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Titanium oxide:fullerene composite films as electron collector layer in organic solar cells and the use of an easy-deposition cathode

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ABSTRACT

Here is reported the use of a titanium oxide:fullerene (TiO_x:$PC_{71}BM$) composite film as electron collector layer in organic photovoltaic devices (OPV cells). OPV cells were fabricated under the bulk heterojunction architecture: the active layer was a blend of either the photoconductor polymer MEH–PPV or P3HT with the fullerene derivative $PC_{71}BM$. As cathode the eutectic alloy of Bi, In and Sn, known as Field's metal, was used. The melting point of this alloy is above 62 °C, which makes it suitable for a vacuum-free deposition process and easy and fast device test. Cell fabrication and testing were carried out at normal room conditions. For OPV cells based on MEH–PPV, the composite thin electron collector layer improved the power conversion efficiency (η) from 1.12% to 2.07%, thus the η increase was about 85%. Meanwhile, for devices based on P3HT the use of the composite film improved the photocurrent in almost 1 mA/cm^2 and the efficiency slightly increase from 2.48% to 2.68%.

1. Introduction

Organic photovoltaic cells (OPV cells) have attracted worldwide attention due to their advantages over inorganic counterparts. Efficiency of such organic devices has been increased in the last years to reach 9–10% [1–3]. These high efficiencies have been achieved not only by means of the design of suitable organic materials, but also by implementing new approaches in the cell architecture [4–6]. The use of an organic or inorganic n-type layer, in between the active-layer and the cathode has been a strategy to increase light absorption, the photocurrent, and stability in OPV cells [7–11]. In the last few years, a solution processable titanium oxide layer has been introduced as an electron collector, hole blocker and optical spacer [10–13] in between the active-layer and the top metal electrode. The route reported for the preparation of TiO_x sol and for the deposition of TiO_x films yields an amorphous phase; however, the electron mobility for these thin layers was estimated about 1.7×10^{-4} cm^2 V^{-1} s^{-1}, which is larger than that for an amorphous film of metal oxide prepared by the typical sol–gel process [11]. Additionally, a TiO_x sheet exhibits an efficient protection against physical damage and chemical degradation of an organic layer, which could results in a more stable performance for OPV cells under aerobic condition [14,15].

On the other hand, fullerene-based derivatives (PCBM) have been recently used as organic material for electron transport layer (ETL) in OPV cells; this ETL enhances the electronic coupling of the organic/inorganic interface leading to an improving fill factor and photocurrent [16–18]. Further, for inverted OPV cells, fullerene self-assembled monolayer (SAM) improves the contact properties between the bulk-hetero junction (BHJ) layer and ZnO or TiO_x film [19,20]. However, it should be observed that a combination of the fullerene derivatives properties with TiO_x in ETLs for OPV cells, has been poorly explored [16,21,22]. Cheng et al. [21] reported the design and synthesis of functionalized fullerene derivatives, anchored onto TiO_x surface to form a SAM; they used a bilayer combination of TiO_x film and fullerene SAM as ETL and reported an enhancement in η from 3.1% to 4.1% for P3HT:PCBM based OPV cells. Xi et al. [22] used single-crystalline TiO_2 nanorods coated with a PCBM layer as ETL in OPV cells with P3HT:PCBM as active layer; here PCBM film onto the TiO_2 nanorods reduced the surface roughness improving the contact between the active layer and the cathode, leading a power conversion efficiency of 3.2%. In these

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approaches of Cheng et al. and Xi et al. is remarkable that both fullerene and TiO_x were deposited into the devices as contiguous layers (bilayer approach), to the best of our knowledge, a blend of these materials in a single layer has never been explored.

In this work, we report the use of a titanium oxide and [6,6]-phenyl C_{71}-butyric acid methyl ester ($PC_{71}BM$) blend and its employ as solution processable electron collector layer in OPV cells. The composite film improved contact properties between the active layer and the cathode leading to a significant increase in the efficiency of 85% for those OPV devices based on MEH–PPV and an enhance for the short circuit photocurrent density (J_{sc}) of about 1 mA/cm^2 and 8% in η for those based on P3HT; in both cases, the active layer contained the electron acceptor $PC_{71}BM$. TiO_x was prepared by the sol–gel method and the blend with $PC_{71}BM$ fullerene was made by mixing TiO_x sol with a fullerene chloroform solution; TiO_x:$PC_{71}BM$ thin films were deposited by the spin-coating technique. Our OPV cells, with the BHJ architecture, were prepared at normal room conditions. For the OPV cells fabrication, the eutectic alloy Field's metal (32.5% Bi, 51% In, 16.5% Sn) was used as cathode. This alloy can be employed as an easy, economical and vacuum-free way to test OPV devices. Furthermore, it is free of the highly toxic cadmium and lead elements, which are contained in the Woods metal previously used in OPV cells [23,24]. This easy and fast deposition process for Field's metal could it makes suitable for possible large area applications.

In our previous work [23,24], we had already demonstrated the suitability of this approach to fabricate and test OPV cells with the use of the eutectic alloy known as Wood's metal (Pb 25%, Bi 50%, Cd 12.5%, Sn 12.5%). As can be seen from its composition, Field's metal is a better choice for a cathode in the sense that it is a heavy metal-free alloy (free of the highly toxic cadmium and lead) and exhibits better adhesion to the organic material yielding a smoother metal surface; it has a melting point above 62 °C. The architecture used for the OPV devices was: ITO/PEDOT:PSS/active layer/(TiO_x or TiO_x:$PC_{71}BM$)/Field's metal (Scheme 1). Cells made in this way reached a η of 2.07% for those based on the active blend MEH–PPV:$PC_{71}BM$ and 2.68% for OPV devices based on P3HT:$PC_{71}BM$.

2. Materials and sample preparation

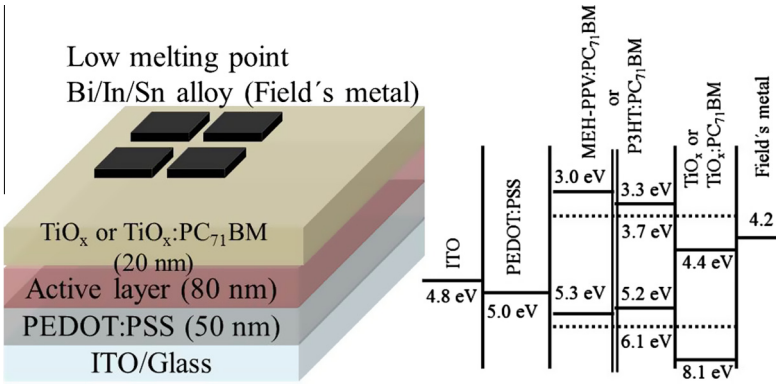
2.1. Materials

Conjugated polymers poly[2-methoxy-5-(2-ethylhexyloxy)-1, 4-phenylenevinylene] (MEH–PPV) (M_n = 150,000–250,000 g/mol) and poly(3-hexylthiophene-2,5-diyl) (P3HT) (M_n = 15,000–45,000 g/mol) as well as titanium isopropoxide and ethanolamine were purchased from Aldrich (Mexico). Polymer poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) was obtained from Heraeus–Clevios (Germany), meanwhile the fullerene derivative [6,6]-phenyl C_{71} butyric acid methyl ester ($PC_{71}BM$) was purchased from SES Research (USA), solvents and reagents were used without further purification process. ITO/glass substrates with 4–10 Ω/square were acquired from Delta Technologies (USA). Field's metal was acquired from Rotometals.

2.2. Sample preparation and testing

TiO_x was prepared by the sol–gel method and diluted with methanol (1:200% v/v) as previously reported [11,25]. For the TiO_x:$PC_{71}BM$ film, a chloroform $PC_{71}BM$ solution (0.25 mg/ml) was mixed with TiO_x sol (volume ratio 1:0.02). The ratio 1:0.02 exhibited the best OPV performance in comparison with larger $PC_{71}BM$ concentration. Despite low solubility of $PC_{71}BM$ in the sol solvents, the mixture at this concentration was stable and the formation of agglomerates was not observed. Moreover, due to the tiny amount of chloroform used in the solution, this mixture does not damage the active layer when is deposited on it. To fabricate the cells, ITO-coated glasses were used as substrates and were ultrasonically cleaned with liquid soap, distilled water, acetone, and ethyl alcohol. A first layer of PEDOT:PSS (about 50 nm thickness) was spin-casted onto the substrate. Blends of MEH–PPV:$PC_{71}BM$ (blend ratio 1:3, 5 mg/ml of MEH–PPV) and P3HT:$PC_{71}BM$ (blend ratio 1:0.8, 6.6 mg/ml of P3HT) were dissolved in chlorobenzene and used to deposit the active layer (thickness: ~80 nm for the blend MEH–PPV:$PC_{71}BM$ and ~90 nm for that of P3HT:$PC_{71}BM$). A thin film of TiO_x or TiO_x:$PC_{71}BM$ blend (about 20 nm) was spin-coated onto the active layer at 5000 rpm. After deposition, each film (PEDOT:PSS, active layer and TiO_x or TiO_x:$PC_{71}BM$) was thermally treated at 120 °C for 20 minutes. For deposition of the mentioned cathode, Field's metal pellets were placed on a metallic container and set on a hot plate preheated at about 100 °C. After some seconds, pellets melted and it quasi-liquid alloy was transfer to a new metallic container, this process removed any scrap metal. This melted material looks like a "mercury drop". It was deposited by dropping onto the top of the OPV device; which was also heated at the same temperature on the hot plate to avoid freezing. The active layer area was 0.03 cm^2

Thicknesses and morphology were analyzed by means of an atomic force microscopy (AFM) easyscan2 from Nanosurf, with a maximum square scanning area of 110 μm, operating in contact mode under ambient conditions. The silicon cantilever was 450 μm long with a force constant of 0.2 N/m. On the other hand, we estimated the work function of the Field's metal used as cathode to be 4.2 eV. This estimation was done by means of a set of experiments to analyze the energy barriers of the Schottky junctions of this metal with the polymer semiconductor P3HT, the study is reported elsewhere [26]. All this process was done at normal room conditions. Solar cells were tested using a Keithley



Scheme 1. Architecture used for the OPV devices and energy levels.