

The spectrochemical behavior of composites based on poly (para-phenylenevinylene), reduced graphene oxide and pyrene



Mirela Ilie ^{a, b, *}, Mihaela Baibarac ^a

^a Lab. Optical Processes in Nanostructured Materials, National Institute of Materials Physics, P.O. Box MG-7, Bucharest R077125, Romania

^b Faculty of Physics, University of Bucharest, P.O. Box MG-11, 077125 Bucharest, Romania

ARTICLE INFO

Article history:

Received 26 January 2017

Received in revised form

29 May 2017

Accepted 1 June 2017

Keywords:

Polymers functionalization

Composites

Conducting polymers

Infrared spectroscopy

UV–Vis spectroscopy

ABSTRACT

A new composite material based on poly (para-phenylenevinylene) (PPV), pyrene (Py) and reduced graphene oxide (RGO) is synthesized using thermal conversion route. The properties of this material are investigated by Raman scattering, photoluminescence (PL), infrared (IR) and ultraviolet–visible (UV–Vis) spectroscopy. Adding Py at PPV precursor solution (PPV PS) containing RGO, yields to important modifications in both vibrational and electronic properties of these composites. The presence of Py into PPV matrix determines a blue shift of PPV PL. According to Raman and IR studies, PPV is non-covalently functionalized with Py which interacts forward with RGO through π - π interactions causing an important modification into the polymer chains conjugation length.

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1. Introduction

Poly (para-phenylenevinylene) (PPV), one of the most representative conjugated polymers, is a good candidate for improving the preparation of solar cells [1]. The PL high efficient and good processability in solution [2] recommend PPV as a starting point for the synthesis of different materials like composites, copolymers, heterostructures or various mixtures with improved optical properties and charge separation.

Special attention was focused on composite materials like PPV-graphene, PPV-graphene derivatives, PPV-carbon nanotubes (mixed or highly separated in metallic and semiconductor entities) [3–8]. Until recently, only several studies on PPV-graphene composite have been reported to use the chemical route [5,9,10], comparing with multitude of papers related to composites based on carbon nanotubes (CNTs) and PPV [8,11–16]. Several studies on the PPV-CNTs composites, synthesized by chemical and electrochemical routes, have revealed the following aspects [8,17]: i) generation of surface plasmons at PPV/metallic CNTs interface [8]; ii) decrease of PPV PL intensity induced by the presence of CNTs

[7,8,11–14]; iii) PL studies have shown that single walled carbon nanotubes (SWNTs) play a role of inhibitor on the annealing conversion of the PPV precursor solution (PPV PS) [15]; iv) shortening of the macromolecular chains of PPV as a consequence of the polymerization process in the presence of CNTs proved by PL studies [18]; v) using IR absorption spectroscopy, the covalent and non-covalent functionalization of SWNTs with PPV has been revealed [8,16,17].

Few papers have been devoted to the functionalization of CNTs with pyrene (Py), but concerning the functionalization of graphene, there are no available studies. Py is used due to its high luminescence [19,20] and good solubility in various solvents, even with simple structure and good volatility, as in the case of ethanol [21]. According to M. J. Niedziolka et al. [22], Py has been used in homogenization and functionalization processes of CNTs and graphene [22]. Py functionalized polymers were shown to be effective for the stabilization of CNTs in polymeric matrices and enables the use of polymer functionalized CNTs. Reinforcing the polymers with CNTs leads to increase their electric properties [23]. The presence of Py in copolymers has a polaron stabilizing effect and allows greater ion mobility compared to the initial macromolecular compound [24,25]. The addition of Py or its derivatives [26,27] at the PPV PS with different amount of CNTs can lead to materials with superior mechanical, electrical and optical properties [28,29].

In this paper, the attention is focused on the chemical synthesis

* Corresponding author. Lab. Optical Processes in Nanostructured Materials, National Institute of Materials Physics, P.O. Box MG-7, Bucharest R077125, Romania.

E-mail address: mirela.ilie@infim.ro (M. Ilie).

and characterization of a new composite material based on PPV, Py and RGO.

2. Experimental

Chemical compounds used in this work are: α,α' -dichloro-*p*-xylene Sigma Aldrich (98% purity), tetrahydrothiophene Sigma Aldrich (99% purity), HCl Alfa Aesar (36 wt%), NaOH flake Alfa Aesar (98% purity), CH₃OH anhydrous J.T. Baker (99.8% purity), Pyrene Alfa Aesar (98% purity), Carbon black acetylene 50% compressed (99.9% purity), KMnO₄ Alfa Aesar (98% purity), NaNO₃ (98 atom % 15 N), H₂SO₄ (98 wt%), H₂O₂ Sigma Adrich (30 wt%), C₂H₅OH Chim. Reactiv (96% purity), and hydrazine monohydrate Aldrich-Sigma (98% purity).

Graphene oxide was prepared according to the protocol published elsewhere [30] and then reduced in the presence of hydrazine to obtain RGO [31]. The PPV PS was prepared using Wessling-Zimmerman route, starting from α,α' -dichloro-*p*-xylene and tetrahydro-thiophene, in methanol and then recrystallized from acetone [32]. To obtain thin films of PPV, PPV-Py, and PPV-Py with different wt.% of RGO, several mixtures were prepared, as follows:

- the PPV-Py blend was prepared by adding Py-Et-OH (0.001 g/mL) solution to a diluted PPV PS in Et-OH (1:2 vol ratio). The mixture was ultrasonicated until it became a homogeneous transparent solution;
- the PPV PS-RGO blends with different weight percentages concentrations of RGO 0, 0.01, 0.05, 0.1, and 0.5 wt%, were prepared and ultrasonicated for 10 min.
- the PPV PS-RGO-Py blends were obtained by adding the same quantity of Py/Et-OH (0.001 g/mL) solution at the PPV PS-RGO blends. These mixtures have been also homogenized by ultrasonication.

Using drop casting method, the solutions mentioned above were deposited on quartz and silicon substrates. After drying at room temperature for 24 h, the films were annealed in vacuum at 110 °C for 48 h.

Raman spectra of PPV, PPV-RGO and PPV-RGO-Py were recorded with a spectral resolution of 2 cm⁻¹ in a backscattering geometry, under excitation wavelength of 1064 nm, using a RFS 100S FT Raman spectrophotometer from Bruker.

The IR spectra of PPV, PPV-RGO and PPV-RGO-Py were recorded on films deposited onto silicon substrate, with a resolution of 4 cm⁻¹, using Vertex 70 FTIR spectrometer.

The UV-Vis spectra of PPV, PPV-RGO and PPV-RGO-Py were recorded on films deposited onto quartz substrate, with a resolution of 1 nm using a dispersive Lambda 950 Perkin Elmer spectrometer.

The PL spectra of PPV, PPV-RGO and PPV-RGO-Py were measured in right angle geometry at room temperature (RT) using a Horiba Jobin Yvon Fluorolog-3 spectrometer, model FL 3-22, under an excitation wavelength of 370 nm.

3. Results and discussion

3.1. Optical properties of PPV-Py material

The UV-Vis absorption spectra of PPV-Py (Fig. 1) consist of the following bands situated at 5.36 eV (231 nm), 3.8 eV (326 nm) and 3.62 eV (342 nm), the former being assigned to arilsulfonium salt and the last two to stilbene-like chromophores [33]. Other bands situated at 3.31 eV (374 nm), 3.15 eV (393 nm) and 2.91 eV (426 nm) correspond to conjugated π -electron system. As it can be seen, adding Py induces a decrease of the UV-Vis bands absorbance

situated between 360 and 450 nm, simultaneous with an increase in the absorbance of the band situated at 291 nm. According to Fig. 1, adding Py at PPV PS leads to a decrease in the PPV absorbance bands, located in the spectral range 350–480 nm, suggesting a lower conjugation length of the PPV MCs [33].

Another consequence of adding Py to PPV PS is observed in Fig. 2 by a slightly blue shift in the PL spectra of the PPV-Py comparing to PPV, fact which suggests a weak interaction between PPV and Py.

Fig. 3a shows the emission spectrum of PPV, obtained by annealing conversion of the PPV PS at 110 °C. The deconvolution of PPV emission spectrum indicates the presence of three emission maxima situated at ~2.55 (labeled k_3), 2.4 (labeled k_2) and 2.25 (labeled k_1) eV which are attributed to electronic transitions of 4, 5 and 7-10 repetitive units (RUs) [36], having the following molecular structures $(-C_6H_4-CH=CH-)_4$, $(-C_6H_4-CH=CH-)_5$ and $(-C_6H_4-CH=CH-)_7-10$, respectively. Fig. 3b shows a decrease in the 5 and 7-10 RUs of PPV with 30 and 35%, respectively, when the Py is added at the PPV PS. This fact can be proved by calculating the I_{k3}/I_{k2} ratio which varies from 1.09 for PPV to 1.29 for PPV-Py. A decrease of only 7% of PPV 4 RUs is reported.

The Raman lines of PPV are situated at 1172, 1324, 1550, 1586 and 1627 cm⁻¹ and they correspond to the following vibrational modes: i) C–C stretching + C–H bending of the phenyl ring, ii) C=C stretching + C–H bending of the vinyl group, iii) C=C stretching of the phenyl ring iv) the C–C stretching of the phenyl ring and v) the C=C stretching of the vinyl group [34]. In Fig. 4, in the case of the PPV-Py Raman spectrum one observed that all the main vibrations of PPV are shifted towards higher wavenumbers from 1172, 1550 and 1586 cm⁻¹ to 1176, 1554 and 1592 cm⁻¹, respectively. In our opinion these modifications can be correlated with the presence of a heavier molecular structure attached to the PPV macromolecular chains (MCs). The presence of a new Raman line situated at 613 cm⁻¹ (Fig. 4), reveals an inhibition of the PPV PS polymerization in the presence of Py. This Raman line was assigned to thiophen C–S–C vibrational mode [35]. The interaction between the phenyl rings of PPV and Py suggests a non-covalent functionalization, via π - π stacking interaction.

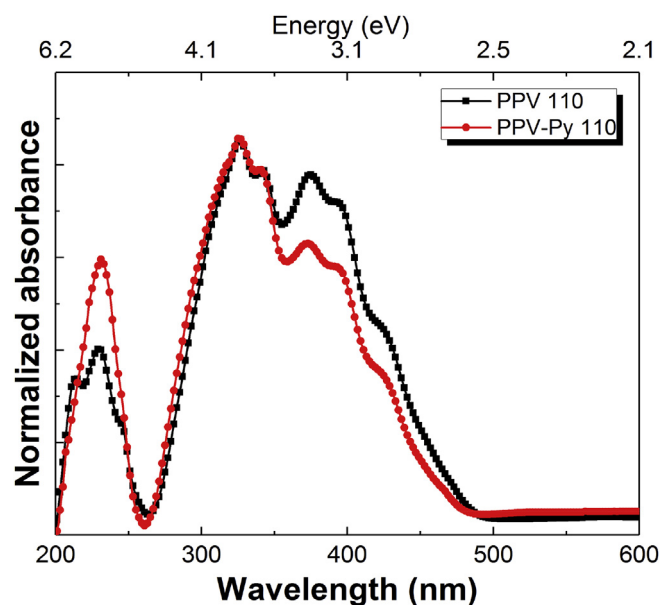


Fig. 1. UV-Vis spectra of the PPV (black curve) and PPV-Py (red curve) films deposited onto quartz support. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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