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Electrochemically crosslinked surface-grafted PVK polymer brushes as a hole transport layer for organic photovoltaics†

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Electrochemically crosslinked surface-grafted poly(*N*-vinylcarbazole) (PVK) brushes as hole transport layers (HTLs) on a photovoltaic device have been demonstrated using SI-RAFT polymerization. Comparable performance to PEDOT:PSS/P3HT:PCBM based devices was achieved. A main advantage is strong adhesion to ITO with a possible long-term stability against acid dopants and oxygen.

Organic semiconductors have been the focus of significant study in the last few decades to determine device applicability in a number of different fields.^{1,2} Semiconducting conjugated polymers are typically used, which can be engineered to fine tune their properties such as spectral absorption, band gap and charge mobility. With these capabilities of conjugated polymers, an incremental power conversion efficiency (PCE) improvement has been observed over the last five years.^{3,4} In addition, a 10% PCE milestone can further be achieved by using multiple semiconductor constituents (multi-tandem cells)⁵ and new device architectures.^{6,7} Unlike silicon or inorganic solar cells, organic photovoltaics usually require the photoactive layer to be sandwiched between two different highly conductive layers (normally a metal such as Al and a transparent oxide such as ITO) for effective charge extraction. The interface between the polymer and the electrodes plays an essential role in determining the final device performance of OPVs—inserting a functional interfacial layer can change the interface properties dramatically.^{8–10} A hole transport layer (HTL) between the polymer/anode interface such as a poly(3,4-ethylene dioxathiophene):poly(styrene sulfonate) (PEDOT:PSS) film, for example, can be incorporated between the ITO electrode and the emissive layer in organic light emitting diodes (OLEDs).^{11,12} The same principle can also be applied to OPVs.^{13,14} When a PEDOT:PSS film is inserted between the ITO anode and the photoactive layer, an improvement of open circuit voltage (V_{oc}) is observed. The increase

of the photovoltage is due to the band bending of the ITO work function (4.5–4.7 eV) by the PEDOT:PSS (5.1–5.4 eV) to match with the highest occupied molecular orbital (HOMO) of the donor in the photoactive layer (~5.1 eV for P3HT). Another important function of PEDOT:PSS is to planarize the ITO surface reducing the occurrence of pinhole defects in the device, which in turn improves device performance (short-circuit current density (J_{sc}) and fill factor (FF)).

Although PEDOT:PSS has been commonly used to improve the performance of both OLEDs and OPVs, the acidic and insulating nature of the PSS imposes problems in terms of device stability.^{15–17} Therefore, in order to fabricate high efficiency OPVs with reasonable lifetimes that can compete with inorganics, new materials for the HTL need to be developed. Ideally, the HTL should maintain all the functions of PEDOT:PSS but without the drawbacks from the dopant (PSS).

The use of poly(*N*-vinylcarbazole) (PVK) as the HTL would be a good substitute for PEDOT:PSS because of its ability to provide the functions similar to PEDOT:PSS while avoiding all the drawbacks mentioned arising from the PSS dopant. First, PVK has become a material of interest in OPVs and OLEDs because of its electro-optical, charge-carrier and good hole-transport properties.^{18,19} It is also known to exhibit photochemical and high thermal stability in air.²⁰ Furthermore, the capability of the PVK to form a linkage at the 3,6-position of its carbazole pendant units^{21,22} makes it a good “precursor polymer” to form conjugated polymer networks (CPNs) of carbazole.^{23–25} This conjugation is an important characteristic that provides better electrical conductivity, adhesion properties, smoothness in morphology, uniformity, and optical quality of the films produced.

In this study, the “precursor polymer” approach was employed in combination with surface-initiated polymerization (SIP) of the precursor polymer PVK (Fig. 1). The use of SIP to tether the PVK brushes on ITO presents an efficient way to yield a good control over the film thickness and a good surface coverage due to the high grafting densities provided by this technique.²⁶ Furthermore, reversible addition-fragmentation chain transfer (RAFT) polymerization was used as the polymerization technique to grow the PVK from the surface, a technique which has likewise been used in carbon nanotube functionalization with polymers.^{27,28} This technique provides even more control on the polydispersity of the polymer chains grafted on the surface in contrast to the conventional free-radical polymerization process. The use of the electrodeposited chain transfer agent (CTA) as the macroprecursor of the brush formation from the surface also

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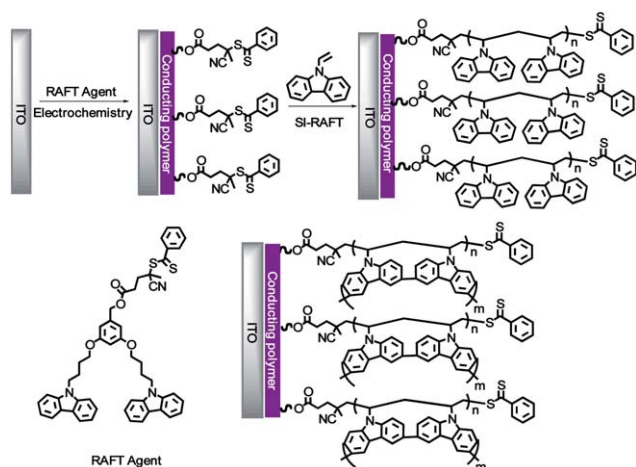


Fig. 1 Synthesis of the PVK HTL on ITO by SI-RAFT followed by electrochemical crosslinking.

provides a selective anchoring point from where the polymer brush would grow, unlike in self-assembled silane initiators, which coats both the glass side and conducting side of the ITO.

ITO modification was performed as depicted in Fig. 1. The electropolymerizable RAFT agent (CBz-CTA) was electrodeposited using a potentiostatic method as reported in our previous study (ESI†).²⁹ Vinylcarbazole (VK) was polymerized from the CTA-modified surface to form the PVK brush on the surface by surface-initiated RAFT (SI-RAFT), which was then cross-linked by cyclic voltammetry (CV) to produce a more conjugated film on the anode interface. The static contact angle of the surface after every modification step was monitored in which the value increased from $\sim 10^\circ$ (clean ITO) to $\sim 72^\circ$ (CTA-modified slide) to $\sim 82^\circ$ (PVK brush) signifying the introduction of relatively hydrophobic materials on the surface. A parallel run on an Au substrate was also carried out to check for the thickness of the film after each step using ellipsometry. The thickness increased from 10.4 nm to 22.7 nm from the electrodeposition of the CTA layer to polymerization of the PVK brush. Attenuated total reflectance infrared (ATR-IR) spectroscopy showed the successful growth of the PVK brush, which displayed peaks at 3100 cm^{-1} (aromatic C–H stretch), $2900\text{--}3000\text{ cm}^{-1}$ (aliphatic C–H stretch of the polymer backbone), 1600 cm^{-1} (C=C stretching),

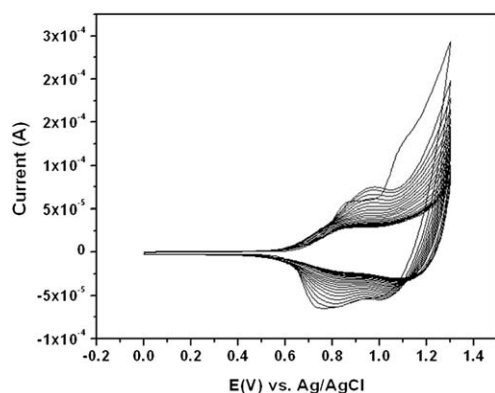


Fig. 2 Cyclic voltammogram during the electrochemical crosslinking of the PVK brush after RAFT polymerization.

1226 cm^{-1} (C–N stretching of vinylcarbazole), $1100\text{--}1150\text{ cm}^{-1}$ (in plane C–H aromatic) and $700\text{--}800\text{ cm}^{-1}$ (out of plane C–H aromatic) (ESI†).

The PVK brush grown from the surface was then electrochemically crosslinked by using CV (Fig. 2). During the first cycle, the first oxidation peak occurred at 0.85 V, which is attributed to the existing crosslinked carbazole moieties from the CTA layer.²⁹ Another oxidation peak at a higher potential (1.1 V) was observed, signifying the presence of uncrosslinked carbazole moieties arising from the grafted PVK brush after polymerization. This oxidation potential is similar to the surface-initiated PVK brush reported by the Advincula group, which used a silane-type free radical polymerization initiator³⁰ and is also expected for the oxidation of a carbazole monomer.^{31,32}

UV-Vis spectroscopy was also employed to monitor the progress of the surface modification (Fig. 3). The presence of the broad peaks at around 400 nm and 800 nm after the electrodeposition of the CTA are assigned to the dicarbazyl radical cation and dicarbazyl dication, respectively,³² confirming the presence of the crosslinked carbazole moieties from the CTA. After SI-RAFT polymerization of the VK, the broad maxima at 400 (3.1 eV) and 800 nm (1.55 eV) are still present (polaron and bipolaron bands) due to the underlying cross-linked carbazole units from the CTA layer. However, a new small peak was observed at 348 nm (3.56 eV), similar to the peak found in the uncrosslinked PVK control film indicating the successful growth of the PVK brush. The disappearance of the peak at 348 nm after the CV process evidenced the subsequent crosslinking of the PVK brush. This result is consistent with the reported electropolymerization of the PVK brush by Fulghum *et al.*³⁰

Atomic force microscopy (AFM) analysis also supported the surface modification as shown by the differences in topography after each step (Fig. 4). Bigger globular domains were formed after the formation of the PVK brush as compared to the electrodeposited CTA. The distinct and regular domains of the PVK brush appeared flattened and relatively smoother after the crosslinking. The line profiles of the AFM images also supported the thicknesses of the films observed in the parallel run on Au surface using ellipsometry (ESI†).

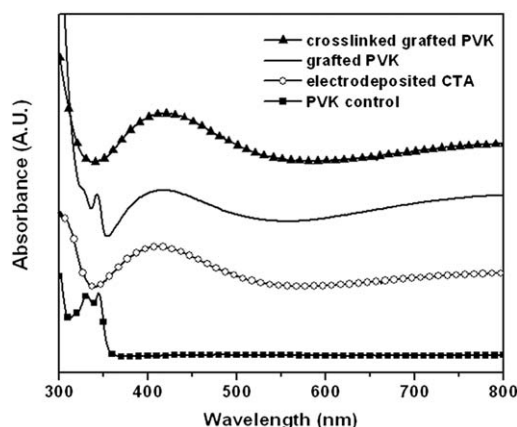


Fig. 3 UV-Vis spectra of the films obtained from the succeeding modification steps. Note: the formation of the PVK brush after RAFT polymerization showed a small peak at 348 nm, similar to the commercially available pure PVK, which was again removed after crosslinking the brush.

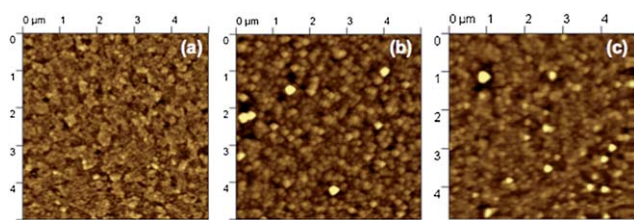


Fig. 4 AFM topography images of the (a) electrodeposited CTA, (b) PVK brush after SI-RAFT and (c) crosslinked PVK brush after CV.

In order to compare the OPV performance between devices using different HTLs, all poly(3-hexylthiophene):[6,6]-phenyl C_{61} -butyric acid methyl ester (P3HT:PCBM) based OPV devices were fabricated under exactly the same processing conditions (sequential spin-coating of P3HT:PCBM on each substrate and thermal evaporation of Al at the same time).³³ It must be noted that the PVK layer was sonicated for over an hour and showed no degradation in the thin film layer clearly indicating the robustness of the adhesion to the substrate. J - V characteristics of the P3HT:PCBM OPVs using the crosslinked PVK brushes or the PEDOT:PSS as the HTL, as well as the control without the HTL, are shown in Fig. 5. The device fabricated without the PEDOT:PSS showed a low V_{oc} (0.45 V), which can be attributed to the mismatch of the ITO work function (4.5–4.7 eV) with the HOMO of P3HT (~ 5.1 eV). In addition, low J_{sc} (3.0 mA cm^{-2}) and reduced FF (0.33) values were observed due to the decrease in the hole transfer rate that is caused by an interface barrier layer between ITO and the active layer.^{13,14} The devices produced using the PEDOT:PSS as the HTL showed improvements comparing to the devices without the PEDOT:PSS, in terms of V_{oc} (0.54 V), J_{sc} (8.0 mA cm^{-2}) and FF (0.51), which is in agreement with other studies.^{13,14} Devices fabricated using the crosslinked PVK brushes as the HTL showed comparable performance (PCE 2.3%) to the PEDOT:PSS devices (PCE 2.1%). A high V_{oc} (0.55 V) suggested that the work function of the PVK HTL is well aligned with the HOMO of P3HT, forming an ohmic contact. This is in agreement with our previous report on the use of electropolymerized and cross-linked PVK as a hole transport material on ITO in which the HOMO was determined to be variable from 5.1 to 5.4 eV.²⁴ A comparable J_{sc} (8.8 mA) and FF (0.47) demonstrated good hole transport property of PVK HTL compared to the reference cells using the PEDOT:PSS. These results suggest that the ITO is well covered with the PVK brush

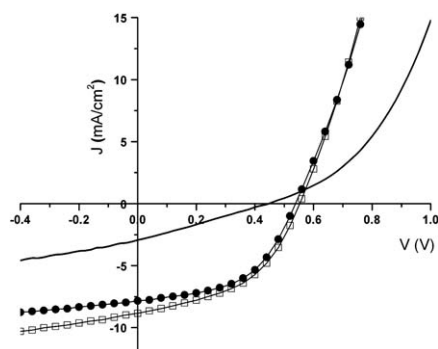


Fig. 5 J - V characteristics of the P3HT:PCBM OPVs using different materials as the HTL: (—) ITO/P3HT:PCBM/Al; (●) ITO/PEDOT:PSS/P3HT:PCBM/Al; and (□) ITO/PVK/P3HT:PCBM/Al.

and that no significant amount of pinholes was present, as depicted in our AFM data. It can also be noted that although the PVK layer is relatively less conductive³⁴ compared to PEDOT:PSS (Clevios PH-1000) used for most OPV devices, it still performed well as a charge carrier material.

Conclusions

In conclusion, we demonstrated a novel route of preparing electrochemically surface-grafted PVK brushes as the HTL on a photovoltaic device. The PVK HTL on ITO prepared by SI-RAFT polymerization followed by electrochemical crosslinking is proven to be a suitable candidate to replace the PEDOT:PSS in OPV applications. Comparable performance of P3HT:PCBM based OPVs was achieved using the PVK as the HTL comparing to the standard devices using the PEDOT:PSS. Because there is no insulating and acidic dopant such as PSS in the PVK HTL, it is expected that the PVK HTL should be more robust with humidity and oxygen exposure, which are the main factors that reduce the lifetime of OPVs. Furthermore, their morphology may be better for ultrathin film devices as compared to spin-coated films. A degradation study of OPVs using the PVK brush as the HTL under controlled conditions is currently underway.

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