

# **“Tunable Luminescence of Graphene Based Nanomaterials: Role of Surfactants and Macromolecules”**

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for the degree Doctor of Philosophy in Science**

**by**

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**Thesis Title: “Tunable Luminescence of Graphene Based Nanomaterials : Role of Surfactants and Macromolecules”**

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## Summary of the Research Work:

The entire work is devoted to the synthesis of graphene based nanomaterial and study of their photoluminescence property. For the first time, Polyaniline (PANI) grafted Graphene Oxide (GO-PANI) nanocomposite exhibits a remarkable change in luminescence band from UV to visible region with the decrease in pH. Exciting at 230 nm, a single emission band at 345 nm is observed and this band is shifted from UV to blue region by decreasing the pH less than 3. Aqueous dispersion of GO-PANI (pH = 4.6) shows dual fluorescence at 345 nm and 405 nm upon excitation at 280 nm indicating the presence of two emissive moieties. At pH < 3, single fluorescence peak at 410 nm is observed by exciting GO-PANI at 280 nm, whereas the emission band is centered at 345 nm when pH is more than 5. Instead of the peaks at 230 nm and 280 nm in alkaline region, a peak at 250 nm has been obtained in the excitation spectra (at pH < 3) monitored at 410 nm. This observation suggests the formation of a new ground state species. Presence of this species is further supported by a fluorescence lifetime components at 410 nm. Appearance of a new emission band in visible region at very low pH may be explained as a result of the formation of a ground state species by electron donor-acceptor interaction between emeraldine salt form of PANI and GO along with  $\pi$ - $\pi$  stacking interactions. Formation of this emissive species in the ground state is supported by the pH dependent emission spectra, fluorescence excitation spectra and life time data. The present work also demonstrates the change in photoluminescence property of GO as a result of interaction between an anionic surfactants (CTAB and SDS) in both acidic and alkaline dispersion. The mode of interaction between surfactants (SDS and CTAB) and GO is different in different pH of the medium. It has been found that the mode of interaction between surfactants and GO, modulating the photoluminescence feature of GO. In the acidic dispersion (pH  $\approx$  2) of GO, the surfactant, SDS is adsorbed on the GO sheets and the critical surfactant aggregation constant (CSAC) is obtained at a SDS concentration greater than 2 mM. Adsorption of SDS on the GO sheets as

hemispherical micelles, at  $\text{pH} \approx 2$  modulates the photoluminescence band of GO due to formation of nonpolar confined environment. As a result of this, the acidic dispersion of GO in presence of 32 mM SDS shows red edge effects which is a common consequence of restricted solvent relaxation process. This results a marked 36 nm blue shift of photoluminescence spectrum. This type of SDS adsorption is prohibited in alkaline medium ( $\text{pH} \approx 10$ ) due to the presence of negatively charged carboxylate ions at the GO edges. But, appearance of a new luminescence band at 303 nm, in the presence of SDS (at  $\text{pH} \approx 10$ ), is possibly due to weakening of  $\pi$ - $\pi$  stacking interaction by the intercalation of SDS within the basal planes of GO. This lead to SDS intercalated largely separated layers of GO moiety which may be responsible for the fluorescence at 303 nm. The blue shift of emission maxima of GO in the acidic medium in the presence of CTAB may also due to the creation of nonpolar environment by the formation of hemispherical surface micelle. It should be mentioned that, we did not carried out the photoluminescence experiment of GO in alkaline medium in the presence of CTAB due to aggregation formation of GO (i.e. unstable dispersion of GO) resulting from the ionic interaction between the positively charged ammonium ions of CTAB head and the negatively charged carboxyl groups of GO. It has been also found that the luminescence of the GO-PANI nano-composite tuned in the presence of an anionic surfactant (SDS). In acidic medium ( $\text{pH} \sim 2.5$ ), GO, grafted by polyemeraldine salt form of PANI, interacts with SDS having concentration above 2 mM and there by hemispherical surface micelles on GO sheets are formed by replacing of some of the PANI chains from GO surfaces. This leads to a non-polar environment around the fluorephoric moiety of the GO-PANI nano-composite. In consequence, relative contribution of the slightly blue shifted luminescence due to charge transfer species in GO-PANI decreases. In addition to this, intercalation of SDS between the GO layers weakens the stacking interaction among the basal planes of GO and as a result of it, two emission bands at 300-310 nm and 330-345 nm, originating due to the functional groups

attached with GO sheets  $sp^2$  conjugated carbon atom in GO, are markedly appeared. In alkaline medium (pH~10.5), polyemeraldine base of PANI remains non interacting with GO and so the effect of SDS on the luminescence is similar with that of alkaline dispersion of GO, in presence of SDS, where SDS intercalated largely separated layers of GO moiety shows two characteristics luminescence bands of GO. The present work also includes that the tunable photoluminescence feature obtained 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  $\pi$ - $\pi$  stacking interaction between GO layer and there by lowered the band gap of GO. The aggregate of GO may be formed in the solution as GO layers become closer with increase concentration of GO by increasing  $\pi$ - $\pi$  stacking interaction between the layers of GO. Hence, the present work shades light on the interesting tunable photoluminescence features of GO and GO-PANI. The work may provide a further insight on the research of GO based pH sensing materials and also the effect of pH on the luminescence properties of GO-PANI may have implications in biological sensing and optoelectronics. The observation of pH dependent fluorescence of GO-PANI may be extended to carbon quantum dots and other nanocomposites. The tunable photoluminescence feature from the synthesised graphene based nanomaterial will help to develop various kinds of GO based optoelectronic devices. This tunable luminescence obtained as a function of the surfactant (SDS) concentration and pH of the medium may also be applied in the photocatalysis.

## Conclusion

- (i) We have synthesised graphene based material GO and GO-PANI with complete characterisation by Raman Spectroscopy, XRD, FT-IR, SEM and TEM. The characterisation data reveals that the GO and GO-PANI material is perfectly synthesised and the composite material (GO-PANI) is new type of nano composite material that we have synthesised. The luminescence feature originated from our synthesised material which makes different from different groups as reported in the literature.
- (ii) For the first time aqueous dispersion of GO-PANI is exhibiting a remarkable change in fluorescence band from UV to visible region with the decrease in pH. Appearance of a new emission band in visible region at very low pH may be explained as a result of the formation of a ground state species by electron donor-acceptor interaction between emeraldine salt form of PANI and GO along with  $\pi$ - $\pi$  stacking interactions. Formation of this emissive species in the ground state is supported by the pH dependent emission spectra, fluorescence excitation spectra and life time data. Hence, this work indicates that the emission of GO-PANI is tuned by the pH of the medium and this is possibly the first report of such pH dependent tuning of luminescence between UV and visible region.
- (iii) The modulation of luminescence of GO in the UV region as a result of interaction between an anionic surfactant (SDS) and a cationic surfactant CTAB in both acidic and alkaline medium is reported for the first time. In the acidic medium (pH  $\approx$  2) of GO, the surfactant, SDS, is adsorbed on the GO sheets and the critical surfactant aggregation constant (CSAC) is obtained at a SDS concentration greater than 2 mM. Adsorption of SDS on the GO sheets as hemispherical micelles, at pH  $\approx$  2 modulates the photoluminescence band by providing a nonpolar confined

environment. Similarly, The blue shift of emission maxima of GO in the acidic medium in the presence of CTAB may also due to the creation of nonpolar environment by the formation of hemispherical surface micelle. As a result of this, the acidic dispersion of GO in presence of 32 mM SDS shows red edge effects which is a common consequence of restricted solvent relaxation process. Observation of the increase in the fluorescence life time of the fluorophoric moiety of GO with increase in SDS concentration is suggesting the decrease in nonradiative decay process due to lower accessibility of solvent molecules near the GO fluorophores. In the alkaline medium, instead of adsorption on GO sheets, intercalation of SDS molecules within the GO layers may occur and these intercalations enhance the distance between successive GO sheets. This leads to the weakening of  $\pi$ - $\pi$  stacking interaction between the basal planes of GO. The time resolved photoluminescence data also supports the entire scenario and indicate the presence of two types of GO moieties, one with weak  $\pi$ - $\pi$  stacking interaction another with almost disrupted  $\pi$ - $\pi$  interaction between GO sheets containing benzoic acid or phenol like structure due to the intercalation of SDS, results dual photoluminescence band in alkaline medium in the presence of SDS. Thus, the both surfactant (CTAB and SDS) modulates the luminescence of GO.

- (iv) Interestingly, the tuning of luminescence of GO-PANI nano-composite also observed by the interaction with a negatively charged surfactant (SDS). The electron donor-acceptor interaction between the polyemeraldine salt form of the PANI and the conjugated  $\pi$  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. But, the presence of SDS in the alkaline dispersion of GO-PANI does not show such interesting observation as the obtained luminescence of the GO-PANI is almost similar to that of GO (pH~10) 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, this is possibly first report of such tuning of luminescence between UV and visible region from aqueous dispersion of GO-PANI interacting with SDS.

- (v) The modulation of photoluminescence is also observed from aqueous dispersion of GO by changing concentration. 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 possibly first time. This observation may be due to increase  $\pi$ - $\pi$  stacking interaction between GO layer and there by lowered the band gap of GO. Thus, the present modulation of photoluminescence (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.



## **Future Aspect:**

The entire work highlighting the modulation of luminescence of GO has been discussed in the thesis. The effect of pH on the luminescence properties of GO-PANI may have implications in biological sensing and optoelectronics and also may provide a further insight on the research of GO based pH sensing materials. Also, the modulation of photoluminescence feature of GO by interacting with the surfactants (SDS, CTAB) may help to develop various kinds of GO based optoelectronic materials. The effect of intercalation of anionic surfactant SDS between GO layers in the alkaline medium. The effect of intercalation of surfactant can be a beneficial route to produce of high-quality single layer graphene oxide nanosheets. The effect of concentration on the photoluminescence feature from our synthesized GO is observed, which 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. Thus, the entire work indicates that GO based material has a wide range of local energy gaps due to the presence of  $sp^2$  clusters which is very useful to the design of nano-optoelectronic and biomedical devices.