Organic Electronics 9 (2008) 1136–1139

Contents lists available at ScienceDirect

Organic Electronics

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

Letter

Polymer solar cells incorporating one-dimensional polyaniline nanotubes

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ARTICLE INFO

Article history:
Received 27 April 2008
Received in revised form 21 July 2008
Accepted 6 August 2008
Available online 15 August 2008

PACS:
71.20.Rv
73.61.Ph
73.63.Fg
73.50.Pz
79.60.Jv

Keywords:
Solar cell
Acid-doped polyaniline
Nanotube

ABSTRACT

We have fabricated polymer solar cell devices based on poly(3-hexylthiophene):[6,6]-phenyl-C_{61}-butyric acid methyl ester (P3HT:PCBM) and incorporating one-dimensional nanostructured acid-doped polyaniline nanotubes (a-PANINs) as an interfacial layer. The power conversion efficiency of an annealed device incorporating the a-PANIN layer reached 4.26% under AM 1.5 G (100 mW/cm^2) illumination, an increase of ca. 26% relative to that of the annealed device lacking an a-PANIN interfacial layer. The incorporation of the a-PANINs in the solution-processed polymer solar cells was reproducible; the high conductivity, controlled tubular nanoscale morphologies, and mobility of the annealed a-PANIN layer led to efficient extraction of photogenerated holes to the buffer layer and suppression of exciton recombination, thereby improving the photovoltaic performance.

The properties of bulk heterojunction structures, which hold great promise for use in high-efficiency polymeric solar cells, are controlled by the nature of their interfaces. Because exciton diffusion lengths in organic solar cells range from 10 to 100 nm [1,2], only those excitons generated within a short distance of the donor–acceptor interface have the possibility of dissociating into free electrons and holes. Although ideally the interface should have as large a contact area as possible, the morphologies of the donor and acceptor should still permit the charge carriers to travel along unrestricted transport pathways to their respective electrodes. Many organic solar cells based on conjugated polymers and soluble fullerenes have been developed since their efficient photo-induced charge separation at donor–acceptor interfaces was first reported simultaneously with the finding of continuous pathways for free charge carriers transport to appropriate electrodes [3,4]. Several techniques related to the preparation of the materials and modification of the device architectures have also been reported [3–6].

Poly(3-hexylthiophene) (P3HT) is at present among the most suitable electron–donor conjugated polymers for use in bulk heterojunction polymer solar cells. When incorporated with double-walled carbon nanotubes [7] or multi-walled carbon nanotubes [8] as an interpenetrating hole-extracting electrode, it improves the photovoltaic performance of solar cells. Polyaniline (PANI) nanotubes have attracted almost as much interest as carbon nanotubes because of the unique chemical and physical properties of their doped and un-doped structures and for their future potential applications in polymeric conducting devices [9]. In addition to PANI nanotubes (PANINs) [10], several other PANI morphologies are known, including needle-like structures [11], hollow microspheres [12], and self-assembled nanofibers [13]. Because of their one-dimensional (1-D)

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doi:10.1016/j.orgel.2008.08.001

nanostructures and metal-like conductivities, conducting polymers, nanotubes, and nanofibers have attracted much attention for their potential applications in nanodevices [14].

In this study, we synthesized acid-doped [15] PANI nanotubes (a-PANINs) for use as the interfacial layer in P3HT:[6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM)-based polymer bulk heterojunction solar cells to collect holes efficiently from the active layer and transport them to the buffer layer under the internal electric fields of the fabricated ITO/buffer/a-PANINs/P3HT:PCBM/Al devices. Regioregular P3HT with 98% HT–HT coupling and PCBM (99.5% purity) were obtained from Aldrich Co. A solution of *n*-dodecylbenzenesulfonic acid (DBSA) (3 g) and ammonium persulfate (6 g) in de-ionized water (30 mL) was mixed with a solution of aniline (1 g) in HCl (ca. pH 1.5, 5 mL). The resulting dark-green mixture was gently stirred for 5 min and then a further charge of aniline (10 g) was added. After 4 h of gentle magnetic stirring, the green/black precipitate of the a-PANINs was suction-filtered and washed with copious amounts of de-ionized water and methanol. Drying under vacuum at 100 °C for 12 h yielded a dark-green powder [16–19]. A 60-nm-thick film of PEDOT-PSS (Baytron AI 4083) was spin-coated at 4000 rpm from an aqueous solution onto pre-cleaned indium tin oxide (ITO)-coated glass (sheet resistance: 15 Ω/□; Ritek) in a clean-room atmosphere (class 10000) and then dried at 180 °C for 5 min. The a-PANIN layer (30–50 nm) was then spin-coated from toluene solution (0.2 mg/mL, 5 mL) onto the ITO/PEDOT-PSS layer. Next, a P3HT:PCBM active layer was spin-coated [P3HT:PCBM, 1:1 (w/w) in *o*-xylene; 30 mg/mL] onto the a-PANIN layer and then the system was dried at 150 °C for 10 min. Subsequently, an Al cathode (200 nm) was deposited on top of the active layer through thermal evaporation at ca. 2×10^{-6} torr through a mask, defining an active area of 3 mm^2, and then dried at 150 °C for 30 min. The work functions of these materials in air were measured through photoelectron spectroscopy (PESA, AC-2). Using a Hall measurement system (ECOPI, HMS-3000), we determined that the electrical conductivities (σ_{RT}) of the as-spun a-PANIN and PEDOT-PSS films were in the ranges 3–4 and 2×10^{-4}–4×10^{-4} S/cm, respectively.

Fig. 1a displays the energy levels of the compounds used in this study. Fig. 1b and d present the device structure and chemical structures of the materials, respectively. The field-emission scanning electron microscopy (FE-SEM) image in Fig. 1c reveals that the product was composed of >12-μm-long tubes having mean and effective diameters in the ranges 300–500 and 400–600 nm, respectively. The inset to Fig. 1c indicates that the well-extended 1-D nanostructure of each a-PANIN had the form of a 1-D nanotube, the hollow tunnel of which could aid in the transport of charges further through the tubular structure, preventing interference, recombination with electrons, or defects. The length scale of phase separation in the photoactive layer is a key factor affecting the performance of polymer solar cells. To achieve high-performance cells based on P3HT:PCBM, the PCBM component must form clusters having lateral dimensions of the order of 20–50 nm within, and continuous pathways through, the whole film [20,21]. The sub-micron scale of the features in the a-PANIN surface was appropriate for the P3HT:PCBM domain, providing a well-defined contact area for the transport of

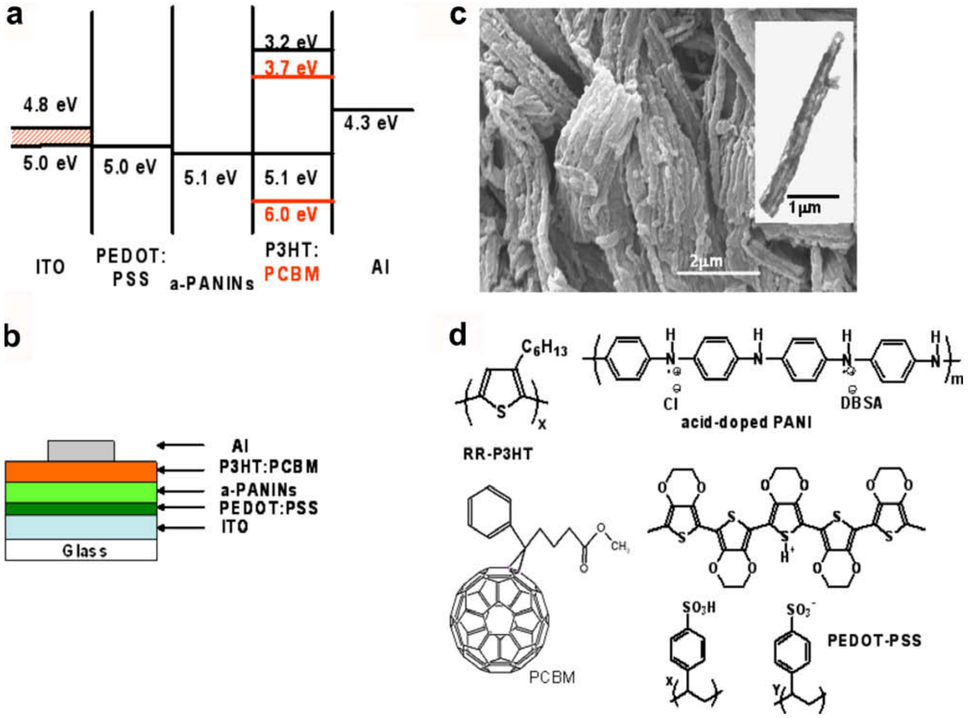

Fig. 1. (a) Energy-level diagram, (b) device structure, (c) FE-SEM image of the a-PANINs (inset: TEM image), and (d) chemical structures of the compounds used in this study.