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Bilayer and bulk heterojunction solar cells with functional poly(2,2′-bithiophene) films electrochemically deposited from aqueous emulsion

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ABSTRACT

Ultra thin films of poly(2,2′-bithiophene) with thickness of 11–33 nm were electrochemically deposited on poly(3,4-ethylenedioxithiophene):poly(styrene sulfonic acid) modified indium tin oxide substrates using a new approach for electrochemical synthesis. Ultrasonic emulsification of aqueous perchloric acid and 2,2′-bithiophene monomer is an effective method to disperse this water insoluble monomer in micro droplets that improved the contact with the electrode. Rigorous control of the poly(2,2′-bithiophene) thickness was achieved by controlling the potential applied and the charge during the deposition. We studied thin films solar cells based on poly(2,2′-bithiophene) polymer as bilayer with C_{60}, resulting a power conversion efficiency of 0.3%, and as buffer layer in bulk heterojunction solar cells. We show that poly(2,2′-bithiophene) films influenced positively the open circuit voltage and increased about 1.6 times the short circuit current, increasing the efficiency from 1.3% up to 2.9% from devices without buffer layer or with 11 nm of poly(2,2′-bithiophene), respectively.

1. Introduction

Organic solar cells have been subject of research due their environmental and cost-effective advantages. The best performance is currently achieved with bilayer, polymer:fullerene bulk heterojunction (BHJ) or tandem cells, yielding power conversion efficiencies of 7–10% [1–3]. One of the important parameters of photovoltaic devices is the short circuit current (J_{sc}), which is related with the amount of absorbed light and the charge collected by the electrodes. In polymer:fullerene solar cells the reduction of J_{sc} have been attribute to leakage of electrons back to the anode electrode [4].

In organic solar cells the use of anode buffer layer (ABL) is a strategic procedure to avoid the leaking of electrons to the indium tin oxide (ITO) electrode and improvement of the anode electrode efficiency in collecting and extracting positive carriers. To work as an ABL the film must be transparent, insoluble in organic solvents, as well displays good mechanical and transport properties [5]. Poly(3,4-ethylenedioxithiophene):poly(styrene sulfonic acid) (PEDOT:PSS) is the most widely used ABL, its performance can be enhanced by using organic additives or via physical methods such as exposure to UV light, thermal annealing or plasma treatments.[5,6] Moreover, instead PEDOT:PSS, poly-aniline [7,8] can also act as ABL. All these ABL_s have influenced positively the resulting open circuit voltage parameter, while maintained fairy good short-circuit current in organic solar cells. Other organic ABL_s can be also used simultaneously with PEDOT:PSS, such as pentacene molecules [9] or poly(thiophene) (PT) [10]. PT and its derivatives have been prepared by electrochemical synthesis and extensively used as active layer [11–14], as well as buffer layer in organic solar cells [10].

PT is one of the most studied conducting polymer and shows good stability to oxygen and moisture in both the dedoped and doped forms but is necessary high potentials for the polymerization of the thiophene monomer that causes an irreversible oxidation of the polymer chains [15]. Lower oxidation potential has been found for bithiophene in comparison with thiophene. As it has been previously reported, in situ FTIR spectra showed that poly(bithiophene) (PBT) films present a regular α,α′-linking of the monomeric units while poly(thiophene) films present a disordered cross-linked polymer structure. The study also suggests that PBT has the highest average conjugation length of the polymer chains [16]. PBT is generally synthesized by electrochemical oxidation of 2,2′-bithiophene monomer in organic media [17,18].

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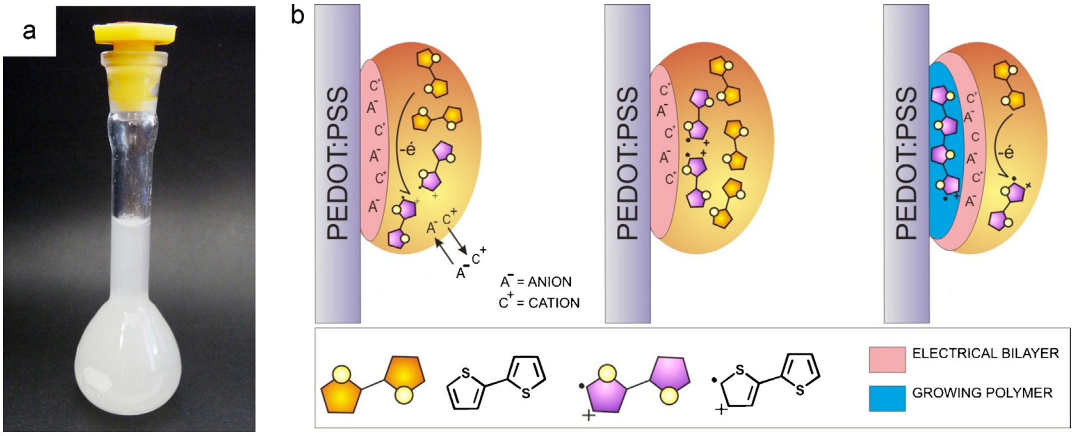

Fig. 1. (a) Image of the emulsion containing micelles of 2,2′-bithiophene monomer achieved after ultrasonic stirring and (b) schematic representation of the electropolymerization of 2,2′-bithiophene onto PEDOT:PSS.

The main reasons which prevent the electropolymerization of this monomer in water are its low solubility and the high reactivity of its radical cation with nucleophilic media [19]. However, there are advantages in using water as a solvent in chemical and electrochemical synthesis which can lower the cost of synthesis, toxicity and waste treatment. Electropolymerization of water insoluble monomers has been performed in aqueous electrolytes using ultrasonic emulsification [20]. It has been reported that PT on ITO could be synthesized by electrochemical polymerization at a lower potential in relatively concentrated aqueous perchloric acid (5 M, $HClO_4$) [21]. Conventional electro-synthesis of PBT in organic medium was also performed in presence of water, without ultrasonic stirring or formation of emulsion [22].

Recently, bilayer solar cells based on poly(2,2′-bithiophene) (PBT) containing all layers deposited by electrochemical method was reported [14]. The authors performed the PBT deposition in organic media, whereas the thickness was controlled by varying the number of cycles. Although the thickness of individual layer is not reported, they achieved power conversion efficiencies of 0.03% and 0.37% from devices having fullerene layer electrochemically deposited or spin coated, respectively.

In this study, PBT was deposited by a new electrochemical method in aqueous medium. It was possible to obtain very thin and homogeneous polymer films onto conductive substrates. Due to its ultra thin thickness, the films were applied in two distinct functionalities: as active layer in bilayer solar cells and, in order to increase the J_{sc} parameter, as buffer layer inserted between the bottom electrode and the active layer polymer:fullerene in BHJ solar cells, yielding promising results.

2. Experimental

2.1. Poly (2,2′-bithiophene) electrosynthesis

Poly(3,4-ethylenedioxythiophene)-polystyrenesulfonic acid (PEDOT:PSS) was filtered in a 0.45 μm filter, spin-coated at 5000 rpm onto the indium tin oxide (ITO) patterned glass substrate, resulting in a film with thickness of 40 nm, and annealed at 100 °C by 15 h, in vacuum. Although the as casted PEDOT:PSS is water soluble, after thermal annealing at 100 °C by 15 h, the adherence on ITO increases thus allowing its use as substrate for electrochemical synthesis in aqueous medium. A layer of PBT was electrochemically deposited onto ITO or PEDOT:PSS modified ITO by using three electrodes cell (WE:ITO|PEDOT:PSS; CE:Pt Plate 1 cm^2 and RE:Ag|AgCl–KCl saturate) applying +0.7 V or +0.6 V, respectively, in aqueous $HClO_4$ (5 mol L^{-1}) and 2,2′-bithiophene monomer (0.01 mol L^{-1}). Before the deposition this mixture was ultrasonically stirred during 10 min resulting in a whitish emulsion showed on Fig. 1(a). For PEDOT:PSS modified ITO, the potential used during the electropolymerization was set at +0.6 V until the system achieves charge of 2.0, 4.3, 5.0 or 7.0 mC, resulting in films with thickness of 11, 24, 28 and 33 nm, respectively. The synthesized PBT films were dedoped, in the same synthesis solution, applying a 0.0 V potential. The films were washed with etanol/water and annealed at 100 °C by 15 min.

Determination of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular level (LUMO) of PBT was performed by means of cyclic voltammograms of the ITO|PBT in a single cell with three electrodes at a sweep rate of 50 mV s^{-1}. The counter electrode was a Pt plate and the pseudo reference electrode was Ag. The electrolyte was a solution of tetramethylammonium tetrafluoroborate ($C_4H_{12}BF_4N$, 0.1 mol L^{-1}) in acetonitrile. The measurements were accomplished with a Microquímica model MQPG-01 potentiostat. The absorption spectras were obtained in a UV-2450 Shimadzu diode UV–vis spectrophotometer, at room temperature. The potentials were measured at the onset of oxidation of the poly(2,2′-bithiophene) and the HOMO level estimated following the method described at Ref. [23].

2.2. Solar cell fabrication

Bilayer solar cells were prepared as follows: the as prepared PBT film, with thickness of 24 nm, received layers of 30 nm of C_{60} and 100 nm of aluminum (Al) thermally evaporated through a shadow mask at vacuum pressure of 6×10^{-6} mbar. For bulk heterojunction solar cells the poly(9,9-dioctylfluorene-*alt*-bithiophene) (F8T2, Aldrich) polymer with number average molecular weight (M_n) >20,000 g mol^{-1} and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM, Aldrich) were used as active layer. BHJ devices were fabricated by spin-coating blend of F8T2:PCBM on the ITO:PEDOT:PSS/PBT substrate. The blend of F8T2:PCBM (1:3) was prepared by dissolving it in chlorobenzene at nitrogen atmosphere, followed by aging at room temperature during 20 h and stirring by 2 h at 50 °C in a sealed flask. The active layer was obtained by spin-coating the blend at 900 rpm for 60 s in nitrogen atmosphere, resulting in film with thickness of 71 nm. Subsequently, the films were annealed at 80 °C by 2 h. Then, 30 nm of calcium and 80 nm of aluminum were thermally evaporated under vacuum, at pressure of 5 × 10 mbar through a shadow mask. Thickness was determined in a Dektak 3 profilometer. Topography images were acquired by using an atomic force microscope (AFM, Shimadzu SPM 9500J3) in dynamic mode. Photovoltaic characterization was performed with