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Layer-by-layer films and colloidal dispersions of graphene oxide nanosheets for efficient control of the fluorescence and aggregation properties of the cationic dye acridine orange

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ABSTRACT

Chemically derived graphene oxide (GO) nanosheets have received great deal of interest for technological application such as optoelectronic and biosensors. Aqueous dispersions of GO become an efficient template to induce the association of cationic dye namely Acridine Orange (AO). Interactions of AO with colloidal GO was governed by both electrostatic and π–π stacking cooperative interactions. The type of dye aggregations was found to depend on the concentration of GO in the mixed ensemble. Spectroscopic calculations revealed the formation of both H and J-type dimers, but H-type aggregations were predominant. Preparation of layer-by-layer (LbL) electrostatic self-assembled films of AO and GO onto poly (allylamine hydrochloride) (PAH) coated quartz substrate is also reported in this article. UV–Vis absorption, steady state and time resolve fluorescence and Raman spectroscopic techniques have been employed to explore the detail photophysical properties of pure AO, AO/GO mixed solution and AO/GO LbL films. Scanning electron microscopy was also used for visual evidence of the synthesized nanodimensional GO sheets. The fluorescence quenching of AO in the presence of GO in aqueous solution was due to the interfacial photoinduced electron transfer (PET) from photoexcited AO to GO i.e. GO acts as an efficient quenching agent for the fluorescence emission of AO. The quenching is found to be static in nature. Raman spectroscopic results also confirmed the interaction of AO with GO and the electron transfer. The formation of AO/GO complex via very fast excited state electron transfer mechanism may be proposed as to prepare GO-based fluorescence sensor for biomolecular detection without direct labeling the biomolecules by fluorescent probe.

1. Introduction

Atomically thin exfoliated graphite oxide or graphene oxide (GO) a non-stoichiometric, two dimensional lattice of sp^3 and sp^2 hybridized carbon network has attracted great attention in recent years [1] in the field of Chemistry, Physics, Materials science and Nanotechnology [2–4]. The extraordinary properties of GO make it suitable for potential applications in electronic devices [5], solar cells [6], sensors [7], Li-ion batteries [8], supercapacitors [9], biosensing devices etc. [10]. GO bears covalently attached epoxide (1, 2, ether) hydroxyl functional groups on either side of basal plane and carboxyl groups on either side of edges [11]. Therefore, GO becomes strongly hydrophilic and easily exfoliated in water due to electrostatic repulsion between their nanosheets forming a stable colloidal dispersions [12]. GO undergoes a complex interplay of various ionic and non-ionic interactions in solution due to the presence of aromatic moieties and specific functional groups [13]. Colloidal GO can be considered as a promising material with a net negative surface charge because of ionizible carboxylic groups and it can be used for fabricating multilayer thin films onto oppositely charged surface based on electrostatic interactions [14]. Borislav Angelov et al. reported the preparation of self-assembled structures of DNA and protein by Lipid Nanocarrier via electrostatic interaction [15,16]. Although Langmuir–Blodgett technique is an elegant choice to precisely control the molecular arrangement in multilayered systems [17,18], layer-by-layer electrostatic self-assembly technique is also becoming promising as it includes wide diversity of materials to fabricate multilayered nanostructured films onto solid substrate [19]. The excellent colloidal dispersibility and stability of GO can make it efficient nanotemplate to support wide range of organic, inorganic and biomaterials on their surface via π–π stacking and/or electrostatic interactions [20]. Some authors reported enzyme immobilization onto the surface of GO for its large surface area [21].

Therefore, the significant colloidal properties of GO sheets in aqueous media may provide a platform for the preparation of ordered structures of organic dye molecules namely dye aggregates. Spectroscopic

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characteristics of organic dyes have shown a lot of fundamental importance since long back [22]. The precise controls of these structures are also very important because of the use of their aggregates in some biological applications [23]. Specific dipole-dipole interactions between the dye monomer units result the formation of dimers or aggregates [24, 25]. This is generally reflected as spectral splitting and spectral shifting or generation of new band in the absorption spectra of dyes when compared to that of their free monomers. Depending on the type of intermolecular association of the monomers, the structure and optical properties, aggregates are classified into two major groups namely H-type (face-to-face arrangement of the monomer) [24] and J-type (head to tail arrangement) [26]. By using simple UV–Vis absorption spectroscopic technique one can easily characterize them. While considering the emission properties of many adsorbed fluorophores onto GO sheets, the emission is certainly quenched due to highly specific interaction between fluorophores and GO and this phenomenon has many possible applications. For example, the GO-based fluorescence quenching has already been demonstrated as an efficient sensing platform for the quantitative detection of nucleotides [27]. The quenching of fluorescence of cationic dye molecules can also be due to the process of excited state electron transfer between dye and some suitable electron acceptor molecules like GO either by static or dynamic quenching mechanism [28,29]. In static quenching, lifetime of the excited fluorophore remains same whereas in dynamic quenching the lifetime decreases [30]. Furthermore, with the increasing attention to energy and environmental issue, many researchers focus on solar cell, which has potential applications in our daily life. The electron transfer after photoexcitation of the electron acceptor moieties is a fundamental process, which could strongly influence efficiency of solar cell. Therefore the charge transfer from sensitizer (may be some cationic dye) to GO or G (electron acceptor) is of particular importance for future technological applications.

In the present article, we have addressed the detail aggregations behavior and fluorescence quenching of a cationic dye namely Acridine Orange (abbreviated as AO) in presence of GO in aqueous media. We also report the preparation of AO/GO layer-by-layer (LbL) self-assembled mono and multilayered film onto a poly(allylamine hydrochloride) (abbreviated as PAH) coated quartz substrates via electrostatic interaction between the positively charged group of AO and negatively charged GO nanosheets from their aqueous solutions and dispersion respectively. AO has a planar heterocyclic aromatic structure which is suitable as electron donor in the excited state when come close enough to an oppositely charged electron deficient materials [31]. AO remains in cationic form in pH below 10 and is completely deprotonated at pH > 10 [32]. Owing to its high photostability, high photoluminescence quantum yield and low cost, it has been widely used as a fluorescent probe in numerous investigations [33]. In this present work, we have explored the detailed aggregation behaviors of AO in a simple ion exchange strategy for electrostatic complexation as well as π–π stacking cooperative interactions with GO and the fluorescence quenching via photo induced electron transfer (PET) mechanism. UV–Vis absorption, steady state and time resolved fluorescence and Raman spectroscopic measurements have been employed to explore their molecular level interactions. AO is known to form H-aggregates as reported by some authors [34]. However, our results confirm the presence of some amount of J-aggregates in AO/GO mixed ensemble with predominant H-aggregates as evidenced by using exciton coupling theory. The aggregation behavior of AO is of particular importance because of their use as molecular probe for intercalation with DNA [35]. Also GO acts as an efficient quencher for the quenching of AO fluorescence due to photoinduced electron transfer from excited AO molecules (electron donor) to GO (acceptor). This electron transfer is a very ultrafast process than the intrinsic fluorescence of AO. We also observed the aggregation of dye molecules in the AO/GO LbL self-assembled films onto the solid substrates as confirmed by UV–Vis absorption spectroscopy.

2. Experimental

2.1. Materials

The cationic dye AO (MW = 265.35 g/mol, purity >99.9%) was purchased from Aldrich Chemical Company, USA and was used as received. The purity of the dye was also checked by UV–Vis absorption and fluorescence spectroscopy before use. The molecular structure of AO is shown in Fig. 1a. The solubility of AO was about 0.7 mg/ml in the ambient temperature and becomes light orange in color in the studied aqueous phase at neutral pH. Natural Graphite powder was purchased from Aldrich chemical co, USA. H_2SO_4, $NaNO_3$ and $KMnO_4$ were purchased from Merck Chemical Company, Germany. PAH was purchased from Polyscience inc., USA and its molecular structure is shown in Fig. 1b. Tripled distilled deionized Milli-Q water (Resistivity 18.2 MΩ-cm) was used to prepare all the solutions in the present work.

2.2. Synthesis of graphene oxide

GO powder was prepared according to modified Hummer's method [36], with natural graphite powder as a starting material. At first, 1 g of graphite powder and 0.5 g of sodium nitrate were mixed together followed by addition of 23 ml of conc. sulphuric acid under constant stirring by a magnetic stirrer. After 1 h, 3 g of $KMnO_4$ was added to the above solution gradually while keeping the temperature less than 20 °C to prevent overheating and explosion. The mixture was then stirred at 35 °C for 12 h and the resulting solution was diluted by adding 500 ml of distilled water under vigorous stirring. In order to confirm the completion of reaction with $KMnO_4$ the suspension was further treated with 30% H_2O_2 solution (5 ml). The Final mixture was washed off with HCl and H_2O subsequently, followed by filtration and drying, graphene oxide sheets were thus obtained. After preparing GO, it was characterized by Field Emission Scanning Electron Microscopy (FESEM), UV–Vis absorption spectroscopy and Raman spectroscopy. FESEM image of GO as shown in Fig. 2 reveals that GO has layered sheet like structure and they are not planner rather having wrinkled morphology. Such sheets are folded or continuous at times. It is possible to distinguish the edges of individual sheets, including kinked and wrinkled areas. UV–Vis absorption and Raman Spectrum of GO are discussed later.

2.3. UV–Vis absorption spectroscopy

UV–Vis absorption spectroscopic measurements were done by a dual beam UV–Vis-NIR absorption spectrophotometer (Model: UV-3600PC, Make: Shimadzu, Japan). For measuring all solution spectra, quartz cuvette of 1 cm path length was used. Absorption spectra of LbL films deposited onto fluorescence grade quartz substrates were recorded by this spectrophotometer at room temperature.

2.4. Steady state and time resolved fluorescence spectroscopy

All the steady state fluorescence measurements were done by a Spectrofluorometer (Model: LS-55, Make: Perkin Elmer, USA). The fluorescence lifetime of the samples were recorded by Time-correlated single photon counting (TCSPC) set up from Horiba Jobin-Yvon, Japan.

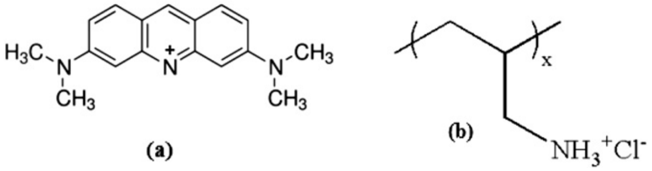

Fig. 1. Molecular structure of (a) AO and (b) PAH.