variation of work function with fluence for different ion beams.](image)

The work functions of GO and low energy ion irradiated GO were measured to correlate ion induced defects with electronic properties. The work function was measured using kelvin four probe method. The obtained values of the work functions are plotted against ion fluence and are shown in figure 6.9. It can be observed from figure 6.9 that the work function of pristine GO is 4.65 eV which is in good agreement with published values [24]. The work function increases exponentially...
with increases in fluence as seen from figure 6.9 and it can be explained as follows. During irradiation, the ion beam deposits energy in GO in the form of electronic stopping power leading to the creation of defects sites in GO and creation of large number of small sp² domains as studied by Raman spectroscopic studies. These sp² domains/defects sites acts are responsible for the increase in work function [23]. The increase in work function is higher for Ar ion irradiated GO indicating the more reduction of GO in this case corroborating the explanation in above sections.

6.3.5 Electrochemical analysis

The electrochemical analysis of GO along with low energy ion beam irradiated GO was carried out in 5 mM potassium ferrocyanide and 5 mM potassium ferricyanide in 0.01 M KCl. Figure 6.10 (a), (b) and (c) shows cyclic voltammograms at a scan rate of 100 mVs⁻¹ for 100 keV H⁺, 350 keV N⁺ and 200 keV Ar⁺ ion beam irradiated GO respectively at different fluences. It can be seen that all the CV curves showed a couple of redox peaks. The oxygen functional groups viz. carbonyl, carboxyl and quinine groups persisting on the surface of GO are responsible for the redox peaks in CV curves. The reduction and oxidation caused by these functional groups in electrolyte solution may be expressed as follows for carbon based materials [20,25],

Quinone + 2H⁺ + 2e⁻ → hydroquinone

It can also be observed that the current for both reduction and oxidation peak increases with increase in ion fluence indicating the removal of more oxygen functional groups as depicted from XPS analysis and increase in sp² domains as studied by Raman spectroscopic analysis. These increased sp² domains with many cross linked connections facilitates the ion and electron transport. Figure 6.10 (d) shows CV curves for H⁺, N⁺ and Ar⁺ ion beam irradiated GO at a fluence of 1 × 10¹⁵ ions cm⁻². It can be observed that at a particular fluence, both reduction and oxidation peak current increased in the following way, H⁺ > N⁺ > Ar⁺. The more current response in case of Ar⁺ ion irradiated GO is due to its more electronic energy loss compared to N⁺ and H⁺ ion irradiated GO.
Figure 6.10: Cyclic voltammograms at a scan rate of 100 mVs$^{-1}$ for (a) 100 keV H$^+$, (b) 350 keV N$^+$ and (c) 200 keV Ar$^+$ ion beam irradiated GO at different fluences; (d) Cyclic voltammograms of GO and low energy ion beam irradiated GO at a fluence of $1 \times 10^{15}$ ions cm$^{-2}$. Electrolyte used was 5 mM potassium ferrocyanide and 5 mM potassium ferricyanide in 0.01 M KCl.

Further, the supercapacitance performance of pristine and ion beam irradiated GO was carried out in 3 M KOH aqueous solution. The CV curves for H$^+$, N$^+$ and Ar$^+$ ion beam irradiated GO at different scan rates is shown in figure 6.11 (a), (b) and (c) respectively. It can be observed from figure 6.11 that all CV curves showed both anodic and cathodic peaks, the current of which increased with increase in ion fluence indicating the reduction of more GO supporting XPS and Raman explanation. Li et al., [20] have reduced graphene oxide by H$_2$/Ar plasma treatment and observed enhancement in specific capacitance of GO to 185.2 Fg$^{-1}$ at a scan rate of 100 mVs$^{-1}$. Recently, Bai et al., [16] have reported that, by using ion beam irradiation nanopores of tunable geometries can be produced in graphene. Even they also argued that the nanopores formation in graphene also depend up on the energy of incident ion beam. The charges can be stored in these nanopores results in the enhancement in the specific capacitance of GO. This is also supported by the increase in work function of
GO after irradiation compared to pristine GO. The enhanced work function for ion beam irradiated GO suggests that this GO will hold more charges inside it results in the enhancement in specific capacitance. In addition to this, the increased numbers of small sp$^2$ domains provide a low resistant network for charge transfer within the electrode, while the inductive effects aroused from the oxygen atoms will cause the polarization of some C–C bonds. As a result, the reversible redox reactions are likely to take place on these polarized sites during charging/discharging processes.

Figure 6.11: Cyclic voltammograms of (a) GO, (b) H$^+$, (c) N$^+$ and (d) Ar$^+$ ion beam irradiated GO. Electrolyte used as 3 M KOH aqueous solution.

Figure 6.12 (a) shows CV curves at a scan rate 100 mVs$^{-1}$ for GO and low energy ion beam irradiated GO at a constant fluence of $1 \times 10^{15}$ ions cm$^{-2}$. It can be observed that GO showed deprived electrochemical performance because of its insulating property. However, ion beam irradiated GO showed more electrochemical performance at the same scan rate and at the same ion fluence than of pristine GO. It is worth noting that both current (i.e. anodic and cathodic peak current) and integrated area under CV curve were increased for all ion beam irradiated GO compared to pristine GO. Such ameliorating capacitive behavior might presumably benefit from the electrochemical active sites by deoxygenation and the improved conductivity by
ion beam irradiation. It is also very interesting to observe that Ar$^+$ ion beam irradiated GO showed more electrochemical performance compared to N$^+$ and H$^+$ ion beam irradiated GO. The more electronic energy loss of Ar$^+$ compared to that of N$^+$ and H$^+$ ions in GO might be responsible for the more deoxygenation in GO resulting in the more conductive network and enhanced electrochemical performance. The specific capacitance ($C_s$) of GO and ion beam irradiated GO at a fluence of $1 \times 10^{15}$ ions cm$^{-2}$ were calculated as explained in experimental section. The $C_s$ for Ar$^+$ ion beam irradiated GO was found to be 202 Fg$^{-1}$ while that of N$^+$ and H$^+$ were found to be 195 Fg$^{-1}$ and 180 Fg$^{-1}$ respectively at a scan rate of 100 mVs$^{-1}$. The more specific capacitance for Ar$^+$ ion beam irradiated GO than of N$^+$ and H$^+$ ion beam irradiated GO supporting the above explanation. The obtained specific capacitance of ion beam irradiated GO is compared with specific capacitance of GO reduced by other techniques and is tabulated in Table 6.3 [20,26-31]. The specific capacitance obtained in this study is considerable compared to other techniques. The reduction of GO by ion beam irradiation technique is simple, clean and doesn’t require high temperature and harsh reducing agent. Also, the specific capacitance of rGO can be tuned by varying the ion beam and ion fluence.

Figure 6.12 (b) shows galvanostatic charging-discharging (CD) curves at a current density of 0.5 Ag$^{-1}$ for GO and low energy ion beam irradiated GO at a fluence of $1 \times 10^{15}$ ions cm$^{-2}$. It is observed from figure that the all the CD curves showed nearly triangular shape indicating the electric double layer capacitance behaviour. At the beginning of discharging process, all ion beam irradiated GO showed a less IR drop indicating that ion beam irradiated GO has less internal resistance which is important for supercapacitance devices since less energy would be wasted to produce undesired heat. The specific capacitance was also calculated using equation (2) and it is found to be 15, 53, 63 and 131 Fg$^{-1}$ respectively for GO, 100 keV H$^+$, 350 keV N$^+$, 200 Ar$^+$ irradiated GO at 0.5 Ag$^{-1}$. The enhanced specific capacitance of ion beam irradiated GO may be due to increased work function, creation of nanopores which will store more charges and formation of large number of small sp$^2$ domains i.e. restored graphene structure that promotes electron and ion migration during the charge/discharge process.
Figure 6.12: (a) Cyclic voltammograms at a scan rate 100 mV s\(^{-1}\), (b) Charge-Discharge at a current density 0.5 A g\(^{-1}\), (c) electrochemical impedance spectroscopy and (d) Capacitance retention (%) of low energy ion beam irradiated GO (1 \(\times\) 10\(^{15}\) ions cm\(^{-2}\)) and pristine GO. (Inset of Figure (c): Equivalent Randels circuit).

Electrolyte used was 3 M KOH aqueous solution.

Table 6.3: Comparison of obtained specific capacitance of ion beam irradiated GO with that of specific capacitance of GO reduced by other techniques.

<table>
<thead>
<tr>
<th>Reduction method</th>
<th>Electrolyte</th>
<th>Cs (F g(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)/Ar plasma treated</td>
<td>6 M KOH</td>
<td>185 (100 mV s(^{-1}))</td>
<td>20</td>
</tr>
<tr>
<td>thermal</td>
<td>1 M BF(_3)/PC</td>
<td>112 (5 mV s(^{-1}))</td>
<td>26</td>
</tr>
<tr>
<td>Chemical</td>
<td>30 wt % KOH</td>
<td>205 (50 mV s(^{-1}))</td>
<td>27</td>
</tr>
<tr>
<td>Microwave</td>
<td>5 M KOH</td>
<td>175 (0.6 A g(^{-1}))</td>
<td>28</td>
</tr>
<tr>
<td>electrochemical</td>
<td>0.1 M Na(_2)SO(_4)</td>
<td>136.8 (100 mV s(^{-1}))</td>
<td>29</td>
</tr>
<tr>
<td>Microbe</td>
<td>0.5 M Na(_2)SO(_4)</td>
<td>117 (1.0 A g(^{-1}))</td>
<td>30</td>
</tr>
<tr>
<td>using urea</td>
<td>6 M KOH</td>
<td>175 (0.5 A g(^{-1}))</td>
<td>31</td>
</tr>
<tr>
<td>Ion beam (Ar(^+))</td>
<td>3 M KOH</td>
<td>202 (100 mV s(^{-1}))</td>
<td>Present work</td>
</tr>
<tr>
<td>Ion beam (N(^+))</td>
<td>3 M KOH</td>
<td>195 (100 mV s(^{-1}))</td>
<td>Present work</td>
</tr>
<tr>
<td>Ion beam (H(^+))</td>
<td>3 M KOH</td>
<td>180 (100 mV s(^{-1}))</td>
<td>Present work</td>
</tr>
</tbody>
</table>
Electrochemical impedance spectroscopy (EIS) was used to study the charge transfer and transport mechanism for GO and ion beam irradiated GO. Figure 6.12 (c) shows the Nyquist plots for GO and low energy ion beam irradiated GO at a fluence of $1 \times 10^{15}$ ions cm$^{-2}$. It can be seen from figure 6.12 (c) that all curves showed semicircle at higher frequencies and nearly straight line at lower frequencies. The ion beam irradiated GO showed less semicircle compared to pristine GO suggesting the less internal resistance in turn indicates more specific capacitance corroborating the cyclic voltammograms and galvanostatic charge-discharge analysis. Among all ion beam irradiated GO, Ar$^+$ ion beam irradiated GO showed less semicircle suggesting the less internal resistance than of other ion beams irradiated GO. Therefore, Ar$^+$ ion beam irradiated GO showed more specific capacitance due to its more $S_e$ in GO compared to $S_e$ of other ion beam in GO.

The EIS spectra were also analysed using semi quantitative fitting program supplied along with BioLogic potentiostat (model: SP 300) on the basis of the Randles equivalent circuit modelling shown in inset of figure 6.12 (c). The Randles equivalent circuit comprised of five elements, the internal resistance ($R_1$), electrical double layer capacitance at the interface of electrode and electrolyte ($C_1$), charge transfer resistance ($R_2$), Warburg impedance ($W_Z$) and pseudocapacitance ($C_2$) which used to account for the faradic reaction. These values were calculated qualitatively from the fittings (mean error of modulus ~0.76%) of experimental EIS spectra and are tabulated in Table 6.4. It can be observed that the internal resistance ($R_1$) is less for Ar$^+$ ion beam irradiated GO than of other ion beam irradiated GO supporting the above explanation. The lower internal resistance may be due to the development of internal nanopores structure in GO during ion beam irradiation [16]. In turn this results also supported by lower value of charge transfer resistance ($R_2$) for Ar$^+$ ion beam irradiated GO compared to other ion beam irradiated GO indicating the significant nanopores distribution. This processes may help to reduce the intrinsic resistance ($R_1$) via development of large number of nanopores structure. The subsequent interpretation is in the increase in kinetics of electron transfer through redox process leading to increase in pseudocapacitance ($C_2$) in ion beam irradiated GO. The lower value of Warburg impedance is attributed to diffusion of electrolyte in nanopores structure of electrode material at lower frequency.
Table 6.4: Electrochemical parameters of different ion beam irradiated GO obtained from impedance analysis based upon the proposed equivalent Randel circuit

<table>
<thead>
<tr>
<th>Ion beam</th>
<th>$R_1$ (Ω)</th>
<th>$R_2$ (Ω)</th>
<th>$C_1$ (mF)</th>
<th>$C_2$ (F)</th>
<th>$W_z$ (Ωs$^{-0.5}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>1.12</td>
<td>6.24</td>
<td>6.89</td>
<td>0.33</td>
<td>0.19</td>
</tr>
<tr>
<td>H$^+$</td>
<td>1.01</td>
<td>5.49</td>
<td>8.12</td>
<td>0.49</td>
<td>0.25</td>
</tr>
<tr>
<td>N$^+$</td>
<td>0.89</td>
<td>5.06</td>
<td>9.36</td>
<td>0.58</td>
<td>0.39</td>
</tr>
<tr>
<td>Ar$^+$</td>
<td>0.74</td>
<td>4.82</td>
<td>10.28</td>
<td>0.64</td>
<td>0.52</td>
</tr>
</tbody>
</table>

Furthermore, the cyclic stability of Ar$^+$, N$^+$ and H$^+$ ion beam irradiated GO at a fluence of $1 \times 10^{15}$ ions cm$^{-2}$ has been carried out over 1000 cycles and is shown in figure 6.12 (d). It can be seen that the capacitance retained by 77%, 69% and 65% by Ar$^+$, N$^+$ and H$^+$ ion beam irradiated GO respectively. The observed large capacitance retention of 200 keV Ar$^+$ ion beam irradiated GO compared with 350 keV N$^+$ and 100 keV H$^+$ ion beam irradiated GO is due to more reduction of GO as Ar$^+$ ion beam electronic energy loss is more than N$^+$ and H$^+$ ion beams.

6.4 Conclusions

GO was reduced by low energy ions via 100 keV H$^+$, 350 keV N$^+$ and 200 keV Ar$^+$ ions. XRD results showed the reduction of GO and formation of rGO. FTIR and XPS analysis revealed the removal of oxygen functional groups from GO after low energy ion beam irradiation. Raman spectroscopic results showed the increase in $I_D/I_G$ ratio with increase in fluences indicating decrease in the crystallite size of sp$^2$ domains. The specific capacitance has increased for irradiated GO corroborating the increased work function for irradiated GO. Also, 200 keV Ar$^+$ ions irradiated GO showed more specific capacitance compared to 100 keV H$^+$ and 350 keV N$^+$ ions irradiated GO due to its more electronic energy loss in it than of other ions. The reduction of graphene oxide by low energy ion irradiation is confirmed as a reliable method by which graphene based materials can be produced.
References


