

Chapter 7

Modulation of Photoluminescence of Graphene Oxide (GO) by Changing Concentration

7.1. Introduction

One of the important limitation of graphene is that it does exhibit photoluminescence (PL) property due to its zero band gap. This limitation is overcome by using the chemically modified form of graphene like graphene oxide (GO), graphene quantum dot (GQD), reduced graphene oxide (RGO) etc. In particular, GO contains variety of chemically reactive functional groups like hydroxyl group, epoxide, carbonyl and carboxyl group. As a result, GO consists of a mixture of sp^2 and sp^3 carbon atom, where the sp^2 hybridised carbon are only bonded to the adjacent carbon atoms where the sp^3 hybridised carbon atom are connected to the adjacent oxygen containing functional groups [1-8] and these oxygen containing functional groups responsible for the opening of band gap in GO sheets and thus PL property originated from GO. It has been reported by the several group of researcher on the origin photoluminescence (PL) and the PL feature of GO in the widespread region from visible to near infrared (NIR) [5, 9-13], but still now, it is a controversial issue to the researcher. Thus, the origin of the PL properties of GO and its variation deserves enormous attention to resolve the ongoing debate. The complicated PL feature of GO is due to the presence of different domains and different functional groups in comparison to organic compounds. The progressive chemical reduction of graphene oxide modulates the band structure of two dimensional π -electronic system and this leads to broadband photoluminescence [11]. Hunt et al. observed that the stacking configuration of multi-layered graphene oxide by proper controlling way may provide a method for tuning its band gap [14]. Luo et al. [11] pointed out that the bond distortions may have contribution to the fluorescence of GO and r-GO. Chien et al. claimed that the broad longer wavelength band arises from the $\pi-\pi^*$ transition [10]. Eda et al [8] considered the broad band PL of GO result from disorder-induced state within the band gap of the sp^2 domains within the sp^3 cluster. The broad band fluorescence observed in GO may be interpreted as the confinement of π -electrons in

localized sp^2 clusters with various sizes [15-17]. Again, it has been found that the several groups has been inspired to study the effect of pH on the fluorescence properties of GO of the aqueous suspension of GO as it contains the functional groups like carboxylic acid and phenoxide groups in the surface and sheet edges respectively [18-21]. According to Zhang and coworkers the pH dependent emission properties at visible region is due to protonation and deprotonation of the fluorophore in GO [20]. Dutta et al. reported a marked blue-shift of the UV fluorescence with increase in pH due to the movement of basal planes and shape modulation of GO sheets [21]. Galande et. al. reported the strongly pH-dependent broad band visible fluorescence from aqueous dispersion and proposed that the PL of GO originated from quasi-molecular fluorophore (containing 50 π -electron and carboxylic acid groups) similar to polycyclic aromatic compounds [18]. It is also very interesting to observe photoluminescence (PL) nature of GO by changing concentration as self-assembly behaviour of GO sheets may tune the band gap. Ozcan et al. [22] reported the effect of functional group and associative behaviour of GO on the fluorescence of graphene oxide. According to them, fluorescence consists of six components and the relative intensity of the six component changes significantly due to reduction. The hydrogen bond suppress the emission from smaller sp^2 domain, while the large domain remain almost unaffected due to reduction [22]. Shao et al. observed fluorescence from chemically derived graphene (CDG). They also studied the effect of self rolling up and aggregation on the PL properties of CDG [23]. Donghe et al. [24] reported the PL nature of GO by changing concentration of GO. They observed that blue band predominated at low concentration and longer wavelength band dominated at high concentration of GO. They explained that longer wavelength band arising from excimer formation. Excitation wavelength dependent as well as pH dependent emission has been reported from GO [7, 21] and we observed three emission band at 305-310 nm, 330-345 nm and 350-390 nm respectively [7,21] from our synthesised GO. It has been also reported that

the emission band at 330-345 nm is pH independent, although other two emission band pH is dependent [21]. Also, we have observed modulation feature of these emission band in the presence of surfactants (SDS, CTAB) [7]. Thus, the modulation feature of electronic band structure of GO has enormous interest. In the present work, we have high lightened the observation of tunable PL property from aqueous dispersion of GO at different concentration.

7.2. Experimental Section

The different instruments used for this experiment are FT-IR, X-ray diffraction study (XRD) spectrofluorimeter, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) and TCSPC and details about instrument has been discussed in chapter 3.

7.2.1. Method of Synthesis

The material required and the method of synthesis of GO has been discussed details in chapter 3. In our experimental work, pH of the aqueous GO (0.02 ml/ml) solution was 4.7 and the pH of the solution was almost remain unchanged with increase concentration of GO. The aqueous dispersion GO based material is acidic due to the de-protonation of its -COOH and -OH functional groups.

7.3. Result and Discussion

7.3.1. Characterization

The GO has been characterised by different spectroscopic technique such as Raman spectrum, FT-IR spectrum, X-ray diffraction study, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) and has discussed details in chapter 3 with figure. Now, we interpret the characterisation result of our synthesized nanomaterial.

In the Raman spectrum of GO, two Raman peaks at 1350 cm^{-1} and 1596 cm^{-1} , named as D band (disordered band, associated with the reduction in size of the in-plane sp^2 domains) and G band (growth band, due to vibrations of hexagonal lattice, characteristic of graphene-like

“honeycomb” structure), respectively are observed [25]. In our GO sample, the Raman spectra [Fig- 1(a), Chapter 3] shows the comparable intensity of D band to that of the G peak at $\sim 1596\text{ cm}^{-1}$ and this spectra is a indicates of significant structural disorder due to the harsh oxidation condition in Hummer’s process. The intensity ratio of the D band to G band (I_D/I_G) of our GO is about ~ 1 and this value is very close to the result obtained from GO from Ganguly et al. [26] and Wang et al. [27]. The FT-IR spectrum of GO indicates the presence of C=O groups in the form of free carboxylic acid and hydrogen bonded carboxylic acid moieties by showing two sharp peaks at $1,726$ and 1622 cm^{-1} respectively, due to the weakening of carbonyl bond in the latter case (Fig. 1b, chapter 3). A broad band having a centre at $\sim 3380\text{ cm}^{-1}$ is appeared mainly due to the stretching mode of vibration of the –OH functional group, which indicates that GO contains the numerous surface hydroxyl groups (-OH group). In the XRD spectrum of GO [Fig. 1c, chapter 3] shows a most intense sharp diffraction peak at $2\theta = 7.97^\circ$ corresponds to the (001) diffraction plane with an interlayer spacing of 1.11 nm . [28] The larger interlayer distance of GO from natural graphite flake might be due to the formation of hydroxyl, epoxy and carboxyl like oxygen-containing functional groups [28]. Another low intense peak appeared at $2\theta = 25.97^\circ$, this value is slightly lower than natural graphite flake which is due the reflection of (002) plane [29]. The SEM and TEM images of GO displayed an exfoliated layer of several micrometers, a curled morphology [Fig. 1(d), 1(e), 1(f), 1(g), chapter 3].

7.3.2. Absorption Spectra

We have measured the absorption spectra at different concentration of GO and we observed broad spectral structures with distinct band around at 230 nm [Fig. 1]. Absorption of the aqueous dispersion of GO below 250 nm may be assigned to $\pi\text{-}\pi^*$ transition of sp^2 network and also a shoulder appeared at 280 nm which is usually assigned as $n\text{-}\pi^*$ transition

of the C=O bond in GO moiety. Although, the absorption spectral pattern remain unchanged with increased concentration of GO but steady state fluorescence affected.

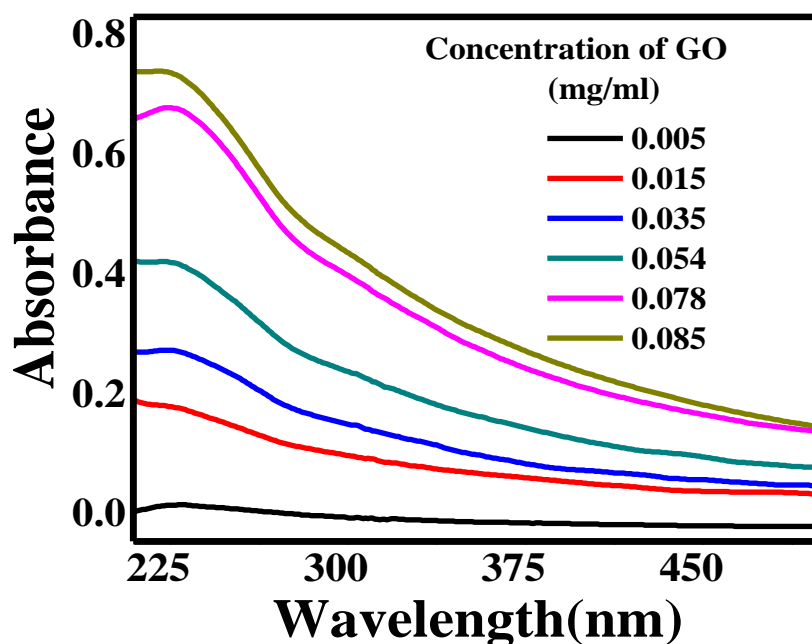


Fig. 1 Absorption spectra at different concentration GO

7.3.3. Steady State Emission Spectra

The photoluminescence property of GO has been reported in the literature review section, which shows that the photoluminescence of GO is different from the typical organic aromatic molecules, for which the emission properties are independent of excitation wavelength. It has been reported that the photoluminescence of GO is complicated and depends upon the excitation wavelength, pH of the medium [20,21,30]. It has been found that the change in concentration should not affect the amount of disorder induced states [10], size of sp² clusters [8], free zigzag sites [31] and the protonation and deprotonation of carboxyl and hydroxyl groups [30,32]. Thus, more detailed investigations are required to explore the

origin of photoluminescence mechanism of GO. So, in the present work, the effect concentration on the photoluminescence of GO has been discussed.

The photoluminescence of aqueous GO dispersion have been measured by exciting the sample at 240 nm (π - π^* band) and at 280 nm (n - π^* band) at different concentration of GO. Interestingly, we have observed 22 nm red shift of the emission band 370 to 392 nm at excitation wavelength 240 nm [Fig. 2(a)] and 38 nm red shift of the emission band 354 nm 392 nm at the excitation wavelength 280 nm [Fig. 2(b)]. This red shift may be due to increase π - π stacking interaction between GO layer with increase concentration of GO and there by lowered the band gap of GO. Shao et al. observed aggregate formation by self-rolling up from chemically derived graphene (CDG) with the increase concentration of CDG. They explained that the CDG sheets get closer and closer so that inter-layer π - π interaction at get stronger, which eventually leads to aggregate formation [23]. The aggregate formation of CDG leads to the rise in PL intensity in the blue region and falling down in PL intensity in the red range with the increase in concentration. Dutta et al. [21] reported the blue shift of UV fluorescence from aqueous dispersion of GO with the increase in pH. When they excited at 240 nm and 280 nm, they observed 32 nm blue shift and 12 nm blue shift respectively with the increase in pH due to the movement of basal planes of GO by the repulsion of carboxylate ions at the edges of GO sheets and weakening of π - π stacking interaction [21]. Thus, the aggregate of GO may be formed in the solution as GO layers more closer with increase concentration of GO by increasing π - π stacking interaction between the layers of GO, resulting in red shift of the emission maxima is observed. We have also observed that the emission maximum is gradually red-shifted as well as the bandwidth became broader with the increase of concentration of GO, which is similar to the observation reported by Zhang et al. [20] that the blue emission band appeared strongly when the concentration of GO is sufficiently low due to self-absorption (i.e. the inner filter effect) to its fluorescence. The

inner filter effect is much prominent in the UV and blue region than the red and NIR range as the absorption of GO in the UV and blue

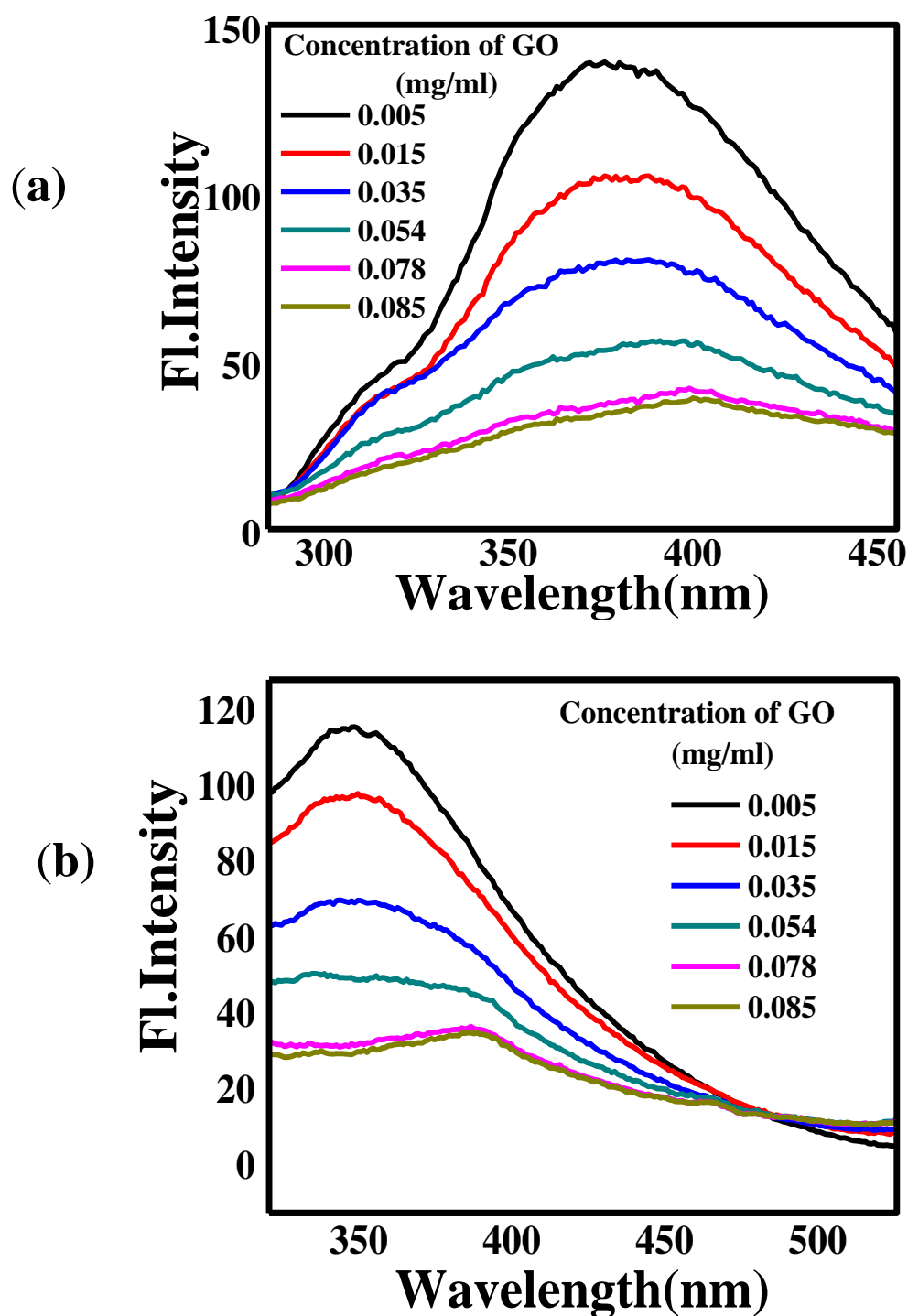


Fig. 2 (a) Emission Spectra of GO ($\lambda_{ex} = 240$ nm) (b) Emission Spectra of GO ($\lambda_{ex} = 280$ nm)

region is much more intense. The emission maximum is gradually red-shifted as well as the bandwidth became broader with the increase of concentration of GO [20].

The origin of photoluminescence feature may be explained on the basis of quasi-molecular electronic structure of sp^2 clusters present within sp^3C-O matrix [9,18,33-35,]. It is evident from quasimolecular study that the center of the emission band is dependent upon the functional groups present at the surface of GO [33,18] decorated with different oxygen containing functional groups like carboxyl ($-COOH$), epoxy ($-O-$), hydroxyl ($-OH$). According to Nourbakhsh et al. after the 25% oxygen coverage on the GO surface, the band gap increases continuously with the decrease in the ratios of carbon to oxygen numbers [36]. Thus, the oxygen coverage at the GO surface modulates the band gap as well as the centre of luminescence peak [36,37]. The local energy gap also depends upon the size of sp^2 clusters present within the material [9] and therefore the wavelength of luminescence. It has been reported that the DFT calculation of $\pi-\pi^*$ energy gap suggests that the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of a single benzene ring is about 7.4 eV (170 nm). This energy gap decreases with the increase in the size of sp^2 clusters, i.e. the increasing number of aromatic rings [9, 34]. Thus, the observed emission band at 345/390 nm from GO in the work may occur from the sp^2 clusters having size less than 2 nm (containing about 10 aromatic rings) and the corresponding energy gap lies within 3.2–3.6 eV [21]. The present work reported here which is in the UV region of electromagnetic spectrum that is different from other groups. It should be mentioned that further investigation using the time resolved study is required to confirm this type of phenomenon.

7.3.4. Excitation Spectra

The fluorescence excitation (FLE) spectra monitored at two emissive wavelength 350 nm and 370 nm respectively at different concentration of GO, which exhibit two distinct peaks at 230/240 nm and 280 nm respectively [Fig. 3(a) and Fig. 3(b)]. These two peak are resembled to first and second singlet-singlet transition in benzoic acid [21]. But the pattern of FLE spectra of aqueous dispersion of GO monitored at concentration of GO 4.45mg/ml and 85.62 mg/ml are different at both emission wavelength of 350 nm and 370 nm respectively.

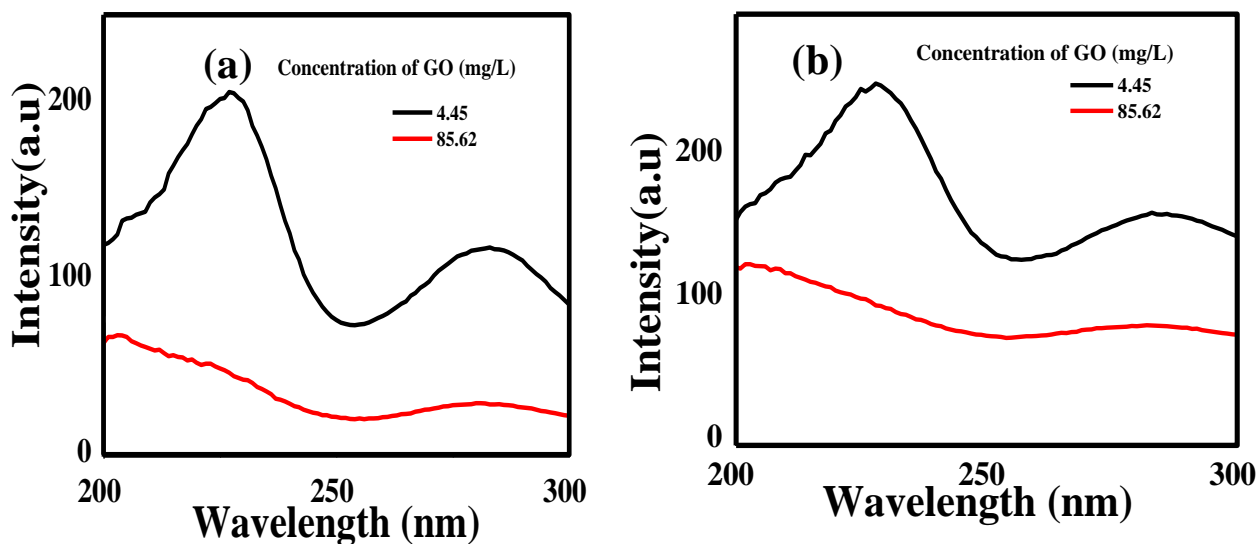


Fig. 3 Fluorescence Excitation Spectra at different concentration of GO at the Emissive Wavelength (a) 350 nm (b) 370 nm

Thus, FLE spectra indicates the existence of different types of fluorescence species present in the sample [21] which is affected, as the intensity 230/240 peak in FLE spectra decreases and also the peak of 230 nm become flatted with the change in concentration. Thus, FLE suggested that there may form an aggregate of GO in the aqueous medium with increase concentration of GO by increasing π - π interaction between the layers of GO, resulting in red shift of the emission maxima is observed.

7.4. Conclusion

The modulation of photoluminescence is observed from GO by changing concentration. For the first time, the red shift of emission maxima as well as the broader of emission spectra in the UV region from aqueous dispersion of GO with the increasing concentration of GO is observed. This observation may be due to increase π - π stacking interaction between GO layer and there by lowered the band gap of GO. Thus, the aggregate of GO may be formed in the solution as GO layers become closer with increase concentration of GO by increasing π - π stacking interaction between the layers of GO. The observed emission band at 345/390 nm from GO in the present work may occur from the sp^2 clusters having size less than 2 nm. It should be mentioned that further investigation using the time resolved study is required to confirm this type of phenomenon. Thus, the present modulation of photoluminescence (PL) PL feature of GO by changing concentration may open a new area of research on PL in the UV region and hence one may use GO material for various optoelectronic devices. The effect of concentration on the photoluminescence observed from of our synthesized GO may have implications in sensing and optoelectronics. The observed phenomenon of excitation wavelength dependent photoluminescence also may open an interest to researcher, since the emission wavelength can be changed simply by varying the excitation wavelength and this type of work may be extended to the carbon based quantum dots material where spectral tuning is found to be identical.

7.5. Reference

- [1] F. Bonaccorso, Z. Sun, T. Hasan, A. C. Ferrari, *Nat. Photonics*, 2010, **4**, 611–622.
- [2] M. Liu, X. Yin, X. Zhang, *Nano Lett.*, 2012, **12**, 1482–1485.
- [3] J. O. Hwang, J. S. Park, D. S. Choi, J. Y. Kim, S. H. Lee, K. E. Lee, Y.-H. Kim, M. H. Song, S. Yoo, S. O. Kim, *ACS Nano*, 2012, **6**, 159–167.
- [4] Z. Yin, S. Wu, X. Zhou, X. Huang, Q. Zhang, F. Boey, H. Zhang, *Small*, 2010, **6**, 307–312.
- [5] X. Sun, Z. Liu, K. Welsher, J. T. Robinson, A. Goodwin, S. Zaric, H. Dai, *Nano Res*, 2008, **1**, 203–212.
- [6] S. He, B. Song, D. Li, C. Zhu, W. Qi, Y. Wen, L. Wang, S. Song, H. Fang, C. Fan, *Adv. Func. Mater.*, 2010, **20**, 453–459.
- [7] P. Saha, D. K. Pyne, S. Ghosh, S. Banerjee, S. Das, S. Ghosh, P. Dutta, A. Halder, *RSC Adv.*, 2018, **8**, 584–595.
- [8] G. Eda, Y. Y. Lin, C. Mattevi, H. Yamaguchi, H. A. Chen, I. S. Chen, C. W. Chen, M. Chhowalla, *Adv. Mater.*, 2010, **22**, 505–509.
- [9] K.P. Loh, Q. Bao, G. Eda, M. Chhowalla, *Nat. Chem*, 2010, **2**, 1015.
- [10] C. T. Chien, S. S. Li, W. J. Lai, Y. C. Yeh, H. A. Chen, I. S. Chen, L. C. Chen, K. H. Chen, T. Nemoto, S. Isoda, M. Chen, T. Fujita, G. Eda, H. Yamaguchi, M. Chhowalla, C. W. Chen, *Angew Chem. Int. Ed.*, 2012, **51**, 6662–6666.
- [11] Z. Luo, P. M. Vora, E. J. Mele, A. T. C. Johnson, J. M. Kikkawa, *App. Phys. Lett.*, 2009, **94**, 111909–13.
- [12] T. V. Cuong, et al. *Mater. Lett.* 2010, **64**, 399–401.
- [13] S. Shukla, S. Saxena, *Appl. Phys. Lett.*, 2011, **98**, 073104.
- [14] A. Hunt, D. A. Dikin, E. Z. Kurmaev, Y. H. Lee, N. V. Luan, G. S. Chang, Moewes, A. *Carbon*, **2014**, 66, 539–546.

- [15] J. Robertson, E. P. O'Reilly, *Phys. Rev. B*, 1987, **35**, 2946-2957.
- [16] K. Erickson, R. Erni, Z. Lee, N. Alem, W. Gannett, A. Zettl, *Adv. Mater*, 2010, **22**, 4467-4472.
- [17] J. Shang, L. Ma, J. Li, W. Ai, T. Yu, G. G. Gurzadyan, *Sci. Rep.*, 2012, **2(792)**, 1–8.
- [18] C. Galande, A. D. Mohite, A. Naumov, W. Gao, L. Ci, A. Ajayan, H. Gao, A. Srivastava, R. B. Weisman, P. M. Ajayan, *Sci. Rep.* 2011 **1(85)**, 1-5.
- [19] D. Kozawa, Y. Miyauchi, S. Mouri, K. Matsuda, *J. Phys. Chem. Lett.*, 2013, **4**, 2035-2040.
- [20] X-F. Zhang, X. Shao, S. Liu, *J. Phys. Chem. A*, 2012, **116**, 7308-7313.
- [21] P. Dutta, D. Nandi, S. Datta, S. Chakraborty, N. Das, S. Chatterjee, U. C. Ghosh, A. Halder, *J. Lumin.* 2015, **168**, 269-275.
- [22] S. Ozcan, S. Vempati, A. Cirpan, T. Uyar, *Phys. Chem. Chem. Phys*, 2018, **20**, 7559-7569.
- [23] X. F. Zhang, S. Liu, X. Shao, *J. Lumin.*, 2013, **136**, 32-37.
- [24] D. Du, H. Song, Y. Nie, X. Sun, L. Chen, J. Ouyang, *J. Phys. Chem. C*, 2015, **119**, 20085 –20090.
- [25] S. Pei, H.-M. Cheng, 2012, **50**, 3210–3228.
- [26] A. Ganguly, S. Sharma, P. Papakonstantinou, J. Hamilton, *The Journal of Physical Chemistry C*, 2011, **115**, 17009–17019.
- [27] S.J. Wang, Y. Geng, Q. Zheng, J.-K. Kim, *Carbon*, 2010, **48**, 1815–1823.
- [28] S. Bykkam, V. K. Rao, S. CH. Chakra, T. Thunugunta, *Int. J. Adv. Biotech. and Research* 2013 **4** 142-146.
- [29] S. N. Alam, N. Sharma, L. Kumar, *Scientific Research Publishing*, 2017, **6**, 1-18.
- [30] S. K. Cushing, M. Li, F. Huang, N. Wu, *ACS Nano*, 2014, **8**, 1002 –1013.
- [31] L. R. Radovic, B. Bockrath, *J. Am. Chem. Soc.* 2005, **127**, 5917 –5927.

- [32] S. Kochmann, T. Hirsch, O. S. Wolfbeis, *J. Fluorescence*, 2012, **22**, 849–855.
- [33] G. Eda, M. Chhowalla, *Adv. Mater.*, 2010, **22**, 2392.
- [34] G. Eda, Y.Y. Lin, C. Mattevi, H. Yamaguchi, H.A. Chen, I. S. Chen, C.W. Chen, M. Chhowalla, *Adv. Mater.*, 2009, **21**, 1.
- [35] C. Mattevi, G. Eda, S. Agnoli, S. Miller, K.A. Mkhoyan, O. Celik, D. Mastrogiovanni, G. Granozzi, E. Garfunkel, M. Chhowalla, *Adv. Funct. Mater*, 2009, **19**, 1.
- [36] A. Nourbakhsh, M. Cantoro, T. Vosch, G. Pourtois, F. Clemente, M.H. van derVeen, J. Hofkens, M.M. Heyns, S. De Gendt, B.F. Sels, *Nanotechnology*, 2010, **21**, 435203.
- [37] H. Haiming, Z. Li, J. She, W. Wang, *J. Appl. Phys*, 2012, **111**, 054317.