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Optical properties of porphyrin – graphene oxide composites

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ABSTRACT

In this work we aim to (via a non-invasive functionalization approach) tune and alter the intrinsic features of optically “transparent” graphene, by integrating water-soluble porphyrin aggregates. We explore the potential to combine porphyrin aggregates and graphene oxide to assess the advantages of such a composite compared to the individual systems. We apply a range of optical spectroscopy methods including photo-absorption, fluorescence assess ground-state and excited state interactions. Our studies show that comparing resonant Raman scattering with optical transmission and fluorescence microscopy that the presence of influences the microscopic structures of the resulting composites.

INTRODUCTION

Considerable amount of research has been undertaken to advance the understanding of optical processes in low dimensional nanomaterials such as quantum dots, nanodisks, fullerenes and carbon nanotubes [1-9]. These materials exhibit a range of interesting physical properties, the study of which potentially advances fundamental science and also areas of applied research such as photonics and sensor development where nanomaterials show great promise. This has been reinforced by advances in optical spectroscopy and imaging methods that has supported the study of nanosystems [10-14]. Graphene is one type of nanomaterial has recently gained considerable interest. Exfoliated graphene oxide sheets (GO) are one form of graphene, such materials are attractive as they are suspendable in polar solvents making them suitable for chemical processing [15,16].

π -conjugated molecule materials have attracted interest due to their structural similarities to photosynthetic antenna systems of green bacteria [17-20]. Such antenna systems channel the energy to the photosynthetic reaction centre where light is converted into chemical energy via a charge separation process. It is believed that the complex self-assembling antenna systems are the reason for the extraordinary light collection efficiency in photosynthesis [20]. In the chlorosomes of green bacteria, bacteriochlorophylls (a porphyrin derivative) assemble to form nanorods, and these chromosomal rods are the most efficient harvesters of light known [21]. One way to produce efficiently porphyrin nanorods is via self-assembly. Self-assembly occurs whereby molecules, atoms or nanoparticles spontaneously form pre-designed structures, typically through non-covalent interactions such as π - π stacking, hydrophobic-hydrophobic interactions H-bonding, electrostatics etc. [22-26]. Nano and micro-structured porphyrin aggregates can self-assemble to form highly stable nano and micro rod or wire like structures. A range of porphyrins have been found to form nanorod like structures for example Reddy et al [27] demonstrated that H₂TPP in acidic environments forms well defined nanorods assigned to occur due to J-aggregation. In porphyrins the formation of J aggregates are reported to result in a red-shift in absorption bands [30-32].

Combining nanomaterials such as GO with π - π aggregated materials has potential for the development of composites with optoelectronic properties ex sensors and catalysis [28,29]. Studies of blends of functionalized graphene with TiO₂ when applied to photovoltaics resulted in an advancement in power conversion efficiency of c.a. five times [28]. Potential exists to ‘marry’ the electrical and mechanical properties of GO with the optical properties of porphyrins however, questions remain in regard to the behaviour of GO in how it interacts with porphyrins and porphyrin aggregates (J or H). In order to achieve this an understanding of how GO and porphyrins interact is required. Wojcik et al [29], studied the optical properties of 5,10,15,20-tetrakis(1-methyl-4-pyridinio)porphyrin tetra(ptoluenesulfonate) (TMPyP) with chemically reduced graphene oxide (RGO). The authors reported the formation of a ground-state TMPyP/RGO complex in solution via absorption spectroscopy, monitoring of the porphyrins B band showed a red-shift with increasing

concentration of RGO along with a reducing of the fluorescence lifetime of the porphyrin from 5 to 1 ns demonstrating potentially excited-state interaction between singlet excited porphyrin and RGO. Xu et al [33] studied complexes of TMPyP molecules and chemically converted graphene (CCG). The authors reported that the complexation of the CCG sheets and TMPyP created a red-shift in the porphyrin B band, which is assigned to the molecular flattening of TMPyP. Here we demonstrate that a strong GO/TMPyP interaction is observed (in solid state porphyrin-graphene oxide composites) even when conditions to form TMPyP J-aggregates are present creating a material with strong constituent molecule interactions.

EXPERIMENTAL

The porphyrins Meso-Tetra (N-methyl-4-Pyridyl) Porphine Tetra chloride (TMPyP) were prepared as thin films with and without graphene oxide (GO). Two sets of samples were prepared as thin films by drop deposition onto a glass slide. The first prepared by deposition of porphyrins directly onto a glass slide under neutral conditions, these samples are hereby referred as sample set N. The second set of samples were prepared by depositing the porphyrins onto a slide in the presence of acid (pH = 0.5), a sample set hereby referred to as set A. In all cases the samples were dried in air. Optical UV-vis absorption spectra were recorded using a Jasco UV/Vis instrument. Fluorescence microscopy studies were performed using a Zeiss inverted microscope system coupled with a 532 nm excitation wavelength, CCD camera and 650 nm band pass filter. The resulting images were fitted with scale bars that indicate length. A Picoquant Microtime 200 fluorescence lifetime imaging microscopy (FLIM) system was used for lifetime imaging. The fluorescence lifetime images were recorded on a Microtime 200 microscope system (PicoQuant GmbH, Berlin, Germany). The measurements were performed using the time-tagged time-resolved methodology[28,29].

RESULTS

Absorption and emission spectra of neutral and acidic TMPyP with and without Graphene Oxide has shown in the figure 1. The absorption spectrum for the n-TMPyP film shows clearly defined bands at 427, 470, 532, 602 and 658 nm. In comparison the absorption spectrum for the n-TMPyP+GO film shows bands at 428, 529, 593 and 646 nm. The optical absorption spectra of n-TMPyP \pm GO shows not only differences in band positions but also in relative band intensities. The presence of GO has altered the position of both the Q bands by blue shifting the Q bands by values ranging from 3 to 12 nm. In addition the relative intensity of the B band has increased while the Q band intensities have decreased when GO is added. The absorption bands for TMPyP in acid are at c.a. 422, 520, 559, 587, and 643 nm which is significantly blue-shifted relative to both n-TMPyP \pm GO films. This indicates that strong TMPyP-TMPyP interactions may occur creating layers. Such layers are potentially similar to H/J aggregates which possess red-shifted absorption bands. When GO is added the degree or magnitude of the red shift (relative to solution studies) is reduced. One explanation for this may be that GO is reducing the TMPyP-TMPyP interaction potential. It is known that porphyrins interact with GO to form a complex eg TMPyP possesses N-methylated pyridine substituents which are ca. perpendicular to the plane of the porphyrin. This enables the molecule to interaction with GO [29]. While it is believed that GO sheets when deposited exist as multi-layers [36]. The porphyrin can intercalate between the GO multi-layers in solution enabling a molecular interaction between the two molecules to effectively occur. The films prepared here were prepared together in water solution before a thin film was prepared. This enables the TMPyP to intercalate with the GO, resulting potentially in an effectively mixed TMPyP/GO film being prepared.

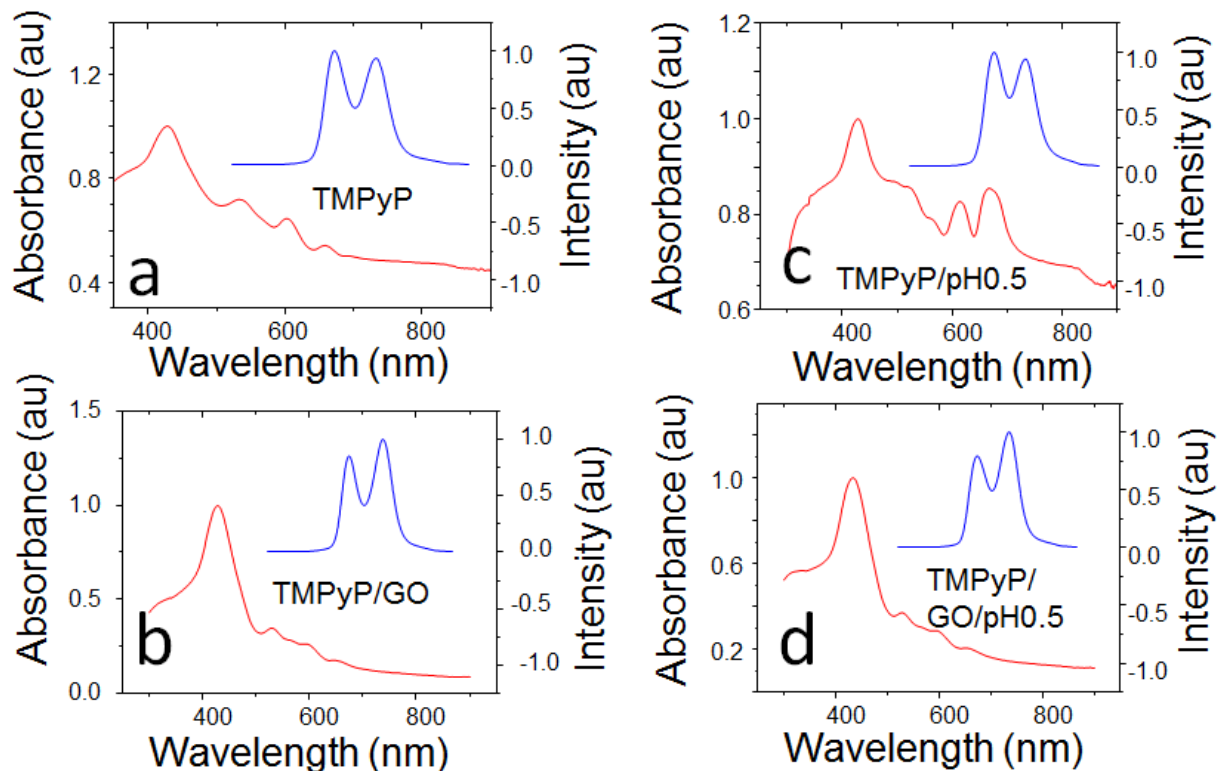


Figure 1. Absorption and emission spectra for all material composites.

When acid is used in the preparation of a TMPyP film, the acidic environment is reported to enhanced the potential for porphyrin-porphyrin interaction eg aggregation [27,37]. Optical absorption spectra of TMPyP film prepared at pH = 0.5, (referred to as a-TMPyP) was recorded and is shown in Fig 1. The absorption spectra for a-TMPyP film possess a distinct spectrum with a broad B (with a peak at c.a. 470 nm) band and relatively intense Q bands with bands at c.a. 375, 428, 470, 565, 615 and 668 nm. These band positions are red shifted compared to the (neutral) n-TMPyP film (as well as TMPyP in solution) and possess band intensities (ie B vs Q band intensities, together with the red-shift) consistent with J-aggregate formation. In comparison the absorption spectrum for the a-TMPyP+GO film shows bands at 430, 528, 595 and 651 nm, (very similar to those for n-TMPyP+GO) ie the presence of GO blue shifts the Q band positions relative to a-TMPyP alone. The optical absorption spectra of a-TMPyP \pm GO shows not only differences in band positions but also in relative band intensities, with the presence of GO increasing the relative intensity of the B band and reducing the Q band intensities, mirroring the spectral features for n-TMPyP+GO.

Microscale and macroscale studies of the structures in the films for the porphyrin/graphene oxide complexes was undertaken using optical microscopy. Fluorescence imaging was applied to all samples; the resulting images are shown in Fig 2. The fluorescence of TMPyP (in line with other free-base porphyrin moieties) consist of two emission peaks (see Fig 1). These peaks are assigned to Q(0,0) and Q(0,1) (mirror images of their respective absorption bands ie Q(0,0) and Q(1,0)). TMPyP in common with other porphyrins possesses a relatively large energy gap between the singlet states S_1 (Q band) and S_2 (B band). The B band corresponds to a strongly allowed transition, resulting in a fast S_2/S_0 radiative transition. TMPyP fluoresces from the S_1 and S_2 states giving rise in turn to two bands this enables fluorescence imaging to occur.

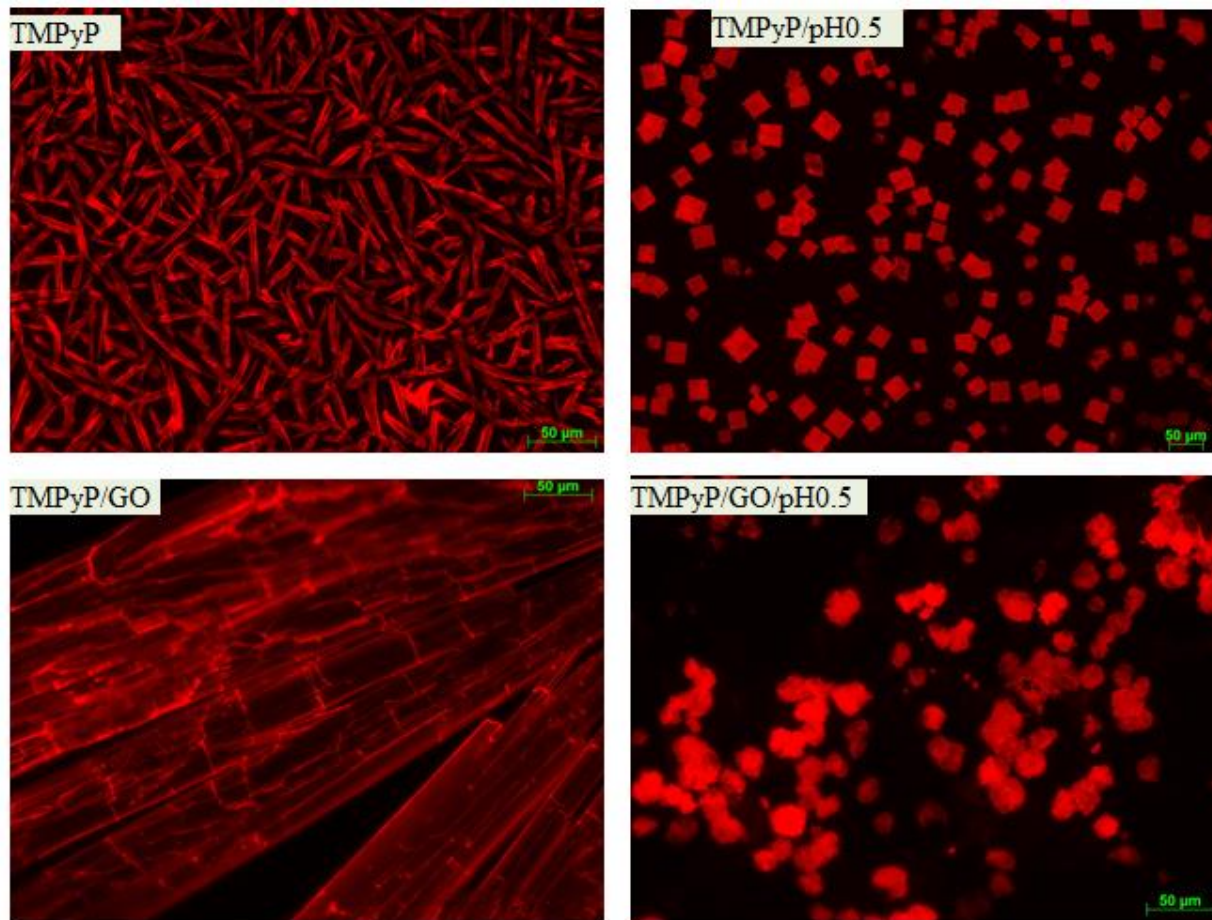


Figure 2. Emission images for all material composites.

The films show well defined structure resulting from self-assembly based processes, these structures possessing features on the tens of micron length scale and upwards. Imaging of n-TMPyP shows well defined self-assembled macroscale structures with rod like formations clearly visible in the image. Fluorescence imaging showing the same features further confirming that n-TMPyP as a film that self-assembles into macroscale ordered structures. For a-TMPyP, possessing relatively stronger J-aggregates there is a clear difference in the resulting self-assembled structures with macroscale square like structures resulting. When GO is introduced for both n and a-TMPyP materials there is a resulting destabilisation of the self-assembled structures. In n-TMPyP, the structures are less well defined, more amorphous and clustered, this is also the case for a-TMPyP.

Nanoscale imaging of the TMPyP+/-GO complexes was undertaken using Scanning electron microscope (SEM). The resulting images are shown in Fig 3. The n-TMPyP SEM image shows structural features in line with fluorescence imaging. It is noted that SEM shows in more detail these micronized/macroscale features. Inspection of the SEM shows how different each of the materials structures are indicating that the introduction of acid or GO significantly changes the resulting materials structure, noting that the fluorescence spectral emission wavelengths do not change.

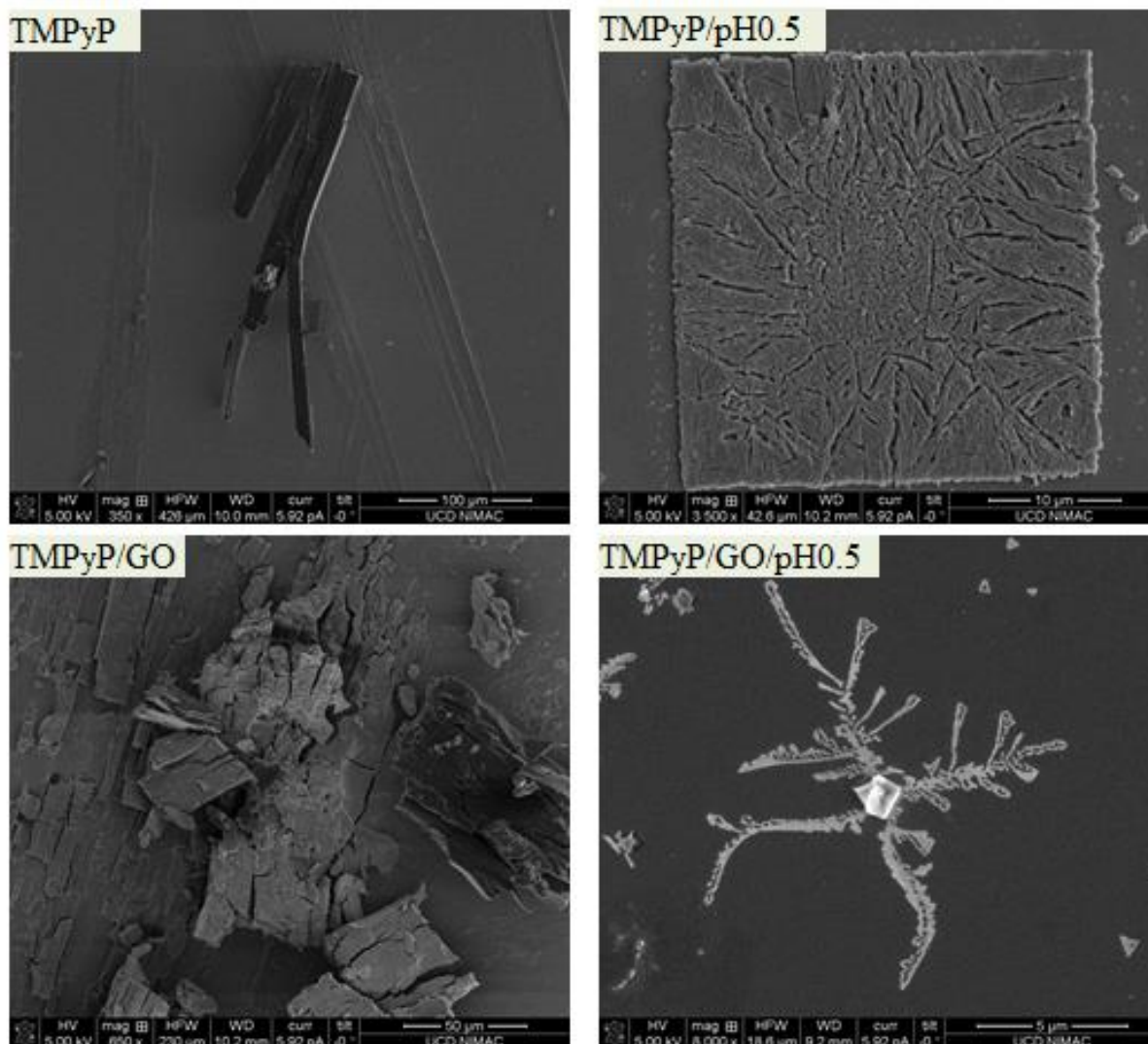


Figure 3. SEM images for all material composites.

Fluorescence images show the self-assembled porphyrins structures are effected, (albeit to a relatively small extend) by the presence of GO. In addition the spectroscopy data (fluorescence and absorption) indicate also that the average optical properties are effected when GO is added. FILM data shows that GO is intercalated within the TMPyP self-assembled structures resulting in the average lifetime shifting downward. Significantly analysis of FLIM data shows that the lifetimes are changed for the majority of the porphyrins when GO is added. This indicates that the porphyrins and GO are well mixed, noting that the self-assembled structures of the porphyrins are approximately maintained which in turn indicates that the porphyrin and GO are interacting in a manner maintaining in general the self-assembled mechanism ex J-aggregate π - π stacking. GO + TMPyP may form a macroscale complex through aromatic π - π stacking whereby the porphyrin is lying flat onto the GO sheet, noting that the other side of the porphyrin can also interact with a GO sheet or interact with a second porphyrin or x number of porphyrins creating an GO-aggregate like complex. If the aggregate complex consists of small number of porphyrins with a single GO sheet, this substructure potentially may form a similar structure to when GO is absent i.e. GO behaves as a porphyrin molecule (in that both are planer in symmetry enabling potentially similar stacking structures such as J-aggregation to occur). The presence of an acid (eg pH=0.5 as used here) is reported to enhance porphyrin-porphyrin interactions i.e. J-aggregation. Even with strong J-aggregation evidence suggests that GO is present within the self-assembled porphyrin structures resulting in the porphyrins optical properties

and also self-assembled structure been effected. Mechanical force studies (using AFM) showed that when GO is present the resulting materials (i.e. for both n and a-TMPyP+GO) was c.a. > magnitude stronger.

In conclusion we demonstrate graphene oxide intercalation into self-assembled (J-aggregate) porphyrin structures. GO-TMPyP interaction is observed even when conditions to form TMPyP J-aggregates are present. Fluorescence lifetime imaging (FLIM) and fluorescence anisotropy imaging were applied along with scanning electron microscopy to study the structure and optical properties from the resulting GO/TMPyP composites. It was seen that the presence of GO alters the macroscale and nanoscale self-assembled structures of TMPyP in addition GOs also alters the optical activity reducing the emission intensity and exciton recombination lifetime. Evidence exists to support a model where planar-symmetric GO and TMPyP co-operate in the formation of self-assembled macro and nanostructures forming a composite with strong GO-TMPyP interaction.

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