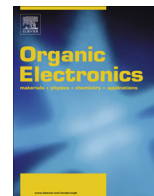




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Letter

In-situ modification of PEDOT:PSS work function using alkyl alcohols as secondary processing solvents and their impact on merocyanine based bulk heterojunction solar cells

Martin R. Lenze^a, Nils M. Kronenberg^{a,1}, Frank Würthner^b, Klaus Meerholz^{a,*}

^a University of Cologne, Department of Chemistry, Luxemburger Str. 116, 50939 Cologne, Germany

^b Universität Würzburg, Institut für Organische Chemie & Center for Nanosystems Chemistry Am Hubland, 97074 Würzburg, Germany

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ABSTRACT

The influence of a series of alkyl alcohols on the work function of PEDOT:PSS thin films is systematically investigated by Kelvin probe measurements. We show that the PEDOT:PSS work function can be increased stepwise from 5.2 eV for pristine PEDOT:PSS to 5.61 eV using either alcohols with different alkyl chain length or varying the amount of alcohol in mixtures with chlorobenzene. Moreover, we demonstrate the effect of work function modification on merocyanine based bulk heterojunction solar cells, resulting in improved values for the open-circuit voltage comparable to those obtained with high work function MoO₃. Thus, the processing method presented herein can potentially serve as a simple, alternative route to adjustable and high work function electrodes while maintaining processability from solution.

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1. Introduction

The extensive research on organic solar cells (OSCs) in the past decade has developed multiple concepts to improve device efficiency comprising synthesis of new photoactive materials, electrode materials, processing conditions and device setups. Power conversion efficiencies (PCEs) of about 9% have been achieved for small molecule [1] as well as for polymer [2] based single-junction solar cells.

For bulk heterojunction (BHJ) solar cells the morphology of the active layer is crucial for efficient generation and transport of charges. Several solvent additives, such as 1,8-diiodooctane [3], 1,8-octanedithiol [4] or nitrobenzene [5], have been identified to improve the morphology and/or crystallinity of the active layer. A common feature of such additives is their higher boiling point compared to the main solvent for active layer deposition combined with different solubilities of the dissolved materials, causing a change in morphology during film formation [3–6]. Furthermore, wide band gap materials such as n-type ZnO [1] or TiO₂ [7] have been implemented at the electron collecting side in the device stack to improve OSC performance. These additional layers often

act as optical spacers, which can increase the fraction of absorbed light within the active layer. Additionally, wide band gap materials can have charge blocking properties preventing the “wrong” charge carriers from reaching the electrode [7]. Recently, conjugated polyelectrolytes (CPEs) emerged as facile method to modify the organic/electrode interface. In most reported cases, thin layers (<5 nm) of CPEs induce a shift in vacuum level that lowers the effective work function of the electrode material and can, therefore, replace low work function metals as top electrodes that are sensitive to air [8]. In terms of OSC characteristics, the reported additives and stack modifications primarily affected the short-circuit current density J_{SC} and the fill factor FF .

The open-circuit voltage V_{OC} of a BHJ organic solar cell is limited by the effective photovoltaic gap, i.e. the difference between the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor. The synthesis of new donors, therefore, tends toward materials with deep HOMO energy levels to reach high values for V_{OC} . To obtain high voltages, however, the work functions of the hole and electron collecting contacts need to be adjusted to the BHJ active layer energy levels as well [9]. Typically, V_{OC} is barely affected by modification of the electron collecting contact most likely due to easily achieved ohmic contact formation of the electrode with the commonly used electron acceptor phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) [10,11].

* Corresponding author.

E-mail address: klaus.meerholz@uni-koeln.de (K. Meerholz).

¹ Present address: School of Physics & Astronomy, University of St Andrews, North Haugh, St Andrews KY16 9SS, Scotland.

On the hole collecting side of OSCs, metal oxides such as high work function n-type MoO₃ [12] and p-type NiO_x [13,14] as well as self-assembled monolayers [15] (SAM) of phosphonic acids on ITO have been employed. However, the conductive polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) PEDOT:PSS still remains the most commonly used material due to its simple processability from aqueous suspension. Although easily processed, PEDOT:PSS often lacks the demand of the active layer for high work function. It is therefore desirable to find a way to adjust the properties of PEDOT:PSS to those needed by the active layer. Plenty of parameters that influence the work function (and most often conductivity) of PEDOT:PSS have been reported including UV light exposure [16] and the processing conditions, e.g. by addition of secondary solvents [17–20]. Moet et al. showed that the work function of PEDOT:PSS, and, thus, the V_{OC} of the corresponding solar cells is reduced upon increasing the pH of the casting solution [21]. Graham et al. reported on V_{OC} enhancement in small molecule based solar cells when adding triethylene glycol to the casting solution of the active layer and suggested an increase of PEDOT:PSS work function due to H-bonding of triethylene glycol to the PEDOT:PSS surface [6]. The Friend group recently showed that polymer OSC performance can be improved by exposing the active layer on top PEDOT:PSS to methanol prior to evaporation of the top electrode [22]. This treatment led to an *in-situ* increase of the PEDOT:PSS work function and resulted in higher values for V_{OC} and hole extraction rates [23].

In this publication, we systematically investigate the impact of various alkyl alcohols on the work function of PEDOT:PSS thin films. Furthermore, we show that our findings for bare PEDOT:PSS films can be transferred to merocyanine based OSCs, which are highly sensitive to changes in the work function of the hole collecting contact.

2. Experimental section

2.1. Materials and device fabrication

The syntheses and characterization data of all MC dyes were reported previously [12,24–27]. PC₆₁BM (≥99.5%) was obtained from Nano-C. Solvents (purity ≥98%) were obtained from commercial sources and used as received. All devices were fabricated on commercial indium–tin oxide (ITO) coated glass (TFD) coated with poly(3,4-ethylene dioxithiophene):poly(styrene sulfonate) (PEDOT:PSS) (Clevios P Al 4083, Heraeus; ca. 40 nm). PEDOT:PSS films were heat treated for 2 min at 110 °C to remove residual water and transferred into a N₂ glove box for subsequent treatment with alcohols or device fabrication. The active layers of BHJ solar cells were spin-coated from chlorobenzene (CB) containing the mixture of MC and PC₆₁BM (20 mg mL⁻¹ each in CB). The secondary solvent was added to the blend solution to yield the desired vol%. After evaporation of an aluminum top electrode (120 nm; Alfa Aesar 99.9%) through a shadow mask, seven solar cells with an active area of 0.0785 cm² were obtained on each substrate.

2.2. Measurements and device characterization

KP measurements were performed using a system by Besocke Delta phi GmbH in an inert argon atmosphere. The contact potential difference between the sample and a vibrating gold grid (reference) was measured. The measurement was calibrated with work functions determined by ultraviolet photoelectron spectroscopy (UPS) of various metals as well as pristine PEDOT:PSS films. The *JV*-characteristics of the solar cells were measured using a Keithley 2425 source measurement unit under simulated AM1.5 illumination provided by a filtered Xe lamp. The light intensity of

100 mW cm⁻² was determined by using a calibrated inorganic solar cell from the Fraunhofer Institute for solar research (ISE) and a reference P3HT:PC₆₁BM cell measured by the same institute. No spectral mismatch factor was included in the calculation of the efficiency. Transmission electron microscopy (TEM) of blend layers was performed with a Leo 912 Omega by Zeiss. UV/visible absorption spectra were taken with a Varian Cary 50 spectrometer in transmission mode. Layer thicknesses were measured by surface profilometry (Veeco).

3. Results and discussion

3.1. Effect of alcohols on the work function of PEDOT:PSS thin films

The effect of alcohols on the work function Φ of PEDOT:PSS thin films was systematically studied by Kelvin probe (KP) measurements. In a first approach, thin films of PEDOT:PSS on ITO were treated with pure alcohols of increasing alkyl chain length from methanol (MeOH), to *n*-pentanol (PeOH). The resulting work functions are displayed in Fig. 1a. The work function of PEDOT:PSS increases steadily with increasing chain length of the alcohol from 5.2 eV for the untreated reference sample (REF) up to 5.61 eV using PeOH, respectively. The only exception from the steady increase is *n*-propanol, yielding a Φ -value, which is less than for the two neighboring chain lengths (5.35 eV compared to 5.45 and 5.50 eV, respectively); the reason for this finding is currently unknown. Unfortunately, the effect of work function increase by the alkyl alcohols was found to be reversible since washing the alcohol treated substrate with chlorobenzene (CB) – a common solvent for the subsequent deposition of active layers – restores the work function to 5.15 eV. This finding is in agreement with the Φ -value of ~5.15 eV for pristine PEDOT:PSS treated with pure CB, which will serve as reference value in the following (see Fig. S1 in the Supporting Information).

To make this finding useful for OSC fabrication, but since most organic materials used in organic photovoltaics are insoluble in alcohols, we tested whether the addition of alcohols to the main casting solvent (here CB) would yield similar results. Indeed, in doing so we were able to increase the work function of PEDOT:PSS even when it is used in mixtures with CB. Exemplarily, Fig. 1b shows the dependence of the PEDOT:PSS work function on the volume fraction of BuOH in mixtures with CB. Φ is stepwise increased using small amounts of BuOH until a saturated value of 5.57 eV is reached at 4 vol% BuOH. Thus, BuOH can potentially be added to the casting solution of the subsequent layer for *in-situ* enhancement of the substrate work function during layer deposition. Similar results were obtained with the other alcohols (Fig. 2).

To further investigate the properties of alcohol-treated PEDOT:PSS, substrates treated with 12.5 vol% BuOH/CB, i.e. in the saturation regime, were exposed (i) to elevated temperatures (150 °C, 10 min, N₂ atmosphere), (ii) to air (90 min, room temperature) and (iii) to vacuum (10⁻⁶ mbar for 1 h), respectively (see Fig. S1 in SI). During heating of the alcohol-treated substrate the work function was restored to 5.15 eV, i.e. the same value as for CB-treated PEDOT:PSS, while a smaller decrease of Φ_{PEDOT} (to 5.35 eV) was found when only exposed to air; it can be assumed, however, that extended times would also restore the work function to that of CB-treated PEDOT:PSS. Finally, after exposing the BuOH/CB treated film to vacuum the initial work function of PEDOT:PSS of about 5.2 eV was measured. Therefore, due to the reversibility under ultra-high vacuum (UHV) conditions the alcohol modified PEDOT:PSS cannot be studied by ultraviolet photoelectron spectroscopy (UPS). This finding opposes the report by Friend et al. for MeOH treated PEDOT:PSS films, where a change

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