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Optical absorption and electron dynamics in reduced graphene oxide-nanostructured porphyrin for active solar cell layers

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ABSTRACT

This work outlines a study to gain further understanding of the interactions of two interesting materials, the reduced graphene oxide, and porphyrin nanostructured. We seek to address the changes occurring in morphological and opto-structural properties of the resultant composite material using different spectroscopies and by changing pH values. The structural analysis by X-ray diffraction suggests an enhancement of the composite structure, which is further confirmed by the scanning electron microscopy. The acidity effect on the resulting properties was investigated by preparing multiple samples with different pH values. The optical properties highlighted the photoluminescence intensities quenching in the composite for optimum pH values, which is a favourable property for inserting in energy applications. Furthermore, the study of electron-hole pair dynamics was conducted by means of Time resolved photoluminescence. Obtained results prove that the excitons exhibit a longer lifetime for the composite sample and therefore confirming the electron transfer from porphyrin nanostructured to reduced graphene.

Keywords : Reduced graphene oxide, Porphyrin, XRD, Luminescence, Absorption, Exciton lifetime

1. Introduction

The two dimension allotrope of carbon, presents one of the most widespread and studied materials in this field since its discovery in 2004 [1], thanks to its outstanding physical and optical properties as well as its potential of use in a multitude of electronic and medical fields [2–5].

The graphene synthesis techniques has known great development in the last years, depending on the desired application varying from epitaxial growth, chemical vapor deposition, and chemical methods that include the synthesis via Hummers method, that we used in this work [6–8]. The tuning of the final properties of graphene is achieved by functionalization and mixing with other organic and inorganic materials [9,10].

Reduced graphene oxide (RGO) is considered as an efficient and easy-synthesis substitute for graphene, thanks to the possibility of production via a chemical reduction of graphene oxide (GO) already prepared by oxidation of pristine graphite using Hummer's method [11,12].

Porphyrins present a kind of conjugated organic molecules based on macrocycle pyrroles linked via methine bonds [13,14]. They have been widely used in composites because of their transferable properties to carbon nanomaterials such as carbon nanotubes and graphene, via functionalization. The strong conjugation of porphyrin comes from the high number of delocalized electrons offering great photophysical properties allowing successful interactions with other conjugated materials [15–17].

The porphyrin, with an extended p-bond system, was mixed with RGO samples that plays the role of electron acceptors thanks to its low bandgap [18], has given rise to a composite with enhanced optical properties translated with higher absorption intensities and photoluminescence (PL) quenching. Electron-hole dynamics were further investigated by time resolved photoluminescence (TRPL), and showed the enhancement of transport and relaxation of the photogenerated excitons. pH effect was investigated to better determine the factors affecting the optical and electronics processes. In this paper, we report also the modification of structure and surface by means of X-Ray Diffraction (XRD) and Scanning electron microscopy (SEM).

2. Setup

We proceed by synthesizing graphene oxide from graphite powder using Hummer's method [11]. After the GO solution is prepared, a reduction step is fulfilled by using hydrazine hydrate. The obtained RGO solution submitted a sonication process in order to better exfoliate the graphene sheets. Porphyrin nanostructured, synthesis procedure is described in our early works [7,19]. Afterwards the final nanocomposite was further sonicated at room temperature for 30 min to ensure homogeneity, and drop casted finally on glass substrates.

X-ray diffraction (XRD) measurements were performed with Bruker's D8 advanced X-ray diffractometer using CuK α radiation

($k = 1.5418^\circ \text{\AA}$). SEM images were obtained using a JEOL JSM 7600F. UV–Vis spectra were measured with a PerkinElmer LAMBDA 950/1050 UV/VIS/NIR spectrophotometers are dual-beam, dual-monochromator instruments equipped with an optional 150 mm integrating sphere accessory. The steady-state photoluminescence spectra were recorded using a Jobin-Yvon fluorolog 3 with $k_{\text{exc}} = 420 \text{ nm}$ and luminescence dynamics spectra were obtained at room temperature using a Jobin-Yvon Fluorolog spectrometer with a CCD detector.

3. Results and discussion

3.1 X-Ray diffraction

XRD is used to understand the structural order and its modification in the RGO–PN composite samples. Fig. 1. shows the XRD patterns of RGO, PN, and RGO-PN composite films. We can see that the characteristic diffraction peak of RGO arises at $2\theta = 23.4^\circ$, which is attributed to the diffraction from the (0 0 2) plane [20–22]. This diffraction peak is wide and thus indicating a good

Fig.1. XRD patterns of RGO, PN, and RGO-PN composite films.

reduction of GO, giving therefore rise to the irregularity in the interlayer spacing at the edges or inside the RGO sheets. In the RGO-PN composite pattern we can see the characteristic peak (0 0 2) of the RGO at $2\theta = 23.4^\circ$ ($d_{\text{spacing}} = 3.78 \text{ nm}$) interfering with the PN peaks. The RGO diffraction peaks intensity exhibit a slight decrease in the composite sample, meaning that the presence of PN changes the structure of RGO which is proved by the increase in d-spacing between the RGO sheets. The increase in the inter-planar distance can be attributed to the effect of PN trapped in RGO layers leading to their expansion and eventually their exfoliation. These results will be better conceived by scanning electron microscopy results.

3.2 Morphological analysis

Scanning Electron Microscopy images of the RGO, PN and RGO–PN composite films are presented in Fig. 2. The RGO sample presented in Fig. 2a exhibits the wrinkled sheet structure generally found in literature [23].

The PN sample is presented in Fig. 2b shows a grain structure agglomerated with a good homogeneity in the surface. The composite exhibited in Fig. 2c shows a modified RGO sheet structure with small PN particles embedded within. Brighter zones in the composite image could be attributed to the arising edges or entire RGO sheets, proving the increase in d-spacing between the RGO sheets already discussed. These results can be explained by the presence of electronic interactions between reduced graphene oxide sheets and PN that will be further investigated by optical studies.

3.3 UV–Visible absorption

The UV–Visible absorption spectroscopy is an important tool to gain a better insight in the optical processes taking place within the composite and the resulting interaction as well as their effect on the optical properties. We conducted a study based on the variation of pH value as a key factor, and observed the absorption by means of UV–Vis absorption spectroscopy on the RGO and RGO–PN solutions at different pH values. In Fig. 3a we can observe in the acidic range from pH 2 to 5 that the characteristic peak of RGO is more pronounced and better resolved, however in the basic range we can see the rise of a shoulder around 300 nm especially when reaching pH 10, as well as a widening of the characteristic band of RGO. The change of the characteristic band at 250 nm is explained by the restoration of RGO's conjugated structure [24–26]. The absorption intensity of the RGO increases gradually with pH value. The RGO UV–Vis absorption spectra presented a dependency of the pH value, which can be attributed to p-p stacking property which can play an important role in the absorption process.

The RGO-PN composite spectra for different pH values are shown in Fig. 3b. For the acidic range from pH 2 to 7 we can always see the RGO characteristic peak around 240 nm and the rise of a new peak and a small shoulder attributed to the PN. Remarkably, the same observations made for the 240 nm peak in the RGO can be attributed to the composite in the acidic range, while an increase in the 420 nm is noted due to both, the PN component and the pH higher levels.

In Fig. 3b in the basic range we observe a declining trend of the intensity of the PN characteristic peak that goes in reverse to the increase trend already observed in the acidic region. This behavior can allow to fix an optimal level of pH value for a maximum level of absorption for the composite which lays around the pH 8. This can be explained by the restoration of the conjugated structure in addition to the improvement of the interaction between the RGO sheets and PN when pH value is increasing up to a pH 8 level.

Fig. 2. SEM images of: (a) RGO, (b) PN and (c) RGO-PN composite films.

Fig. 3. (a) UV-Vis absorption of RGO (b) RGO-PN composite.

3.4 Steady state photoluminescence

The PL spectroscopy is an effective way to probe the electronic structure of materials. Steady state PL measurements were conducted in order to observe the evolution of PL spectra of the RGO and PN samples and how it relates to the generated electron-hole pairs properties. Fig. 4 shows the PL spectra of RGO, PN and the PN-RGO composite.

The Fig. 4 exhibits PN spectrum, that is characterized by two key bands at 650 and 714 nm [7], while the RGO sample shows a large emission over the red and near infrared region, rather than distinct bands. The compound PL spectrum present two main peaks at 620 and 690 nm, these emissions can be attributed to the presence of isolated sp² groups in the sp³ carbon matrix, as well as resulting from the electron recombination already generated on the PN, with the holes generated and concentrated in the RGO surface [11,27].

Fig. 4. PL spectra of RGO, PN and the PN-RGO composite.

The composite PL spectrum exhibits a more distinct emission peak at 650 nm which is attributed to higher absorption in the composite as well as the interface interaction between the RGO and the PN which facilitates the emission of the already absorbed energy. This intensity of the composite is obtained for pH7 which makes it a perfect value for both application in absorption and emission purposes.

The quenching observed for the composite PL spectrum can be attributed to the interaction between RGO and PN. This extinction can be explained by an efficient charge/energy transfer between the two components.

3.5 3D PL mapping

The 3D photoluminescence mapping of the RGO, PN and RGO- PN composite is shown in Fig. 5. the false color images show qualitatively that the PL emission intensity presents some changes when RGO is inserted in the PN matrix. These results confirm the quenching effect already observed in the steady state PL in the previous section. The photogenerated excitons decline spectra are subsequently extracted from these 3D PL mapping images.

3.6 TRPI

TR-PL spectroscopy is a strong tool to extract useful information about the dynamics and lifetimes of photogenerated excitons as well as the mechanisms taking place between RGO and PN components in the excited state. The PL decay measurements of PN and the RGO-PN composite in solutions were extracted from the false color image in Fig. 5. which are excited at a wavelength of 400 nm and a probe wavelength of 620 nm Fig. 6.

The PN component exhibits two different exciton lifetimes obtained for $S_1 = 16$ ps and $S_2 = 315$ ps mentioned in Table 1. The key changes in exciton dynamics created in PN after their interaction with RGO was perceived in the increase in the larger component S_2 , which increased from 315 to 396 ps Table 1. This can be interpreted by the alteration of their energy band structure due to the role of RGO related to the size of the sp² clusters, leading to a retardation in recombination of the interband carriers [28].

The TRPL measurements bring into light the important effect of PN particle size and their aggregation on the excitons lifetime. Consequently we can infer a considerable change of the composite optical properties. Furthermore, the results of this work showed notable emission extinction and an increase in the average lifetime of excitons. These results constitute a proof to the presence of energy/ charge transfer between PN and RGO sheets, which is very appealing for optical applications [29,30].

Fig. 5. False color images of RGO, PN and RGO-PN.

Fig. 6. The PL decay time spectra of PN and the RGO-PN composite.

Table 1
Excitons lifetime of PN and RGO- PN.

Sample	$S_1(a_1)$	$S_2(a_2)$	$S_{\text{avg}}(\text{ps})$
PORPHYRIN	16(2.20)	315(0.23)	217
RGO-PN	27(3.12)	396(0.41)	270

4. Conclusion

To sum up, our results show that RGO-PN composite presents an enhanced structural order as well as better absorption and emission properties. XRD spectroscopy results imply the improvement of the overall structure after inserting RGO in the PN Matrix. The pH effect study suggests an enhanced optical absorption for higher pH up to a slightly basic value. Furthermore, the results of the PL measurements in steady state and time resolved showed a notable emission quenching and an increase in the photogenerated excitons lifetime. This study have provided further evidence of an overall enhancement of the optical properties that can be achieved by monitoring the pH value in order to obtain electron transfer between the two components of the composite.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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