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Defected graphene nano-platelets for enhanced hydrophilic nature and visible light-induced photoelectrochemical performances

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ABSTRACT

This paper reports an optimized electron beam irradiation (60 kGy and 90 kGy) approach for defects-related engineering of graphene nano-platelets for optical and structural properties dependent photoelectrochemical performances. The defects in the electron beam irradiated pristine graphene nano-platelets were studied, analyzed and confirmed using standard characterization techniques such as, diffuse reflectance spectroscopy (DRS), X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), Brunauer-Emmett-Teller (BET), high resolution-transmission electron microscopy (HR-TEM) and contact angle measurements. DRS clearly revealed the increment in the absorption band using electron beam irradiation doses of 60 kGy and 90 kGy. Contact angle measurements confirm the additional hydrophilic nature of the defects engineered graphene nano-platelets in comparison with pristine graphene. The photoelectrochemical performances such as linear sweep voltammetry and electrochemical impedance spectroscopy further confirms the enhancement in the optical, spectroscopic, and photoelectrochemical properties of the 90 kGy defected graphene in comparison to pristine graphene nano-platelets. Therefore, the proposed method is a reliable way of fine-tuning the properties (optical, spectroscopic and photoelectrochemical) of pristine graphene nano-platelets using electron beam irradiation for enhanced photoelectrochemical performance.

1. Introduction

Graphene nano-platelets is a one-atom thin two-dimensional (2D) structure of carbon atoms that is highly conducting (~2.02 x 10^6 S cm⁻¹). In addition, it has an extremely high charge carrier mobility (200000 cm² V⁻¹ s⁻¹), enormous specific surface area, high transparency, and great mechanical strength [1,2]. This substance is considered one of the most promising materials for the next generation of optoelectronic materials on account of its extremely high charge carrier mobility. On the other hand, graphene nano-platelets lack a suitable band gap around the Fermi level, which is a decisive feature of semiconducting materials and essential for controlling the conductivity by electronic means [2,3]. Therefore, graphene nano-platelets are expected to be an ideal material for photo-electronic applications, energy storage and conversions [1–4]. The unique sheet-like structure gives graphene a range of superior properties, such as high charge carrier transport and thermal conductivity [1,5,6] good transparency, great mechanical strength, inherit flexibility, and huge specific surface area (SSA) [7–9]. Therefore, graphene nano-platelets has attracted considerable attention in recent years in the fields of optoelectronics and micro/nanoelectronics devices [4,10,11] energy storage materials [9,12,13] electrocatalysts [14,15] polymer composites [16] and ultra-strong paper-like materials [17–20].

Up-to-date studies have shown that pristine (defect-free) graphene nano-platelets exhibit an ultra-high elastic modulus and unsurpassed strength [1,2]. Recently, it was reported that the electrical conductivity of pristine graphene nano-platelets can be modified by metal ion doping, adding impurities, noncovalent modifications, and chemical functionalization [21–23]. Pristine graphene nano-platelets have a Young’s modulus of ~1 TPa and a tensile strength of more than 100 GPa [24,25]. Graphene nano-platelets and its composites are used for a range of potential applications, such as chemical sensors, ultra-capacitors, transparent electrodes, photovoltaic cells and biodetectors [26–34]. On the other hand, the emergence of defects in the graphene nano-platelets lattice is inevitable either because of the production process or because of the environmental and operating conditions under which the graphene material based device operates [35–37]. Very few studies have shown that electron beam irradiation can be used for the synthesis of different metal nanoparticles and thin films of metal oxides with the desired properties [38,39]. This approach has
several advantages over other methods as a defects engineer, such as an ability to interact effectively with the materials through coulomb interactions produced by charged particles, i.e., electrons [38–40].

Defects engineering in pristine graphene nano-platelets is performed not only to modify its properties, but also to extend its functionality by providing sites for chemical reactions, which involves the intentional self-doping at specific points [1,41–43]. If a large number of atoms are missing from the pristine graphene nano-platelets, the defect configurations could become more complicated, and the graphene nano-platelets could be energetically unstable. If the number of missing atoms is even, the carbon atoms could be reconstructed completely, leaving no dangling bonds. In contrast, if an odd number of atoms are missing, there will be dangling bonds that make the graphene more unstable and provide reactive sites [44]. These dangling bonds in the graphene nano-platelets layers could be useful sites for doping with impurities or functionalizing them with different atoms or molecules for other types of graphene nano-platelets based applications. Defective graphene nano-platelets are also used in nanoelectronic applications for opening a band gap [45]. Band gap opening can be interpreted in terms of either the hybridization of the electronic state at the K and K’ points in the Brillouin zone or symmetry breaking of the A and B sublattices by external or internal perturbation [46]. Given that defects are ubiquitous in the operational environment of graphene nano-platelets based devices, it is important to understand how the defects in graphene nano-platelets affect its elastic properties and intrinsic strength. Several studies have revealed the formation and structural evolution of defects in graphene using both experimental and theoretical tools [47–49]. On the experimental side, however, few studies have examined how the density and type of defects affect the mechanical properties of graphene using an electron beam as a defects engineer [48,49]. Therefore, it is important from a fundamental standpoint and for practical applications to understand how the optoelectronic properties of graphene nano-platelets can be influenced by defects formed by electron beam irradiation. The contact angle measurement could be an effective technique to check the hydrophobic/hydrophilic nature of pristine graphene nano-platelets or graphene related material [22]. The interaction of pristine graphene nano-platelets with aqueous solution of salts strongly depends on the wetting properties of graphene nano-platelets. Pristine graphene has already been recognized as a hydrophobic material [50]. However, quantitative knowledge of its wetting properties is still missing. Therefore, the specific standard characterization of these properties is of crucial importance and became a topic of investigation recently [22,50]. Electron beam irradiation offers the possibility to improve the aqueous dispersibility of pristine graphene nano-platelets, which means an improvement in hydrophilicity. In this study, according to the author's knowledge, this is the first report of the use of an electron beam technique at optimum doses like, 60 kGy and 90 kGy to produce defects in pristine graphene nano-platelets in an aqueous dispersion in a controlled manner. For example, devices made from a zero band gap material are difficult to switch off, losing the advantage of the slow static power consumption of complementary metal oxide semiconductor (CMOS) technology [51]. Therefore, maintaining sizeable and well-tuned optical properties in graphene nano-platelets is particularly important with the materials through coulomb interactions produced by charged particles, i.e., electrons [38–40].

Pristine graphene nano-platelets were purchased from Iljin Nano Tech, Seoul, Korea (7–8 layers graphene with mean length of 500 nm). Ethanol (C2H5OH) was acquired from J. T. Baker. Sodium sulfate (Na2SO4) was supplied by Duksan Pure Chemicals Co. Ltd., South Korea. Ethyl cellulose and α-terpineol were obtained from KANTO Chemical Co. Fluorine-doped transparent conducting oxide glass (FTO; F-doped SnO2 glass; 7 Ω/sq) was purchased from Pilkington. The above mentioned reagents used in this study were of analytical grade and used as received. All solutions were prepared from DI water obtained using a PURE ROUP 30 water purification system.

2.2. Methods

An electron beam accelerator (ELV-0.5, BINP, Russia) with a maximum beam power, maximum beam current, and maximum beam energy of 28 kW, 40 mA, and ~0.7 MeV, respectively, was used to modify the pristine graphene. The UV–Vis diffuse reflectance spectra (DRS) of the powdered samples were obtained using a UV–vis–NIR double beam spectrophotometer (VARIAN, Cary 5000, U.S.A.) equipped with a diffuse reflectance accessory. XRD (PANalytical X’pert PRO-MPD, The Netherlands) was performed using Cu Ka radiation (λ=0.15405 nm). Raman spectroscopy was performed on a HR800 UV Raman microscope (Horiba Jobin-Yvon, France). XPS (ESCALAB 250 XPS System, Thermo Fisher Scientific U.K.) was conducted using the following X-ray source: monochromated Al Kα, λv = 1486.6 eV, X-ray energy: 15 kV, 150 W and spot size: 500 μm at KIBSI. The microstructures of the samples were measured by HRTEM (JEM-2100 JEOL) at an operating voltage of 200 kV. Selected-area electron diffraction (SAED) images were recorded by HRTEM. The BET specific surface area of the samples was measured using a Belsorp II mini (BEL, Japan Inc.). The contact angles were measured using a video based contact angle device, OCA-20 (Dataphysics, Germany).

The photoelectrochemical measurements, such as LSV (photocurrent) and EIS (impedance) were conducted using a 400 W lamp with an intensity of 31 mW/cm2 (3 M, λ > 420 nm, USA). The LSV and EIS measurements were performed using a potentiostat (Versa STAT 3, Princeton Research, USA) comprising of a standard three-electrode system. Ag/AgCl (3 M KCl), a Pt gauge and FTO glass coated with pristine graphene, 60 kGy-graphene and 90 kGy-graphene, were used as the reference, counter and working photoelectrodes, respectively. The experiment was performed in a 0.2 M Na2SO4 solution as the electrolyte at room temperature. The projection area of the photodec- trode was 1 cm2. The working electrodes for CV were prepared as follows: 50 mg of each sample was mixed thoroughly by adding 0.05 g ethyl cellulose as a binder and 0.05 g of α-terpineol as the solvent for preparing a paste. The obtained paste was then coated on carbon paper using the doctor-blade method and dried overnight under a 60 W lamp. The resulting electrode was used as a photoelectrode.

2.3. Defects engineering in pristine graphene nano-platelets using electron beam irradiation

Pristine graphene nano-platelets was modified using an electron beam accelerator in integral mode with electron beam energy of 0.7 MeV and an initial electron beam current of 2 mA/sec in DI water at room temperature and atmospheric pressure. Two 75 mL aqueous dispersions of pristine graphene nano-platelets (0.25g) were prepared using a low sonication system (Branson 2800, low power sonication instrument). The initial pH of the aqueous dispersions was 7.61. The
final pH of the aqueous dispersions was 3.76 and 4.17 after exposure to electron beam doses of 60 kGy, (power 1848 mA s and real time 16.46 min) and 90 kGy (power 2724 mA s and real time 23.40 min), respectively. The resulting dispersions were centrifuged and washed twice with DI water in both cases. The 60 kGy-graphene and 90 kGy-graphene powdered samples were dried overnight in an oven at 60 °C for further characterization.

2.4. Photoelectrochemical measurements (LSV and EIS)

The photoelectrochemical measurements of the pristine graphene nano-platelets, 60 kGy-graphene and 90 kGy-graphene sample were examined by LSV and EIS under ambient conditions in the dark and under visible light irradiation. Both of the experiments were performed in 50 mL of an aqueous 0.2 M Na₂SO₄ solution in the dark and under visible light irradiation at room temperature. The photocurrent response was examined by LSV in the dark and under visible light irradiation at a scan rate of 50 mV s⁻¹ over the potential range of −0.4–1.0 V. EIS was performed in the dark, and later under visible light irradiation (λ > 420 nm) with frequencies ranging from 1 to 10⁴ Hz at 0.0 V vs. Ag/AgCl in potentiostat mode.

3. Results and discussion

Generally, for the functionalization or decoration purposes of graphene nano-platelets or graphene oxides sheets, researchers have used a range of methods, involving various expensive and toxic chemicals that give noxious side products as environmental pollutants. On the other hand, in the present study, an electron beam was used as a green “defect engineer” approach because it is a very helpful tool for producing defects, and imparting novel characteristics, such as tuned optical properties to defected graphene nano-platelets for improved visible light-induced photoelectrochemical performance without producing harmful pollutants [44,45]. This protocol does not involve any expensive and toxic chemicals, which make this modification process quite useful and efficient in the field of the defects engineering of pristine graphene. The entire process took place in DI water at room temperature and under atmospheric pressure.

Fig. 1 presents a schematic model illustrating the defects formed in pristine graphene nano-platelets using electron beam irradiation at doses of 60 kGy and 90 kGy, which is a simple, fast and efficient process [53,54]. The electron beam irradiation process revealed exposed regions of the graphene nano-platelets sheets. The irradiation process was designed in such a way that only the graphene matrix is exposed to the electron beam, while there was no interaction with the side contacts.

3.1. Optical analysis of pristine graphene nano-platelets and defects engineered graphene nano-platelets

The richness of optical properties of pristine graphene nano-platelets attracts enormous interest. Pristine graphene nano-platelets have high mobility and optical transparency. The optical diffuse absorbance/reflectance spectra (DRS) of the pristine graphene nano-platelets and defects engineered graphene (60 kGy-graphene and 90 kGy-graphene) were measured at room temperature over the wavelength range, 200–800 nm and shown by Fig. 2. The absorption spectra shows the absorbance peak at (~246.3 nm), which is generally
due to the exciton-shifted van Hove singularity in the graphene density of states [23]. In defects engineered graphene (60 kGy-graphene and 90 kGy-graphene), the absorption features can be seen at higher visible light absorption region, which is highlighted by circle with arrow as compared to the pristine graphene nano-platelets [55].

The increase in the absorption band in defects engineered graphene (60 kGy-graphene and 90 kGy-graphene) is because of the electrons that are confined to a much smaller space than in a (practically infinite) crystal (or other macroscopic solid state object). Instinctively, from quantum mechanics, this confinement leads to a shift in the energy levels, which can affect the optical properties [56,57]. Graphene has a two dimensional band structure. Therefore, the difference between the highest occupied levels and the lowest unoccupied level (or band of levels) may shift. Accordingly, the optical behaviour is changed when a transition from “infinite” solid to nano-scale material is made [54–57].

### 3.2. Structural analysis of pristine graphene nano-platelets and defects engineered graphene nano-platelets

The phase and purity of the pristine graphene nano-platelets and defects engineered graphene nano-platelets were examined by XRD (Fig. 3) to identify the changes in the phases and structure of the defects engineered graphene. All XRD peaks of pristine graphene nano-platelets, 60 kGy-graphene and 90 kGy-graphene nano-platelets were well matched with the planes (JCPDS No. 79–1470) [23]. The XRD peaks at ~26.53° 2θ (002) and ~54.7° 2θ (100) confirmed that the graphene structure had been maintained. No other peak for any impurity was detected. The XRD patterns of 60 kGy-graphene and 90 kGy-graphene were similar to the pristine graphene nano-platelets except for minor differences in the peak position, peak intensities and peak broadening. This shows that when pristine graphene nano-platelets were treated with electron beam irradiation, the basic structure of pristine graphene had not changed, even though the successive increase in the intensities of 60 kGy-graphene to 90 kGy-graphene indicates an increase in the crystallinity of the structure of the graphene layers. A very small peak shift towards high 2θ angles were observed (inset in Fig. 3), which confirmed the changes or modifications in the graphene layers. This shift was also attributed to the increase in crystallite size of the engineered defective graphene, which further confirmed the defects formed in the pristine graphene nano-platelets using different doses of electron beam irradiation.

The mean crystallite size of the pristine graphene nano-platelets, 60 kGy-graphene and 90 kGy-graphene nano-platelets were calculated using Scherer’s formula, $D = \frac{\beta \lambda}{\sin \theta}$, where $\kappa$ is the shape factor and $\lambda$ is the wavelength (Cu Kα = 0.15405 nm), $\beta$ is the full width at half maximum of the most intense peak (in radians), and $\theta$ is the peak position [23]. The most intense peak of pristine graphene nano-platelets, 60 kGy-graphene and 90 kGy-graphene at 26.53° 2θ, 26.55° 2θ, and 26.63° 2θ revealed a crystallite size of 20.71 nm, 21.95 nm, and 23.50 nm, respectively (Table 1). The most intense peak shift towards a higher 2θ angle indicating an increased crystallite size with increasing electron beam irradiation doses. The peak intensity of the defect engineered graphene (60 kGy and 90 kGy) revealed increased intensity and the lattice parameters $a$ and $c$ in 60 kGy-graphene and 90 kGy-graphene were slightly larger than those of pristine graphene nano-platelets with the increased effect of electron beam irradiation. Therefore, Table 1 lists the experimentally calculated structural parameters, which were obtained from the XRD data. The lattice constant $a$ of pristine graphene nano-platelets were 2.47 Å, whereas $c$ was 6.70 Å and the lattice constants $a$ and $c$ were (a = 2.48, c = 6.71) slightly expanded monotonously in the case of the 60 kGy-graphene and 90 kGy-graphene samples. The slight increase in the lattice parameters suggests that lattice defects had formed in the sample. Extended defects, such as threading dislocations, were also reported to increase the lattice constant [58].

The inset in Fig. 3 shows that the intensity of the peak increased after electron beam irradiation at 60 kGy-graphene and 90 kGy-graphene nano-platelets compared to the pristine graphene nano-platelets, and the crystallite size increased compared to pristine graphene nano-platelets. This suggests that an electron beam could be a good tool for modifying the required XRD parameters of the graphene layers without altering its basic structure.

### 3.3. Raman analysis of pristine graphene nano-platelets and defects engineered graphene nano-platelets

Raman spectroscopy provides valuable information on the electronic and structural properties of graphene nano-platelets. To determine the type and density of defects in the graphene layers quantitatively, the samples were characterized using this technique. In graphene nano-platelets, the Stokes phonon energy shift caused by laser excitation produces two main bands in the Raman spectrum: G (1590 cm$^{-1}$), a primary in-plane vibrational mode, and 2D (2729 cm$^{-1}$), and in a second-order overtone of a different inplane vibration, D (1350 cm$^{-1}$) [23]. The assignment of the D and G peaks is straightforward for a “molecular” picture of carbon materials. These bands are present in all poly-aromatic hydrocarbons [59]. The 2D band position is highly sensitive to the number of layers present in the sample and is one method for determining layer thickness or number of layers. The G peak is due to the bond stretching of all pairs of sp² atoms in both rings and chains. The D peak is due to the breathing modes of sp² atoms in the rings. The D peak was first assigned to an $A_{1g}$ breathing mode at K, activated by the relaxation of the Raman fundamental selection rule q.

### Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>2θ (degree)</th>
<th>Lattice parameters ($\lambda$)</th>
<th>Crystallite size (n.m.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine graphene nano-platelets</td>
<td>26.53</td>
<td>$a = 2.47$</td>
<td>20.71</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$b = 2.47$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$c = 6.70$</td>
<td></td>
</tr>
<tr>
<td>60 kGy-graphene nano-platelets</td>
<td>26.55</td>
<td>$a = 2.48$</td>
<td>21.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$b = 2.48$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$c = 6.71$</td>
<td></td>
</tr>
<tr>
<td>90 kGy-graphene nano-platelets</td>
<td>26.63</td>
<td>$a = 2.48$</td>
<td>23.51</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$b = 2.48$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$c = 6.71$</td>
<td></td>
</tr>
</tbody>
</table>
The peak was then linked to maxima in the vibrational density of states of graphene at the M and K points. As expected, the peak indicates band disorder. The number of layers decreased with increasing doses of electron beam irradiation, while the two dimensional (2D) band slightly shifted and strengthened, which confirms the slight modification in the pristine graphene.

Fig. 4(a) shows the Raman spectra of pristine graphene nano-platelets, 60 kGy-graphene and 90 kGy-graphene nano-platelets at an excitation wavelength of 514 nm. The characteristic peaks of the D and G bands at ~1350 cm$^{-1}$ and ~1590 cm$^{-1}$ were observed. In the case of the 2D band, a broad 2D band at ~2729 cm$^{-1}$ was observed in the spectra. The Raman spectra of the 60 kGy-graphene and 90 kGy-graphene were similar to the pristine graphene except for the peak intensities and broadening, which confirm the defects formed in the pristine graphene nano-platelets [60]. Fig. 4(b) shows the zoom Raman spectra of G bands, in which the intensity and broadening of the G bands decrease with increasing electron beam dose, which further support the defects created in the pristine graphene layers. The ratio of the 2D-G band I(2D)/I(G) is ~1.71, which shows a sp$^3$ defects regime and a decrease in the number of layers of graphene nano-platelets towards the single layer of graphene sheets. The slight peak intensity decreased the 2D band, which supports the decrease in the layer thickness of the electron beam irradiated graphene samples. Several factors might have affected the changes in the Raman band position and broadening including phonon confinement, strain, and broadening associated with the defects creation. These findings further support the DRS and XRD studies and confirm the defect formation in pristine graphene.

### 3.4. XPS analysis of pristine graphene and defects engineered graphene nano-platelets

XPS can be used as a complementary technique for the complete characterization of graphene-based materials. The technique provides information on the chemical quantification, impurity identification, layer thicknesses, and depth composition variations [61].

Fig. 5(a) shows the high resolution survey spectra and the inset shows the O 1 s spectra of all the graphene nano-platelets and defect engineered graphene nano-platelets. Fig. 5(b) shows the C 1 s spectra at the characteristic binding energy (B.E.) of ~284.4 eV for the pristine graphene nano-platelets, 60 kGy-graphene and 90 kGy-graphene samples, in which the peak associated with C 1 s became predominant and a very small peak observed at 533.1 eV for oxygen [23]. The oxygen peak might have appeared because of the interaction of solvent (DI water) with graphene. No any other peaks for other elements were observed except for C and a small amount of O, which indicated the
The intensity of the oxygen peak reduces as electron beam irradiation dose increases, which proves the loss of oxygen and also indicates that the electron beam helps reduce contamination, such as oxygen groups from the edge part of the graphene layers (inset Fig. 5(a)). Fig. 5(b) shows the C 1s peaks associated with the carbon at ~284.4 eV and that the peak intensity is increasing from pristine graphene nano-platelets to 60 kGy-graphene and 90 kGy-graphene sheets samples. This suggests that the electron beam irradiation results in the formation of defects, which are more efficient in the optical properties tuning of highly conducting materials, such as graphene.

3.5. Transmission electron microscopy analysis of pristine graphene nano-platelets and defects engineered graphene nano-platelets

In addition to Raman and XPS analysis, HR-transmission electron microscopy (HR-TEM) characterization was also carried out. In Fig. 6(a) a TEM image of pristine graphene nano-platelets with some overlapped region by inter domain-merging, some folded region but without defects. Fig. 6(b) shows a HR-TEM image that indicates few defects in the pristine graphene nano-platelets sample by 60 kGy electron beam irradiation, which is encircled (yellow colour) in the image, whereas Fig. 6(c) clearly shows defects (representing the defect regime) in the pristine graphene after the 90 kGy electron beam irradiation dose. The orange colour circle representing the defects appeared in the graphene layer. These images confirm that sp$^3$ point defects in the form of holes are generated in the sp$^3$ defect regime. Moreover, the defects in the treated graphene nano-platelets samples increase with increasing dose of electron beam irradiation [62,63]. Fig. 6(d, e and f) shows the elemental mapping (C-K) of the selected area of graphene sheets. Fig. 6(g) presents the energy dispersive spectroscopy (EDS) data of the 90 kGy-graphene sample, which confirmed that mainly carbon atoms are present in the graphene sheets without any other impurities.

3.6. Brunauer-Emmett-Teller and specific surface area analysis of pristine graphene and defects engineered graphene nano-platelets

The Brunauer-Emmett-Teller (BET) surface area and pore volume were obtained from the nitrogen adsorption-desorption measurements. This further supports the engineered defects formed in pristine graphene nano-platelets using 60 kGy and of 90 kGy electron beam irradiation. The specific surface area obtained for pristine graphene, 60 kGy-graphene, and 90 kGy-graphene were 12.7290 ± 0.2446 m$^2$/g, 14.7772 ± 0.5694 m$^2$/g, and 30.5581 ± 0.3141 m$^2$/g, respectively.

Table 2 presents the pore volume of the pristine graphene nano-platelets (0.038249 cm$^3$/g), electron beam irradiated 60 kGy-graphene (0.041042 cm$^3$/g) and 90 kGy-graphene (0.069200 cm$^3$/g), which increases with increasing electron beam dose. The BET measurements (Table 2) shows that surface area and pore volume increase with...
increasing electron beam dose. Therefore, the measured surface areas of the samples are consistent with a previous report showing the separation of graphene layers [62]. For stacked and agglomerated graphene layers or real bulk samples, a significant amount of surface area is unavailable for nitrogen adsorption due to overlap or stacking of graphene layers [64]. Therefore, BET analysis further proves that the pore volume has increased with increasing electron beam irradiation doses. This was attributed to the increase in the properties of the pristine graphene after the defect is formed. The above results prove and further support the defect formation in the electron beam-irradiated graphene nano-platelets.

3.7. Contact angle measurement of pristine graphene nano-platelets and defects engineered graphene nano-platelets

The contact angle measurement is the simple way to report the wetting properties of pristine graphene nano-platelets and graphene related material with respect to water and it is used to measure the contact angle of a water droplet deposited on an isolated graphene surface [50]. The liquid sessile drop method was used to determine the contact angle of the pristine graphene and defects engineered graphene. An image of a water drop formed on the material as a substrate was recorded by a video camera with an initial waiting period of 10 s to stabilize the water drop on the surface of the pristine graphene nano-platelets and the defects engineered graphene (60 kGy-graphene and 90 kGy-graphene) as a substrate. An image analysis system was used to measure the contact angle ($\theta$) from the shape of the water drop [22,50]. Here, static contact angle analysis, as shown in Fig. 7(a, b and c), was performed on the shape of the water drop formed to examine the impact on the hydrophobic/hydrophilic features of the pristine graphene nano-platelets and defects engineered graphene (60 kGy-graphene and 90 kGy-graphene). In Fig. 7(a) pristine graphene displayed a hydrophobic nature and it shows the contact angles of the left 89.6° and right 87.9°, which reflects its hydrophobic nature, whereas for the defects engineered graphene (60 kGy-graphene), Fig. 7(b) shows relatively hydrophilic nature with contact angles of left 72.5° and right 70.2°. It suggests that the hydrophilic characteristic can indeed be obtained by modifying the surface of graphene using electron beam irradiation. Fig. 7(c) displayed the contact angles left 53.2° and right 53.4° and it shows the increment in hydrophilic nature of electron beam treated graphene. The overall contact angle measurement confirms the defects created by electron beam irradiation which further proves the defects engineered graphene displayed hydrophilic in nature. This hydrophilic nature of graphene plays a crucial role in optoelectronic devices.

4. Photoelectrochemical performance measurements (LSV and EIS)

4.1. Photoelectrochemical measurements (LSV and EIS) of pristine graphene nano-platelets and defects engineered graphene nano-platelets

The demand for applications of graphene nano-platelets in optoelectronic and micro/nanoelectronic devices is huge, in which opening the band gap of pristine graphene nano-platelets is the most important issue [65]. Introducing defects by electron beam irradiation is promising for the tuning of optical properties of pristine graphene. In the present study, more attention was paid to an understanding of the defects of graphene in the vicinity of the surface, interface, reactant, and environment, which are responsible for enhanced visible light-induced properties. Electron beam irradiated defects in pristine graphene nano-platelets are also very important, which will provide new insights into the structures and properties of graphene, and boost further exploration of graphene-based micro/nanoelectronics applications [54,65].

<table>
<thead>
<tr>
<th>Sample name</th>
<th>BET surface area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine graphene nano-platelets</td>
<td>12.7290 ± 0.2446</td>
<td>0.038249</td>
</tr>
<tr>
<td>60 kGy-graphene</td>
<td>14.7772 ± 0.5694</td>
<td>0.041042</td>
</tr>
<tr>
<td>90 kGy-graphene</td>
<td>30.5581 ± 0.3141</td>
<td>0.069200</td>
</tr>
</tbody>
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Fig. 7. Static contact angle measurements of (a) pristine graphene nano-platelets and defect engineered (b) 60 kGy-graphene and, (c) 90 kGy-graphene as a substrate.
The photoelectrochemical measurements of the carbon based visible light active material can be determined by the light-harvesting capacity of nanomaterials [66–68]. Complementary information regarding the photocurrent response of the pristine graphene nano-platelets, optimized dose of 60 kGy-graphene and 90 kGy-graphene were obtained from LSV and EIS. LSV was performed over the potential range, –0.3–1.0 V, in the dark and under visible light irradiation to examine the visible light response of the pristine graphene nano-platelets, 60 kGy-graphene and 90 kGy-graphene for photocurrent measurements. Fig. 8(a) presents LSV plots of the pristine graphene nano-platelets, 60 kGy-graphene and 90 kGy-graphene as a photoelectrode under visible light irradiation, in which the 60 kGy-graphene and 90 kGy-graphene showed an enhanced photocurrent performance compared to the pristine graphene nano-platelets. The defects formed by electron beam irradiation can tune the optical properties of pristine graphene nano-platelets, which explain why the 60 kGy-graphene and 90 kGy-graphene samples showed an increase in the visible light induced carrier transport rate.

EIS was performed in the dark and under visible light irradiation to understand the transport properties of pristine graphene nano-platelets, 60 kGy-graphene and 90 kGy-graphene as photoelectrode. Fig. 8(b) shows EIS Nyquist plot ($Z_{\text{real}}$ vs. $Z_{\text{imag}}$) of the pristine graphene nano-platelets, which originates from the resistance and capacitance components of the electrochemical cell. In general, the typical Nyquist plots include one or more semicircular arcs with the diameter along the $Z_{\text{real}}$ axis. The semicircular arc observed in the high and low frequency regions correspond to an electron-transfer process, and its diameter represents electron transfer or charge transfer resistance [68,69]. In the case of 60 kGy-graphene and 90 kGy-graphene, a semicircular arc with a smaller diameter that observed with pristine graphene nano-platelets indicated a rapid electron-transfer process. In particular, the smaller radius of the arc in the EIS spectra indicates smaller electron transfer resistance at the surface of the photoelectrodes, which normally corresponds to faster interfacial charge transfer. The smaller arc radius of the EIS Nyquist plots for 60 kGy-graphene and 90 kGy-graphene (Fig. 8(b)) compared to pristine graphene nano-platelets under visible light irradiation indicates faster interfacial charge transfer at the 60 kGy-graphene and 90 kGy-graphene as a photoelectrode. These results show that electron beam irradiation could be an effective tool for modifying the optical properties of pristine graphene nano-platelets, which enhances the visible light-induced charge transfer efficiency of the 60 kGy-graphene and 90 kGy-graphene. The EIS findings further confirmed that the defects engineered graphene can be used as an effective material for visible light active photoelectrodes. Finally, these results showed that the defects engineered graphene could be used as an effective material for photocurrent, capacitance, and optoelectronic devices.

4.2. Proposed electron transfer mechanism in the dark and under visible light irradiation

Generally, in the case of a semiconducting material, visible light irradiation plays an important role in the excitation of electrons from the valence band to the conduction band. In this case, however, the optimized dose of electron beam engineered defective graphene (60 kGy-graphene and 90 kGy-graphene) shows semiconducting behaviour because of the tuned optical properties. In the photocurrent measurements, two half-reactions occur on the working and counter electrodes. During this process, electrons can be extracted or injected from the electrodes into the electrolyte solution. As shown in Fig. 9, visible light irradiation was focused on the as-prepared electrode, which was dipped in the electrolyte solution. The electrolyte solution acts as a donor or acceptor to contribute or receive electrons from the electrodes. The defects engineered graphene sample showed higher photocurrent performance because of its tuned optical properties compared to the pristine graphene nano-platelets. The counter and reference electrode measure the photocurrent with the help of the electrolyte solution [69,70]. An understanding of the electron transfer mechanism by this novel electron beam-assisted, optical properties and defect-engineered graphene could play an important role in designing a new generation of optoelectronic devices in a low-cost and facile manner.

5. Conclusions

In summary, this paper reports an optimized dose of electron beam irradiation (60 kGy and 90 kGy) approach for defects related engineering in pristine graphene nano-platelets for improved visible light-induced photoelectrochemical performance. The formation of defects was confirmed by DRS, XRD, Raman spectroscopy, XPS, BET, contact angle measurement and HR-TEM. The structural and spectroscopic analyses confirm the purity and quality of the pristine graphene nano-platelets. Optical analyses and contact angle measurements confirm the optical properties and hydrophilic nature of the defect engineered graphene which further supports the enhancement in photoelectrochemical performance. The as-modified defected graphene were tested
for the photocurrent and EIS measurements in the dark and under visible light irradiation to check their performance and indicated an increase in the use charge carrier mobility as well as hand opening properties, which is associated with an increase in the visible light-harvesting ability of the defected graphene. The 90 kGy defected graphene showed improved photocurrent performance than the 60 kGy defected graphene, which may have applications in the fabrication of commercial and industrial optoelectronic and nano/microelectronic devices. Defects engineered graphene can provide a range of options and it will be exciting to witness how defected graphene will revolutionize/expand the materials used for future energy-related applications. These results confirm that the as-modified defected graphene nano-platelets will bring significant advancement for high performance in photoelectrochemical energy systems such as photo based electronic applications.

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References

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