



Blocking layer optimisation of poly(3-hexylthiophene) based Solid State Dye Sensitized Solar Cells

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ABSTRACT

The optimisation study of the fabrication of a compact TiO₂ blocking layer (via Spray Pyrolysis Deposition) for poly(3-hexylthiophene) (P3HT) for Solid State Dye Sensitized Solar Cells (SDSCs) is reported. We used a novel spray TiO₂ precursor solution composition obtained by adding acetylacetone to a conventional formulation (Diisopropoxytitanium bis(acetylacetonate) in ethanol). By Scanning Electron Microscopy a TiO₂ layer with compact morphology and thickness of around 100 nm is shown. Through a Tafel plot analysis an enhancement of the device diode-like behaviour induced by the acetylacetone blocking layer respect to the conventional one is observed. Significantly, the device fabricated with the acetylacetone blocking layer shows an overall increment of the cell performance with respect to the cell with the conventional one ($\Delta J_{sc}/J_{sc} = +13.8\%$, $\Delta FF/FF = +39.7\%$, $\Delta PCE/PCE = +55.6\%$). A conversion efficiency optimum is found for 15 successive spray cycles where the diode-like behaviour of the acetylacetone blocking layer is more effective. Over three batches of cells (fabricated with P3HT and dye D35) an average conversion efficiency value of 3.9% (under a class A sun simulator with 1 sun A.M. 1.5 illumination conditions) was measured. From the best cell we fabricated a conversion efficiency value of 4.5% was extracted. This represents a significant increment with respect to previously reported values for P3HT/dye D35 based SDSCs.

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1. Introduction

Owing to the use of potentially low cost materials and relatively easy fabrication processes, Dye-Sensitized Solar Cells (DSCs) are an attractive photovoltaic technology candidate for large scale production [1,2]. A basic DSC configuration is obtained juxtaposing between two conductive and transparent substrates (generally FTO/glass) a nanocrystalline TiO₂ film (nc-TiO₂) sensitized to the visible light by means of an absorbing dye (attached on the nanocrystals surface) a liquid electrolyte (a redox couple in a liquid solvent) and a catalytic layer (conventionally made of Pt).

Large area devices are obtained interconnecting single cells. An electron injected from the dye into the nc-TiO₂ film after dye photoexcitation diffuses through the substrate and an external load, generating electrical power. Finally the electron is again available for the dye regeneration through a redox reaction (catalysed by the Pt).

Although a conversion efficiency (PCE) value higher than 12.3% has been reached over small area [3] several demanding issues should be addressed before the commercial exploitation of DSC technology [4–7].

Here we mention in particular the increase of device life time and long term stability which is, amongst the other, connected to the mechanical and electrochemical stability of the liquid electrolyte. In fact, being the latter quite volatile (conventionally composed by the redox couple I₃⁻/I⁻ and a

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solvent such as MPN, ACN or VN) DSC devices suffer from leakage induced problems such as insufficient ionic diffusion current and corrosion of metallic contacts [8,9]. Furthermore, it has been shown that in reverse bias conditions liquid electrolyte will deteriorate with consequent fatal effects on the cell performances [10]. Several alternative strategies have been proposed to tackle these issues including the use of less corrosive redox couple (such as Co(II) Co(III)), solvent free electrolyte and polymer gel electrolyte [3,11–14]. Highly promising are the so called Solid State DSC (SDSC) where the electrolyte is replaced by an hole transport material (HTM) with the straightforward advantage of resolving all the here mentioned problems [15–18]. Being in SDSC the electron recombination rate at the interface nc-TiO₂/HTM higher than nc-TiO₂/electrolyte, dye regeneration is optimised reducing the nc-TiO₂ thickness (down to few μm) with the drawback to reduce the device light harvesting [19,20]. In this case, dyes with a high extinction molar coefficient ϵ (such as the tri-arylamine-based D35 Dye with $\epsilon = 30,000 \text{ mol}^{-1}$) have been shown to have a positive impact on the device performances [21–23].

High performances have been obtained using an organic, transparent, p-type doped, small molecule compound called Spiro-OMETAD, although the high production cost makes its employment prohibitive for large area devices [19–23]. Very recently a PCE = 10.2% has been measured from a SDSC (in which photonic crystals were embedded) using a p-type inorganic semiconductor CsSnI₃ (HTM) and Ru-based dye (N719) [24]. Amongst organic HTM compounds, P3HT is a promising option in order to obtain high performing SDSC devices [25–29]. In fact, its hole conductivity may be higher respect to pristine Spiro-OMETAD [28] making it a promising and cost effective alternative to Spiro-OMETAD. Snaith et al. have shown that by an accurate engineering of the interface TiO₂/P3HT promising performance can be obtained (PCE = 2.81%) [27]. Hagfeldt and co-authors extracted from a cell using a P3HT/dye D35 a PCE = 3.2% [28]. It has been shown that for SDSC, holes (in the HTM) and FTO surface electrons recombination processes originates a remarkable current leakage path (back transfer) [30–32]. It becomes therefore crucial in SDSC device fabrication to engineer a compact (c) blocking layer (BL) between FTO/nc-TiO₂ with the aim to induce a diode like behaviour (or current rectification) consisting in a drastic reduction of the back transfer recombination rate but letting the photo-extracted electrons to be efficiently collected. Several techniques have been utilised for the BL fabrication, including Magnetron Sputtering, Atomic Layer Deposition, Sol–Gel Process and Electrodeposition [26,33–35], although, for a low cost processing, Spray Pyrolysis Deposition (SPD) of a precursor solution (conventionally consistent of Diisopropoxytitanium bis(acetylacetonate) dissolved in a solvent such as isopropyl alcohol or EtOH) is a prominent option and a nearly 100 nm thick c-TiO₂ layer is conventionally adopted as an optimum condition [29–31]. It has been shown that the thickness, morphology and electromechanical bonding with respect to the upper and lower interfaces are the key parameters to optimise, having a huge bearing on the BL electrical properties and therefore on the final device performance [36,37].

Here for the first time a c-TiO₂ BL was fabricated by SPD technique utilising a novel precursor composition obtained

by adding acetylacetonate (ACAC) to Diisopropoxytitanium bis(acetylacetonate) hereinafter referred as ACAC-BL. By Scanning Electron Microscopy (SEM) we show not only that a TiO₂ film with a compact morphology is obtained but also that P3HT is uniformly interpenetrated all along the nc-TiO₂. Moreover, by Tafel plot analysis an enhancement is observed of the BL rectifying properties.

In fact, compared to conventional BL, both a lower value of the exchange current I_0 (indicative of the BL thickness, morphology and interface adhesion) and a lower anodic transfer coefficient β_a (proportional to the transfer resistance at the interface nc-TiO₂/HTM) were observed.

Furthermore average values of electrical parameters (J_{sc} , V_{oc} , PCE, FF) measured from a batch of cells fabricated with a ACAC-BL were compared with those extracted from a second batch of cells fabricated with a conventional BL. In spite of a negligible variation of V_{oc} ($\Delta V_{oc}/V_{oc} = -1.8\%$) a remarkable enhancement is observed for the value of J_{sc} ($\Delta J_{sc}/J_{sc} = +13.8\%$) and even more of FF ($\Delta FF/FF = +39.7\%$) resulting in an overall increase of the PCE value ($\Delta PCE/PCE = +55.6\%$).

The whole SPD process for ACAC-BL fabrication in SDSC was shown to observe an optimum in terms of final device PCE when the number of successive SPD spray cycles was $n = 15$.

Tafel plot analysis indicates that in correspondence of $n = 15$ not only the thickness of the BL reached an effective value but also shows optimal rectifying properties (high β_c and low β_a). By Electro Impedance Spectroscopy (EIS) analysis the variation of the FTO surface left uncovered by BL obtained with various n and for both precursor composition has been analysed. Finally from three batches of cells fabricated with P3HT/D35, an ACAC-BL and $n = 15$ an average PCE value higher than 3.7% was extracted (for batch iv, v and vi) and IPCE measurements were carried out on a representative device showing a PCE = 3.9%. The best cell we fabricated shows a PCE = 4.5% which is a significant improvement respect to all previously reported values for SDSC utilising the same set of materials.

2. Experimental

FTO/glass substrates (Pilkington, $15 \Omega/\square$, 25 mm × 25 mm) were etched via raster scanning laser (Nd:YVO₄ pulsed at 30 kHz average output power $P = 10 \text{ W}$) to form the desired electrodes pattern. Four cells were formed on each substrate. Patterned substrates were cleaned with detergent, de-ionized water and ethanol, in an ultrasonic bath. By SPD technique a c-TiO₂ film was deposited onto FTO surface. During the deposition the substrate temperature was fixed at 450 °C, the distance between the substrate positioned flat and the aerograph (tilted about 45° respect to the substrate) was fixed to 20 cm. To let an effective pyrolysis of TiO₂ precursor solution we waited 10 s before to carry out the successive spray cycle [30]. Number of successive spray cycles n was varied between 0 (i.e. no BL) and 50. Six batches of cells were fabricated with the same set of materials but with different BL. Batch (i) consisted of two set of three cells each. For the first set the composition of the precursor spray solution consisted of 0.16 M Diisopropoxytitanium bis(acetylacetonate) (TAA) in 0.16 M

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