

Chapter 6

*Study of Photoluminescence of GO-PANI
in the Aqueous Medium in the Presence
of an Anionic Surfactant (SDS) at Both
Acidic and Alkaline Medium*

6.1. Introduction

The presence of high surface area of GO as well as the presence of several functional groups (epoxy, hydroxyl, carboxyl) on the surface and sheet edges, researcher are interested to synthesis GO based nano-composite to explore their outstanding compatibility with many organic, inorganic, biomolecules, polymers [1-10]. Again, conducting (conjugated) polymers like polyaniline (PANI) has a broad attention to the researcher to synthesis GO based composite nano material. PANI exists in different oxidation state from the most reduced leucoemeraldine form to the half oxidized emeraldine and fully oxidized pernigraniline form [11] depending on the pH of the medium. Thus, the different oxidative form of PANI can be controlled by doping acid. Rana et al. have reported a synthetic method for emeraldine salt formation of PANI by using the carboxylic acid of GO as a dopant acid rather than using any additional acids [12]. Among these different form of PANI, only the emeraldine form which exit at low pH, is very interesting due to the presence of different form either bipolaron [13] or polaron [14] or coexistence of the both types of charge carriers [15]. This emeraldine salt state is also responsible for showing electrical conductivity due to its highly delocalized charge carriers. Therefore, PANI may be an excellent promising candidate for developing graphene based nano-composite material through possible interactions like π - π stacking, electrostatic interactions, hydrogen bonding and donor-acceptor interactions [16]. Maser and co-workers have prepared a reduced GO-PANI by using 1:1 GO to aniline mass ratio through in situ polymerisation where the simultaneous reduction of GO sheets covered by a thin layer of PANI leads to formation of a solid state charge transfer complex between reduced GO and PANI [16]. They have explained that the formation of charge transfer complex is responsible for the enhanced conductivity of the material and the material is also highly water dispersive and stable [16]. Thus, polyaniline grafted graphene oxide nano-composites (GO-PANI) has particular interest, especially to study the optical property. We have already reported the

effect of pH on the photoluminescence of GO-PANI [5] which has been described in chapter 4. Again, it is also important to mention that surfactant may be adsorbed on the GO surface and electrostatic repulsion or steric interaction may occur by the charged head groups of adsorbed ionic surfactants and this may have significant effect on the photoluminescence of GO and GO based nano composite. We have also studied the effect of anionic surfactant sodium dodecyl sulphate (SDS) on the photoluminescence of GO at different pH [17] which has been discussed in chapter 5. We have found a marked 36 nm blue shift in the acidic medium and intercalation of SDS between GO layers resulting an enhancement of photoluminescence intensity at 303 nm in the alkaline medium. Similarly PANI may also interact with the anionic surfactant (SDS) due to the presence of hydrophilic and hydrophobic moieties of PANI. This interaction may have significant effect on the properties of GO-PANI. Vaidya et al. have observed lower conductivity of PANI-SWNT (single wall carbon nano tubes) nano-composite with processable dispersion in organic solvent in the presence of anionic surfactant SDS [18]. They have also reported the significant modulation of the band of PANI and localisation of charge carrier by using UV-visible spectroscopic study [18]. Using electrochemical study, Torresi et al. have studied the interaction between PANI and SDS and the interaction leads to the modification of the species in the aqueous medium by increasing participation of water molecules [19]. Aoki et al. have prepared a PANI/DBSA (DBSA-dodecyl benzene sulphonic acid) conductive ion complex and the ion complex shows monolayer behaviour at the air-water interface and formation of LB (Langmuir-Blodgett) films on solid surfaces [20]. According to their work, the conductivity of PANI/DBSA LB films depends on the number of layers in case of less than four layers and its conductivity becomes similar to the bulk conductivity, 0.5 S/cm, for more than five layers [20]. Interesting electrical property of such materials, one may think about the tuning of optical property by surfactant. Although, the effect of anionic surfactant (SDS) on the luminescence of GO has

been reported by Saha et. al [17] but the effect of SDS on the luminescence of the GO-PANI nano-composite is not still investigated. In this work, we have studied the effect of SDS to tune the luminescence of GO-PANI in acidic and alkaline medium.

6.2. Experimental Section

The concentrations of GO-PANI dispersions (both acidic and alkaline pH) for the spectroscopic (UV-Visible absorption and emission) were 0.01 mg/ml. pH of the aqueous GO-PANI dispersion was controlled by using very low amount of dilute HCl and dilute NaOH.

6.2.1. Material and Method

The material required and the method of synthesis of GO-PANI has been discussed details in chapter 3 in section 3.2.

6.3. Result and Discussion

6.3.1. Characterisation

The GO-PANI has been characterised by different spectroscopic technique such as Raman spectrum, FT-IR spectrum, X-ray diffraction study, XPS spectra, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) and has been discussed details in chapter 4.

6.3.2. Absorption spectra

UV-visible absorption spectra of the aqueous dispersion of GO-PANI are measured both in the acidic medium (pH~2.5) and the alkaline medium (pH~10.5). In the acidic medium, one band appears at 280 nm and another at 438 nm in the absence of SDS, as shown in [Fig. 1(a)]. The absorption band at 280 nm is due to the $n-\pi^*$ transition of GO moiety and another band at 438 nm appears is due to transition from polaron state to π^* of PANI [5] suggesting PANI is present as polyemeraldine salt form of GO-PANI [12, 21]. But, with the

addition of anionic surfactant (SDS) up to 20 mM to the aqueous dispersion of GO-PANI, an interesting change in the UV-visible spectra is observed. Absorption band of the polaron to π^* transition is ~ 20 nm blue shifted along with an enhancement of intensity.

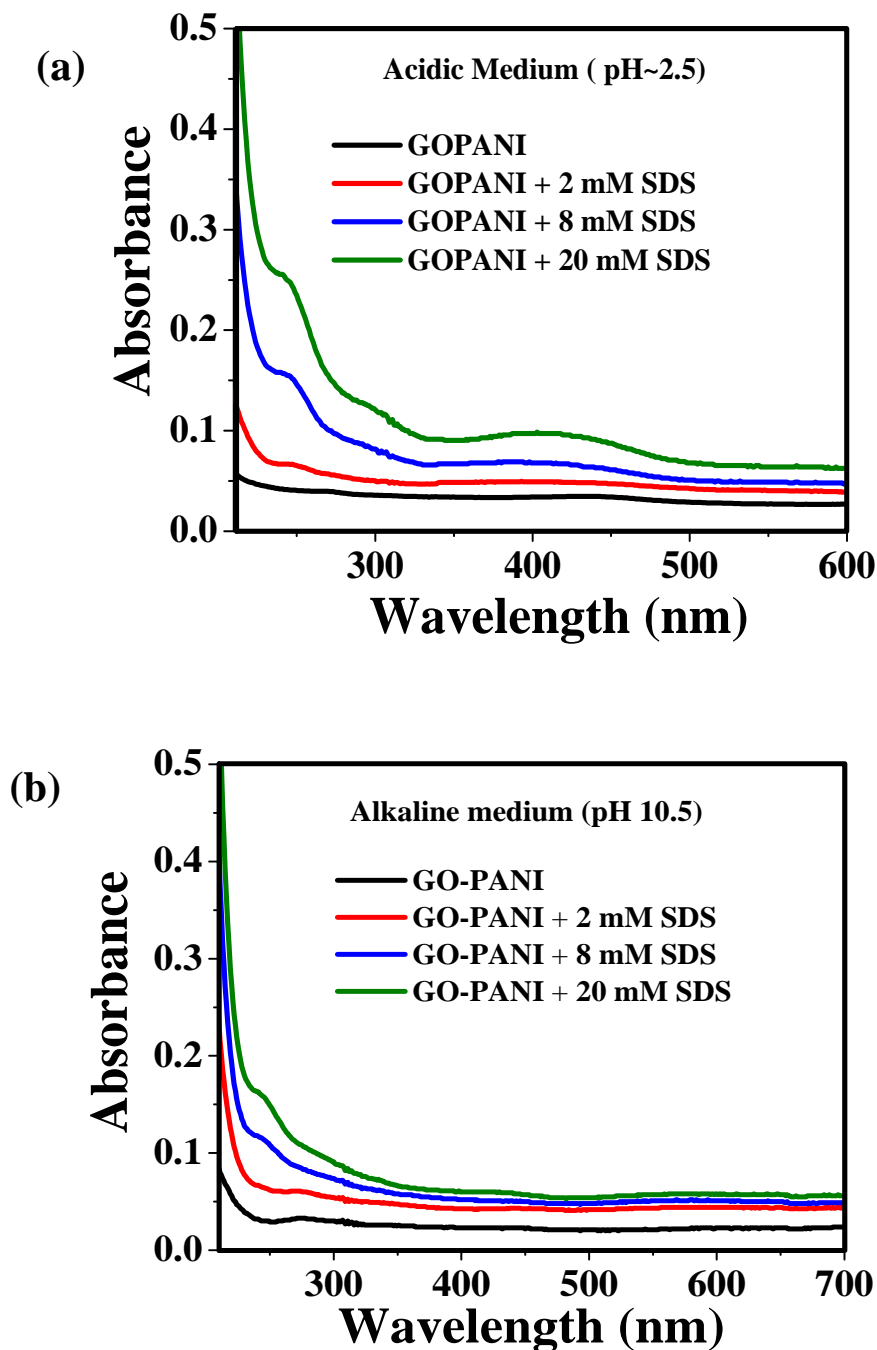


Fig-1 (a) Absorption spectra of GO-PANI dispersion (pH \approx 2.5) (b) Absorption spectra of GO-PANI dispersion (pH \approx 10.5) at different SDS concentration

This blue shift may be due to the change in the configuration of the PANI backbone by adsorption of SDS as well as a creation of nonpolar environment by formation of hemispherical SDS micelles. This blue shift [Fig. 1(a)] indicates the transformation of the PANI chains from compact coil to expanded coil conformation leading to the reduction of π -conjugation defects [22]. The adsorption of SDS on GO-PANI sheets results an increase in the dispersibility of GO-PANI which increases the intensity of the absorption band.

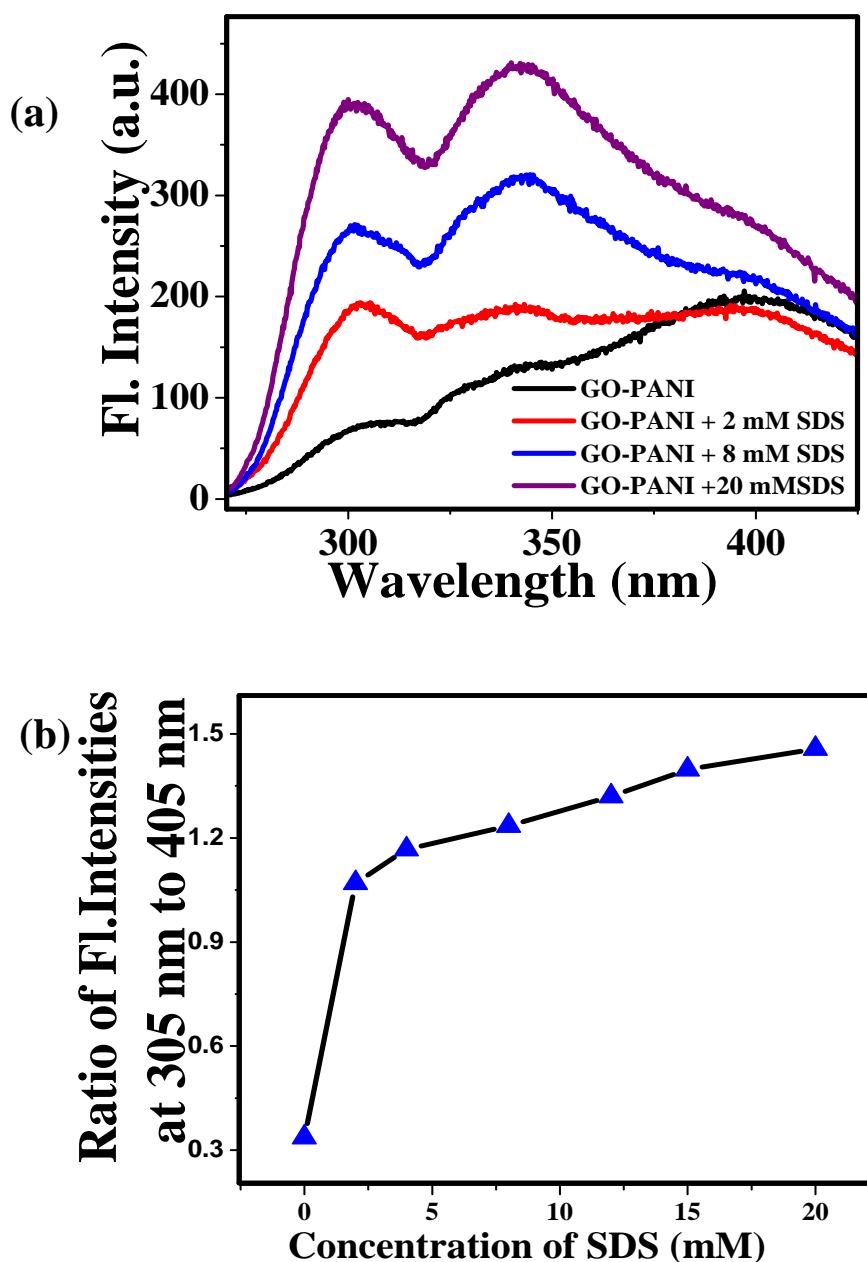
In the alkaline medium (pH~10.5), one absorption band appears at 275 nm due to $n-\pi^*$ transition of GO moiety as shown in [Fig. 1(b)]. Absence of the band at 438 nm indicates that polyaniline (PANI) is present as polyemeraldine base form [5]. The presence of anionic surfactant (SDS) up to 20 mM, no significant spectral change is observed indicating the absence of hydrophilic interaction between polyaniline chain and SDS molecules. But, a peak at 230 nm is appeared in the presence of SDS due to $\pi-\pi^*$ transition of GO moiety. The absorption spectra of GO-PANI in alkaline medium looks like GO may be due to the high surface negative charge on GO in GO-PANI arising from deprotonation of the carboxylic acid group in alkaline medium hinders the SDS adsorption on GO-PANI moiety [23].

6.3.3. Luminescence property of GO-PANI dispersion

Luminescence of GO and GO based nano material has great attention to the scientist due to their excellent tunibility by pH and other external additives. The interesting feature of emission property arises mainly due to intrinsic inhomogeneity within the GO based nanomaterial [5,17,23]. In the previous work, we have described the pH dependent luminescence of GO-PANI in chapter 4. But, the luminescence behaviour of GO-PANI nanocomposite in presence of anionic surfactant SDS, is yet to be observed. In the present work, we have studied the effect of an anionic surfactant (SDS) on the luminescence of the aqueous GO-PANI dispersion in the both acidic medium (pH~2.5) and alkaline medium (pH~10.5).

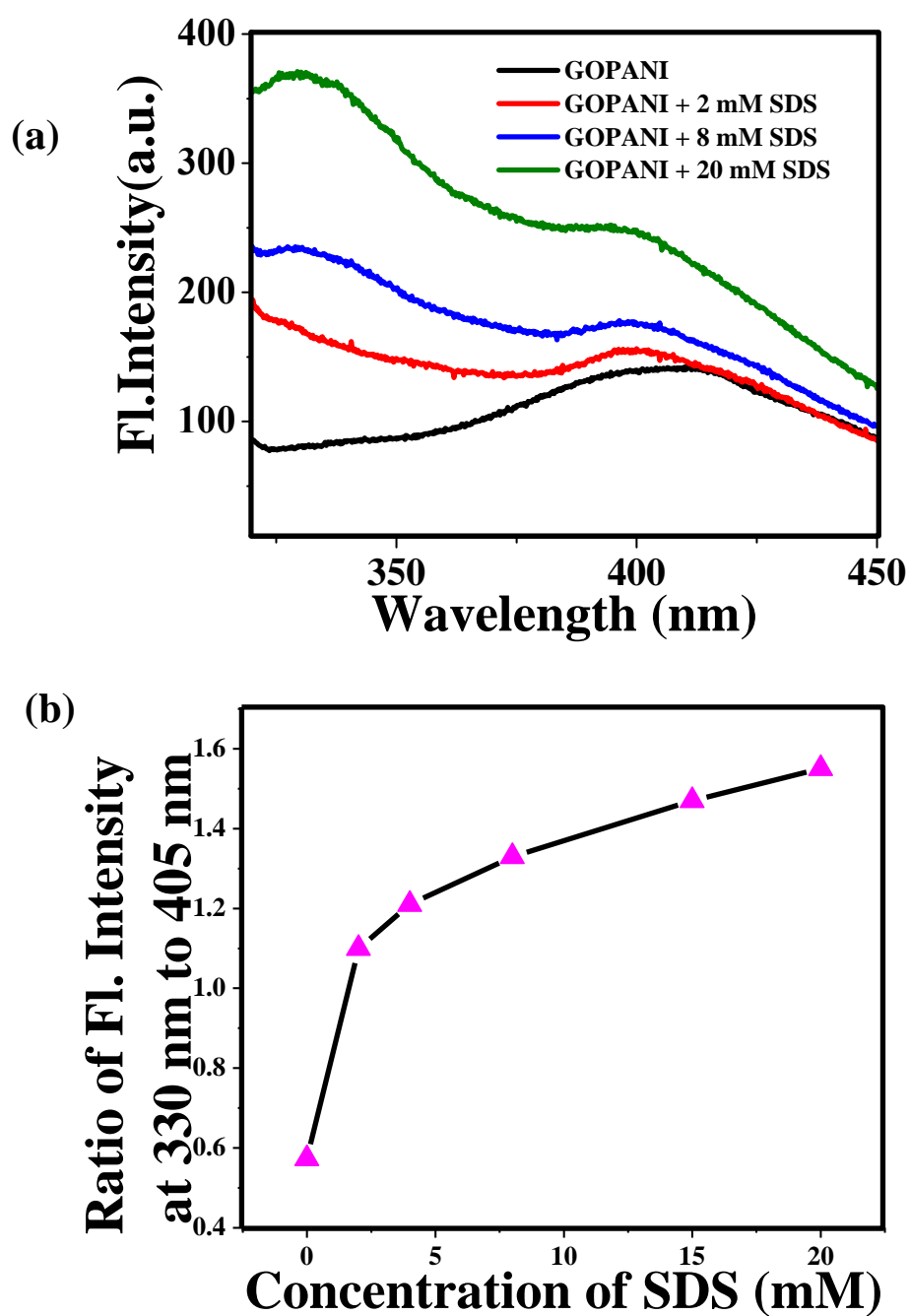
In the acidic medium (pH~2.5), exciting the aqueous dispersion of GO-PANI at 230 nm, one major peak appears at 405 nm with two distinct low intense shoulders at 305 nm and 345 nm [Fig. 2(a)].

Fig-2



(a) Photoluminescence Spectra of acidic dispersion of GO-PANI with different SDS concentration ($\lambda_{ex} = 230$ nm), (b) Plot of ratio of fluorescence intensities at 305 nm to 405 nm vs concentration of SDS ($\lambda_{ex} = 230$ nm)

Fig-3



(a) Photoluminescence Spectra of acidic dispersion of GO-PANI with different SDS concentration ($\lambda_{\text{ex}} = 280 \text{ nm}$), (b) Plot of ratio of fluorescence intensities at 330 nm to 405 nm vs concentration of SDS ($\lambda_{\text{ex}} = 280 \text{ nm}$)

The luminescence peak at 405 nm obtained by exciting at both 230 nm and 280 nm below the pH~2 is described in chapter 4 and it is due to the fluorophoric species formed by the charge transfer interaction between polaron state of PANI and GO, as the polyemeraldine salt of PANI existing at very low pH consists of the polaron state. But, addition of anionic surfactant (SDS) up to 2 mM, we have observed that the intensity of the emission band at 405 nm is almost constant with the enhancement of intensity of the emission bands at 305 nm and 345 nm. Above 2 mM concentration of the anionic surfactant (SDS), intensity of the emission band at 305 nm and 345 nm increases up to 20 mM SDS concentration. Interestingly, a slight blue shift of the 405 nm emission band to 395 nm is found at the concentration of SDS above 2 mM. But, the increase in intensity of this luminescence band is relatively lower than that of the emission bands at 305 nm and 345 nm. This is clear from the plot of the ratio of fluorescence intensity at 305 nm to 405 nm vs SDS concentration as shown in [Fig. 2(b)]. [Fig. 3(a)] exhibits the steady state emission of acidic dispersion (pH~2.5) of GO-PANI at the excitation wavelength of 280 nm. Along with one major emission band at around 405 nm, a new emission band centred at 330 nm is appeared by the addition of 2 mM SDS as shown in [Fig. 3(a)]. Intensity of the emission band at 405 nm is found to be almost constant up to ~2 mM SDS. But, when the concentration of SDS is above 2 mM, intensity of both the emission band at 330 nm and 405 nm increases but relative enhancement of intensity of 330 nm is considerably greater than that of the 405 nm emission band. This is shown by plotting the fluorescence intensity at 330 nm to 405 nm vs SDS concentration in [Fig. 3(b)] These observations suggest that there are three regions of luminescence in GO-PANI nano-composite, one at 300-310 nm, another two at 330-345 nm and ~405 nm and the relative contribution of the fluorophoric moieties changes with the concentration of anionic surfactant SDS. In the absence of SDS, the region of luminescence at 300-310 nm and 330-345 nm remain suppressed in case of the GO-PANI nano-composite. So, to explore the origin of the

emission feature of GO-PANI in presence of anionic surfactant SDS, we have to consider the mode of interaction between the anionic surfactant (SDS) and GO-PANI in the acidic media (pH~2). Constancy of the intensity of the emission band at 405 nm up to 2 mM concentration of SDS indicates that the charge transfer interaction between GO and emeraldine salt form of PANI is unaffected within this concentration range and this observation also suggests that the emission band of 405 nm is not modulated up to this concentration of SDS. But, when the concentration of SDS is above 2 mM, the interaction of SDS with the PANI results the change in the conformation of PANI from compact coil to expand coil form. This change in conformation of PANI decreases the number of PANI moieties interacting with GO by the replacement of PANI chains due to the formation of hemispherical surface micelles on the GO sheets. Because of the decrease of the PANI moieties at the GO surface, the contribution of the intensity of the luminescence band at 405 nm due to donor-acceptor interaction between PANI and GO decreases with respect to the intensity at both 305 nm and 345 nm emission bands. The observation of slight blue shifted luminescence at ~395 nm may be interpreted as a result of creation of nonpolar environment due to hemispherical surface micelles formed by the adsorption of SDS, around the fluorophoric moiety. Again, the intercalation of the SDS molecules between the GO layers may weaken the stacking interaction among the successive basal planes of GO. So, the appearance of two emission bands at 305 nm and 345 nm (excitation wavelength = 230 nm) may be due to weakening of the stacking interaction among the successive GO layers. Similar type of appearance of small shoulder at 305 nm in the luminescence spectra of acidic dispersion of GO in the presence of SDS (concentration ≥ 4 mM) has been already interpreted as a consequence of very weak π - π stacking interaction due to the intercalation of SDS between GO layers [17]. With increase concentration of SDS, the extent of intercalation increases between GO layers results more and more emission intensity at the 300-310 nm and 330-345 nm.

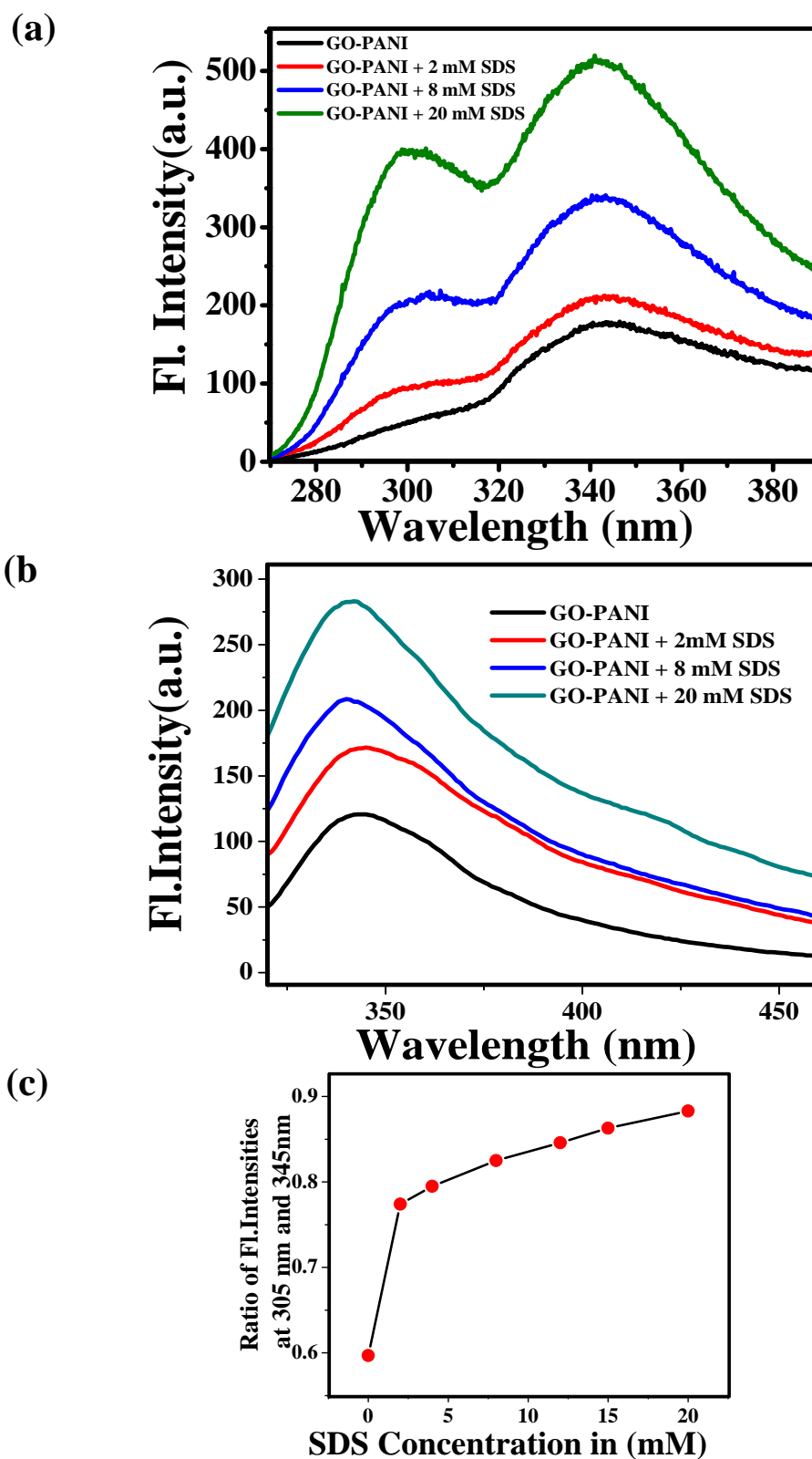


Fig-4: PL Spectra of GO-PANI in alkaline dispersion ($\text{pH} \approx 10.5$) at different SDS concentration (a) $\lambda_{\text{ex}} = 230 \text{ nm}$ (b) $\lambda_{\text{ex}} = 280 \text{ nm}$ (c) Plot of ratio of PL intensities at 305 nm to 405 nm vs concentration of SDS ($\lambda_{\text{ex}} = 230 \text{ nm}$ at $\text{pH} \sim 10.5$)

The origin of the emission around 300-310 nm and 330-345 nm will be explained in details after the discussion of the luminescence patterns in alkaline medium. But interestingly, the enhancement of the intensity of the luminescence band at around 300-310 nm of GO-PANI in acidic medium is considerably greater than the GO dispersion in acidic medium in the presence of 20 mM SDS. So, this observation is suggesting that PANI chains may have a significant role for the appearance of the luminescence at 300-310 nm in the acidic medium (pH~2.5) of aqueous GO-PANI dispersion in the presence of SDS. The photoluminescence spectra obtained by exciting the aqueous dispersion of GO-PANI in the basic medium (pH ~10.5) at 230 nm [Fig. 4(a)] shows a major luminescence band at 345 nm and a small shoulder at 305 nm in the absence of SDS. By exciting the aqueous dispersion of GO-PANI at 280 nm, photoluminescence peak is obtained at 345 nm [Fig. 4(b)]. The emission band at 345 nm at basic medium is due to the fluorephoric moiety of GO [5]. The low intense but distinct shoulder around 305 nm in the alkaline medium of GO-PANI dispersion may be appeared from the benzoic acid or phenol like structure of the GO moiety [17]. But, addition of SDS up to 20 mM, the intensity of the emission band at 305 nm is significantly enhanced along with the emission band at 345 nm [Fig. 4(a)]. The charge transfer interaction between GO and PANI is not possible in the alkaline medium, as PANI exist as polyemeraldine base form. The steady state emission feature of the aqueous GO-PANI dispersion in the alkaline medium is resembled to the aqueous GO dispersion of pH~10.5 in the presence of SDS up to 20 mM [17]. To interpret the enhancement of the intensity of the photoluminescence band at 305 nm, we have to consider the mode of interaction between GO and SDS at highly alkaline pH. The zeta potential values of aqueous GO dispersion [24] at various pH indicates that GO contains negative surface charges [25] arising from the carboxylate groups at the edges. Hence, adsorption of SDS on the GO surface is prohibited due to repulsion between negative head groups of SDS and negatively charged carboxylate groups. But, surfactants may be

intercalated between GO layers [26] and this intercalation disrupts the π - π stacking interaction between the successive GO sheets. Song et al. have reported the intercalation of anionic surfactant to increase the dispersion stability of functionalized graphene [27]. However, the disruption of π - π stacking interaction because of the intercalation SDS within the basal plane of GO may lead to largely separated GO layers [17]. With the increase in the distance between basal planes of GO, the band gap of GO moiety increases [23]. Increase in intensity of the luminescence band at 305 nm may be due to the increase in the band gap of GO and the largely separated GO layers induces the pronounced effect of the luminescence band of the benzoic acid or phenol like species present in the GO sheets. Plot of ratio intensities at 305 nm and 345 nm of alkaline dispersion of GO against SDS concentration [Fig. 4(c)] shows that with increase in SDS concentration photoluminescence intensity at 305 nm is enhanced as a result of weakening of π - π stacking interaction due to increase in the extent of SDS intercalation within GO layers and this leads to the observation of more prominent emission from benzoic acid or phenol like moiety as the interaction between the two successive GO layers is negligibly small in the presence of SDS. Onyang and co-workers have interpreted long wavelength excimer photoluminescence band due to π - π overlapping between successive GO sheets and another blue shifted photoluminescence band of monomeric GO species without interlayer π - π interaction at very low concentration of GO [28]. Similar type of observation is also found for polyaromatic compounds [29]. But, further investigation using the time resolved study is required to confirm this type of observation.

6.3.4. Comparative Luminescence

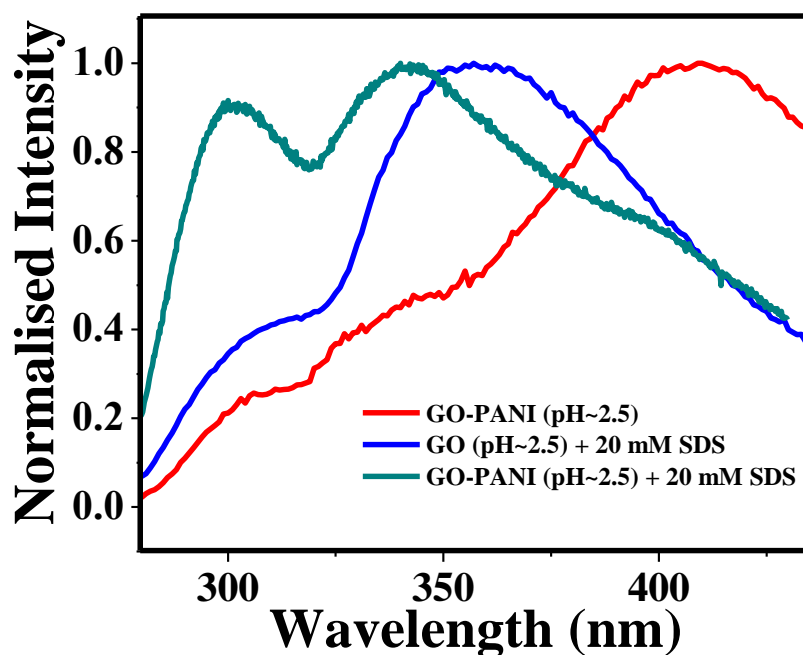
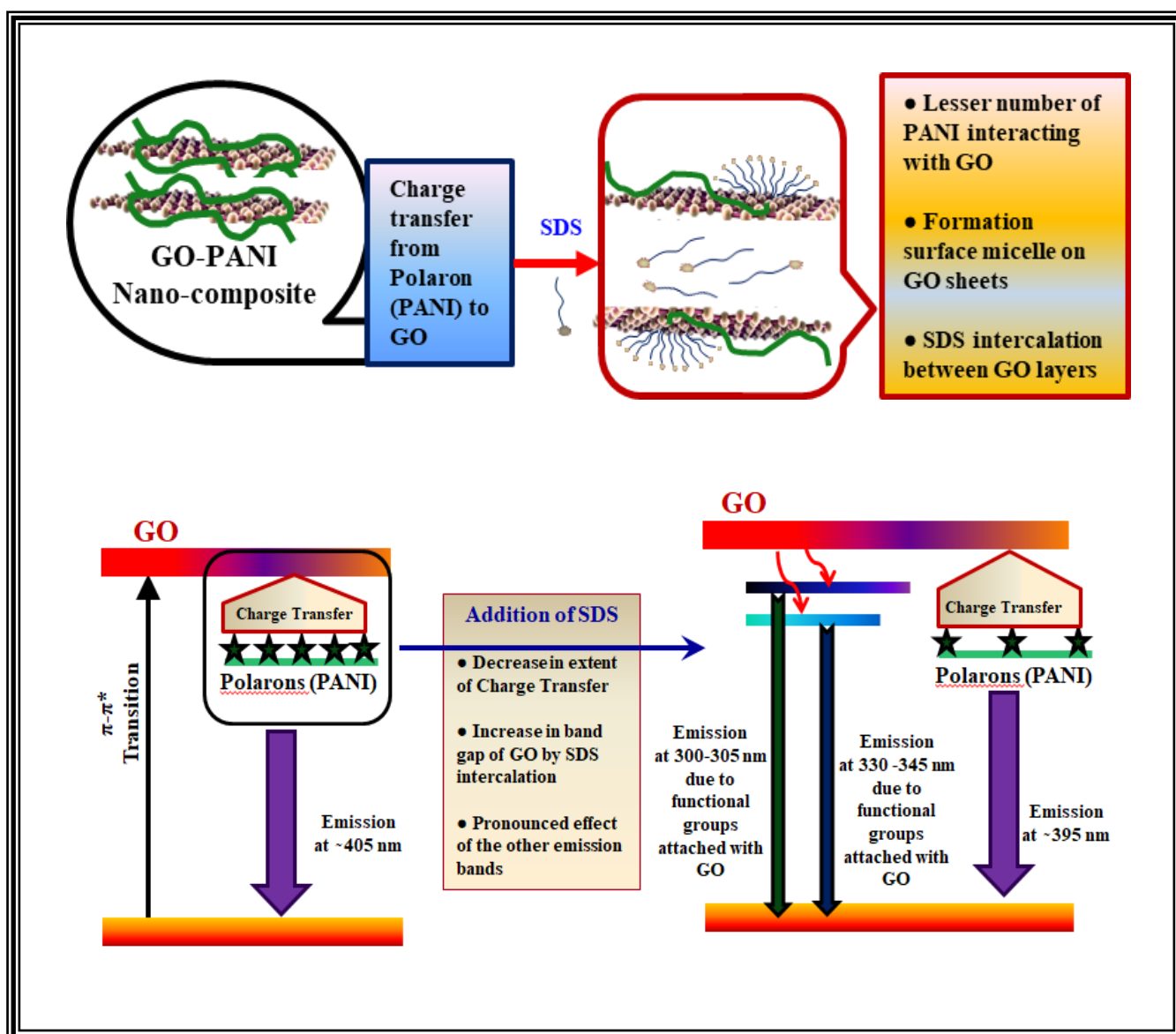


Fig. 5 Normalized photoluminescence spectra of aqueous dispersion of GO-PANI (pH \approx 2.5), GO (pH \approx 2) and 20 mM SDS, GO-PANI (pH \approx 2.5) and 20 mM SDS (λ_{ex} = 230 nm)

On the basis of our experimental findings, we may explain the effect of an anionic surfactant (SDS) on the tunability of the luminescence spectra of both GO and GO-PANI in acidic (pH~2.5) and alkaline (pH~10.5) dispersions by comparing with the results of our previous work as represented in [Fig. 5] which is described in chapter 4 and chapter 5 respectively. Using this comparison a qualitative idea about the various types of tunable luminescence bands may be drawn. In general, the luminescence of GO may be originated from the presence of functional groups of the GO sheets, isolated cluster of conjugated sp^2 carbon and interlayer stacking interaction, as the defect in the electronic band structure of graphene based nano material may be induced by all these three reasons [30-32]. Interacting basal plane with oxygen containing functional groups forming the layer structures of GO may be responsible

for the UV emission around 380-390 nm which is blue shifted as a result of movement basal planes from each other by increasing pH [23]. The luminescence at the region 300-310 nm and 330-345 nm arises due to oxygen containing mono-functional and bi-functional groups along with conjugation within the sp^2 carbon network, respectively. Matsuda and co-workers have already observed UV luminescence band of GO [30]. According to them, the emission is originated as a result of sp^2 fragments consisting of small numbers of aromatic ring with oxygen containing functional groups [30]. Among these two regions, the emission around 300-310 nm is mostly suppressed when the GO layers are not much separated. So, the intensity at this region is very small for GO only in both acidic and alkaline medium. But in presence of SDS (concentration ≥ 4 mM) the intensity of this luminescence band is starting to increase even in acidic pH due to intercalation of SDS between the basal plane of GO [17]. In alkaline medium, when the SDS intercalation between the GO layers, which are already separated by the repulsion between carboxylate groups, is favourable, π - π stacking interaction among the successive GO layers is practically disrupted to produce largely separated GO sheets. In consequence, luminescence around 300-310 nm is more pronounced [17]. Now in case of GO-PANI nano-composite at $pH < 2$, the intensity of luminescence peak at 405 nm, arising from electron donor-acceptor moiety is high, compared to the luminescence at 300-310 nm and 330-345 nm as GO sheets are grafted by PANI and thereby suppressing the luminescence due to oxygen containing functional groups at the GO surface and the conjugated network of sp^2 carbon atoms. But when SDS molecules form hemispherical surface micelle on the GO sheets by replacing some PANI chains from GO layers, the number of polyemeraldine salt form of the PANI moiety interacting with the GO decreases. This leads to the decrease in the contribution of GO-PANI charge transfer species along with a slight blue shift due to relatively nonpolar environment created by SDS surface micelle. [Fig. 5]

Fig. 6



Schematic diagram representing the interlayer spacing between GO-PANI sheets and effect of SDS on the emission at acidic medium ($\text{pH} \approx 2.5$)

Again, the replacement of some PANI moiety from the GO sheets and intercalation of SDS between the basal plane of GO lead to the pronounced effect of the oxygen containing functional groups at the GO surface and the conjugated network of sp^2 carbon atoms and so the enhancement of luminescence at the region of 300-310 nm and 330-345 nm. The entire physical process is schematically represented in [Fig. 6]. Since, PANI is almost non-interacting in the alkaline medium (pH~10.5) as polyemeraldine salt is de-protonated to form polyemeraldine base, the effect of SDS on the luminescence spectra of GO-PANI resembles to that of alkaline dispersion of GO in presence of SDS exhibiting significant luminescence at 305 nm due to largely separated GO layers.

6.3.5. Fluorescence Excitation Spectra

The fluorescence excitation spectra (FLE) of aqueous dispersion GO-PANI in the acidic medium (pH~2.5) in presence and absence of SDS monitored at 345 and 330 nm respectively, shows two distinct bands at 230 nm and 280 nm [Fig. 7(a) and Fig. 7(b)]. This observation clearly suggests that both the emission bands appeared at 330 nm and 345 nm are originated from same fluorophoric moiety present in the ground state. In this context, it can be mentioned that the observed FLE bands at 280 nm and 230 nm resemble to the first and second singlet-singlet transition in benzoic acid, respectively [17]. Since, the chemically functionalized GO contains carboxylic groups attached with the hexagonal sp^2 hybridized carbon atoms, the appearance of FLE band at 280 nm and 230 nm is quite natural. The FLE monitored at the wavelength of 405 nm of GO-PANI dispersion in the absence and presence of 20 mM SDS [Fig-7(c)], appearance of a major band at 250 nm suggests that the species emitting at 405 nm absorbs at 250 nm [5] and adsorption of SDS does not completely destroy the fluorophoric species obtained due to charge transfer interaction in GO-PANI nano-composite.

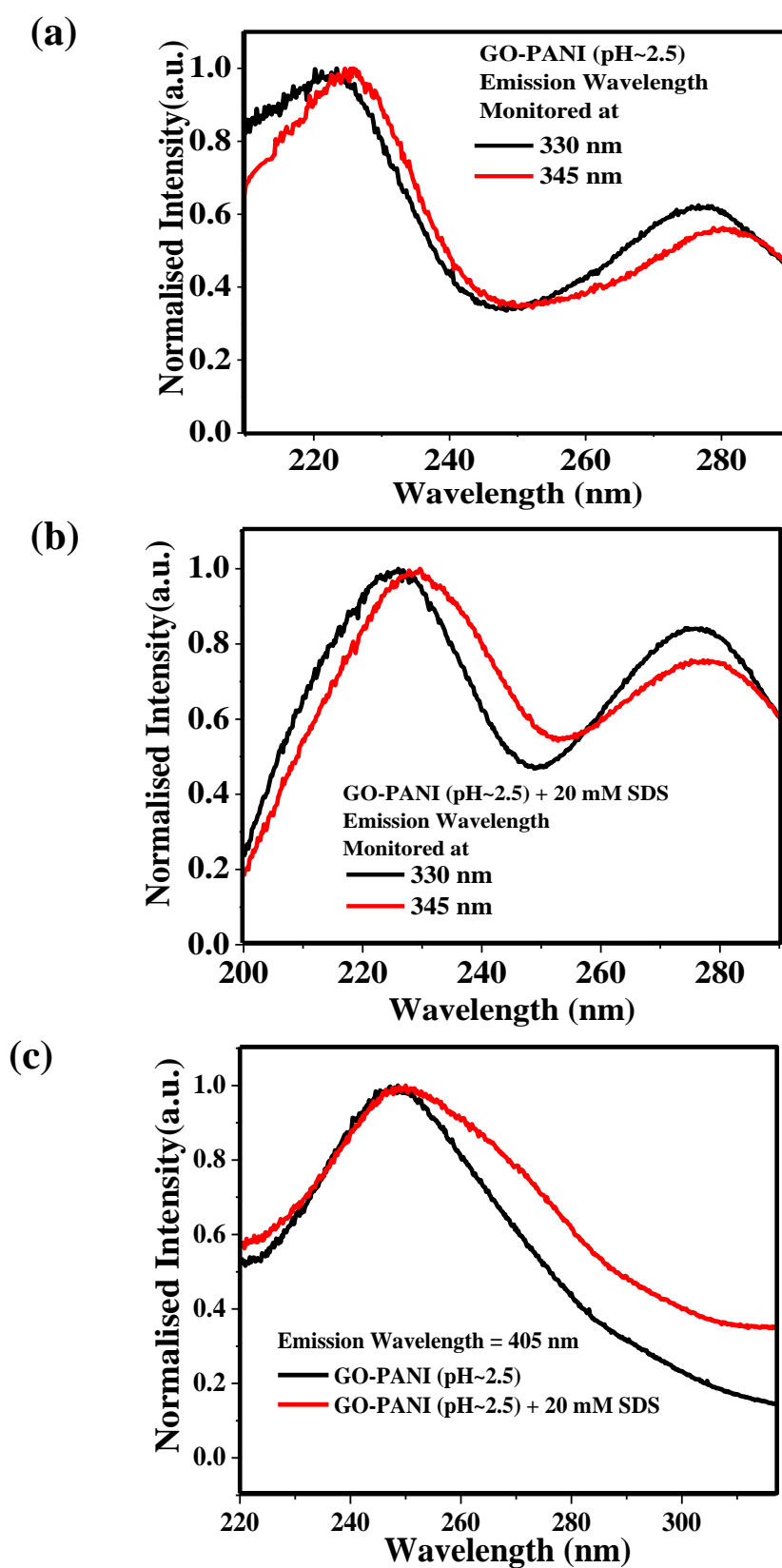


Fig. 7 (a) Excitation Spectra of GO-PANI Dispersion (pH \approx 2.5), (b) Excitation Spectra of GO-PANI Dispersion (pH \approx 2.5) in presence of 20 mM SDS, (c) Excitation Spectra of GO-PANI Dispersion (pH \approx 2.5) in presence and absence of SDS at 405 nm

6.3.6. Fluorescence Life Time of GO-PANI dispersion

Fig. 8a shows the fluorescence decay at 405 nm obtained by exciting the aqueous GO-PANI dispersion (pH~2.5) at 280 nm, in absence and presence of SDS. The fluorescence decays are fitted well with bi-exponential function. In the absence of SDS, the life time of the fast decay process is 2.4 ns with 69% contribution and life time of the slow decay process is 5.3 ns with 31% contribution as given in Table 1. The appearance of the 2.4 ns component and the long-lived component (more than 5 ns) in the fluorescence decay at 405 nm may be from a new species, which is formed by the charge transfer interaction between GO and PANI in the acidic medium [5]. But, the addition of SDS above 2 mM, the life time of the fast component decreases to ~ 900 ps with 90% contribution and the life time of the long-lived component increases to ~ 6.0 ns with 10% contribution. The decrease in the life time may be interpreted by considering the interaction of SDS with the GO-PANI. As the SDS molecules interact with GO-PANI, the conformation of PANI changes from compact coil to expanded coil. This change in conformation of PANI in presence of SDS decreases the number of PANI moieties interacting with GO. Because of the decrease of the PANI moieties at the GO surface, the luminescence life time of the fast component (2.4 ns) of the charge transfer moiety disappears. So, the observed life time of the fast component with ~900 ps may be obtained from fluorophoric moiety of GO which is not interacting with PANI as a result of its conformational change in presence of SDS. But, the slow decay process with life time with ~ 6.0 ns may be obtained due to radiative combination processes from both the luminescent GO moiety surrounded by hemispherical surface micelles and GO-PANI charge transfer species.

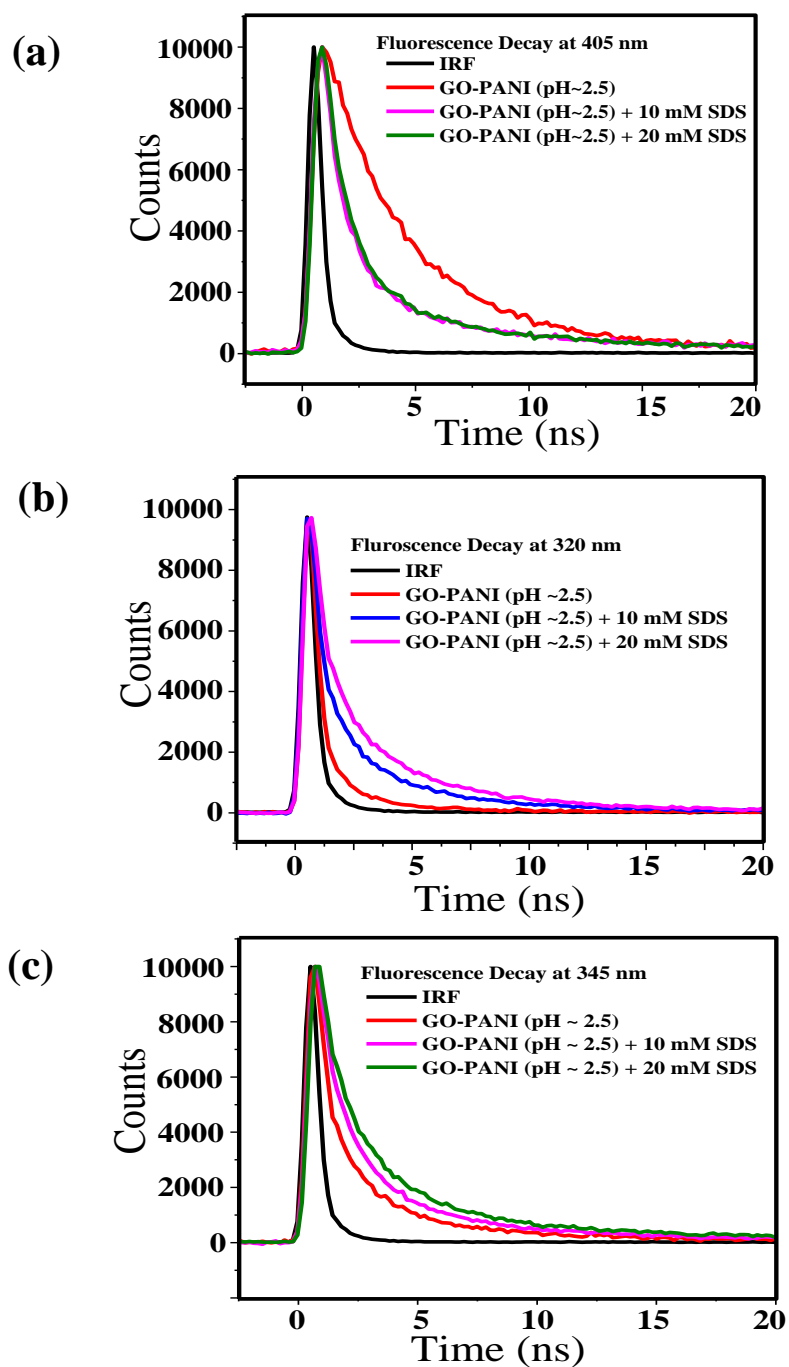


Fig. 8 Fluorescence decays of aqueous dispersion of GO-PANI (pH \approx 2.5) in presence and absence of SDS (a) at 405 nm (b) 320 nm (c) 345 nm

expanded coil form of PANI chains, is replaced from the GO sheets by SDS surface micelles. The fluorescence decays of the acidic dispersion (pH~2.5) of GO-PANI, obtained at 320 nm and 345 nm, both in the presence and absence of SDS, are found to be bi-exponential in nature (Fig. 8b and Fig. 8c). As the excitation wavelength of our TCSPC set up is 280 nm, the fluorescence decays of the acidic dispersion of GO-PANI are recorded at 345 nm and 320 nm (instead of 305 nm to avoid any interference from Raman scattering). In the presence and absence of SDS, the short-lived life time of the fluorescence decay process of GO-PANI in acidic medium is less than 1000 ps which is due to non-radiative re-combination process and the life time of the slow radiative decay process is 3-3.5 ns at 320 nm. But, the decrease in the contribution of the fast component and increase in the component of the slow component with the increase in the SDS concentration (Table 2) clearly suggests the suppression of the non-radiative process of the luminescent moiety of GO [17] due to non-polar environment by the formation of hemispherical SDS micelles. Since, the intercalation of SDS at high concentration (20 mM) ruptures the interlayer stacking interaction in GO, the fluorescence decay of acidic dispersion of GO-PANI in the presence of 20 mM SDS at 320 nm arising from the luminescence of well separated GO layer consists of benzoic acid or phenol like structure, is almost identical with that of acidic dispersion of GO with 20 mM SDS [17]. Again, the decrease in the contribution of the short-lived decay component and increase in the contribution of the long-lived decay component at 345 nm (Table 2) with the increase SDS concentration indicates the enhancement of the life time of the luminescent moiety consists of clusters of the sp^2 hybridised carbon atoms attached with oxygen containing bi functional groups as luminescent moiety is surrounded by SDS surface micells. The similarity of the fluorescence decay characteristics of the acidic dispersion of GO-PANI in presence of 20 mM SDS with that of

Fluorescence decay Parameter of aqueous dispersion of GO-PANI (pH \approx 2.5) in presence and absence of SDS

Table-1

Concentration of SDS (mM)	Wavelength Monitored at 405 nm	
	τ_1^a	τ_2^a
0	2.4 ns (69%)	5.3 ns (31 %)
2	950 ps (90%)	5.86 ns (10 %)
10	965 ps (87%)	6.02 ns (13 %)
20	850 ps (88%)	6.03 ns (12 %)

a \pm 10 %

The life time (τ^a) can be reproduced within \pm 10 % uncertainty

Table-2

Concentration of SDS (mM)	Wavelength Monitored at 320 nm		Wavelength Monitored at 345 nm	
	τ_1^a	τ_2^a	τ_1^a	τ_2^a
0	390 ps (97%)	3 ns (3%)	800 ps (85%)	4.9 ns (15%)
2	400 ps (92%)	3.1 ns (8%)	830 ps (84%)	4.9 ns (16%)
10	620 ps (81%)	3.4 ns (19%)	1090 ps (82%)	5 ns (18%)
20	840 ps (75%)	3.5 ns (25%)	1100 ps (76%)	5.3 ns (24%)

a \pm 10 %

acidic dispersion of GO-PANI only [5] is indicating that the luminescence band at 345 nm is mainly originated from the fluorephoric moiety of GO. The longer life time of the slow component at 345 nm and at 320 nm may be explained by the symmetry argument. Du et al. have mentioned that the origin of the longer life time is related to the symmetry of the electronic states of excimer wave function [28]. According to Conwell et al. the similar parities of the ground state monomer and excimer is responsible for such longer life time [34]. We have also studied the fluorescence decay at 320 nm and 345 nm of GO-PANI aqueous dispersion in the alkaline medium (pH~10.5) by exciting at 280 nm. The existence of dual luminescence bands at 305 nm and 345 nm is already discussed in the photoluminescence section. The fluorescence decays at two wavelengths 345 nm and 320 nm are distinct in nature both in the presence and absence of SDS and fitted well by bi-exponential decay function. Since, PANI present as a polyemeraldine base form, does not interact with either GO [5] or SDS, only GO moiety of GO-PANI interacts with SDS molecules in the alkaline pH. As a result of this interaction between GO and SDS, the fluorescence decay and decay parameters of GO-PANI in the presence of SDS at 320 nm and 345 nm are almost same as obtained from aqueous GO dispersion in the alkaline medium in the presence and absence of SDS [17]. The details of fluorescence decay parameters of the alkaline dispersion of GO-PANI in presence and absence of SDS are discussed in chapter 5.

6.4. Conclusions

The most important finding of this work is the tuning of luminescence of GO-PANI nano-composite by the addition of a negatively charged surfactant (SDS). The electron donor-acceptor interaction between the polyemeraldine salt form of the PANI and the conjugated π network of the GO is affected by the anionic surfactant and this leads to the pronounced emission from the fluorophoric moiety of GO due to mono-functional and bi-functional oxygen containing functional groups attached with the sp^2 hybridised carbon

atoms of GO as a consequence of the intercalation of SDS molecules between the successive GO layers. But, in spite of the structural change in the PANI chains from compact coil to expanded coil form in presence of SDS, luminescence due to GO-PANI charge transfer species is not disappeared as some of the PANI chains are still interacting with GO even in presence of 20 mM SDS. However, relatively non polar surroundings created by the hemispherical surface micelles on the GO sheets, around the luminescent moiety produced by charge transfer interaction, results a slight blue shift. Thus, the luminescence in UV as well as visible regions by the excitation of the acidic dispersion of GO-PANI at UV regions may open up an illuminating pathway to produce various types of light emitting devices by using GO based nano-composites. But, the presence of SDS in the alkaline dispersion of GO does not show such interesting observation as the obtained luminescence of the GO-PANI is almost similar to that of GO itself exhibiting two luminescence bands in the UV region due to largely separated GO sheets produced by the weakening of layer to layer stacking interaction as a result of SDS intercalation between the basal planes of GO. Hence, the present work helps to understand the tunability of the luminescence of GO-PANI nano-composite and thereby enlightens the area for the development of optoelectronic materials.

6.5. Reference

- [1] H. B. Lee, A. V. Raghu, K. S. Yoon, H. M. Jeong, *J. Macromol. Sci. Phys.*, 2010, **49**, 802–809.
- [2] J. Wang, X. Wang, C. Xu, M. Zhang, X. Shang, *Polym. Int.*, 2011, **60**, 816–822.
- [3] C. Bao, Y. Guo, L. Song, Y. Hu, *J. Mater. Chem.*, 2011, **21**, 13942–13950.
- [4] P. Dutta, J. Afalla, A. Halder, S. Datta, K. Tominaga, *J. Phys. Chem. C*, 2017, **121**, 1442–1448.
- [5] P. Saha, D. K. Pyne, M. Pal, S. Datta, P. K. Das, P. Dutta, A. Halder, *Journal of Luminescence*, 2017, **181**, 138–146.
- [6] B. Xu, Y. Ovchenkov, M. Bai, A. N. Caruso, A. V. Sorokin, S. Ducharme, B. Doudin, P. A. Dowben, *Appl. Phys. Lett.*, 2002, **81**, 4281–4283.
- [7] F. Yakuphanoglu, B. F. Şenkal, *J. Phys. Chem. C*, 2007, **111(4)**, 1840–1846.
- [8] S. Virji, J. Huang, R.B. Kaner, B.H. Weiller, *Nano Lett.*, 2004, **4**, 491–496.
- [9] R. Karthik, S. Meenakshi, *Chem. Eng. J.*, 2015, **263**, 168–177.
- [10] N. C. S. Vieira, A. Figueiredo, A. D. Faceto, A. A. A. De Queiroz, V. Zucolotto, F. E. G. Guimaraes, *Sensor and Actuator B*, 2012, **169**, 397–400.
- [11] D.D. Nicolas, E.F. Poncin, *Anal. Chim. Acta.* 2003, **475**, 1-15.
- [12] U. Rana, S. Malik, *Chem. Comm.*, 2012, **48**, 10862-10864.
- [13] D. S. Galvao, D. A.D. Santos, B. Laks, C. P. De.Melo, M. J. Caldas, *Phys. Rev. Lett.*, 1989, **63**, 786-789.
- [14] S. Stafstrom, J. L. Bredas, A. J. Epstein, H. S. Woo, D. B. Tanner, W. S. Huang, A.G. MacDiarmid, *Phys. Rev. Lett.*, 1987, **59**, 1464-1467.
- [15] E.M. Genies, M. Lapkowski, *J. Elektroanal. Chem.*, 1987, **220**, 67-82.
- [16] C. Valles, P. Jimenez, E. Muñoz, A.M. Benito, W.K. Maser, *J. Phys. Chem. C*, 2011, **115**, 10468-10474.

- [17] P. Saha, D. K. Pyne, S. Ghosh, S. Banerjee, S. Das, S. Ghosh, P. Dutta, A. Halder, *RSC Adv.*, 2018, **8**, 584–595.
- [18] S. G. Vaidya, S. Rastogi, A. Aguirre, *Synthetic Metals*, 2010, **160**, 134–138.
- [19] S. I. De. Torresi, S. L. De Al. Maranhao, R. M. Torresi, *Synthetic Metals*, 1999, **101**, 797.
- [20] A. Aoki, R. Umehara, K. Banba, *Langmuir*, 2009, **25**, 1169-1174.
- [21] K.M. Molapo, P.M. Ndangili, R.F. Ajayi, G. Mbambisa, S.M. Mailu, N. Njomo, M. Masikini, P. Baker, E.I. Iwuoha, *Int. J. Electrochem. Sci.*, 2012, **7**, 11859-11875.
- [22] Y. Chunming, F. Zheng, Z. Pingmin, *J. Cen. Sou. Univ. Tech.*, 1999, **6**, 128-129. [23] P. Dutta, D. Nandi, S. Datta, S. Chakraborty, N. Das, S. Chatterjee, U. C. Ghosh, A. Halder, *Journal of Luminescence*, 2015, **168**, 269–275.
- [24] H. Hosoya, J. Tanaka and S. Nagakura, *J. Mol. Spectrosc.*, 1962, **8**, 257- 275.
- [25] D. Li, M. B. Mülle, S. Gilje, R. B. Kaner and G. G. Wallace, *Nat. Nanotechnol.*, 2008, **3**, 101-105.
- [26] K. Zhang, L. Mao, L. L. Zhang, H. S. O. Chan, X. S. Zhao and J. Wu, *J. Mater. Chem.*, 2011, **21**, 7302-7307.
- [27] Y. Song, H. Lee, J. Ko, J. Ryu, M. Kim and D. Shon, *Bull. Korean Chem. Soc.*, 2014, **35**, 2009 – 2012.
- [28] D. Du, H. Song, Y. Nie, X. Sun, L. Chen and J. Ouyang, *J. Phys. Chem. C*, 2015, **119**, 20085-20090.
- [29] W. T. Yip, D. H. Levy and *J. Phys. Chem.*, 1996, **100(28)**, 11539–11545.
- [30] D. Kozawa, Y. Miyauchi, S. Mouri, K. Matsuda, *J. Phys. Chem. Lett.*, 2013, **4**, 2035-2040.

- [31] 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.
- [32] Q. Mei, K. Zhang, G. Guan, B. Liu, S. Wang, Z. Zhang, *Chem. Commun.*, 2010, **46**, 7319–7321.
- [33] K. Zhang, Li Li Zhang, X. S. Zhao, Jishan Wu, *Chem. Mater.*, 2010, **22**, 1392– 1401.
- [34] E. Conwell, *Phys Rev. B: Condens Mater Phys.*, 1998, **57**, 14200-14202.