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Unravel the interaction of protoporphyrin IX with reduced graphene oxide by vital spectroscopic techniques

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ABSTRACT

Probing interaction between dyes and reduced graphene oxide (rGO) is of contemporary research interest. Since, rGO is widely used as electron acceptor in photovoltaic and optoelectronic devices. Hence, we have investigated the interaction between protoporphyrin IX (PPIX) and rGO by vital spectroscopic techniques. The adsorption of PPIX on rGO is studied by Attenuated total reflection-Fourier transform infrared (ATR-FTIR) and X-ray photoelectron spectroscopic (XPS) measurements. The fluorescence quenching measurements are also performed and the fluorescence intensity of PPIX is quenched by rGO. The quenching of PPIX with rGO is evaluated by the Stern–Volmer equation and time-resolved fluorescence lifetime studies. The results revealed that the fluorescence quenching of PPIX with rGO is due to the static quenching mechanism. The dominant process for this quenching has been attributed to the process of electron transfer from excited state PPIX to rGO. Fluorescence lifetime measurements were used to calculate the rate of electron transfer process between excited state of PPIX and rGO. Transient absorption studies demonstrated the formation of PPIX cation radical for the evidence of electron transfer between PPIX and rGO.

1. Introduction

Graphene [1], an allotrope of carbon with two-dimensional arrangement of atoms was experimentally discovered in 2004. It has superior electronic and mechanical properties due to its unique structure which can be useful for diverse applications [2]. These high quality graphenes are obtained from numerous methods i.e., chemical vapour deposition of hydrocarbons [3], micromechanical cleavage [4] and epitaxial growth on silver carbide [5] etc. A physical method does not give any defects in graphene structure however, when prepared from chemical oxidation-reduction methods, a higher degree of defects are introduced in graphene structure results high conductivity. The defect related graphene sheets are generally produced from graphene oxide (GO) which consists of highly oxygenated carbon, bearing hydroxyl, epoxide, diol, ketone and carboxyl functional groups [6]. On the other hand, the chemical reduction of GO removes the oxygen containing functional groups [7], results reduced graphene oxides (rGO) and it has received much attention due to its high conductivity [8,9] of 16,000 Scm^{-1} and also acts as an excellent host material owing to its high flexibility [10].

The reduced graphene oxide (rGO) exhibits many physical properties similar to graphene, being considered in electronic, sensor, and catalytic applications [11–13]. The important quality of rGO is its ability to capture and shuttle electrons through its sp^2 network, showing an attractive perspective of applications in photovoltaic devices [14]. For instance, incorporation of graphene sheets into TiO_2 nanoparticle films used as photoanodes in dye-sensitized solar cells (DSCs) gave five times higher power conversion efficiencies than those obtained from TiO_2 nanoparticle films without graphene sheets [15]. Imahori et al. developed the efficient hierarchical electron transfer cascade system on a semiconducting electrode in a bottom-up manner by using rGO sheet to anchoring organic/inorganic hybrid materials for the first time [16]. This hierarchical electron transfer cascade system exhibited remarkably high photocurrent generation with an incident-photon-to-current efficiency (IPCE) of up to 70% compared with the reference device without rGO sheets. Kamat et al. reported the photoanodes assembled from CdSe–graphene composites in quantum dot sensitized solar cells display improved photocurrent response (~150%) over those prepared without rGO [17]. Therefore, studies on the interaction between sensitizers and rGO is significant. Several applications, including energy storage, molecular imaging, biological and chemical sensing, and drug delivery, take advantage of the electronic interactions of organic molecules with graphene-based materials [18,19]. Numerous studies have been exploited that graphene can strongly interact with a variety of organic

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dyes and has a superior quenching efficiency [20–25]. The interactions in the excited state are followed through fluorescence quenching, diminished excited state lifetimes, and monitoring the formation of electron transfer products. In our previous report [26], PPIX have been successfully used for DSC applications and the power conversion efficiency of 0.8% was achieved. The lower power conversion efficiency of PPIX is due to faster electron cation recombination. In order to minimize this channel, the electron shuttle between PPIX and TiO_2 is suggested to enhance the rate of electron injection from PPIX to TiO_2 conduction band. Hence, here we have employed rGO sheets as an electron shuttle. Before making a real device (PPIX/rGO/TiO_2), it is very necessary to study the interaction between PPIX and rGO sheets. From this study, one can gain the knowledge about fundamental process of PPIX-rGO complex.

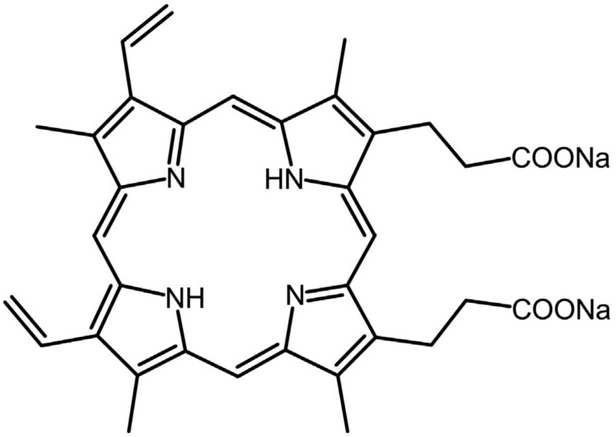
In the present manuscript, the molecular interaction of Protoporphyrin IX disodium salt (PPIX, Scheme 1) with rGO is investigated using various spectroscopic techniques. The characterization of rGO sheets is also presented. We have demonstrated the experimental evidence for ground and excited state interaction between PPIX and rGO sheets. The quenching property of the rGO on the fluorescence intensity of PPIX in an aqueous solution was evaluated using the Stern-Volmer equation and the time-resolved fluorescence studies. As a consequence of this work, PPIX-rGO material can be used for DSC applications.

2. Materials and Methods

Protoporphyrin IX disodium salt (≥90%) was purchased from Sigma-Aldrich.

2.1. Preparation of Reduced Graphene Oxide

For the preparation of reduced graphene oxide (rGO), first we prepared the Graphene oxide (GO) using modified Hummers method [27]. 2 g of Graphite powder (Alfa Aesar > 99%) and 1 g of $NaNO_3$ (Merck >99%) were thoroughly mixed, then transferred into concentrated H_2SO_4 (96 mL; Merck, 98%) in an ice bath. Under vigorous stirring, $KMnO_4$ (6 g) was added gradually, and maintain the temperature of the mixture below 20 °C. The mixture was stirred at 35 °C in a water bath for 18 h after removing the ice bath. The mixture became pasty with a brownish colour as the reaction progressed. Successively, 150 mL of H_2O was slowly added to the pasty mixture which is kept in an ice bath to maintain the temperature below 50 °C. After dilution with 240 mL of H_2O, 5 mL of 30% H_2O_2 was added to the mixture, and the diluted solution colour changed to brilliant yellow along with bubbling. After continuous stirring for 2 h, the mixture was filtered and washed with 10% HCl aqueous solution (250 mL), DI water, and ethanol to remove other ions. Finally the resulting mass was dried by vacuum. The rGO was synthesized through simple reduction method using $NaBH_4$ as a reducing agent. Briefly, 1 g of GO was dispersed in 50 mL of distilled water using ultrasound in an ultrasonic bath (Model PCi analtics, 230 V, 50 Hz) for 1 h to obtain uniform dispersion. To this dispersion, $NaBH_4$ (0.02 mol) was added drop by drop under continuous stirring and again exposed to ultrasound for 30 min, and then collected the black colour solid by filtration. The resulting solid was dried in oven for 1 h and subjected to structural characterization.



Scheme 1. Structure of protoporphyrin IX disodium salt.

2.2. Instrumentation

The morphology and microstructure of the composites were characterized by TEM analysis (FEITecnai-20 G2). SEM measurement is done by using Nova NanoSEM 600 from FEI Company, Netherlands and EDS analysis is with EDAX system. X-ray photoelectron spectra of PPIX were recorded in an ESCA-3 Mark II spectrometer (VG Scientific Ltd., UK) using Al Kα (1486.6 eV) radiation as the source. All spectra were referenced to the C1s major peak at 284.5 eV. The dynamic light scattering measurements were done by using Malvern DLS instrument to determine the particle size and zeta potential of rGO respectively. The electronic absorption spectra of the samples were recorded using CARY 100 Bio UV–Visible spectrophotometer. The fluorescence spectral measurements were carried out using Fluoromax-4P spectrofluorometer (Horiba Jobin Yvon, Singapore). Time resolved picosecond fluorescence decays were obtained by the time-correlated single-photon counting (TCSPC) technique with microchannel plate photomultiplier tube (Hamamatsu, R3809U) as detector and femtosecond laser as an excitation source. The second harmonics (400 nm) output from the mode-locked femtosecond laser (Tsunami, Spectra physics) was used as the excitation source. The instrument response function for TCSPC system is ~50 ps. The data analysis was carried out by the software provided by IBH (DAS-6), which is based on deconvolution technique using non-linear least-squares methods. Transient absorption experiments were carried out using nanosecond laser flash photolysis (Applied Photophysics, UK). The third harmonic (355 nm) of a Q-switched Nd:YAG laser (Quanta-Ray, LAB 150, Spectra Physics, USA) with 8 ns pulse width and 150 mJ pulse energy was used to excite the samples. The transients were probed using a 150 W pulsed xenon lamp, a Czerny-Turner monochromator, and Hamamatsu R-928 photomultiplier tube as detector. The transient signals were captured with an Agilent infiniium digital storage oscilloscope, and the data were transferred to the computer for further analysis. Infrared spectrometer (IR) spectra of PPIX powders were recorded on BRUKER VERTEX 70 Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) spectrometer.

3. Results and Discussion

3.1. Characterization of Reduced Graphene Oxide

Fig. 1a and Fig. S1 presents the SEM and EDS analysis of rGO respectively. It appears as folded flakes which looks like wrinkled sheet morphology. EDS analysis of rGO confirms the presence of carbon (63%) and oxygen (28%) in rGO sheets. Sodium (9%) also presents in the synthesized material as a result of graphene oxide reduction process with $NaBH_4$. Fig. 1b**&1c** shows the TEM image and SAED pattern of rGO. The size of the sheets varies from 500 to 800 nm. The amorphous nature of the rGO is confirmed through SAED pattern which shows vaguely appeared solid rings. Characterization of rGO in solution using DLS is an important aspect to know the particle size as well as the degree of stability. Fig. 1d presents the DLS spectrum of rGO. From this figure, it is very clear that the particle size of rGO is 723 nm (PDI 0.575) which is in good agreement with TEM observations. In general, particles with Zeta potential more positive than +30 mV or more negative than −30 mV are considered to form stable dispersion due to interparticle electrostatic dispersion [28,29]. Here, the Zeta potential is −31.4 mV