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Full Length Article

pH dependent tunable photoluminescence of Polyaniline grafted Graphene Oxide (GO-PANI) nanocomposite

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ABSTRACT

Polyaniline (PANI) grafted Graphene Oxide (GO), GO-PANI nanocomposite exhibits interesting pH dependent tunable photoluminescence. 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. The presence of this species is further supported by a fluorescence lifetime components at 410 nm. From the luminescence behavior of GO-PANI and electronic characteristics of GO and PANI at low pH, one may consider the formation of the species as a result of charge transfer interaction between GO and PANI.

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Effect of an anionic surfactant (SDS) on the photoluminescence of graphene oxide (GO) in acidic and alkaline medium†

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An anionic surfactant (SDS) modulates the photoluminescence of graphene oxide (GO) in both acidic and alkaline medium. In the acidic medium (pH = 2), formation of hemi spherical surface micelles on the GO sheets creates a non-polar environment around the fluorophoric moiety of GO and hinders the solvent relaxation. This leads to a significant 36 nm blue shift of the photoluminescence band, whereas in alkaline medium (pH = 10), SDS interacts with GO sheets in a different way due to the presence of negatively charged carboxylate ions at the GO edges. The repulsion between the negatively charged GO sheets and the intercalation of SDS within the basal planes of GO may weaken π - π stacking interaction which produces largely separate layers of GO. The largely separated GO sheets due to very weak stacking interactions among successive layers may behave almost like isolated functionalized GO, resulting in an enhancement of the photoluminescence intensity at 303 nm.

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Introduction

Graphene, a monolayer of sp^2 -hybridised carbon atoms with a two dimensional honeycomb sheet structure, and graphene based nano materials have become a popular research topic in nanomaterials science due to their unique optical and mechanical properties^{1–6} and many technological^{7–9} and biological applications,¹⁰ since its discovery in 2004. Functionalized graphene sheets or graphene oxide (GO) obtained by treating graphite with strong oxidizers, was primarily considered only as a precursor for graphene, but as a result of oxidation, the band gap of graphene is enhanced and graphene oxide has drawn tremendous research interest for its optical properties^{11–18} which are somehow limited for graphene because of its zero band gap. On the other hand due to the availability of several oxygen containing functional groups (epoxy, hydroxyl, carboxyl) on the surface and sheet edges^{19,20} and high surface area, GO interacts with many organic, inorganic, biomolecules, polymers^{21–23} and surfactants^{24–26} to produce several GO based nanomaterials and nanocomposites. Adsorption of surfactants

on the GO surface plays an important role for many practical applications in Li-ion battery electrodes^{24,26} and metal-oxide films.^{21,22} Introduction of electrostatic repulsive or steric factors increases the stability of the aqueous GO system.²⁸ This can be obtained by increasing the pH of the medium above the pK_a of the carboxylic groups through the utilization of electrostatic repulsion between the negative charges of carboxyl groups on the edges of the GO sheet.^{29,31} But when the carbon to oxygen ratio is high, pH adjustment is not practically possible. In this situation, stability of the aqueous GO system may be enhanced by using surfactants. The charged head groups of adsorbed ionic surfactants may provide electrostatic repulsion or steric interaction. Considering this fact in mind, the different research groups investigated the stability of GO in aqueous medium in the presence of sodium dodecyl sulphate (SDS) by various methods and also studied the interaction between GO and SDS. Hsieh *et al.* observed the adsorption behavior of SDS on functionalized graphene sheet (FGS) by conductometric titration.²⁷ According to them, the surface of FGS is complete covered by monolayer adsorption of 12 μ M SDS concentration, when FGS has carbon to oxygen ratio is 18 and they found the critical surface aggregation concentration (CSAC) for surface micelle formation on FGS as 1.5 mM.²⁷ In another work, related to the stability of FGS in the presence of SDS by optical microscopy and UV-vis study, Aksay and coworkers showed that FGS achieved significant stability in aqueous medium above the monolayer adsorption concentration ($\approx 40 \mu$ M) of SDS.²⁸ Glover *et al.* reported the charge driven selective adsorption of SDS on graphene oxide by atomic force microscopy and showed that the amount of selective adsorption of SDS depends on the degree of

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Tunable luminescence of graphene oxide-polyaniline nano-composite: Effect of an anionic surfactant

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ABSTRACT

Luminescence of the graphene oxide-polyaniline (GO-PANI) nano-composite has been found to be tuned in the presence of an anionic surfactant (sodium dodecyl sulphate, SDS). In acidic medium (pH~2.5), graphene oxide (GO), grafted by polyemeraldine salt form of polyaniline (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 fluorophoric 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.