Solar Energy 174 (2018) 743–756

Contents lists available at ScienceDirect

Solar Energy

journal homepage: www.elsevier.com/locate/solener

Interface engineering of G-PEDOT: PSS hole transport layer via interlayer chemical functionalization for enhanced efficiency of large-area hybrid solar cells and their charge transport investigation

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ARTICLE INFO

Keywords:
G-PEDOT:PSS
Organic-inorganic hybrid solar cell
Press technology
Interlayer functionalization

ABSTRACT

In this study, in order to minimize the recombination current of free charge carriers in a large-area organic-inorganic hybrid solar cell (O-IHSCs), we improved the electrical conductivity of a graphene (G) and poly(3,4-ethylenedioxy thiophene)–poly(styrenesulfonate) (G-PEDOT:PSS) hole transport layer (HTL) by introducing various concentrations of synthesized graphene (G) into poly(3,4-ethylene dioxythiophene):poly(styrenesulfonate) (PEDOT:PSS). The electrical conductivity of G-PEDOT:PSS was enhanced to 932781.17 S m^{-1} via the addition of 2 mg/mL of G to PEDOT:PSS. The O-IHSCs fabricated with the highly conductive G-PEDOT:PSS composite as HTL enhanced the power conversion efficiency (PCE) to 3.90%, a 70% increase compared to O-IHSCs fabricated with pristine PEDOT:PSS HTL. However, the accumulation of G at a higher concentration (2.5 mg/mL) degrades the performance of the solar cell, which generated further defects or film aggregation, interfering with the fast transport of free charge carriers toward their respective electrodes. The G-PEDOT:PSS composite contained various types of functionalization via interfacial reaction between the G and PEDOT:PSS based on Raman and X-ray photoelectron spectroscopy studies. These chemical functionalizations provide an additional mechanism of charge transport via bridges enhancing the carrier mobility and suppression of recombination of free charge carriers, resulting in significant improvement in photovoltaic performance of the O-IHSCs.

1. Introduction

Over the last two decades, organic solar cells (OSCs) have been the focus of attention in the area of renewable energy. Their significant advantages include low cost, easy fabrication such as through spin coating, light weight, easy-fabricated process overall, and high mechanical flexibility (Günes et al., 2007; Yang and Loos, 2007; Scharber and Sariciftci, 2013; Brabec et al., 2001; Dennler et al., 2009). Organic solar cells are designed with different structures such as single-layer OSCs and bilayer OSCs; however, the most appropriate and efficient structure is the bulk heterojunction (BHJ) (Tang, 1986; Blom, 2007). In BHJ OSCs, the photoactive layer is formed by spin coating the blended solution of the conjugated polymers such as Poly(3-hexylthiophene-2,5-diyl) (P3HT), Poly({4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl}{3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b] thiophenediyl}) (PTB7), and/or Poly[(5,6-dihydro-5-octyl-4,6-dioxo-4H-thieno[3,4-c]pyrrole-1,3-diyl)[4,8-bis[(2-ethylhexyl)oxy]benzo [1,2-b:4,5-b′]dithiophene-2,6-diyl]] (PBDTTPD) (donor) and fullerene such as [6,6]-Phenyl C61 butyric acid methyl ester (PCBM), [6,6]-phenyl-C71-butyric acid methyl ester (PC71BM), and/or indene-C60 bisadduct (ICBA) (acceptor) as a single layer between electrodes with different work functions (Ecker, 2011; Jagadamma, 2014; Kumar, 2014; Van Bavel, 2010). BHJ OSCs share a work design similar to that of the bilayer solar cell; however, the excitons in BHJ OSCs are easily dissociated into free charge carriers due to the presence of donor and acceptor interfaces occurring randomly throught the whole film (Khan and Sayyad, 2011; Spanggaard and Krebs, 2004).

Furthermore, various materials have been used as the hole transport layer (HTL) and as the electron transport layer (ETL) between the photoactive layer and metal electrodes in order to facilitate the transport of free charge carriers towards specific electrodes. For the most part, poly(3,4-ethylenedioxy thiophene)–poly(styrenesulfonate) (PEDOT:PSS) has been extensively exploited as HTL in OSCs and in organic light-emitting diodes (OLEDs) (Baran, 2017; Rafique, 2017; Seo, 2017; Seo, 2017). It exhibits high optical transparency in the visible region, easy aqueous solution processability, and effective work

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https://doi.org/10.1016/j.solener.2018.09.031
Received 17 August 2018; Received in revised form 10 September 2018; Accepted 12 September 2018

function (Zhao, 2015; Po, 2011; Nardes, 2008). Conversely, PEDOT:PSS is acidic and hygroscopic in nature and easily interacts with air molecules, resulting in decomposes the photoactive materials (P3HT:PCBM) and drastically reduced lifetime of the devices (Chen, 2015; De Jong et al., 2000; Choi, 2015). Consequently, the shortcomings associated with PEDOT:PSS have been addressed by various research groups using high work function metal oxide-based materials such as MoO_3, NiOx, V_2O_5, and WO_3 as the HTL (Yang, 2012; Park, 2010; Meyer, 2011). Although these materials did increase the lifetimes of the OSCs and OLEDs (Chen, 2012; Li, et al., 2015), the addition of metal oxide-based materials is associated with its own limitations. For example, the techniques used for the deposition of metal oxide-based materials such as ion beam deposition, pulsed laser deposition, and magnetron sputtering require high vacuum, high temperature, and careful operator attention (Gallasch, 2011; Meng et al., 1993; Wu, 1992), which increases the expense and complexity of the techniques compared to those of liquid-based techniques such as spin coating, doctor blading, and dip coating (Wantana, 2017; Habibi et al., 2017).

Accordingly, the development of a cost-effective, liquid-based method has gained significance. Several research groups have introduced solution processible graphene oxide (GO) into PEDOT:PSS used as HTLs in the application of OSCs, OLEDs, field effect transistor (FETs) and sensors (Yu, 2011; Yu, 2010). However, the homogeneous dispersion of pristine PEDOT:PSS carries PSS as an insulating moiety, and the addition of GO diminishes conductivity due to the availability of oxygen (Zhiqiang et al., 2018). Therefore, using GO as an additive may not be an appropriate option, which may further decrease the conductivity of the PEDOT:PSS. In order to increase the conductivity of PEDOT:PSS, several research groups have added graphene alone (G), which significantly enhanced the electrical conductivity of the PEDOT:PSS film(Soltani-kordshuli et al., 2016; Yoo et al., 2014; Xu, 2009). Alongside, the power conversion efficiencies and lifetimes of PEDOT:PSS-based OSCs, perovskite solar cells, organic-inorganic hybrid solar cells (O-IHSCs), and OLEDs were also enhanced (Park, 2015; Yin, 2010; Gomez De Arco, et al., 2010; Choe, 2010; Geng, 2010; Wang, 2011; Un Jung, 2012; Kim, 2014; Chen, 2014; Murray, 2011). The O-IHSCs have been fabricated by several research groups using pristine PEDOT:PSS, GO-PEDOT:PSS, rGO-PEDOT:PSS, or graphene-PEDOT:PSS composites as the HTL in many device architectural structures such as (Al/n-Si/PEDOT:PSS/Ag-nanowire), (Au/Si-NWs/PEDOT:PSS/Ag), (Al/n-Si/PEDOT:PSS/Ag-metal grid), (Cs2CO3/PEI/n-Si/PEDOT:PSS-DMSO/Ag grid), (InGa/c-Si/PEDOT:PSS + GO/Ag), and (Ti/Pb/Ag/Si pillar array/graphene/Ti/Au) (Ozdemir, 2011; Ikeda, 2016; Thomas and Leung, 2016; Zhang, 2015; Jiang, 2017; Yin, et al., 2014).

In these structures, the deposition of p-type polymers such as PEDOT:PSS on the n-Si wafer was of interest because of the simple fabrication process as well as the fact that the result was free from contamination and convenient for commercialization (Yu, 2013; Schmidt et al., 2013). Additionally, in these structures the electron-hole pairs were generated in the n-Si instead of in the organic layer, and depletion occurred when the PEDOT:PSS was deposited on the surface of n-Si (Jäckle, 2016). Since the intrinsic charge carrier mobility of n-Si was very high i.e., 1600 $cm^{-2} V^{-1} s^{-1}$, the free charge carriers rapidly reached anode and cathode. Moreover, in these structures, the PEDOT:PSS acts by blocking electron transport, inducing hole transportation, and through the surface passivation and light antireflection layer in the O-IHSCs (Jäckle, 2015; Sheng, 2014). These properties of the organic layer further increase the number of excitons generated in the n-Si and suppress the recombination of the charge carriers. Therefore, the O-IHSCs fabricated by Zielke et al demonstrate a high PCE value of 20% (Zielke, 2015). Additionally, several groups have used the well-known organic polymer with fullerene (P3HT:PCBM) to design a hybrid solar cell. Eisenhawer et al also fabricated a hybrid solar cell by introducing the Si nanowires (SiNWs) into a P3HT:PCBM blender resulting in a significant improvement in the power conversion efficiency of P3HT:PCBM-based solar cells due to the improved charged separation and transportation at the interface between SiNWs and P3HT:PCBM (Eisenhawer, 2011).

Dietmueller et al. studied the charge transfer mechanism in hybrid composites such as Si/P3HT, Si/PCBM, and P3HT:PCBM through measuring their light-induced electron spin resonance (LESR) and demonstrated that the generation and separation of electron-hole pairs at the Si/PCBM interface require a lower light energy than those at the P3HT:PCBM interface (Dietmueller, 2009). Additionally, they established that organic materials with better energy level alignment with Si effectively separate photogenerated electron-hole pairs. Based on these characteristics, the Si/PCBM and Si/P3HT interfaces represent promising organic-inorganic hybrid solar cells. Similarly, Avasthi et al fabricated hybrid solar cells based on n-Si/P3HT and demonstrated 10.1% PCE. They also found that this well- known polymer with Si is a better option for blocking the electron recombination at anode because of the large offset between the lowest unoccupied molecular orbital (LUMO) level of P3HT and Si conduction band (CB) (Avasthi, 2011).

Although diverse types of photovoltaic cells with the very small active area have been designed (Ozdemir, 2011; Ikeda, 2016; Thomas and Leung, 2016; Zhang, 2015; Jiang, 2017; Yin, et al., 2014) but by the pressing technology no one yet fabricated a hybrid solar cell with a large active area (1 cm^2) based on two photoactive or exciton-generated layers i.e., n-Si and P3HT:PCBM. Similarly, several efforts have focused to enhance the conductivity of PEDOT:PSS and the performance of PEDOT:PSS based devices by preparing the composites of PEDOT:PSS with carbon-based materials (Yoo et al., 2014; Pathak et al., 2016; Xiong, 2015; Kim et al., 2012; Dehsari, 2014; Seol, 2012; Eda et al., 2008; Chen, 2009; Park, 2017). However, there is no report available in which the author increased the conductivity of PEDOT:PSS films near to 1 million S/m by the addition of G. Therefore, the purpose of the present study is to address the two important scientific problems. Firstly, to employ a very simple and novel device architecture, i.e., ITO/G-PEDOT:PSS/P3HT:PCBM/n-Si/Al, for the fabrication of O-IHSCs, where we are expecting two large barriers for the recombination current, i.e., $\Delta Ec \sim 0.5$ eV and $\Delta Ev \sim 1.1$. One for the flow of electrons between the CB of n-Si and LUMO level of the P3HT ($\Delta Ec \sim 0.5$ eV) and second for the flow of holes between the n-Si valence band (VB) and work function of Al ($\Delta Ev \sim 1.1$ eV). These two (LUMO-Ec and LUMO-Ev) offsets significantly blocked the recombination of electrons and holes at the cathode and anode, respectively. Another benefit of this new architecture is the existence of a negligible energy barrier between the VB of n-Si (5.17 eV) with the highest occupied molecular orbital (HOMO) level (5.1 eV) of P3HT and with the work function of HTLs (5.1 eV) that significantly increased the flow of holes to the ITO by reducing the series resistance. Further, the CB of Si (4.05 eV) also containing a very low offset with LUMO level (3.8 eV) of PCBM and closely aligned with the work function of Al (4.06 eV) improved the efficiency of electron transportation to the Al.

Secondly, to improve the conductivity as well as the stability of the PEDOT:PSS and PEDOT:PSS based hybrid solar cells. we incorporated the various concentrations of the highly conductive (70,000 S/m) synthesized graphene (G) with PEDOT:PSS and used that G-PEDOT:PSS composite as HTLs. The introduction of G to PEDOT:PSS as a conductive platform effectively decreased the resistance of pristine PEDOT:PSS as well as increased the photovoltaic performance of O-IHSCs through the functional groups at the interface of graphene and PEDOT:PSS. The addition of 2 mg/mL concentrated G to PEDOT:PSS increased the electrical conductivity close to 1 million (S/m), which represented an almost (63%) enhancement compared with the conductivity of pristine PEDOT:PSS. It, therefore, enhanced the PCE of O-IHSCs to 3.90%, which was a 70% enhancement compared with bare PEDOT:PSS-based O-IHSCs.