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# Infiltration and Selective Interactions at the Interface in Polymer-Oxide Hybrid Solar Cells

R Ferragut<sup>1,2†</sup>, S Aghion<sup>1,2</sup>, F Moia<sup>1,2</sup>, M Binda<sup>3</sup>, E V Canesi<sup>3</sup>, G Lanzani<sup>3</sup> and A Petrozza<sup>3</sup>

<sup>1</sup> LNESS and Dipartimento di Fisica, Politecnico di Milano, via Anzani 42, 22100 Como, Italy

<sup>2</sup> Istituto Nazionale di Fisica Nucleare, via Celoria 16, 20133 Milano, Italy

<sup>3</sup> Center for Nano Science and Technology @Polimi, Istituto Italiano di Tecnologia, Via Pascoli 70/3, 20133 Milano, Italy

E-mail: rafael.ferragut@polimi.it

**Abstract.** Positron annihilation spectroscopy was used to characterize polymer-based hybrid solar cells formed by poly(3-hexylthiophene) (P3HT) finely infiltrated in a porous TiO<sub>2</sub> skeleton. A step-change improvement in the device performance is enabled by engineering the hybrid interface by the insertion of a proper molecular interlayer namely 4-mercaptopyridine (4-MP). In order to obtain depth-resolved data, positrons were implanted in the sample using a variable-energy positron beam. The characteristics of the partially filled nanoporous structures were evaluated in terms of the depth profile of the positronium yield and the *S*-parameter. A quantitative evaluation of the pore filling in the deep region is given from the analysis of Coincidence Doppler Broadening taken at fixed implantation energy. We note a remarkable difference in terms of the positronium yield when the 4-MP interlayer is introduced, which means a better covering of P3HT on the porous surface.

## 1. Introduction

Hybrid solar cells are characterized by thin films composed by a combination of organic and inorganic materials. This new generation of thin-film is based on a very favourable price/performance ratio and the possibility to manufacture flexible and large-area modules.

We present a polymer-based hybrid photovoltaic cell composed by poly(3-hexylthiophene) (P3HT) finely infiltrated in the metal oxide mesoporous structure TiO<sub>2</sub>. Previous attempts using nanoporous [1] or nanorods [2] structures filled by similar conjugated polymers could not reach power conversion efficiency above 0.5%. Attention has also been paid to the use of possible interlayers whose main role was to control the energy offset at the oxide/polymer interface [3]. By modifying the TiO<sub>2</sub> surface through a commercial and inexpensive molecule such as 4-mercaptopyridine (4-MP) (see inset in Figure 1), which is optically transparent, we are able to impressively enhance the photocurrent extracted from the nanostructured solar cell, inducing a step change in the overall efficiency. In Figure 1 is shown the current-voltage characteristics for devices with and without 4-MP. When the molecular interlayer is added, the photocurrent (current density when the voltage is zero) is increased, from 1.4 mA/cm<sup>2</sup> to 3.7 mA/cm<sup>2</sup>, together with an enhancement of the V<sub>oc</sub> (voltage when the current density is

<sup>†</sup> To whom any correspondence should be addressed.



null) from 0.51 V to 0.60 V. This result proves an improvement in the device performance that is enabled by engineering the hybrid interface by the insertion of a proper molecular interlayer [4].

Positron annihilation spectroscopy (PAS) is an established method for investigating porous oxides [5], polymers [6] and other systems [7, 8]. There are several advantages of PAS over other methods (Grazing incidence X-ray diffraction, TEM and SEM); it is nondestructive and is not limited in-plane spatial resolution. In recent years, PAS with a variable-energy positron beam has emerged as a powerful tool for the investigation of porous thin films (tens nm up to several  $\mu\text{m}$  in thickness). Depth-profiling with PAS has proven to be an ideal way to measure the interconnection length of pores and explore porosity hidden beneath dense layers [5].

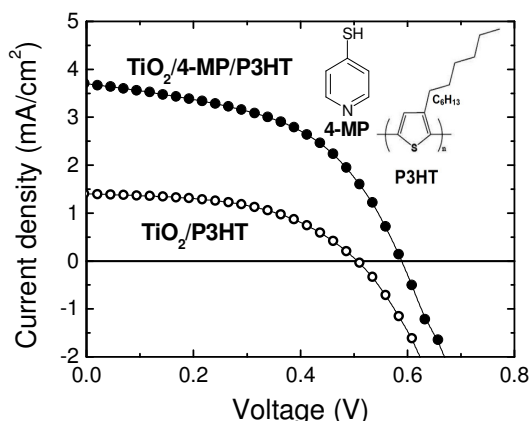
In this work, PAS enables a nanometer scale mapping over the hybrid solar cells. We have found out that, contrary to common knowledge, pore filling of the oxide mesoporous structure is not the more important factor for the device performance. The interlayer 4-MP favors a better covering of P3HT on the porous surface. These results are extremely important moving the focus of the investigation to the nature of the polymer/porous oxide hybrid interface.

## 2. Experimental procedure and methodology

The devices were prepared following the procedure reported in Ref. 4. In the case of devices provided with 4-MP interlayer, the porous  $\text{TiO}_2$  substrates (800 nm in thickness) were immersed in a saturated solution of 4-MP in chlorobenzene for about 20 hours. Immersion was followed by rinsing with pure chlorobenzene. A monolayer of 4-MP is expected to remain at the surface. In order to promote the P3HT infiltration inside the mesoporous  $\text{TiO}_2$  (with and without 4-MP) the polymer was spin coated onto the substrates at 1000 rpm for 60 s from a 30 mg/ml chlorobenzene solution.

In order to obtain depth-resolved data, positrons were implanted in the sample at various depths using a variable-energy positron beam (from 0.1 to 17 keV) at the VEPAS laboratory (LNESS Centre - Politecnico di Milano). The PAS measurements were performed at room temperature at a vacuum level around  $10^{-7}$  mbar. Two hyperpure Ge gamma detectors (ORTEC – relative efficiency  $\sim 50\%$  at 1.33 MeV) were used to measure the spectrum of the annihilation radiation. Results of the  $S$ -parameter, i.e. the fraction of annihilating positron–electron pairs with momenta  $p_L \leq 0.456$  atomic units (energy range  $511 \pm 0.85$  keV), are presented. The tails of the two-gamma peaks at high Doppler shift, which come from annihilation with inner atomic shells, are more sensitive than the  $S$ -parameter to the average chemical composition in the annihilation region and are suitable for quantitative compositional analyses. However, the low counting rate in the high momentum region requires background suppression by adopting the coincidence Doppler broadening technique (CDB), i.e. to take both annihilation gammas in coincidence. CDB spectra with about  $2 \times 10^7$  total counts were measured with a peak/background ratio of  $10^5$ – $10^6$ . The momentum resolution (FWHM) was  $3.7 \times 10^{-3} m_0c$ . The experimental procedure and the data analysis used in this study are similar to those described in Refs. 9 and 10.

An additional PAS parameter, sensitive to the presence of free volume and to the extension of inner pore surface, is the positronium ( $P_s$ ) fraction.  $P_s$  fraction measurements were performed using the well-known “ $3\gamma$  method” [11, 12].

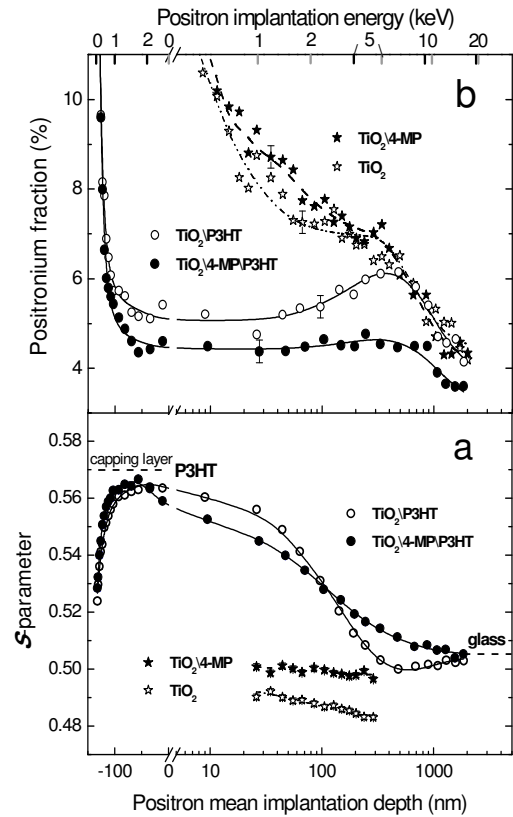


**Figure 1.** Current density/voltage characteristics of the P3HT/ $\text{TiO}_2$  and P3HT/4-MP/ $\text{TiO}_2$  devices under illumination with simulated solar light. The P3HT and 4-MP chemical structure are shown in the inset (after Canesi et al. [4]).

### 3. Results and discussion

Positron annihilation spectroscopy was used to monitor the effect of 4-MP on the penetration of P3HT in the porous TiO<sub>2</sub>. The *S* and *P<sub>s</sub>* yield profiles are reported in Fig. 2. Figure 2.a displays an evolution from the high *S*-value characteristic of P3HT (*S* ≈ 0.57) toward lower values expected for porous TiO<sub>2</sub> with or without 4-MP (full and open stars, respectively).

The zero of the depth scale is fixed at the surface of the porous oxides. Grey and black ticks are presented in the upper frame of Fig. 2.b (positron implantation energy), that correspond to the devices without and with a capping layer of P3HT, respectively. The positron mean implantation depth profile of the oxides infiltrated with P3HT was calculated using the estimation of the polymer concentration infiltrated in the oxide taking into account the density of each layer (see Ref. 4). The curves through the experimental points are the result of a fitting procedure (VEPFIT [13]) which identifies four layers in the explored structure: a solid P3HT cap, a thin porous layer heavily infiltrated with P3HT, a second thick porous layer containing less P3HT and the glass substrate. Table 1 shows the most relevant parameters of the fit. From the results of the first and the second infiltrated layers we can conclude that there is a P3HT concentration gradient within the oxide in both samples, with and without the interlayer; however, in presence of 4-MP the degree of P3HT infiltration is reduced in the first layer and enhanced in the deeper region. A quantitative evaluation of the deep region is given from the analysis of CDB taken at fixed energy (5 keV, see Ref. [4]). CDB is sensitive to the average chemical composition in the annihilation region [9, 10, 14].



**Figure 2.** *S*-parameter (a) and *P<sub>s</sub>* yield (b) profiles for P3HT embedded in porous TiO<sub>2</sub> without and with 4-MP together with the reference values for P3HT and for TiO<sub>2</sub> with and without 4-MP. The continue lines through the data are obtained using VEPFIT. The lower scale before the break at zero is linear.

**Table 1.** Results obtained in the heterostructure after the polymer implantation from the positron lineshape profiles (Fig. 2.a) using VEPFIT. Thickness *Z<sub>i</sub>*, positron diffusion length *L<sub>i</sub>* and *S<sub>i</sub>*-parameter. Fixed parameters are marked with the letter F.

TiO <sub>2</sub> /	<i>Z<sub>CL</sub></i> (nm)	<i>S<sub>CL</sub></i>	<i>L<sub>CL</sub></i> (nm)	<i>Z<sub>1st</sub></i> (nm)	<i>S<sub>1st</sub></i>	<i>L<sub>1st</sub></i> (nm)	<i>Z<sub>2nd</sub></i> (nm)	<i>S<sub>2nd</sub></i>	<i>L<sub>2nd</sub></i> (nm)	<i>S<sub>glass</sub></i>	<i>L<sub>glass</sub></i> (nm)
P3HT	130(20)	0.568(3)	20(5)	70(10)	0.564(4)	15(3)	730F	0.486(3)	60(10)	0.505(3)	40F
4-MP/P3HT	135(20)	0.569(3)	17(5)	43(10)	0.542(5)	10(3)	757F	0.510(4)	60(10)	0.505(3)	40F

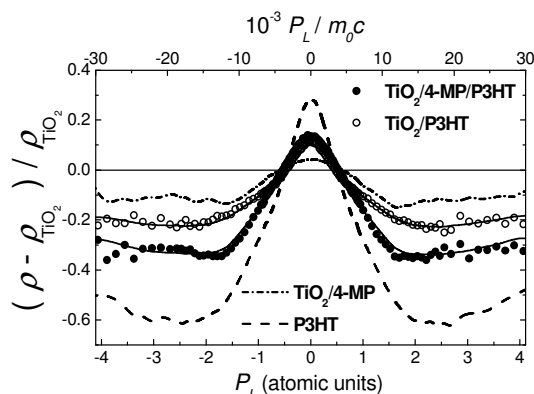
In Fig. 3 the CDB spectra are presented in terms of relative change respect to the reference spectrum of the porous TiO<sub>2</sub>. The curves for TiO<sub>2</sub>/P3HT and TiO<sub>2</sub>/4-MP/P3HT are fitted using synthetic spectra formed as linear combinations

$$\rho = w\rho_{P3HT} + (1-w)\rho_{TiO_2}^* \quad (1)$$

of the spectra taken separately for P3HT ( $\rho_{P3HT}$ ) and for TiO<sub>2</sub> or for TiO<sub>2</sub>/4-MP ( $\rho_{TiO_2}^*$ ), depending if the oxide contains or does not contain 4-MP. The physical meaning of the weight (*w*) in the linear combination is the fraction of positron annihilating in a P3HT environment and therefore is a good index of infiltration. The weights *w* obtained from the linear combination procedure are 0.37 ± 0.03 and 0.44 ± 0.03 respectively for TiO<sub>2</sub>/P3HT and for TiO<sub>2</sub>/4-MP/P3HT. It can be concluded that the presence of 4-MP increases P3HT infiltration at the selected depth, although the effect is barely beyond the

error margin. The  $w$  weights are univocally related to the pore filling factor [4]. The limited difference observed in terms of  $w$  indicates that the presence of the 4-MP does not affect sizably the polymer filling factor suggesting that the pores filling by itself is not the limiting factor controlling the device performances shown in Fig. 1.

On the other hand, remarkable differences in terms of the positronium fraction can be observed when the 4-MP interlayer is introduced. In fact, the  $P_s$  depth profile of Fig. 2.b drops drastically when  $\text{TiO}_2$  is infiltrated with P3HT, specially in presence of 4-MP (a monolayer of 4-MP in bare  $\text{TiO}_2$  does not reduce the  $P_s$  yield). In particular, the bump in the  $\text{TiO}_2/\text{P3HT}$  sample (open circles) which appears in the deeper region (200nm-800nm) is decreased in presence of 4-MP.  $P_s$  yield reduction can be the consequence of: *i*) a better pores filling that favours 2- $\gamma$  annihilation and/or *ii*) a larger P3HT covering of the free inner titania surface where  $P_s$  is formed. In both cases the polymer induces  $P_s$  inhibition and ortho- $P_s$  quenching [15]. The limited difference in the filling factors measured in the deeper region by CDB in samples with and without 4-MP cannot explain the large reduction in  $P_s$  yield. Moreover, if we look at the shallowest region, the  $S$ -parameter shows a lower concentration of the P3HT phase in presence of the 4-MP monolayer, while the  $P_s$  yield is again reduced. Therefore, we conclude that the  $P_s$  fraction reduction is due to a reduction of free  $\text{TiO}_2$  surface, which means a better covering of P3HT on the porous surface. The presented information, inaccessible by optical and electron microscopy techniques previously used, coincides with an improvement of charge generation and device photocurrent. The interpretation is in agreement with X-ray photoemission spectroscopy and with atomistic simulations results [4]. This study indicates that tailoring the interaction between the polymer and metal oxide is the critical area to focus attention to improve these hybrid solar cells.



**Figure 3.** CDB spectra of  $\text{TiO}_2/\text{P3HT}$  and  $\text{TiO}_2/4\text{-MP}/\text{P3HT}$  taken at a fixed implantation energy (5 keV). The dashed lines represent P3HT and  $\text{TiO}_2/4\text{-MP}$ . The continues lines are calculated using a linear combination of the reference spectra (eq. 1) [4].

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