Chapter 1

Introduction

1.1. General Introduction

Carbon based nano materials has tremendous interest to the researcher due to their unique structural and physical properties, availability, low cost and easier to synthesis. Again, Enhancement of energy production is one of the major challenge in 20^{th} century to the whole world, so carbon based nano materials are the most promising candidate to the scientist to accept this challenge. It is also found that carbon-based nano materials exist in all dimensions in nature, like fullerenes as zero-dimensional, carbon nanotubes (CNTs) as one-dimensional and graphene as two-dimensional [Fig.1].

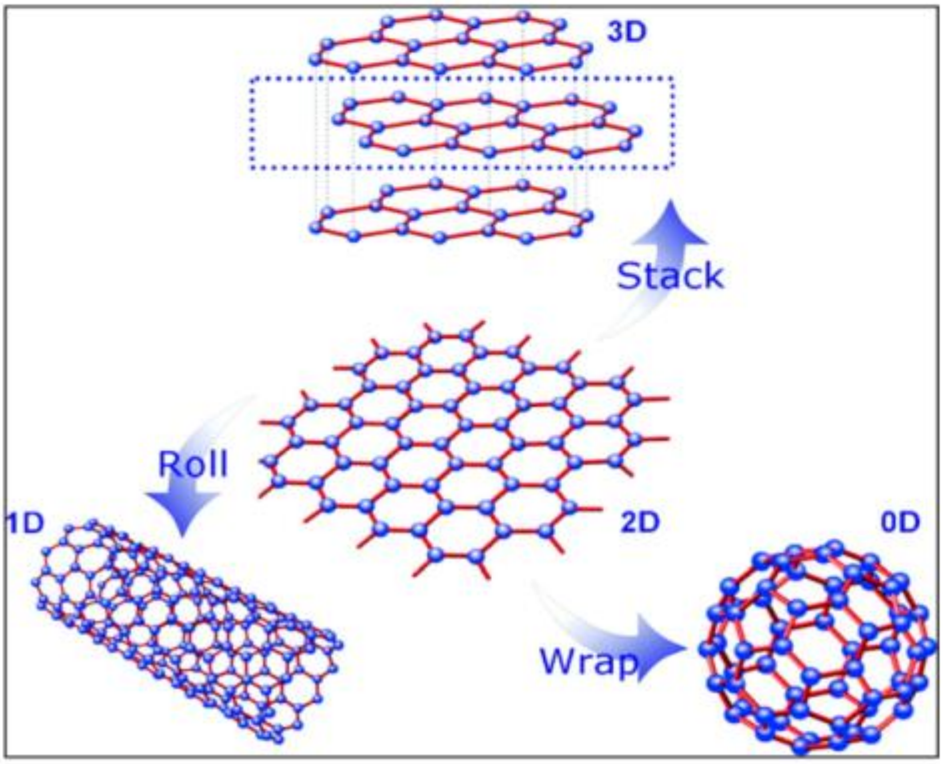

Fig. 1 Different forms of carbon

The unique morphology, size and shape, molecular structure, physical and chemical properties of these nano carbon materials are differ from each other. So, these nano materials have been considered to be the most promising with excellent mechanical, thermal, optical, magnetic and electrical properties and have great potential applications in different fields such as solar cells, catalysis, photocatalysis, optical devices, drug delivery, sensors, bio- imaging, electronics devices, energy harvesting and storage etc. Again, one of the major limitation of two dimentional graphene material is to apply in the field like optical devices, optical sensor etc due to its zero band gap. This limitation is overcome by functionalization of graphene as it opens the band gap of graphene. Graphene Oxide (GO) is one of such functionalization products and possible intermediate for the manufacture of graphene. The opening of band gap of graphene by functionalization produces broad band photoluminescence (PL) property which has been discussed in chapter 2 and this PL property has various application in the optical field. Again, the presence of different functional group in the GO helps to the researcher to prepare different nano composite material with inorganic, organic and biomolecules. The different method of synthesis of graphene oxide has been discussed in chapter 2.The different applications of the PL property of GO, the PL property of graphene based material has tremendous attention to the researcher. So, we have focused on the PL property of graphene based material for our experimental research work.

1.2. Motivation

After the Discovery of graphene from graphite in 2004, scientists are attracted much intention in the field of nanomaterial science especially in carbon based nano material due to their potential applications in both science and technology. There are different forms of graphene-based materials exist in nature. They are graphene oxide, reduced graphene oxide, exfoliated graphite, functionalized graphene oxide, functionalised reduced graphene oxide and graphene quantum dots have been reliably produced in high scale for various application. The outstanding properties together with the ease of processibility and functionalization, demonstrated graphene-related materials as ideal potential candidates for incorporation into a variety of functional materials. So, this novel nano material is one of the attractive research topic in nanomaterial science due to their unique optical and mechanical properties [1-6] and many technological [7-9] and biological application [10]. However, graphene is a zero band gap semiconductor material which creates a challenge for implementation in optoelectronic devices. So, due to absence of band gap in graphene, the possibility of observation of luminescence property from graphene is also highly unlikely. But, this limitation can be overcome by using chemically derived graphene oxide (GO), which not only a precursor for the manufacture of graphene but also it has many excellent properties which helps to apply in various field such as solar cell application[11], dielectric layers in optoelectronic devices[12] polymer composite[13], biological application[14], DNA analysis [15]. It has been observed by several researcher that most of the graphene properties are sensitive to structural defects, functional groups and the number of layers [16-18]. It is also demonstrated that the physical properties of graphene and its derivatives are related to their surface functional groups. Again, the opening of band gap in GO has tremendous interest to the researcher due to its optical property [19-23]. The band gap of GO depends on the method of synthesis and controlled oxidation and that is why GO exhibits broadband photoluminescence. Several group of researcher have already reported significant broadband PL properties of GO in the UV, visible, and near infrared spectral region [19-23], and the details has been discussed in this chapter in the section PL property of GO. Again, the presence of several oxygen containing functional groups (epoxy, hydroxyl, carboxyl) on the surface and sheet edges and high surface area which makes GO a promising material to synthesis GO based nano material and nano-composites by interacting with many organic, inorganic, biomolecules, polymers [24-25] and surfactants [26-27]. Thus, tuning the properties of graphene and its derivatives like GO, RGO by functionalization with organic and inorganic materials is very interesting and important for various applications. The GO based polymer nano composite has also great attention and the physical properties of graphene based polymer composite material are highly tuning in nature which depends on the method of synthesis and the interaction between graphene and polymer.

So, graphene is an exciting platform in carbon based material science which inspired me to study the photoluminescence property of chemically functionalised graphene (GO) and GO based polymer nano composite material. However, to the best of our knowledge only few group of researcher have been reported the PL property of GO and GO based polymer nanocomposite material which I have been high lightened in the literature review section. So, I think to explore the origin of PL property of GO and GO based polymer nano composite material and also to study the optical tunability of the functionalised graphene , more details investigation is necessary which may help to the scientist to apply in different field like optoelectronic devices, biological sensing application and also in photo catalysis.

1.3. The objective of the work

It has been found from the literature survey that the photoluminescence (PL) of graphene oxide and graphene oxide based polymer nanocomposites material is an upcoming subject of interest and may provide a wide variety of applications in future. So there is enough scope to do work in this field.

So, the objective of the work:

- To synthesize of modified graphene Oxide (GO) with different chemical funtionalities.
- To synthesize graphene oxide based polymer nanocomposites.
- To characterize the material graphene Oxide (GO) containing different chemical functionalities using various spectroscopic techniques
- To characterize the GO based polymer composites using various spectroscopic techniques.
- To modulate the photoluminescence property of newly synthesis nanomaterials.
- To understand the role of surfactants and macromolecules to modulate the photoluminescence of the synthesized GO based nanomaterial.

1.4. Plan of the Work

The plan for the work can be summarized as follows

i) Synthesis of graphene oxide (GO) from graphite flake by modified Hummer's method.

ii) Preparation of graphene oxide polyaniline (PANI) nanocomposites material (GO-PANI)

iii) Characterizations of the newly synthesis nanomaterial by X-Ray Diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, Ultraviolet and Visible (UV-Vis) absorption spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS),Transmission electron microscopy (TEM) , Scanning Electron Microscopy(SEM).

iv) Study the photoluminescence property (PL) of the newly synthesis nano materials by the interacting with surfactants like sodium dodecyl sulphate (SDS) and cetyl trimethyl ammonium bromide (CTAB)

1.5. Outline of the thesis

This thesis addresses the synthesis of graphene based nano materials with tunable PL nature. The modulation of luminescence of GO also described by changing concentration, pH of the medium, presence of surfactants like sodium dodecyl sulphate (SDS), cetyl trimethyl ammonium bromide (CTAB) and also by the presence of polyaniline (PANI). The goal of the work described in eight chapter in this thesis.

Chapter 1 deals with the general introduction and brief description of the summary of the research work. The motivation, objectives and plan of the present investigation are also stated in this chapter.

Chapter 2 describes the properties and structure of both graphene and GO. The different method of synthesis of graphene and GO has been also included in this chapter. The literature review on the photoluminescence properties of GO, reduced GO (R-GO), graphene quantum dot (GQD) and GO based polymer nano composite and their application are briefly described in this chapter till 2019.

Chapter 3 describes briefly about the principle of experimental technique that has been used to investigate the present work. The method of synthesis and characterization of GO and GO-PANI nanocomposite are also introduced in this chapter.

Chapter 4 discusses the photoluminescence (PL) properties of GO-PANI nano composite in the aqueous medium. The effect of pH on the PL properties of GO-PANI nano composite are also described. The interaction between polyanilne and GO changes with the change in medium from acidic to alkaline, which strongly affects the PL of the GO-PANI nanocomposite are described in this chapter.

Chapter 5 deals the study of PL of GO in the aqueous medium in the presence of surfactants such as sodium dodecyl sulphate (SDS) and cetyl trimethyl ammonium bromide (CTAB at different concentration. The interaction between GO and surfactant strongly depends on the pH of the medium which modulates the band gap of GO, has been described in this chapter.

Chapter 6 includes the study of PL of GO-PANI in the aqueous medium in the presence of an anionic surfactant (SDS) at both acidic and alkaline medium. The interaction between GO-PANI and SDS is different in different medium which modulates the PL of the GO-PANI nanocomposite material has been described in this chapter.

Chapter 7 describes the band gap modulation of GO by changing concentration of the medium which affects the PL property of the material.

Chapter 8 is the concluding chapter of the thesis which includes the major findings and future aspect of the present work.

1.6. 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 emraldine salt form of PANI and GO along with π-π 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 ≈ 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 ≈ 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 (pH ≈ 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 pH ≈ 10), is possibly due to weakening of π-π 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 (pH~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 π-π 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 π-π 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.

1.7. Reference

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