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Computational comparison of conventional and inverted organic photovoltaic performance parameters with varying metal electrode surface workfunction

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ABSTRACT

Inverted polymer-based bulk-heterojunction organic photovoltaic (BHJ-OPV) device designs have enabled a breakthrough in operational lifetime through use of stable electrode materials. To date, there have not been systematic performance parameter comparisons between conventional and inverted devices that consider a range of different metal electrodes and presence of native metal oxides at the organic-metal interface. Here, we systematically compute optical and electronic performance parameters for both conventional and inverted BHJ-OPV devices for 15 different electrode types covering a range of workfunctions. We quantitatively demonstrate that (1) high-workfunction metal electrodes (Au, Pd, Ni) are ideal for high-efficiency inverted device performance; and (2) native metal oxide on metal electrodes (e.g., CuO/Cu, Ag_2O/Ag, NiO/Ni), which dramatically reduce conventional device efficiencies, can result in highly efficient inverted BHJ-OPV devices (efficiency of up to 6.7% for the P3HT:PCBM system). This work is an important advance over prior studies as it predicts the electrode materials and configurations that can lead to both high efficiency and high stability BHJ-OPV devices.

1. Introduction

In conventional bulk-heterojunction organic photovoltaic (BHJ-OPV) devices, the organic active layer is sandwiched between a low-workfunction metallic cathode (or electron collector) and a higher workfunction transparent anode (or hole collector, Fig. 1a). In recent years, a number of studies have demonstrated that low workfunction metallic cathodes are a primary contributor to device performance degradation for conventional BHJ-OPVs left in air [1–5]. In particular, degradation arises since, as metals oxidize or age, their workfunction increases (i.e., many have *p*-type semiconductor characteristics) [1,2,6–8], making them less effective electron collectors, which results in a marked reduction in the open-circuit voltage over time [7]. In inverted BHJ-OPVs, the polarity of the device is reversed: the metal acts as the anode and the transparent electrode acts as the cathode (Fig. 1a), usually through the use of high workfunction metals and/or the incorporation of appropriate transport layers. Thus, device degradation due to electrode oxidation is circumvented in inverted devices by the use of metals as anodes, where the formation of a *p*-type metal oxide can allow for more effective hole collection. While low workfunction metals have conventionally been chosen to match the lowest unoccupied molecular orbital (LUMO) (~4 eV) of the electron acceptor (typically a fullerene derivative such as phenyl-C_{61}-butyric acid methyl ester, PCBM) [9–13], for inverted devices, the metal workfunction must match the highest occupied molecular orbital (HOMO) (~5 eV) of the electron donor (typically, poly (3-hexylthiophene), P3HT) [14–20]. As a result, inverted device designs have been shown to be substantially more air-stable than their conventional counterparts [1,2,5,21]. A secondary benefit of the inverted design is the elimination of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) layers, which are widely used in organic optoelectronics to improve the electrical properties of the anode [22–24], but are known to be corrosive to the transparent electrode [24,25].

Although the operational lifetimes of inverted BHJ-OPVs have been dramatically improved over conventional BHJ-OPVs [1,2,5,21], especially when left in air, the efficiency of inverted BHJ-OPVs has typically remained lower than that of comparable conventional devices – inverted devices based on a P3HT:PCBM blend typically reach ~3–4% efficiency [2,15,17–21,26–31] whereas the efficiency of conventional devices based on the same blend can reach 4–5% [10,32–37]. Although there have been many studies focused on optimizing the device structure of conventional

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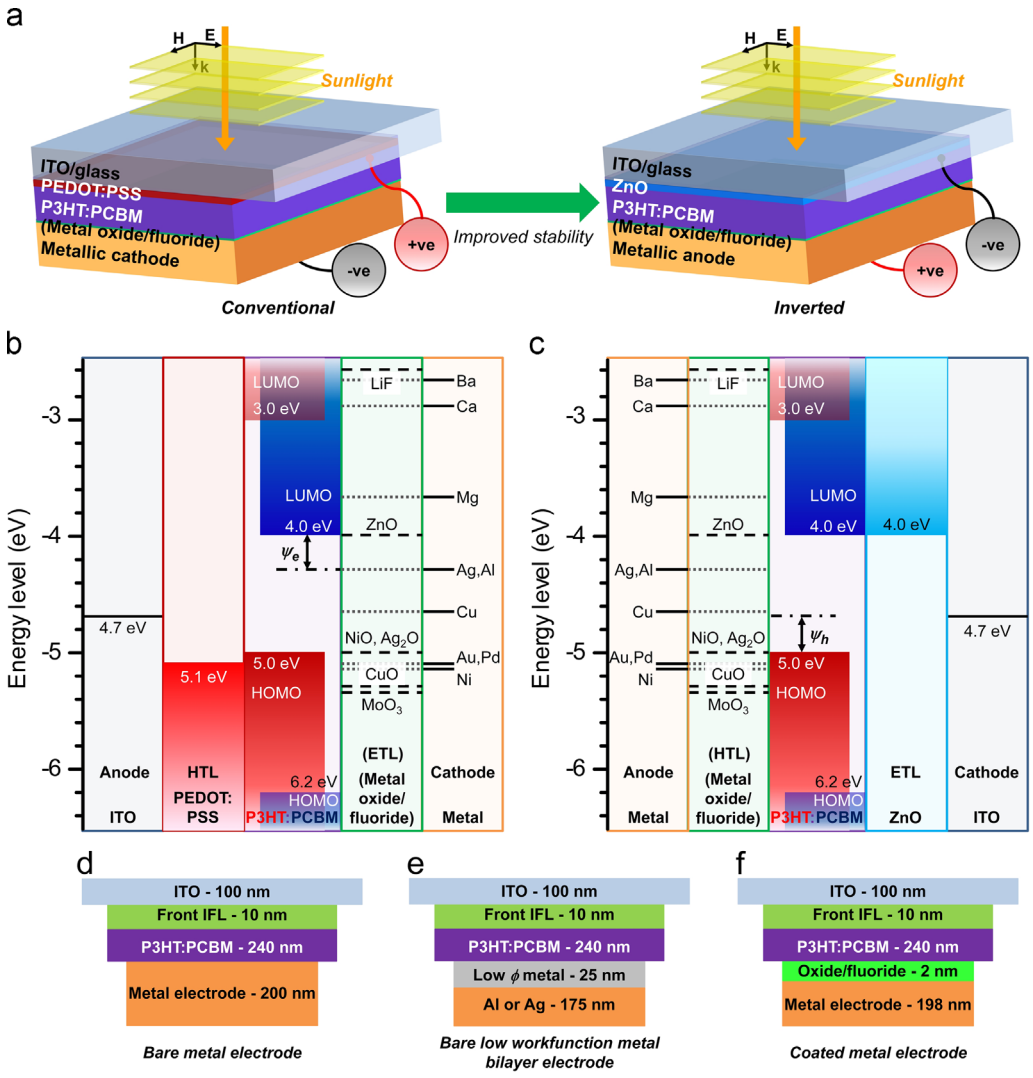

Fig. 1. (a) Schematic illustrating the different configurations for the BHJ-OPV devices studied here: conventional devices (left) and inverted devices (right) which may lead to improved BHJ-OPV device operational lifetime. A metal oxide/fluoride layer was present in 6 of the electrodes studied, but not present in the studies involving bare metal electrodes. (b)–(c) Energy level diagrams (flat-band conditions) for the corresponding (b), conventional and (c), inverted devices (magnitude of the energy levels is shown). The range of metals and metal oxides studied and their associated workfunctions are: LiF (2.6 eV) [60]; Ba (2.7 eV) [61];Ca (2.87 eV) [61]; Mg (3.66 eV) [61]; ZnO (4.0 eV, see below); Ag (4.26 eV) [61]; Al (4.28 eV) [61]; Cu (4.65 eV) [61]; NiO (5.0 eV) [36,62]; Ag_2O (5.0 eV) [6,91,63–65]; Au (5.1 eV) [61]; Ni (5.15 eV) [61]; CuO (5.3 eV) [66,67]; MoO_3 (5.35 eV) [31,45,68–71] (data is given for polycrystalline materials). Note that although the workfunction of ZnO is typically cited between 4.1 and 4.4 eV [17,30,46,69,72–74], it is known to form an ohmic contact to PCBM [46,75], potentially due to formation of an interface dipole [75]. Other energy level data was obtained/averaged from the following references: ITO (4.7 eV) [36,43,45,68,69,76]; PEDOT:PSS (5.1 eV) [31,36,43,68,77]; P3HT HOMO (5.0 eV) [12,21,30,31,36,47,68,76,78–82]; PCBM LUMO (4.0 eV) [12,17,21,30,31,36,47,68,75,76,78–82].

BHJ-OPVs [9,12,32–36,38–42], there have been fewer studies to date where the device structure of inverted BHJ-OPVs has been optimized [2,16,19,28,29,43–46]. In one study by Schumann et al., inverted P3HT:PCBM devices consisting of electrodeposited ZnO as the electron transport layer (ETL) and WO_x-coated Al as the hole transport layer (HTL)-coated anode reached an efficiency of ~4.8% [46]. In another study by Hau et al., the optimized thickness and blend ratio for an inverted device consisting of ZnO prepared by the sol–gel method resulted with inverted device efficiency (~3.5%) exceeding that of a similarly fabricated conventional device (~2.4%, consisting of PEDOT:PSS as the HTL and LiF/Al as the ETL-coated cathode) [2]. A similar active layer blend ratio optimization was performed for a different active layer morphology (a low bandgap polymer blended with $PC_{71}BM$), in which the ideal blend ratio for the inverted configuration was different than that of the conventional configuration, and the optimized inverted device efficiency (5.97%) exceeded that of a similarly fabricated conventional device (5.41%), but was still lower than that of the optimized conventional device efficiency (6.24%) [44]. Further inverted BHJ-OPV device optimization is necessary in order to achieve device efficiencies that can perform as well as, or better than, comparable conventional devices.

There have been a number of studies comparing the performance of BHJ-OPVs using different metal cathodes in a conventional configuration [9,39–41] and different metal anodes in an inverted configuration [16]. Hadipour et al. recently compared, experimentally and computationally, the performance parameters of BHJ-OPVs incorporating different interfacial layers (IFLs), including the low workfunction metal, Ca [38]. In their study, the authors suggested that many low workfunction metals have large parasitic optical absorption, and that their elimination can further improve device efficiency [38]. However, while all of these studies have considered a range of metal workfunctions, there has not yet been a systematic study comparing the performance