

Template role of polyhexylthiophene nanowires on efficient bilayer photovoltaic cells



Rita Rodrigues^{a,*}, Quirina Ferreira^a, Ana Luísa Mendonça^a, Jorge Morgado^{a,b}

^a Instituto de Telecomunicações, Instituto Superior Técnico, Av. Rovisco Pais, P-1049-001 Lisboa, Portugal

^b Department of Bioengineering, Instituto Superior Técnico, UL, Av. Rovisco Pais, P-1049-001 Lisboa, Portugal

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ABSTRACT

Nanowires of the conjugated polymer poly(3-hexylthiophene) (P3HT) were produced by solution self-assembly and incorporated into bilayer photovoltaic devices with PCBM as the electron-acceptor material. Atomic Force Microscopy enabled a full assessment of the self-assembled P3HT fibrils network. It also revealed the effect the pre-existing nanowires have on the evaporated PCBM overlayer, strongly suggesting a master role. The power conversion efficiency of the bilayer with P3HT nanowires dramatically increases, when compared to the non-structured bilayer photovoltaic devices of P3HT. Photovoltaic devices characterization ensured a comparative overview of the performance parameters for both structured and non-structured P3HT:PCBM bilayers and blend devices.

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1. Introduction

The conjugated polymer poly(3-hexylthiophene), commonly referred to as P3HT, has been one of the most studied polymers in organic photovoltaic devices (OPVs), leading to high power conversion efficiencies upon combination with electron-accepting fullerenes (such as PCBM) in bulk-heterojunction devices [1,2]. Improvements of OPVs performance face multiple challenges. Recognized efficiency bottlenecks are poor light capture, significant charge recombination and limited charge extraction [3]. One of the research avenues presently followed in tackling recombination and extraction problems is the incorporation of structured films, maximizing exciton separation efficiency and charge carrier percolation paths [4,5].

The most efficient photovoltaic devices are based on a bulk heterojunction (BHJ) or blend, where the donor:acceptor intermixing leads to effective exciton separation though charge transport is often hampered by limited percolation pathways [6]. In the case of bilayer devices, the contact between acceptor and donor materials is restricted to a well-defined interfacial area. Lower power conversion efficiencies are obtained, mainly due to the limited generation of charges, while its extraction is favoured due to the existence of continuous phases [7]. These limitations lead to poorer

performances which lowers the research potential, but residual examples remain in literature [8,9].

A recent trend in P3HT research has been nanostructuring: it is possible to produce different morphologies in film, from crystallization enhancing aggregates [10–12] to variable length nanowires. For instance, a higher hole mobility has been reported for these P3HT nanowires when comparing with that measured in films [13,14,16].

Processes for nanostructuring can be roughly divided into self-assembly or template assisted. The first group elbows on P3HT aggregation phenomena prior to deposition. Methods include controlled cooling [17,18], electric field-assisted assembly [19], solvent vapour pressure [20] and solvent mixtures in which a poor solvent is minority [21] or marginal [16,22]. Although it is largely assumed that the major morphological changes occur in solution prior to deposition, Verilhac et al. have demonstrated that the nature of the polymer assembly can also be manipulated via the deposition method with a clear link to the molecular weight of the P3HT used [23]. Template assisted methods use commercial or anodized alumina templates and the process can evolve through simple filling of the membrane with solution or by capillary action using the melt temperature of the polymer [24–26]. Combination of both self-assembly and template methods is also possible using the ‘stick-slip’ motion procedure [27,28]. Here, we investigate the fabrication of OPVs based on P3HT nanowires formed in solution prior to its deposition. The study is mainly focused on bilayer OPVs, but BJH-type are also studied to provide a comparison basis. In particular, we find that the use of P3HT nanowires leads to an increase

* Corresponding author. Tel.: +351 218418454.

E-mail address: rita.rodrigues@lx.it.pt (R. Rodrigues).

of the power conversion efficiency (PCE) of bilayer photovoltaic devices with evaporated PCBM as the acceptor layer. Moreover, the nanowires not only determine the morphology of the evaporated PCBM acceptor layer but also play a role in the self-assembly of PCBM in the active layer of the P3HT:PCBM blends, as evidenced by Atomic Force Microscopy (AFM) studies. Charge carrier mobilities, in field-effect transistors and unipolar devices, were determined to assess its relevance on the power conversion efficiencies.

2. Materials and methods

RR-poly(3-hexylthiophene) was obtained from Aldrich and used as received. All solutions and spin coated films (1800 rpm/80 seg) were prepared in air. Nanowires of P3HT and P3HTnw:PCBM blends were formed in solution following the general procedure of Kim et al. [21]. Films with a thickness of 185 nm, as measured with a Dektak 6M profilometer, were prepared from these solutions by spin coating for the nanowires bilayers (identified as nwbilayers). Non-structured (identified as planar) bilayer devices were similarly produced from 1% (w/w) P3HT solutions in chlorobenzene (thickness of the films deposited by spin coating is 213 nm). P3HT:PCBM non-structured blends films were produced from 1% (w/w) solutions in chlorobenzene with a P3HT/PCBM weight ratio of 1:0.5 (thickness of 85 nm), no annealing procedure was used so as to ensure comparison between devices.

To fabricate the bilayer photovoltaic cells with structured donor/acceptor interface, ITO-coated glass substrates, previously cleaned and treated with oxygen plasma, were first coated with a 25 nm thick layer of PEDOT:PSS (poly(3,4-ethylenedioxythiophene) doped with polystyrene sulphonic acid) prepared by spin coating and heated at 125 °C for 10 min over a hot-plate. P3HT nanowires were deposited over this PEDOT:PSS layer by spin coating and a PCBM layer is then thermally deposited on top. PCBM nominal thicknesses were 20 and 70 nm, (as determined with a quartz crystal monitoring system and confirmed by profilometer measurements on films deposited on glass substrates). The photovoltaic devices are completed with a 1.5 nm thick LiF layer and an Al capping layer of ca. 70 nm, both deposited by thermal evaporation at a base pressure of 2×10^{-6} mbar.

UV-vis absorption spectra were recorded with a Cecil 7200 spectrophotometer. Fluorescence spectra were determined with a Spex Fluorolog 2121 in the s/r mode. All spectra were corrected for instrument response.

Photovoltaic characterization was made under inert atmosphere conditions. The solar response was acquired using an Oriol Instruments Solar Simulator 92250A-1000 (AM 1.5 G, 60 mW cm⁻², as determined with a calibrated silicon solar cell).

Atomic Force Microscopy (AFM) studies were carried out with a Molecular Imaging Agilent (model 5100) using non-contact mode with cantilevers having resonant frequencies between 200–400 kHz and silicon tips of under 10 nm radii. Gwydion (version 2.26) software was used for data processing.

Bottom- and top-gate field-effect transistors (FETs) were prepared with films of both P3HT and the network of P3HT nanowires. Bottom-gate FETs were prepared on a 675 nm thick SiO₂ dielectric whose surface was treated with HMDS (1,1,1,3,3,3-hexamethyldisilazane, [(CH₃)₃Si]₂NH). The deposition of the P3HT-based active layers was done in air. Top source and drain contacts were made of MoO₃ (ca. 20 nm thick) covered with 50–60 nm thick aluminium layer, deposited through a shadow mask defining a channel with length $L = 120 \mu\text{m}$ and width $W = 5.1 \text{ mm}$ in a thermal evaporator placed inside a glove box, at a base pressure of 2×10^{-6} mbar. Top gate FETs were prepared by depositing first source and drain gold (40 nm thick) contacts on glass, defining a channel with dimensions $L = 138 \mu\text{m}$ and $W = 8 \text{ mm}$, followed by the

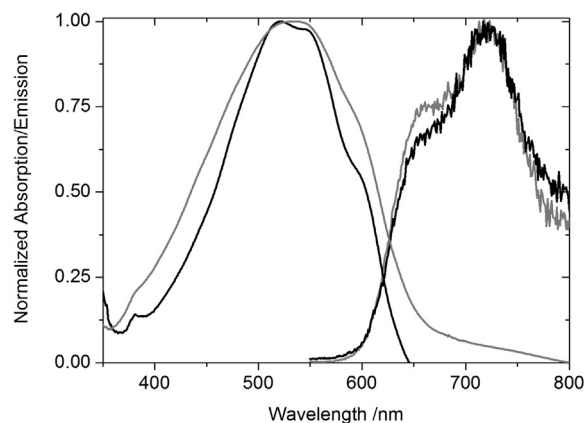


Fig. 1. Normalized absorption and fluorescence (PL) spectra ($\lambda_{\text{exc}} = 515 \text{ nm}$) of films of P3HT deposited on spectroil discs from chlorobenzene/cyclohexanone mixture (black) and from chlorobenzene (grey) solutions.

deposition of the active layer in air. A film of 670 nm thick PMMA (polymethylmethacrylate) was spin coated over that active layer, to serve as dielectric. The structure was completed with the deposition of a gate contact of aluminium (50 nm thick) in the same evaporator as above. Both types of FETs were tested inside the glove box using a HP4140B semiconductor parameter analyzer.

Hole-only and electron-only devices were fabricated using either ITO/PEDOT:PSS or aluminium, respectively, as bottom contact. The active layer (thickness values ranging from 70 to 100 nm) was spin coated on top, in air. The devices were then transferred to the evaporator inside the glove box. Top contacts made of MoO₃ (ca. 20 nm thick) covered with 50–60 nm thick aluminium layer, for the hole-only devices, or barium (40 nm thick) protected with 80 nm thick aluminium, for the electron-only devices, were deposited through a shadow mask. The active area is 4 mm². The current–voltage characteristics were measured with a K2400 source measure unit under vacuum.

3. Results and discussion

The absorption spectrum of P3HT in a film cast from chlorobenzene (Fig. 1, in grey) consists, as expected, of a broad band centered at 525 nm with poor vibrational definition. The addition of cyclohexanone, an extremely poor solvent for P3HT, is expected to induce the growth of polymer nanowires [21]. The absorption spectrum of a P3HT solution aged in a mixture of chlorobenzene and cyclohexanone is shown, in black, in Fig. 1. As can be observed, there is, overall, a clear narrowing of the spectrum and an increase in vibrational definition with a maximum at 521 nm and two red-shifted shoulders at 564 nm and 603 nm. This spectral evolution was previously associated with P3HT nanostructure growth, whether in nanowire [21] or aggregate [10] form.

The fluorescence spectra (PL, Fig. 1) of P3HT films, prepared either from a chlorobenzene solution (grey) or from the chlorobenzene/cyclohexanone mixture (black) (where nanowire formation occurs) have a maximum in the second vibronic at 720 nm and show a decrease in the first vibronic when going from the P3HT/chlorobenzene film to the nanowires-based film. These observations in the emission spectra of P3HT have been associated with aggregation related phenomena in the literature [29].

The morphological nature of P3HT cannot be directly extrapolated from the absorption or fluorescence emission. It is only with Atomic Force Microscopy (AFM) that nanostructuring becomes evident. The AFM topography and phase images (Fig. 2) of a film prepared by spin coating from a filtered solution of P3HT in chlorobenzene/cyclohexanone, aged for a period of 24 h, displays

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