Novel approach to enhance light absorption of porphyrin/graphene oxide composites by PH and concentration modification for energy applications

O. BAJJOU1, 3, A. BAKOUR1, M. KHENFOUCH2,3, M. BAITOUL1, B. MOTHUDI2, M. MAAZA4,5, E. FAULQUES6

1 University Sidi Mohamed Ben Abdellah, Faculty of Sciences Dhar el Mahraz, Laboratory of Solid state Physics, Group of Polymers and nanomaterials, PO Box 1796 Atlas Fez 30 000, Morocco.

2 Physics department, College of Science, Engineering and technology Science Campus, Corner of Christiaan de Wet Road & Pioneer Avenue, Florida, 1709, Johannesburg, South Africa

3 Africa Graphene Center, Physics department, Eureka building, College of Science, Engineering and Technology, Science Campus, University of South Africa, Cnr Christiaan de Wet & Pioneer Avenue Florida 1709, Johannesburg, South Africa.

4 iThemba LABS-National Research Foundation of South Africa, Old Faure Road, PO Box 722, Somerset West 7129, Western Cape Province, South Africa.

5 UNISA Africa Chair in Nanosciences-Nanotechnology, College of Graduate Studies, University of South Africa, Muckleneuk ridge, PO Box 392, Pretoria, South Africa.

6 Institut des Matériaux Jean Rouxel, Nantes, 2 rue de la Houssinière, BP32229, 44322 Nantes, Cedex3, France.

Corresponding authors: bajjou.omar@gmail.com

Abstract

Graphene oxide (GO) decorated with nanostructured porphyrin (PN) was synthesized and the interfacial interaction between these two components were investigated by using Scanning electron microscopy (SEM), X-ray, and UV-Visible absorption spectroscopy. These techniques showed good dispersion of GO and PN as well as a π-π intermolecular interaction confirming the energy/charge transfer. Moreover, X-ray diffraction study confirmed the intercalation of PN in GO and their disaggregation. The UV-Visible results showed an important interaction between GO and porphyrin nanorods under different pH values and concentrations resulting in the enhancement of optical absorption of GO-PN. The findings presented here are important to achieve the functionalization of graphene oxide with PN for various optoelectronic applications.

Key words: Graphene, Porphyrin, SEM, XRD, UV-Visible absorption.

1. Introduction

Graphene, a two-dimensional carbon sheet, has attracted tremendous attention and research interest because of its exceptional physical properties. Graphene has high mobility and optical transparency. Graphene-based materials have great potential for practical applications in nanoelectronics, energy harvesting and storage [1, 2], liquid crystal devices and transparent...
conductive film, nanoelectro-mechanical devices[3]. Recently GO has emerged as a new material based on carbon at the nanoscale. Structurally, the GO is similar to the graphene with a base having groups containing oxygen [4]. GO could be figured as graphene fragment, whose edge is mainly decorated with carbonyl and carboxyl groups, and basal plane with epoxide and hydroxyl groups. As these groups have a strong affinity for water molecules, therefore graphene oxide is hydrophilic and can be easily dissolved in water and other solvents.

Recently, organic-based supramolecular nano-assemblies in terms of porphyrin building blocks have been attracting great interest due to their potential application. The porphyrins nanorods are aromatic macrocycles with a cyclic-tetrapyrrrole structure, electron rich, characterized by remarkably high extinction coefficient in the visible range. On the other hand, porphyrins have attracted much attention due to their outstanding photophysical, photochemical and electronic properties, which make them promising alternatives in areas of nonlinear optical materials[5, 6]. In addition, they can adsorb strongly on graphite surfaces. In addition, porphyrin nanorods are of potential interest, and play a major role in achieving a rapid transfer of energy and with a minimum of loss[7, 8]. Given the advantages of functionalization, which can avoid destruction of π-conjugated skeleton and loss of electronic properties of GO, the process used in this work allows to have a functionalization of GO with porphyrin nanorods obtained by self-assembly.

The prepared GO/porphyrin nanorods samples were characterized by SEM, and X-ray diffraction in order to probe the interfacial bonding and electronic interaction between GO and PN. Optical absorption properties of the composite are discussed in terms of effect pH and concentration the interaction between the GO and PN.

2. Experimental setup

Graphene oxide was synthesized by our modified Hummer’s method [9, 10]. The well dispersed GO sheets were prepared using (KMnO₄/H₂SO₄), and then the precipitate was washed many times with deionized water. The final solution was diluted and sonicated for a major exfoliation of the oxidized sheets. GO solutions with different pH varying from 2 to 11 by means of HCl and NaOH, as well as different concentration solutions were prepared. PN were synthesized via an ionic self-assembly technique by mixing aqueous solutions of two porphyrin precursors using the same procedures developed by Wang and al.[11, 12]. Meso-tetrakis (4-phenylsulfonicacid) porphyrin (H₄TPPS₂⁺) dihydrochloride and Sn(IV) tetrakis(4-pyridyl)porphyrin (SnTPyP²⁺) dichloride were purchased from Frontier Scientific and used without further purification. To obtain porphyrin self-assembly nanorods, equal volumes of an acidified H₄TPPS₂⁺ solution (10.5 µM) and a Sn (IV)-tetrakis (4-pyridyl) porphyrin (Sn(IV)TPyP²⁺) dichloride solution (3.5 µM) were mixed and left undisturbed in the dark for ~72 hours at room temperature. 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 pH ~ 2. First, the solution of the porphyrin nanorods was mixed with different GO solutions. Finally, thin films of the GO-PN composite were deposited by drop casting on glass slide and left to dry in ambient temperature.

SEM images were obtained using a JEOL JSM 7600F. X-ray diffraction (XRD) patterns of GO, porphyrin nanorods and composites were performed with Bruker’s D8 advanced X-ray diffractometer using CuKα radiation (λ=1.5418 Å). UV–vis spectra were measured on a PerkinElmer LAMBDA950/1050 UV/VIS/NIR spectrophotometers are dual-beam, dual-monochromator instruments equipped with an optional 150 mm integrating sphere accessory.
3. Results and discussion

3.1 SEM

Scanning Electron Microscopy images show graphene oxide layers, and GO-porphyrin nanorods. The GO images (Figure 1.a) present a network of randomly oriented sheet-like structures, a wrinkled texture was observed. The SEM images of the GO-porphyrin nanorods composite materials demonstrate that at a micrometer order of magnitude, a good exfoliation of GO sheets as well as a good degree of homogeneity was achieved resulting in the uniform and dense surface observed in figure 1.c.

![Figure 1. SEM images of GO, PN and GO-PN](image)

3.2 X-Ray diffraction

Figure 2. shows the XRD patterns of GO, PN, and GO-PN. GO spectrum exhibits an intense and strong peak at $2\theta = 11.4^\circ$ which is attributed to the (001) lattice spacing of 0.78 nm due to the interlamellar water trapped between the hydrophilic graphene oxide layers [13-15]. For porphyrin nanorods the XRD patterns shows a strong peak $2\theta = 31.75^\circ$ attributed to the (701) [16, 17]. The GO-PN composite shows a peak at $2\theta = 10.03^\circ$ (d-spacing = 0.881 nm), this can be explained by the increase of the inter-planar distance (001) due to the effect of PN trapped by GO.

![Figure 2. XRD patterns of GO, PN and GO-PN](image)
3.3 optical absorption

UV–Vis absorption spectra of the GO, GO-PN solutions are given in Figure 3, with different pH and GO concentrations. The absorption spectrum of PN in solution (Figure 3b) shows characteristic absorbance peaks at 356, 432, 494 nm that are specific for these nanorods, which are attributed to the Soret band, as well as a weak absorption band in the (500,800 nm) range, associated to the Q-band[18, 19]. Additionally, the peaks at 494 and 715 nm are the characteristics of J-aggregate structures, particularly in porphyrin nanorods. The peak at 432 nm is attributed to H-aggregates and the absorbance feature between 432 and 494 nm is most likely due to a mixture of aggregates and monomers [12, 20], where the peak at 644 nm is originating from monomers transitions. The peaks at 553 and 591 nm are assigned to Sn(IV)TPyP3+ . These absorption bands are a result of electronic transitions from ground state (S0) to the two lowest singlet-excited states S1 (Q state) and S2 (S state). Exciton theory states that 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, and since the S band of H4TPPS4− is red-shifted upon aggregation (J-aggregate), it implies that planar porphyrin molecules are stacked in an arrangement where individual porphyrin units are not positioned directly on each other’s top.
Figure 3. UV-visible Absorption spectra of different pH: (a) GO solutions, (b) GO-PN composites, and different concentration spectra of (c) GO; (d) GO-PN composites.

In Figure 3.a we present the study of the pH effect for the GO solution, for a pH ranging from 2 to 11. A peak is noted at 226 nm, can be attributed to the π-π* absorption. The broad peak at 306 nm corresponds to n-π* transition of the C=O bond. We note a widening of the characteristic band of GO when going from pH2 to pH11. The redshift noted while increasing the pH can be understood in terms of the restored electronic conjugation pulling the highest occupied molecular orbital and lowest unoccupied molecular orbital. The variation of GO solution concentration is studied also by means of UV-Vis absorption, the obtained spectra presented in Figure 3.c., we note an increase in the intensity of the GO characteristic band when increasing the concentration.

The UV–vis absorption spectra of GO-PN composite solutions presented in figure 3.b and 3.d, shows that the interaction between these two components has a big effect on the total absorbance. GO absorption peak was red-shifted to 232 nm, can be explained by a change of its band gap structure related to an increase of the π-conjugated domains. On the other hand, it may be due to the presence of unreacted electrons withdrawing group in the GO. Porphyrin nanorods peaks show a remarkable decrease of intensity except the peak located at 434 nm. Moreover, the redshifted B-band at 421 nm, figure 3.b., when increasing the solution pH can be interpreted in terms of the restored electronic conjugation pulling the highest occupied molecular orbital and lowest unoccupied molecular orbital. Moreover, in the GO-PN composite spectra we observe a change in the overall intensity in the different composites when going from pH2 to pH11, this behavior can be explained by the fact that intramolecular donor-acceptor structure usually allows charge-transfer interaction or the (HOMO)- (LUMO) transitions to occur. The study of the GO concentration effect in the GO-PN composites on the absorption spectra is presented in figure 3.d., the main observation is that the GO as well as PN band intensities show an overall increase while inserting different GO
concentrations, proving the insertion of GO created an interface leading to an efficient electron-hole separation. These results prove that the interaction between the photogenerated electrons and holes is strong and the excitons tend to be localized almost exclusively on porphyrin. The efficiency of this energy transfer is inversely proportional to the sixth power of the distance between donor and acceptor. Therefore, the energy transfer rate depends on the strengths of the electronic transitions of the donor and acceptor molecules.

4. Conclusion

PH and concentration effect on optical properties of PN and their interactions with GO were investigated, as well as the morphological, structural properties. SEM showed good adhesion and exfoliation of GO in PN. Moreover, the interaction with GO alters the aggregated structure of the PN. The strong π-π interaction and charge/energy transfer between PN and GO were confirmed by UV-Visible spectroscopy, suggesting that GO functionalized with PN nanostructure with their structural and optical properties can open a new window for optic limiting, optoelectronics and photovoltaic devices.

References

[1] S. Das, P. Sudhagar, S. Nagarajan, E. Ito, S. Kang, W. Choi, Synthesis of graphene-CoS electro-catalytic electrodes for dye sensitized solar cells, 2012 Carbon, 50 4815-4821.
[2] H. Chang, H. Wu, Graphene-based nanocomposites: preparation, functionalization, and energy and environmental applications, 2013 Energy & Environmental Science, 6 3483-3507.
[3] T. Kuila, S. Bose, A. Mishra, P. Khanra, N. Kim, J.H. Lee, Chemical functionalization of graphene and its applications, 2012 Progress in Materials Science, 57 1061-1105.
[4] S.P. Daniel R. Dreyer, W. Bielawski and Rodney S. Ruof, The chemistry of graphene oxide, 2010 Chem.Soc.Rev., 391-13.
[5] D. Narayana Rao, Excited state dynamics in porphyrins in relevance to third-order nonlinearity and optical limiting, 2003 Optical Materials, 21 45-49.
[6] M.K. Panda, K. Ladomenou, A.G. Coutsolelos, Porphyrins in bio-inspired transformations: Light-harvesting to solar cell, Coordination Chemistry Reviews, 256 (2012) 2601-2627.
[7] J.L.J. Ricardo Franco, b Haorong Wang,c Zhongchun Wang, Krisztina István, Neil E. Schore,b Yujiang Song, w Craig J. Medforthc, and John A. Shelnutt, Molecular organization in self-assembled binary porphyrin nanotubes revealed by resonance Raman spectroscopy, 2010 Phys. Chem. 12 1-6.
[8] O. Bajjou, A. Bakour, M. Khenfouch, M. Baitoul, M. Maaza, Charge Carrier Dynamics and pH effect on optical properties of anionic and cationic porphyrin-graphene composites, 2018 J.of electronic materials, 47 2897-2904.
[9] O. Bajjou, A. Bakour, M. Khenfouch, M. Baitoul, M. Maaza, Synthesis and opto-structural characterization of reduced graphene oxide and meso-tetrakis(4-phenylsulfonic-acid) porphyrin composites, 2018 J. of Materials Science: Materials in Electronics, 29 8594–8600.
[10] M. Khenfouch, M. Maaza, Raman study of graphene/nanostructured oxides for optoelectronic applications, 2013 Optical Materials, 4 20-28.
[11] N. Nametso Mongwaketsi, Alexander Nechaev, Malik Maaza, and Raymond Sparrow, Ionic self-assembly of porphyrin nanostructures on the surface of charge-altered track-etched membranes, 2010 Journal of Porphyrins and Phthalocyanines, 14 1-7.
[12] N. Mongwaketsi, B. Klumperman, R. Sparrow, M. Maaza, Synthesis and characterization of
porphyrin nanotubes/rods for solar radiation harvesting and solar cells, 2012 Physica B, 407 1-5.

[13] V.R.K. Satish Bykkam, Shilpa Chakra CH. and Tejaswi Thunugunta, SYNTHESIS AND CHARACTERIZATION OF GRAPHENE OXIDE AND ITS ANTIMICROBIAL ACTIVITY AGAINST Klebsiella AND Staphylococcus, 2013 International Journal of Advanced Biotechnology and Research, 4 1-5.

[14] M. Khenfouch, M. Maaza, White photoluminescence from a grown ZnO nanorods/graphene hybrid nanostructure, 2012 Optical Materials, 34 1320–1326.

[15] P. Viet Hung Pham, T. Truong Dang, S. Hyun Hur, E. Kim, B. Seon Kong, S. Kim and Jin Suk Chung, Chemical reduction of an aqueous suspension of graphene oxide by nascent hydrogen, 2012 The Royal Society of Chemistry, 22 10530-10536.

[16] G. Jin-Song Hu, H. Lian, L. Wan, Three-Dimensional Self-Organization of Supramolecular Self-Assembled Porphyrin Hollow Hexagonal Nanoprisms, 2005 J. AM. CHEM. SOC., 127 17090−17095.

[17] J. Liang Wang, Controlling the growth of porphyrin based nanostructures for tuning third-order NLO properties, 2014 Nanoscale, 6 1-8.

[18] W. Chen, R. Hu, Y.- Xu, Q.- Luo, Y. Dai, S.Huang, P.Guo, Photophysical and electrochemical properties of a novel lanthanide tetra(4-sulfonatophenyl)porphyrin, 2015 J IRAN CHEM SOC,12 937−942.

[19] S. Jo, S. Kim, E. Cho, D. Lee, J. Kim, S. Lee, J. Joo, Photoluminescence and Optical Waveguiding Characteristics of Bisalkoxy Tin(IV) Porphyrin Microcrystals, 2012 Chemistry – An Asian Journal, 7 2768−2771.

[20] M. Khenfouch , M. Baitoul , M. Maaza, Photoluminescence and dynamics of excitation relaxation in graphene oxide-porphyrin nanorods composite, 2014 Journal of Luminescence, 145 33−37.

[21] X. Pyng Yu, Y. Toh, Y. Chieh Lee, K.Yen Huang, S. Huang, S. Shrestha, G. Conibeerb and J. Tang, Efficient electron transfer in carbon nanodot–graphene oxide nanocomposites, 2014 J. Mater. Chem. C, 2 2894−2901.

[22] M. Khenfouch, O. Bajjou, M. Baitoul, N. Mongwaketsi, M. Maaza, J. Wery Venturini, Optical properties and dynamics excitation relaxation in reduced graphene oxide functionalized with nanostructured porphyrins,2015 Optical Materials, 42 479-483.

[23] S. Vempati, T. Uyar, Fluorescence from graphene oxide and the influence of ionic, [small pi] interactions and heterointerfaces: electron or energy transfer dynamics, 2014 Physical Chemistry Chemical Physics, 16 21183-21203.