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A futuristic strategy to influence the solar cell performance using fixed and mobile dopants incorporated sulfonated polyaniline based buffer layer

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ABSTRACT

In this work, we hypothesized and demonstrated a new strategy to tune/modulate the electrochemical, microstructural and opto-electronic properties based on the manipulation of the intentionally included external dopant ion (X^-) within the sulfonated polyaniline (SPANs). Through our new strategy, we developed a different type of SPANs comprising of internal (fixed) and external (mobile) dopant. The X^- included SPANs were prepared through a sequential doping, dedoping and redoping processes and designated as SPAN-R (X^-) (where X^- is the anion of toluene sulfonic acid (TSA) or camphor sulfonic acid (CSA) or napthalene sulfonic acid (NSA)) by modifying the structure of 4-aminodiphenylamine-2-sulfonic acid with additional polyaniline chains to accommodate X^-. SPAN-R(X^-) polymers were characterized by cyclic voltammetry, UV–visible spectroscopy, attenuated total reflectance-Fourier transform infrared spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy and Atomic force microscopy to elucidate the influence of X^- on the electrical, optoelectronic, microstructural properties and surface properties on the performance characteristics of polymer solar cells (PSCs) fabricated with SPAN-R(X^-) as a buffer layer. The electrochemical band gap, degree of doping (DD), electrical conductivity and degree of crystallinity (CD) were evaluated and correlated to understand the influence of X^- on them. The power conversion efficiency (PCE) of PSCs featuring SPAN-R(TSA^-) as a buffer layer showed a ~3.2 times improvement in the overall PCE, compared with the PSCs having pristine SPAN (not containing X^-) as a buffer layer and is higher than that of SPAN-R(CSA^-) and SPAN-R(NSA^-) based devices. The superior photovoltaic (PV) characteristics observed for SPAN-R(TSA^-) is due to the synergistic contributions from appropriate energy-level/work function alignment, higher conductivity, higher DD and induced molecular order with the photoactive layer. Importantly, PSCs with SPAN-R(X^-) buffer layer processed at low temperature (30 °C) (without thermal treatment) exhibited improved PV characteristics and better air-stability as compared to the device having poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) (thermally annealed at 150 °C) as buffer layer. As buffer layers, SPAN-R(X^-) polymers, containing fixed and mobile dopants, are most attractive because of low temperature processability and improved solar cell performance.

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1. Introduction

Polymer solar cells (PSCs) have received increasing attention and have demonstrated potential as renewable, mechanically flexible, light-weight and low cost energy sources [1]. The power conversion efficiency (PCE) of polymer:fullerene solar cells has been increased upto a record value of over ~11% by various

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performance improving strategies such as adopting novel low bandgap donors, morphology control and charge selective buffer layers [2–5]. It is known that the buffer layer plays a crucial role in achieving highly efficient PSCs [6–8]. The buffer layer is usually placed between the electrode and the photoactive layer that transports the photogenerated carriers (holes or electrons) in PSCs. From existing reports, the contributions of the buffer layer can be summarized as follows: adjusting the work function of the electrode [9], offsetting the vacuum level between the active layer and the electrode [10], protecting the active layer from the hot electrode during annealing processes [11] and increasing the built-in electric field through the formation of a tunneling junction [12]. Studies have done on the various processing approaches for buffer layers to induce the optimal microstructural, optical and electronic properties to enhance charge carrier collection [13]. It must be noted that simultaneous tuning of the microstructural, optical and electronic properties of the interfacial buffer layer can be one of the most important approaches to improving the PCE of PSCs, and such studies with new structural polymers are scarce and highly warranted.

Poly(ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) is widely used as a standard anode buffer layer in PSCs because of its excellent transport properties, high transparency and textured surface [14,15]. However, there are few important issues related to using PEDOT:PSS as a buffer layer in PSCs. The acidic and hygroscopic nature of PEDOT:PSS can cause chemical interactions with adjacent layer and thereby degrade the device stability. Commercially available photovoltaic grade PEDOT:PSS exhibits low electrical conductivity (~10^{-3} S/cm) and is not cost-effective. In addition, the hole collection of the PEDOT:PSS film is inhomogeneous over different regions due to possible variations in electrical conductivity within the film. As alternative to PEDOT:PSS, several metal oxide interlayers have been tried as buffer layers in PSCs, which either require thermal annealing or plasma/UV–ozone treatment that contradicts the processing requirements for buffer layers and hence not viable for roll to roll processing [16–19]. The possibility of using a water soluble, annealing free conducting polymer (CP) based buffer layer has triggered researchers to explore suitable alternatives to PEDOT:PSS.

Polyaniline (PANI) is an attractive polymer because of its ease of synthesis, environmental stability, tunable electrical properties and comparatively low cost. PANI based CPs have been reported as a replacement for PEDOT:PSS in PSCs due to their transparency, chemical stability, and high conductivity [20]. PANI, in solar cell configurations, provides an interface with the buffer layer and the active layer, augments photocarrier separation and transports the free charge carriers. In addition, PANI can function as oxygen barrier, inhibits electrical shorts and improves device life time. PANI has shown to be more efficient as a buffer layer in PSCs than PEDOT:PSS under certain conditions [21]. However, the great advantages of using PANI in PSCs over PEDOT:PSS are masked by its restricted solubility in common organic solvents.

Introducing –SO_3H groups on the PANI chain affects the physico-chemical properties of PANI without substantially sacrificing conductivity compared to PANI. Sulfonated PANIs (SPANs) offer good processability in a wide range of solvents [22]. SPANs have received great interest in PSCs for several reasons compared to their counterpart, PANI [23]. The stability of the parent PANI structure is improved by the electron withdrawing properties of the –SO_3H group on the phenyl ring in SPANs. Specifically, SPANs differ from the parent PANI, through the specific role of the –SO_3H group in the crystallographic, steric, and electronic properties. Being able to dope themselves, SPANs have enhanced optical and electrical responses compared with the parent PANI [24]. Fully sulfonated PANIs (SPANs with 100% sulfonation in aromatic rings) were prepared from aniline sulfonic acids monomers such as methane sulfonic acid [25], metallinic acid [26], 2, 5 diaminobenzenesulfonic acid [27], poly(aniline-co-2,5-dimethoxyaniline) [28], dithiodianiline [29], and 2-methoxyaniline-5-sulfonic acid [30]. However, the chemical/thermal stabilities of fully sulfonated SPANs prepared from aniline sulfonic acids are relatively low as they are known to have lower chain lengths compared to pristine PANI. Few studies have been reported on the use of sulfonated poly(diphenylamine) as a hole collecting layer in PSCs [31,32]. SPANs with enhanced chain lengths and adaptable structures for improved optical and electronic properties are expected to resolve the problems with fully sulfonated SPANs.

The structure and/or conformation of PANIs strongly influence the conductivity, electronic and transport properties. The conductivity of acid doped PANI strongly depends on the polymer main-chain conformation of its emeraldine salt (ES) form [33]. The ES PANI with an extended coil conformation of the polymer chain shows a conductivity improvement over the PANI chain with a compact coil conformation [34]. For most of the CPs, carrier transport is primarily controlled by the inter-chain and intra-chain hopping processes and follows the variable-range hopping (VRH) model. According to the VRH model, the average hopping distance (mean free path) is directly related to the conformation and arrangement of polymer chains. As regards SPANs, various studies on the polymer main-chain conformations have been carried out since MacDiarmid and Epstein reported conformational changes during secondary doping of the PANI chain with –SO_3H group [35]. Conformational change in SPANs is likely to be induced by the counter cation of the sulfonate moiety [36]. In the case of SPANs, the solvation, steric hindrance and steric repulsion effect of the –SO_3H group decide the inter-chain interactions between the polymer chains. It has been reported that the thermoelectric properties could be enhanced by increasing the ordered arrangement of polymer chains [37]. In our earlier reports, we demonstrated the structural influence of PANI/substituted PANIs on the optical, electronic and electrochemical properties [38,39].

The nature of the dopants employed in the electrochemical or chemical synthesis of PANI significantly influences the structure, the conformation of polymer chains, and the physico-chemical properties of the PANI. Wynne et al. [40] and Diaz et al. [41] reported that the nature of the counter ions affects the quality and the mechanical properties of the polymer films. Wernet et al. [42] and Yamaura et al. [43] suggested that the counter ions employed in the electrochemical preparation have a direct impact on the molecular organization of the SPANs. Self-doping, as in SPANs, and external doping, in the case of PANI, are rather different. In SPANs, the –SO_3H groups are covalently bonded to the PANI structure, which neutralizes the positive charges generated in the PANI structure [44]. Thus, no anion exchange between the polymer and surroundings occur during oxidation or reduction of the polymer chain. In contrast, doping of PANI always accompanies counter anions coming in (or out of) polymers. For the simple PANI structure, it is well known that its reversible oxidation and reduction is accomplished with the movement of anions into, or out of the bulk of the polymer. The external doping of PANI generates, in principle, high conductivity primarily by increasing the charge carrier concentration, leading to conjugation defects in the polymer chain. However, the electrical conductivity of the self-doped form of PANI is lower than that pristine PANI due to steric restriction from the internal dopant. Also, the conductivity of the pristine PANI is more strongly affected by changes in pH, i.e., conductivity is very low at neutral and basic pHs [45]. In contrast, SPANs exhibit stable conductivities over a wide pH range (pH=4–8). Considering the fact that external and self-doped PANIs have different advantages for tuning device parameters, it would be interesting to explore the utility of PANI comprising both fixed

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