On the origin and tunability of blue and green photoluminescence from chemically derived graphene: Hydrogenation and oxygenation studies

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ABSTRACT

We report on the identification of structural defects and oxygenated functional groups responsible for blue and green photoluminescence (PL) from the chemically derived graphene (CDG) thin films with the help of Raman imaging/spectroscopy, high resolution transmission electron microscopy (HRTEM), Fourier transform infrared spectroscopy (FTIR) and PL analyses. In particular, we probe the role of in-plane and edge oxygenated functionalities on the evolution of visible PL emissions from CDGs after controlled hydrogenation and oxygenation studies. The assignments of the various PL bands were corroborated from thermogravimetric and FTIR analyses in the CDGs and are directly correlated with the Raman analysis. Our studies reveal that the PL emission spectrum in CDGs can be tuned by controlled hydrogen and oxygen treatments. Two green emission bands in the range of ~497–502 nm and ~534–551 nm are assigned to the COOH and C=O sub-band energy states belonging to the edge sites, while the blue emission is attributed to the localised states of sp²/sp³ domains and epoxy related in-plane functional groups in the CDG materials. Our study demonstrates the tunability of PL spectrum from CDG materials through selective manipulation of the functional groups at the in-plane defects and edge sites.

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1. Introduction

Chemically derived graphene (CDG) is a new class of functional carbon nanomaterial that exhibits interesting optical characteristics for the potential applications in the field of photovoltaics, photocatalysis, bioimaging etc. [1–3]. Fabrication of CDG functional materials such as graphene oxide (GO), reduced-GO (rGO), graphene quantum dots (GQD) and graphene oxide nanoribbons (GONR) using chemical approaches and understanding their intriguing photoluminescence (PL) properties are important for the photovoltaic and photoconductive devices, which open up a new era of 2D nanomaterial research [4,5]. The absence of band gap in graphene necessitates the use of CDGs grown by simple chemical methods, which show numerous interesting optical properties by tuning the in-plane and edge oxygen functionalities [6,7]. In CDGs, plenty of oxygenated functionalities are covalently attached at the graphene basal planes as well as at the edges [1]. On the other hand, the graphene grown by conventional chemical vapour deposition (CVD) does not exhibit PL due to large coverage of sp² carbon without any conjugated network of oxygenated functionalities, although it may possess structural defects.

The band gap engineering of CVD graphene and GO ultra-thin films has been explored through various means, such as reactive gas annealing and plasma treatments in certain doping environments (e.g., boron, nitrogen, oxygen and fluorine etc.) to induce visible to near infrared (NIR) PL for optoelectronic applications [8–10]. The CDGs can show enhanced PL emission due to the carbon and oxygen covalent and non-covalent functionalization [1,11]. In fact, the electronic structure of graphene can be altered by chemical approaches depending upon the size distribution of sp² and sp³ domains and by tuning the selective oxygenated surface along with the edge functionalities on pristine graphene layer [12]. The commonly observed oxygenated functional groups that are responsible for the PL in these kind of CDG materials are hydroxyl (–OH), epoxy (O–C–O) and (O–C==C) groups on the basal plane of graphene and ring type functionalities, such as carboxylic (COOH),

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2.1. Growth of graphene by thermal CVD

Large area single layer graphene is synthesized by thermal CVD on a 25 μm thick Cu foil. The full experimental details on CVD growth of graphene is discussed in the supporting information (see section SI1).

2.2. Preparation of chemically derived graphene (CDG)

Simple chemical exfoliation techniques are employed for the preparation of GO based CDG samples with different carbon source materials. The processing steps and full details of the experimental parameters used for the preparation of CDGs are described in the supporting information (Sections SI2, SI3 and SI4).

2.3. Preparation of thin films of CDGs

As prepared CDGs were dispersed in a polar solvent (methanol) followed by a mild tip sonication for controlled dispersion. The CDG solution was spin coated on the quartz and Si/SiO₂ substrates with uniform thickness. The quality of thin films has been assessed primarily by micro-Raman spectroscopy analysis.

2.4. Hydrogenation and oxygenation of CDG samples

For a better understanding of in-plane and edge functional groups on the evolution of PL spectra from CDGs, we have performed the hydrogenation and oxygenation of the powder and thin film samples of CDGs including CVD graphene under the controlled flow of high purity H₂ and O₂ gas, respectively. The samples were kept in an alumina boat and loaded in a tubular quartz chamber inside a muffle furnace. GO and rGO coated on Si/SiO₂ and quartz substrates were annealed under identical conditions. Initially, the chamber was pumped down to a pressure of 4.0 × 10⁻⁶ mbar, and the temperature was ramped up to 550 °C with heating rate 6 °C min⁻¹. The temperature was maintained at 550 °C during the annealing in H₂/O₂ flow. The flow rate for both the gases used for annealing was 200 SCCM (standard cubic centimeters per minute) for the duration of 2 h. Note that the sample codes used for the oxygenated and hydrogenated samples of CDGs are represented by a suffix ‘O’ and ‘H’, respectively. For example, GOO refers to oxygenated GO, GOH refers to hydrogenated GO etc.

3. Characterizations

The morphology and crystal structure of CVD graphene and CDG samples are mainly characterized by HRTEM and micro-Raman spectroscopy. Raman measurements have been performed with a high resolution spectrometer (Horiba, LabRam HR) with excitation wavelengths (λex) 514.5 nm (Ar⁺ ion laser) and 632.8 nm (He–Ne laser). Excitation source was focused with 100X objective lens, spot size of 2 μm, laser power 1 mW to avoid laser heating and damage to the sample. The Raman signal was collected by a CCD in a back scattering geometry sent through a multimode fibre grating of 1800 grooves per mm. HRTEM measurements were conducted with a JEOL 2100 (Japan) microscope operating at 200 kV. Degree of oxidation and crystallinity of pristine CDG samples were assessed by an X-ray diffractometer (Rigaku, RINT 2500 TRAX-III, Cu Kz₂ radiation). Photoluminescence (PL) measurements were carried out at room temperature with a commercial fluorimeter (AB2, Thermo Spectronic) using 355 nm and 405 nm external laser excitation sources. The UV–vis–NIR absorption spectroscopy measurements were recorded using a commercial spectrophotometer (Perkin Elmer UV Win Lab, UV–3101PC). TGA measurements have been conducted using an STA 449 F3 Jupiter TGA analyser (Netzsch, Germany) equipped with high temperature tungsten furnace with temperature range from room temperature to 2400 °C. The maximum temperature chosen for TG measurement was 900 °C in a controlled flow (60 SCCM) of high purity oxygen (99.999%) gas atmosphere with a heating rate 5 °C min⁻¹. The initial weight of the CDG sample was taken as 2–3 mg in each measurement. FTIR measurements were carried out using a commercial spectrometer (Perkin Elmer, Spectrum BX) with KBr as a reference. Thin circular KBr pellets of diameter 10 mm were prepared by using KBr pellet machine for the FTIR measurement.
4. Results and discussions

4.1. Raman studies of CVD graphene and CDGs

Raman spectroscopy is an important non-destructive tool to evaluate the crystal structure and covalently attached surface moieties on the \( sp^2 \) and \( sp^3 \) carbon nanomaterials. From Raman finger prints and Lorentzian line shape analyses, we have probed the structural imperfections arising from the intrinsic defects and oxygenated functionalities on graphene basal plane and edges. The intrinsic defects are naturally grown during the CVD growth process and are unavoidable. In case of CDGs, various oxygenated functional groups selectively nucleate on the basal plane as well as at the edges of CDGs during the oxidation/reduction with KMnO4, \( \text{H}_2\text{SO}_4 \) and \( \text{HNO}_3 \). This creates a continuous disruption of \( \pi \) network on the basal plane and graphene interlayers depending upon its \( sp^2 \) and \( sp^3 \) crystallite size. In general, the covalent attachment of these functionalities preferentially takes place at the defect sites and \( sp^3 \) carbon domains. Fig. 1 presents a comparison of Raman spectra for defect free graphene (GR), defective single layer graphene (DGR) and CDG functional materials. Note that the Raman spectra are scanned with 514.5 nm laser excitation for all the samples at room temperature. The atomic models of CDGs corresponding to each spectrum are presented on the right side panel of Fig. 1. These atomic models were simulated from Atomic Model Kit (ATK 11.8.2, Quantumwise) software. The Raman spectrum of bulk graphite film (GF) is shown in Fig. 1(a) for comparison. Note that the absence of D band and a sharp symmetric G band in GF imply the highly ordered graphitic layers (\( sp^2 \) hybridized) present in the starting carbon precursor. The nature of intrinsic defects in the CVD grown GR is shown in Fig. 1(b) and (c). The most commonly identified in-plane and edge defects that are formed in the CVD growth are carbon vacancies (e.g., single, bi- and multiple), extended defects (line, edge reconstruction due to the weak dangling bonds leading to formation of pentagon and heptagon defects). Various kinds of such defects are schematically represented by the atomic models as shown in Fig. 1 [18].

Further, the characteristic Raman features of GO, rGO, GQD and GONR, such as broad D (1350 cm\(^{-1}\)), G (1595 cm\(^{-1}\)), D’ (1620 cm\(^{-1}\)), 2D (2700 cm\(^{-1}\)), D + D’ (2940 cm\(^{-1}\)) and 2D’ (3240 cm\(^{-1}\)) bands are shown in Fig. 1(d, e, f, g), respectively and these bands signify the presence of both \( sp^2 \) and \( sp^3 \) carbons. In CDGs, the variation of these carbon bonds is associated with the oxygenated surface functionalities. Interestingly, in the case of QGD and GONR, an additional sharp feature (D’) at the higher frequency side of the D band at \(-1450 \text{ cm}^{-1}\) has been found, for the first time (see Fig. 1(f–g)) and it is tentatively assigned to the covalently attached carboxyl (COOH) and carbonyl (C=O) functional groups at the edges of GQD and GONR. Note that D’ band is absent in case of GO and rGO samples. Our FTIR studies along with the TGA/DTG studies reveal that the COOH functional groups can be removed partially after oxygenation/hydrogenation, while C=O functionalities can covalently rearrange due to weak dangling bonds of carbon atoms. This might be due to the lower thermal stability of COOH compared to that of the C=O functionalities [19].

In general, the carbon atoms present at the graphene edges are bonded with weak dangling bonds that usually take part in the edge reconstruction. Edge atoms are primarily observed in GQD and GONR due to their edge confinement at the weakly bonded C–C edges [20,21]. Tuning these edge sites with oxygen or nitrogen by controlled chemical or physical functionalization will allow wide range of PL in the visible to NIR wavelength in GQD and GONR samples [20,22]. In the present case, GQD and GONR samples show a strong green PL emission due to the attachment of COOH and C=O functionalities at the edges. Note that the COOH and/or C=O functionalities are distinguished based on their FTIR signatures and the thermal stability of the functional groups at the edges in pristine and hydrogenated GQD and GONR through the TGA analysis.

![Fig. 1. Typical Raman spectra of different CDG materials: (a) graphite flake (GF), (b) pristine CVD graphene (GR), (c) defective CVD graphene (DGR), (d) GO, (e) rGO, (f) GQD, and (g) GONR. The characteristic Raman modes are denoted as D, D’ (Oxygen functionalized \( sp^2 \) carbon), G, D’, 2D, D + D’ and 2D’ bands. Note that all the spectra were recorded with 514.5 nm laser excitation. The right hand panel shows the corresponding molecular models of each sample elucidating the various functional groups and extended defects formed during the preparation process. (A colour version of this figure can be viewed online.)](image-url)
However, Raman features of GO and rGO show the broad line shape of D and G bands that reveal the high degree of disorder due to the continuous in-plane and inter layer disruption and plenty of in-plane oxygen functional groups on the basal plane (sp² defect sites).

The contribution of various in-plane and edge oxygen functionalities and surface defects in each sample was quantified with Lorentzian line shape analysis of D, G, D' and 2D Raman bands, as shown in Fig. S1 (supporting information). D and G bands are fitted with two Lorentzian peaks each, namely D, D' (new Raman feature at ~1450 cm⁻¹), G and D' bands (see Fig. S1). Note that in all the CDG samples, the D band is broader than that of the CVD graphene, which significantly denote the disorder due to in-plane oxygenated functionalities attached at the sp² carbon sites. Interestingly, edge confinement effect due to COOH or C=O functional groups is understandable from the evolution of D' band in QGD and GONR. Attachment of these functional groups is more probable with edge carbon atoms due to the presence of weak dangling bonds leading to the continuous edge reconstruction [18]. Note that the FWHM (full width at half maxima) of D' band is nearly double for QGD and GONR as compared to that of GO and rGO, which implies the nucleation of oxygen functionalities significantly at the edges, mostly due to the COOH and C=O functional groups. This Raman signature is fully consistent with the strong green PL emission from the QGD and GONR, which is significant for the sub-band energy states of COOH and C=O. Further, the change in the position of G-band (~1590 cm⁻¹) due to the in-plane lattice strain and disorder caused by the functionalization of graphene sheets and presence of D' (at ~1620 cm⁻¹) band are attributed to the intrinsic edge reconstructed defects [18]. In addition, D + D' and 2D' band features are strong in case of GO and rGO, while these are weak in QGD and GONR (see Fig. 1). These two features reveal a higher interlayer distance between the graphene layers in GO and rGO due to covalent attachment of in-plane epoxi/OH functional groups and formation of extended defects, respectively. Further, the variation of oxygenated functionalities and crystalline structure of the pristine CDGs were estimated from the XRD analysis, as shown in the supporting information (see Fig. S2). Fig. S2 represents the XRD pattern from various CDGs, such as GO, rGO, QGD and GF, showing reflections from the C(001) and C(002) planes. The inset shows the magnified view of XRD pattern in the range 40–50°, which shows the weak reflections from C(100) and C(101) planes due to the functional groups in GO, rGO and QGD. A sharp XRD peak at 26.4° corresponds to a (002) plane of sp² hybridised carbon atoms is significant for the highly ordered graphic structure of the starting precursor. The intensity of (002) peak is reduced in all the CDGs (see Fig. S2) due to continuous oxidation process leading to intercalation of various in-plane and edge oxygenated functionalities [23]. Further, presence of (100) and (101) planes reveal the increased interlayer distance between the graphene layers in all the CDGs, which is consistent with micro-Raman results.

4.2. HRTEM studies

The spatial uniformity and disorder due to defects on the basal plane and edges of the graphene layer and CDGs are extensively investigated from the HRTEM analyses. Fig. 2(a) represents the TEM image of GR transferred on to a TEM Cu grid and corresponding SAED pattern showing the hexagonal lattice spots corresponding to (002) plane. The arrows indicate the formation of wrinkles on the graphene basal plane that are formed during the wet transfer process [18]. Upper inset shows the hexagonal lattice pattern of the GR implying the perfect sp² hybridization without any significant intrinsic defects, which is consistent with the Raman spectrum shown in Fig. 1(b). Note that multiple SAED patterns were acquired at several locations of Fig. 2(a) and it revealed the uniform coverage of GR. Further, the spatial distributions of in-plane and edge defects are illustrated in Fig. 2(b) that shows the vacancy type defects and extended defects and these are formed during the CVD growth. Various colour arrows indicate the following: green-edge defects; red-line defects; pink-point defects.

Fig. 2(c) represents the HRTEM image of the cross section of multilayer GO (~30 layers) showing the distribution of layers and the lattice distortion present in the layers. The inverse fast Fourier transform (IFFT) image (upper right inset) is extracted from the region I, which clearly shows the layer distortions along the GO sheets and the shaded region may be due to the oxygenated functionalities and disorder in the layers of GO. The multiple electron diffraction spots arise from the GO basal plane, as shown in the lower right inset of Fig. 2(c). Fig. 2(d) shows a TEM image of rGO sheet and corresponding SAED pattern shown in the inset signifies the few-layer graphene sheet. Further, Fig. 2(e) represents the distribution of as-synthesized QGD fabricated from the GO precursor using simple solvothermal technique (supporting information, SI4). The average size of the QGD was estimated as ~9 nm. Upper left inset in Fig. 2(e) represents the HRTEM image focused on an individual QGD that shows the (002) lattice plane of sp² hybridised carbon atoms with a d-spacing of 3.3 Å. The SAED pattern is significant for the few layer graphene present in the as-prepared QGDs. The TEM image of the GONR prepared from the multiwall carbon nanotubes (MWCNT) is shown in Fig. 2(f). Inset shows a HRTEM image of the GONR and arrows indicate the unzipped portion of the MWCNT during the oxidation/reduction process. Note that the dark regions denote the presence of metal catalyst nanoparticles and amorphous carbon.

4.3. Optical absorption

Optical absorption measurements have been carried out on CVD graphene and CDG materials in order to understand the effect of surface functionalities and intrinsic defects on graphene. Comparison of the absorption spectra from different graphene samples coated on quartz substrates is shown in Fig. 3. It is evident that the GR is completely transparent over the entire range of visible–NIR region as compared to the CDG materials showing some absorption in the visible region. We have also measured the absorption spectra in DGR, which is almost identical to that of GR, though it contains intrinsic defects on the basal plane and at the edges (see the HRTEM image, Fig. 2(b)). Note that GO, rGO and GONR show a broad visible absorption. Interestingly, the QGD has sharp UV absorption bands at 273 and 340 nm. The absorption band at 273 nm signifies two important contributions, i.e., transition from π−−π* electronic states of graphene basal plane formed by partially overlapped p-orbitals in the sp² hybridised carbon and due to the size effect of QGD (diameter ~ 9 nm, see HRTEM image, Fig. 2(e)) showing the band edge absorption [1,24]. Further, this is different from the broad UV–visible absorption in GO due to the stacking of various in-plane oxygenated functional groups corresponding to defect induced intermediate energy states (sub-bands), i.e., transition from n−−n* states (see supporting information Fig. S3) [111]. On the other hand, the strong absorption at 340 nm is attributed to the sub-band gap energy states arising from the edge functionalised states of COOH and C=O functionalities in QGD and GONR, detected for the first time, and it is fully consistent with the Raman spectra and other experimental results.

4.4. PL studies of CDG thin films

The PL spectra from all the CDG thin films have been acquired with 355 and 405 nm laser excitations. In general, CDG samples
may show the excitation wavelength dependent PL due to the distribution of various conjugated aromatic rings of sp$^2$ crystallites with different sizes, separated by the sp$^3$ matrix which are associated with $\pi-\pi^*$ energy states and sub-band energy states ($n-\pi^*$) of oxygen functionalities [1,17]. Fig. 4(a–d) illustrates the room temperature PL features of GO, rGO, GQD and GONR thin films, respectively, with 355 nm laser excitation. The PL spectra of these samples with 405 nm laser excitation are similar to that of the 355 nm excitation (see supporting information: Fig. S4 and S5). The PL spectrum in each case was fitted with the three Gaussian peaks, namely one blue and two green emissions, P1 at ~437–440 nm, P2 at ~497–500 nm and P3 at ~537–551 nm. Interestingly, P1 and P2 are common to all CDG thin films, while relative position and intensity of P3 changes from sample to sample. Note that the solid blue line represents the fitted curve and symbols correspond to the experimental data. The peak positions and line shapes are
dissimilar in different cases due to the difference in nature of in-plane and edge functionalities in the CDG thin films. The origin of blue PL emission (P1) from GO related functional materials is studied well in the literature and it arises from the localised energy states of crystalline sp² domains separated within the sp³ matrix [11]. P1 at ~440 nm from disordered GO is a representative of π states of crystalline sp² clusters within the sp³ carbon sites. These sp³ sites are associated with in-plane oxygenated functionalities on the graphene basal plane, mostly epoxy and CO related functionalities. The nature of blue emission also depends on the degree of in-plane oxygenated functionalities nucleated at the sp³ sites [9]. In the present case, the line shape of the P1 peak does not change significantly for different CDG samples. On the other hand, P2 and P3 peaks are likely to originate from the defect induced sub-band energy states, which are mostly confined at the edge sites of the CDGs [20,21]. These sub-band energy states may arise from the covalent attachment of COOH and C=O functional groups at the edges, which is consistent with the new Raman band at 1450 cm⁻¹ (D'). The line shape of the PL from these sub-bands may be different in different CDG samples due to the variation in COOH and C=O functionalities. Note that the P2 and P3 emissions are strong in case of GQD and GONR, where edge states are likely to be dominant. Interestingly, the evolution of P1, P2 and P3 with annealing reveals that the in-plane and edge functionalization (COOH and C=O) of CDGs is giving rise the sub-band gap energy states. The precise nature and evolution of oxygenated functionalities on the in-plane edge sub-band gap emissions were monitored by the controlled hydrogenation and oxygenation (annealing) experiments and the results are discussed later.

Fig. 3. Comparison of optical absorption spectra of CVD graphene and CDGs: GR, GO, rGO, GQD, and GONR. The vertical dotted lines represent the absorption peaks corresponding to the π–π* transition and sub-band energy states (due to edge functionalization with COOH and C=O), respectively. The curves are vertically shifted for clarity. (A colour version of this figure can be viewed online.)

Fig. 4. Room temperature PL spectra from CDG thin films excited with 355 nm laser: (a) GO, (b) rGO, (c) GQD and (d) GONR. The symbol refers to the experimental data and the solid blue line corresponds to the fitted data in each case; centres of the fitted peaks are denoted in nm unit. (A colour version of this figure can be viewed online.)
4.5. TGA/DTG studies

A quantitative understanding of the in-plane and edge functional groups in CDGs was developed from the analysis of the TGA/DTG results, as illustrated in Fig. 5. The nature of the functional group defects has been assessed from the thermal stability behaviour of each CDG sample analysed from TGA and DTG exothermic curves (black and red curves), as depicted in Fig. 5(a–d) for GF, GO, rGO and GQD, respectively. The oxidation temperatures (T0) and the ratio of sp2, sp3 and functionalized sp3 carbon (TD) content in all the CDG samples were calculated using Gaussian line shape fitting of DTG peaks (see the insets of Fig. 5) and it provides a clear picture on the evolution of the specific in-plane oxygen functionalities and COOH or C=O edge functional groups. The complete details of the DTG peak position, integrated area and the ratio of sp3, functionalized sp3 (TD) to sp2 carbon and functional group identity (tentative) are presented in Table 1. The T0 for GF is very high (829 °C), which is attributed to the highly ordered graphitic layers with covalently bonded sp2 hybridised crystalline carbon. On the other hand, GO, rGO and GQD show much lower decomposition temperature (DTG peaks) for sp2 and sp3 carbon that may be due to the interlayer distortions and in-plane/edge oxygenated functional groups (see Fig. 2(c)). The multiple DTG peaks in the range of 100 and 400 °C can be ascribed to the in-plane and edge oxygenated functionalities. A sudden drop in the weight % of GO at 160 °C arises from the evaporation of water (hydroxyl–OH) and weakly bonded in-plane epoxy (–O–) functional groups [23]. The ratio of sp3/sp2 content is higher in GQD as compared to that in GO and rGO, which signifies more oxygenated functionalities at the edge sites of the GQD. Various peaks of DTG profiles for different samples are extracted from Gaussian fitting and are tabulated in Table 1. Note that both rGO and GQDs show higher oxidation temp (T5, T6) for sp2 and sp3 carbon (see Fig. 5(b) and (c)) as compared to that of GO. This implies the formation of carbonyl related (C=O) functionalities at the edges of GQD and GONR, as it possesses higher thermal stability [19]. A similar TGA/DTG characteristic is expected for the GONR, based on the Raman analysis (see Fig. 1). These results are consistent with the evolution of blue PL emission in GO and rGO and enhanced green emissions in GQD and GONR after hydrogenation and oxygenation, respectively.

4.6. FTIR studies

Identity of various in-plane and edge oxygen functional groups in CDGs is further confirmed from the FTIR analysis. The FTIR bands associated with the various CO related oxygen functional groups and sp2 (C=C) and sp3 (C–C) carbons can be distinguished from the spectra shown Fig. 6. These features are compared for as-grown and hydrogenated CDG samples. All the CDG samples show the characteristic IR active vibrational modes of covalently bonded carbon and oxygen atoms, besides the sp3 and sp3 hybridized carbon. The complete details of the FTIR bands for each sample and their physical significance are presented in Table 2. The two weak modes at 2886 and 2936 cm−1 signify the C–H stretching at the edge of the graphene layer. It can be clearly seen that these modes are prominent in GQD and GONR, while in case of GO and rGO they are insignificant due to the saturation of oxygen species on the basal plane [26]. Interestingly, a key feature of the functionalization on the basal plane of the graphene was obtained from the important vibrational feature of sp2 crystalline carbon at 1589 cm−1, and it is attributed to the in-plane stretching of covalently bonded carbon atoms of CDGs. This band is common to as-prepared GO and rGO, and after hydrogenation (at 550 °C) it is significantly enhanced due to the removal of in-plane covalent oxygen functionalities. Another mode at 1655 cm−1 was observed in GO and rGO and after hydrogenation, it becomes stronger. Interestingly, the 1655 cm−1 band is strong and sharp in case of GQD and GONR, and it is attributed to the COOH or C=O functionalization at the edge sites. Note that the C=C (1589 cm−1) mode is not prominent in GQD and GONR due to strong presence of COOH and C=O edge functional

Fig. 5. TGA/DTG thermogram profiles of CDG materials measured in high purity oxygen atmosphere: (a) GF (b) GO, (C) rGO and (d) GQD. The DTG peaks are denoted in degree °C unit. Note that the insets of Fig. 5(b–d) represent the Gaussian line shape fitting for the DTG peaks of sp3, sp2 and functionalized sp3 carbon (TD). (A colour version of this figure can be viewed online).
groups. Additionally, the evidence for the contribution of C=O is revealed from the enhancement of 1655 cm\(^{-1}\) mode after hydrogenation of GO, while the strong vibrational modes at ~1105, 1254 and 1393 cm\(^{-1}\) in GQD and GONR are attributed to the C\(=\)O related alkoxy and epoxy stretching vibrations at the edge sites. However, attachment of OH functional groups is more significant during the initial stage of oxidation in the CDG materials. The continuous oxidation treatment leads to the formation of COOH and C\(=\)O functionalities along with the enhanced sp\(^3\) carbon content due to the intercalation of the graphene layers [23]. The formation of covalent COOH/C\(=\)O functionalities are more favourable in case of GQD and GONR, which is evidenced from the higher sp\(^3\)/sp\(^2\) ratio and it’s consistent with the FTIR analyses [9,23]. The two additional bands at 660 and 866 cm\(^{-1}\) may be attributed to the residual C\(=\)O related vibrations on the graphene basal plane. Thus, the FTIR results reveal the actual nature of edge functionalities, such as COOH or C\(=\)O in GQD and GONR samples and the evolution of in-plane oxygenated functionalities in GO and rGO, which are fully consistent with the PL analysis. FTIR results reveal that the GQD and GONR have additional functional groups as compared to that of GO and rGO due to domination of the edge sites. This is consistent with the higher intensity of green PL in GQD and GONR after annealing (discussed later).

4.7. Raman and TGA/DTG studies of hydrogenated CDGs

The evolution of oxygen functional groups with hydrogenation treatment was substantiated from the Raman signatures of CDGs and these results are compared with the TGA/DTG analyses. Fig. 7(a) represents a comparison of Raman characteristic bands of various hydrogenated CDGs and the hydrogenated CVD graphene. The ratio of integrated intensities I\(_{2D}/I_{G}\) and I\(_{D}/I_{G}\) reveals considerable reduction in the oxygenated functional groups on the graphene basal plane as well as at the edges and improves the sp\(^2\) crystallinity of GO and rGO after hydrogenation, as evidenced by the sharp G and 2D band shown in Fig. 7(a), in comparison to the as pristine CDG samples (see Fig. 1). The reduction in intensity of D + D’ and 2D’ bands in hydrogenated CDGs is an evidence for the reduction of in-plane and interlayer epoxy/COOH functional

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</table>

**Table 1**

Summary of the DTG profiles of the different CDGs before and after hydrogenation treatment. The peaks in the range 160–400 °C are attributed to the various oxygenated functional groups attached to the sp\(^2\) sites of graphitic structure and those in the range 400–900 °C represent sp\(^3\), sp\(^3\) and oxygen functionalized sp\(^3\) carbon (T\(^4\)). Here, T\(_1\), T\(_2\), ..., T\(_6\) represent the successive oxidation temperatures obtained from the DTG peaks in each sample. The ratio of integrated intensities I\(_2D/IG\) and I\(_D/IG\) reveals considerable during the oxygenation treatment leads to the formation of COOH and C\(=\)O functionalities along with the enhanced sp\(^3\) carbon content due to the intercalation of the graphene layers [23]. The formation of covalent COOH/C\(=\)O functionalities are more favourable in case of GQD and GONR, which is evidenced from the higher sp\(^3\)/sp\(^2\) ratio and it’s consistent with the FTIR analyses [9,23]. The two additional bands at 660 and 866 cm\(^{-1}\) may be attributed to the residual C\(=\)O related vibrations on the graphene basal plane. Thus, the FTIR results reveal the actual nature of edge functionalities, such as COOH or C\(=\)O in GQD and GONR samples and the evolution of in-plane oxygenated functionalities in GO and rGO, which are fully consistent with the PL analysis. FTIR results reveal that the GQD and GONR have additional functional groups as compared to that of GO and rGO due to domination of the edge sites. This is consistent with the higher intensity of green PL in GQD and GONR after annealing (discussed later).

**Table 2**

Summary of the vibrational modes of the various carbon and oxygen covalent functionalities in different CDG materials extracted from the FTIR spectra.

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**Fig. 6.** FTIR spectra of GO, GOH, rGO, GQD and GONR showing the presence of covalently attached oxygen functional groups, sp\(^3\) (C=\(=\)C) and sp\(^2\) (C=C) carbon attached on the basal plane and edges of CDGs. (A colour version of this figure can be viewed online.)
groups. The Raman analysis is consistent with the changes in PL spectra of hydrogenated CDs, as discussed below. The disappearance of D band at ~1450 cm⁻¹ in hydrogenated and oxygenated GQD and GONR clearly reveals the removal of COOH functionalities and the asymmetry in the line shape may be due to the presence of residual C=O at the edge sites of GQD and GONR that enhances the green PL emissions (discussed below).

Further, the above Raman results were correlated with the TGA/DTG analysis of hydrogenated CDG samples. Fig. 7(b) represents the thermal analysis of hydrogenated GO and rGO extracted from the TGA/DTG profiles. Inset in each case represents the deconvolution of sp², sp³ and functionalized sp³ (T°) carbon DTG profiles with Gaussian line shape fitting. Here, two important observations can be made on GOH and rGOH: (i) an increase in the ratio of sp³/sp², (ii) a reduction in the T° (ΔT° – 49 °C for GO and ΔT°– 77 °C for rGO) signifying the removal of in-plane epoxy/OH related functionalities on the graphene basal plane. Here ΔT° is the change in the oxidation temperature of sp² carbon before and after hydrogenation. An additional DTG peak at 437/416 °C for GO/rGO and a sudden weight loss at 337 °C were observed. These observations imply that the additional DTG peak might be due to the residual C=O functionalities, which is fully consistent with the FTIR result of hydrogenated GO sample. Note that the PL emission intensity was strongly reduced after hydrogenation that might be due to the large number of sp² crystallites within the sp³ domains. This may be due to the high temperature of annealing that may have removed the covalently bonded oxygen functionalities. These results help us to identify the specific PL bands from in-plane and edge functionalized CDs.

4.8. PL studies on oxygenated and hydrogenated CDGs

The contribution of in-plane and edge functional groups to the visible PL was further investigated from the PL studies on the oxygenated and hydrogenated CDG samples. Fig. 8(a–d) represents the room temperature PL spectra from various CDG thin films before and after the oxygenation/hydrogenation treatment. Fig. 8(e–f) represents the Gaussian line shape fitting of the PL spectra for oxygenated and hydrogenated GQD and GONR samples. A comparison of the relative change in PL intensity is made on the basis of the Gaussian peak fitting of the PL data. Note that all the samples show strong blue emission before annealing and it is highly reduced in GO/rGO after H₂ annealing, which might be due to the removal of in-plane oxygenated functional groups from the GO/rGO basal plane during the high temperature annealing (550 °C) (See Fig. 5(a) and (b)) [19]. Though there is an overall reduction in the PL intensity after oxygenation, the relative blue intensity of PL is high with respect to the green PL in rGO, while the blue PL intensity is very low in GO. Improved sp² crystallinity was observed from the annealed CDs, which were evidenced from the FTIR, micro-Raman and TGA/DTG results. The evolution of COOH and C=O functionalities in the GQD and GONR correlates well with the evolution of the PL peak intensity. The peak parameters and their physical origin (tentative) are presented in Table 3. These assignments are supported by the FTIR and Raman results discussed in the previous section. Note that the peak positions of the blue (peak 1, P1) and green emissions (peak 2 and peak 3, P3) lie in the range of 437–443, 497–502 and 534–551 nm, respectively. The hydrogenation and oxygenation of CDG samples reveal the improved sp² crystallinity in case of GO and rGO, while in case of GQD and GONR evolution of COOH and C=O functionalities were observed. The Gaussian line shape parameters for the GQD and GONR reveal a considerable increase in the C=O functional groups after oxygenation, while COOH functionalities were less in the case of annealed GQD and GONR (see Table 3). Table 3 shows that after annealing, relative intensity of P1 reduces with respect to that of P2 and P3. Recent report on the photo thermal reduction of GO showed the reduction of defect induced emissions based on the gradual movement of PL peak from blue to red along with narrowing of line width [17]. Based on our experimental observations and literature reports on the PL evolution of CDs, we have tailored the blue and green emissions by monitoring the sp² crystallinity and monitoring the COOH and C=O functionalities at the edge site of CDG materials. We tentatively assign the two green emissions: P2 at ~497–502 nm and P3 at ~534–551 nm in CDG materials to the defect induced energy states of COOH and C=O functionalities, respectively.
5. Conclusion

The spatial distribution and identification of intrinsic and functional group defects at the in-plane and edge sites in graphene and CDG materials were established from the micro-Raman, FTIR and HRTEM analysis to elucidate the origin of blue and green PL emissions from the CDG thin films. The evidence for the specific functionalities at the edges and basal plane that gives rise to the blue and green emission in CDGs have been obtained from the combined analysis of micro-Raman and TGA/DTG results from the as-grown, hydrogenated and oxygenated CGDs. The defect induced two green emissions from the CDG materials at ~497–502 nm and ~534–551 nm are assigned to COOH and C=O functionalities, respectively, while the blue emission is attributed to the localised states of sp2/sp3 domains and epoxy related in-plane functional groups. These experimental findings are very important for tuning the optical properties and band gap engineering of CDG thin films for photocatalysis and sensing applications of graphene based functional materials.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.carbon.2015.08.036.

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