



Solvent-resistant ITO work function tuning by an acridine derivative enables high performance inverted polymer solar cells

Yanfeng Liu ^a, Nabi Aghdassi ^b, Qi Wang ^b, Steffen Duhr ^b, Yi Zhou ^{a, **}, Bo Song ^{a, *}

^a Laboratory of Advanced Optoelectronic Materials, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China

^b Institute of Functional Nano & Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Soochow University, Suzhou 215123, China

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ABSTRACT

In order to avoid an interpenetration of the buffer and the photoactive layers during preparation of polymer solar cells (PSCs), solvent-resistant buffer films were chemically modified on indium tin oxide (ITO) surface. The conjugated aromatics acridine orange base (AOB) was introduced into the films using 3-bromopropyltrimethoxysilane (BrTMS) as coupling agent. Upon ITO surface modification, the respective work functions show a significant decrease. The modified ITO substrates were implemented in inverted PSCs based on PBDDTT-C-T:PC₇₁BM. With the modification, the power conversion efficiency (PCE) was improved significantly from 4.10% (for the inverted PSC without this buffer layer) to 7.56%. The PCE enhancement is mainly caused by the increase of the open-circuit voltage (43%). These results indicate that the solvent-resistant film is able to facilitate electron collection and transportation, thus providing a novel route to high efficient PSCs by surface engineering.

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1. Introduction

The development of bulk heterojunction polymer solar cells (BHJ-PSCs) has progressed steadily during the past years [1–6]. Owing to the diversity of organic materials, the record of power conversion efficiency (PCE) kept increasing with the evolution of the respective donors and acceptors [7–9]. Up to now, the highest PCE has exceeded 10% [10–12]. The rapid progress promises a potential prospect for the practical application of PSCs. In addition to the exploration of new materials, the structural optimization and interfacial engineering has to be considered concurrently [13–16]. Of the two dominating structures, conventional (ITO as anode material) and inverted (ITO as cathode material) PSCs, the latter possesses advantages such as better stability and higher efficiency when the devices constructed with these two structures use the same photoactive materials [17–20].

Regarding inverted PSCs, bare ITO is not suitable to be used as cathode material owing to its relatively high surface work function (WF) [21–23]. A surface modification by a thin oxide layer is usually

carried out to lower the WF and facilitate electron collection and transportation. Inorganic materials, such as zinc oxide (ZnO) [24,25], titanium oxide (TiO_x) [26,27], aluminium oxide (Al₂O₃) [28] and cesium carbonate (Cs₂CO₃) [29,30], have been widely used as interfacial materials due to their solution processability and favorable electron extraction properties [31]. However, the required high temperature post-annealing (usually over 100 °C) is incommensurate with both typical printing methods and flexible organic substrates. In this respect, organic materials, particularly polymers, show superior properties. The typical polymers used for this purpose include conjugated polymers (e.g. poly [(9,9-bis(3'-(*N,N*-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) [32]) and non-conjugated polymers (e.g. polyethylenimine (PEI) [33,34] and polyethylenimine ethoxylated (PEIE) [35]). However, if the polymer is not resistant to the solvent used for dissolving the photoactive materials, interpenetration of the buffer and photoactive layers may occur during the preparation of the upper layer. The interpenetration results in a dramatic decrease of the PCE. In order to solve this problem, Song et al. [36] introduced self-assembled monolayers (SAMs) of 3-aminopropyltriethoxysilane (APTES) as electron transport layer (ETL). Their results show a moderate improvement of the performances. Later on, the usage of surface grafting hyper-branched polymer of aziridine (SGHPA), as

* Corresponding author.

** Corresponding author.

E-mail addresses: yizhou@suda.edu.cn (Y. Zhou), songbo@suda.edu.cn (B. Song).

well as its incorporation with APTES as ETLs were demonstrated [37]. Due to electron donating amine groups in SHGPA and APTEs, the WF of ITO was effectively reduced and the respective PCE of the device was greatly improved.

APTES and aziridine contain no conjugated moieties and may hamper thus efficient charge transport characteristics [38]. Herein, we attempt to improve the conductivity by introducing conjugated aromatics. We assume that the combination of chemical bonding and the additional conjugated aromatics leads to an ideal buffer layer for high performance PSCs. In this paper, ITO substrates were chemically modified with acridine orange base (AOB) using 3-bromopropyltrimethoxysilane (BrTMS) as the coupling agent. AOB has been proven to be effective to reduce the WF of Au electrodes by forming an interfacial dipoles [39]. Moreover, on ITO the film shows very good solvent-resistant properties. After being modified with this film, the WF of ITO was significantly lowered by up to 0.82 eV. Inverted PSCs based on PBDTTT-C-T [40]:PC₇₁BM show great enhancement in terms of the PCEs as well as the performance characteristic.

2. Results and discussion

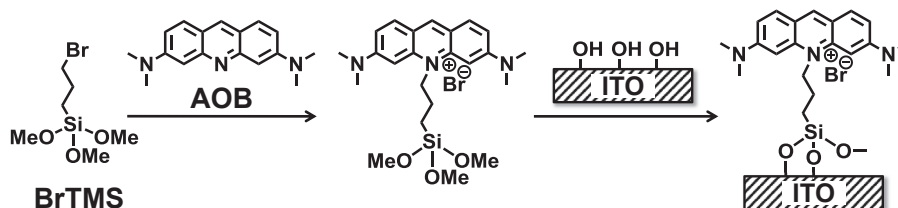
Scheme 1 summarizes the procedure which has been used to modify the ITO substrates by AOB and BrTMS. It turned out that the modification sequence makes a very big difference on the grafting of AOB component in the films. As shown in this scheme, the AOB molecules could react with BrTMS under stirring for 24 h, and the ITO substrates have been immersed into the solution for surface grafting of AOB-BrTMS. For further details the reader is referred to the experimental section. After the treatment, the substrates were thoroughly rinsed with toluene, acetone, chloroform and ethanol to remove physisorbed molecules. By this means of operation, the AOB moieties could be successfully modified on ITO substrates, which as evidenced by X-ray photoelectron spectroscopy (XPS) and UV–vis spectrometer. In contrast, ITO substrates were immersed into the solution of BrTMS for surface grafting, after that, the BrTMS modified ITOs were immersed into AOB solution for the reaction of AOB and anchored BrTMS. Unfortunately, in this modification procedure, the AOB moieties cannot be effectively grafted (indicated by XPS in Fig. S1 in supporting information (SI)). The corresponding device performances (Fig. S2 in SI) were also poor, reflecting that the modification is NOT successful. The deficiency has to be attributed to certain characteristics of AOB and BrTMS coupling. D. Kurth et al. [41] demonstrated that it is difficult to substitute bromine in surface-anchored BrTMS. The coupling of these two compounds is an S_N2 substitution. The reaction only occurs when there is enough space for AOB to attack bromide atoms from the alkyl chain direction. As being anchored to the surface, the mobility of BrTMS is limited, and thus the steric hindrance inhibits the S_N2 transition state, i. e., the reaction probability.

To check if AOB was chemically attached onto the ITO surfaces, they were characterized by XPS and UV–vis spectra. Fig. 1a shows

high-resolution XPS scans of several energetic regions for bare as well as modified ITO surfaces. The mono-peaks centered at 400 and 103 binding energy can be assigned to N 1s and Si 2p, which correspond to the tertiary amines [42,43] and the Si–O bond [44]. But in the Br 3d signal as shown in Fig. 1b, however, showed that not only Br[−] ion (68.2 and 69.1 eV) was present as expected, but also a contribution from C–Br (70.2 and 71.3 eV) was evident [45,46]. The presence of ionic Br contribution indicated the formation of chemical bond between AOB and BrTMS. And the appearance of all these peaks indicates the successful surface modification of ITO by AOB-BrTMS. Nevertheless, the indium signals of In 3d and In 4d originated from ITO were also observed even from the spectra of modified ITO, as shown in Fig. S3 in SI. For related organic thin films the information depth of XPS is around 10 nm by using lab sources. Thus, the nominal film thickness is in the range of a few nanometers, which was also confirmed by ellipsometry (see below).

The chemical coupling between AOB and BrTMS was further verified by UV–vis spectrometer. Fig. 1c presents the absorption spectra of AOB in solution, reaction mixture of AOB and BrTMS in solution and an AOB-BrTMS film on ITO substrate. The maximum absorption of AOB in toluene (good solvent for AOB) is located at around 425 nm [47], showing a mono-peak in the range of 400–700 nm. On the other hand, the corresponding spectrum of an AOB and BrTMS solution, exhibits two new absorption bands located at 475 and 507 nm after a reaction time of 24 h, suggesting the formation of onium salt. For the ITO substrate modified with AOB-BrTMS, the peak attributed to AOB disappears whereas the peaks corresponding to onium salt remain. Since the substrates were thoroughly washed (by ultrasonic cleaning in toluene, acetone, chloroform and ethanol for 10 min each) after surface reaction, it can be concluded that on the ITO substrate only the chemically bonded AOB and BrTMS were left. The transmittance spectrum of AOB-BrTMS modified film (Fig. S4 in SI) showed average transmittance of ~80% in the visible light region, which is comparable with the bare ITO glass. The slight loss of absorption did not cause apparent decrease of device performance as being discussed later in this study.

The thicknesses of AOB-BrTMS thin films obtained after different reaction times were determined by optical ellipsometry. Herein, since silicon is crystalline flat, and has similar reactivity to ITO with silane groups, the silicon slides were used as substrates to compare the thicknesses. The films got thicker with increasing reaction time. As the reaction time increase from 1 h to 5 h, the thickness of film grows from 4 nm to 11 nm. It is worth to note that even for a reaction time of only 1 h, a film thickness of more than 4 nm was obtained, which exceeds the length of fully extended AOB-BrTMS. Since the films have been thoroughly rinsed in several solvents as mentioned above, physisorbed adsorbates on the substrates are rather unlikely. Therefore, we assume that the prepared films were not ideal AOB-BrTMS monolayers. More likely, owing to the trifunctional silane groups of BrTMS, polymers or oligomers of AOB-BrTMS formed in the solution prior to the covalent surface



Scheme 1. The procedure used for modifying AOB-BrTMS thin films on ITO substrates.

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