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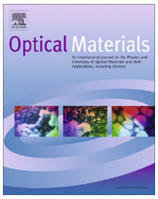

Optical properties and dynamics excitation relaxation in reduced graphene oxide functionalized with nanostructured porphyrins

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ABSTRACT

Few layers of reduced graphene oxide (FRGO) were functionalized with porphyrins self assembled nanostructure. These new hybrid nanocomposites were investigated using Transmission Electron Microscopy (TEM), UV–visible, Raman scattering, Fourier transform infrared (FT-IR) and photoluminescence. The structural and morphological results show strong interactions between these hybrids components. Moreover, steady state photoluminescence (PL) of both porphyrin nanorods (PN) and (PN)/FRGO composite show clearly the PL quenching confirming a charge transfer from porphyrin molecules to graphene sheets. In addition, the relaxation kinetics of the PN and (PN)/FRGO were studied by means of time resolved photoluminescence (TR-PL) and the excitation density in the sample was of 10^{17} cm^3/pulse. The major change of the carrier dynamics in porphyrin nanorods after their interaction with FRGO was in the increase in the fast time constants, which found to be slower at 650 nm, $\tau_1 = 196$ ps and $\tau_2 = 1171$ ps. This has been explained by the change in their energy band gap due to the role of FRGO as doping related to the size of the nanometer-scale sp^2 clusters, which leads to a slower interband carrier recombination.

1. Introduction

Porphyrins and related tetrapyrroles have been extensively studied because of their importance in biological processes and they are often used in the development of photocatalysts [1], artificial light-harvesting [2], energy conversion [3], sensors systems [4] and many others. They possess many desirable structural and functional properties and are attractive components for the preparation of self-assembled nanomaterials [5,6]. They are also interesting from a fundamental point of view, as systems to study the nature and dynamics of excited states in molecular assemblies of reduced dimensionality, as well as models for understanding the photophysics of natural light-harvesting complexes [7]. The extraordinary optical properties of these molecular aggregates are to a large extent governed by exciton delocalization, transport, and relaxation phenomena. To develop these properties, composites based on those structures show their potentials for optic and optoelectronic applications by the association of porphyrin properties to carbon nanotubes, polymers and other molecular materials [8,9].

On the other hand, since graphene was isolated by mechanical exfoliation in 2004, many promising properties have been reported, such as extremely high electron mobility [10]. Furthermore, graphene's strong interactions with photons [11] and electrons, and chemical functionalization ability could add more functions to photoactive composites. The interfacial charge transfer across heterostructures and the implication on the optical properties of graphene derivatives such as graphene oxide (GO) or reduced graphene oxide (RGO) are very useful because of their diverse potential applications.

In this paper, we report on the combination of FRGO and nanostructured porphyrin properties obtained by self assembly. The interfacial interactions and their effects on the optical and emission properties were elucidated by using Transmission Electron Microscopy (TEM), UV–visible transmittance Raman and infrared spectroscopy, and stationary and time-resolved photoluminescence measurements.

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2. Setup

First, we have synthesized graphene oxide from graphite using Hummer's method [12], and then the obtained solution was reduced with hydrazine hydrate after been washed many times with deionised water. The final solution was diluted and sonicated for 30 min in the goal of a total exfoliation of these graphene sheets (solution1: Few layered reduced graphene oxide: FRGO). Porphyrin nanorods (PN) were synthesized via an ionic self-assembly technique by mixing aqueous solutions of two porphyrin precursors Meso-tetrakis(4-phenylsulfonicacid) porphyrin ($H_2TPPS_4^{2-}$) dihydrochloride and Sn(IV) tetrakis(4-pyridyl)porphyrin (Sn(IV)$TPyP^{2+}$) dichloride using the procedures developed by Thema et al. [12] and used in our previous work Khenfouch et al. [31]. Rod formation is very sensitive to solution conditions, especially pH, because it alters the charge balance and hence the synthesis was conducted under acidic conditions of pH $\sim$ 2. After mixing PN and FRGO solutions, a grey solution was formed (Fig. 1) and then was put into an ultrasound bath for 15 min at room temperature to ensure its homogeneity. Finally, a glass slide, was rinsed with distilled water and acetone, and dried in an oven for 10 min, upon which a thin films of the composite (FRGO-PN) and PN were deposited by drop casting process for Raman and FTIR measurements.

For the characterization: TEM images were obtained using a FEI/Tecnai F20 Cryo TWIN FEGTEM, transmittance spectra were recorded at room temperature using a Cary UV–visible-near-infrared spectrometer. The Raman spectra were carried out using Bruker spectrometer SENTERRA Raman Stokes and spectral range of 90–3200 cm^{-1} with an excitation wavelength $\lambda = 785$ nm and for our samples the laser power is adjusted to a low power 10 mW. Infrared absorption measurements are performed using Fourier transform VERTEX 70 Series FT-IR spectrometer of Bruker Rock Solid interferometer based on well known and the ideal entry-level systems for advanced research applications.

The steady-state PL spectra were performed using a Jobin-Yvon fluorolog 3 with an excitation wavelength of 420 nm.

Luminescence dynamics spectra were recorded at room temperature using a Jobin-Yvon Fluorolog spectrometer with a CCD detector.

Time-resolved photoluminescence (TR-PL) experiments were acquired with a regenerative amplified femtosecond Ti: Sapphire laser system (Spectra Physics Hurricane X). This setup generates 100 fs pulses at 800 nm with a repetitive rate of 1 kHz and a power of 1 W. The laser line is frequency-doubled (tripled) with thin BBO crystals to obtain an excitation line $\lambda_{exc} = 400$ nm (3.1 eV) (or $\lambda_{exc} = 266.6$ nm (4.6 eV)). The pump energy pulse is controlled to ensure that the excitation density in the sample did not exceed 10^{17} cm^{-3}, to avoid bimolecular annihilation process and sample photodegradation. The emission is temporally resolved with a high dynamic range Hamamatsu C7700 streak camera coupled to an imaging spectrograph with a temporal resolution to be estimated 20 ps and processed using the HPDTA Hamamatsu software. The excitation wavelength used for the TR-PL was of 400 nm and the probe wavelengths were at 650 nm and 500 nm.

Fig. 1. Solutions of FRGO, FRGO-PN and PN.

3. Results and discussion

3.1. Morphological analysis

Transmission Electron Microscopy images (Fig. 2) show FRGO and FRGO-PN like islands and as prepared PN. The composite structures found to be relatively isolated and composed of porphyrin nanoparticles (PNps) deposited on the top of graphene sheets and show no transparency, which mean that graphene sheets are totally covered by PNps. On the other hand, the size of rods decreases due to the interaction with graphene sheets causing a loss of agglomeration. This serious contact between graphene sheets and porphyrin nanorods will have an important effect on the properties of their composite.

3.2. UV–VIS measurements

These nanostructured antennas of porphyrin are known by their light harvesting properties. Fig. 3 shows UV–VIS spectra of porphyrin nanorods, graphene and the resulting composite in solution. The main several transmittance peaks identified in the spectrum for these nanorods 419, 438, 492, 647 and 705 nm are similar to what has been reported before [13–15]. The peaks at 492 nm and 705 nm are characteristic of J-aggregate structures, particularly porphyrin nanorods [13]. The peak at 438 nm is attributed to H-aggregates and the transmittance feature between 492 and 419 nm is most likely due to a mixture of aggregates and monomer [13]. These transmittance bands result from electronic transitions from ground state (S_0) to the two lowest singlet-excited states S_1 (Q state) and S_2 (S state) [16,17].

According to exciton theory, when molecules lie in a head-to-tail arrangement (J-aggregation), the allowed state is lower in energy, hence producing a red-shift to the monomer [17], and since the S band of $[H4TPPS4]^{2-}$ is red-shifted upon aggregation (J-aggregate), it implies the planar porphyrin molecules are stacked in an arrangement where individual porphyrin units are not positioned directly one on top of the other [13].

On the other hand UV–VIS spectrum of FRGO solution shows a peak at 284 nm, which was clear in absorption measurements (not shown in this paper), strongly red-shifted compared to that of regular GO at 230 nm due to the successful exfoliation of graphite and reduction of graphene oxide by hydrazine; The overall absorption was greatly increased. This is consistent with the color change of the colloidal dispersion from brown to black, similar to what has been observed with regular GO [18].

The spectra show also that porphyrin nanorods solution is more transparent than FRGO and FRGO-PN solutions. FRGO-PN spectrum shows a decrease in light transmittance as well as in nanorods peaks intensities.

Porphyrin nanorods peaks observed at 500 nm and 700 nm show a dramatic modification of the relative intensity with respect to the band situated at 434 nm. This could be related to the rods disaggregation and to the difference of PN concentration as well. This change due to interaction between graphene sheets and PN