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ScienceDirect

Energy Procedia 60 (2014) 13 – 22

Energy Procedia

E-MRS Spring Meeting 2014 Symposium Y "Advanced materials and characterization techniques for solar cells II", 26-30 May 2014, Lille, France

ITO-free anode with plasmonic silver nanoparticles for high efficient polymer solar cells

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Abstract

In this work we improved the performance of ITO-free polymer solar cells (PSCs) by incorporating silver nanoparticles (AgNPs) in the highly conductive (HC) PEDOT:PSS anode. The AgNPs were synthetized *in-situ* in the PEDOT:PSS water dispersion. This anode was used to realize PSCs with the following geometry: glass/HC-PEDOT:PSS/PEDOT:PSS/PBDTTT-C:[70]PCBM/Ca/Al. All the devices were characterized by UV-VIS spectroscopy, impedance spectroscopy, IV light, IV dark and quantum efficiency measurements. The presence of AgNPs in the HC-PEDOT:PSS anode contributes to improve the absorption of the photoactive layer and to lower the resistivity of the anode.

Peer-review under responsibility of The European Materials Research Society (E-MRS)

Keywords: polymer solar cells, silver nanoparticles, plasmonic effect, impedance spectroscopy, ITO-free.

1. Introduction

Polymer solar cells (PSCs) are a promising alternative to silicon-based devices because they have several advantages like the good flexibility, the light-weight and the low-cost manufacturing that can be reached by roll-to-

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Peer-review under responsibility of The European Materials Research Society (E-MRS)
doi:10.1016/j.egypro.2014.12.336

roll printing and coating techniques [1-4]. Recently, power conversion efficiency (PCE) surpassing 9% has been reported [5]. The most successful device configuration is based on the bulk heterojunction (BHJ) concept where an interpenetrating network, with nanometer phase separation, of electron donor and acceptor materials is placed between two contact with different work function [6, 7]. However, the PCE of these devices need to be enhanced even more before PSCs can be commercially viable. One of the main limits of the PCE is the insufficient light absorption due to the narrow absorption range of the photoactive materials and the ultrathin film thickness. A promising approach used to improve this bottleneck is the introduction of metallic nanoparticles (NPs) inside the layers of the PSCs in order to increase the light harvesting and the PCE of the devices. This enhancement is mainly due to the plasmonic effects of these NPs ascribed to near-field enhancement and light-scattering [8].

In the most used device configuration, indium tin oxide (ITO) is used as transparent conducting anode but it is not desirable for PSCs fabrication for the increasing cost of indium [9], the limited mechanical flexibility and the patterning that involves a lot of chemicals. Recently, poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) polymer has been investigated as innovative material for replacing ITO due to its high transparency in the visible region, long-term stability and solution process ability [10, 11].

In this work, we improved the performance of ITO-free PSCs by incorporating silver nanoparticles (AgNPs) in the highly conductive PEDOT:PSS anode. The AgNPs were synthetized *in-situ* in the PEDOT:PSS water dispersion. This anode was used to realize PSCs with the following geometry: glass/HC-PEDOT:PSS/PEDOT:PSS/active layer/Ca/Al). The active layer was a blend of poly[(4,8-bis-(2-ethylhexyloxy)-benzo[1,2-b;4,5-b']dithiophene)-2,6-diyl-alt-(4-(2-ethylhexanoyl)-thieno[3,4-b]thiopene)-2,6-diyl] (PBDTTT-C) and [6,6]-phenyl C_{71} butyric acid methyl ester ([70]PCBM). When PBDTTT-C is used as donor material in conventional PSCs, PCE up to 6% has been reached [12]. All the devices were characterized by UV-Vis spectroscopy, impedance spectroscopy (IS), IV light, IV dark and external quantum efficiency (EQE) measurements. We made a comparative study of the electrical behavior of different PSCs in order to investigate the influence of AgNPs on the absorption of the photoactive layer and on the resistivity of the anode.

2. Experimental

2.1. Materials

To realize ITO-free PSC devices the following materials were used as received: Corning® Eagle XG 1 mm thick boro-aluminosilicate glass substrate (Delta Technologies, LTD), Clevios™ PH 1000 and Clevios P AI4083 PEDOT:PSS aqueous dispersions (Heraeus Precious Metals GmbH), dimethyl sulfoxide (Sigma-Aldrich Co.), $AgNO_3$ (≥ 99.5%) (Sigma-Aldrich Co.), $NaBH_4$ (≥99%) (Sigma-Aldrich Co.), PBDTTT-C (Solarmer), [70]PCBM (Solenne BV), anhydrous 1,2-dichlorobenzene (Sigma-Aldrich Co.), diiodooctane (DIO) (Sigma-Aldrich Co.), Calcium (Sigma-Aldrich Co.), Aluminum (Kurt J. Lesker). Blend of donor: acceptor was prepared prior to device fabrication. PBDTTT-C:[70]PCBM solution (ratio 1 : 1.5) was obtained, inside a nitrogen glove-box, by dissolving both components in 1,2-dichlorobenzene with an initial donor concentration of 15 mg/ml. The solution was left stirring overnight at 40 °C. After 24 h the corresponding amount of DIO (3% v/v) was added. The new solution was stirred 1 h at 70 °C just before film deposition. Moreover, before realization of devices, the highly conductive polymer dispersion used as anode was prepared by doping with dimethyl sulfoxide (DMSO) (5% v/v) the commercial aqueous PEDOT:PSS dispersion (HC-PEDOT:PSS) [13].

2.2. AgNPs synthesis

Silver nanoparticles (AgNPs) were synthesized directly into the HC-PEDOT:PSS aqueous dispersion (in situ preparation) by chemical reduction of Ag^+ of silver nitrate ($AgNO_3$) to Ag^0 using as reducing agent sodium borohydride ($NaBH_4$). 15 mL of HC-PEDOT:PSS aqueous dispersion was added to 1 mL of a 29.4 mM deionized water solution of $AgNO_3$ (5 mg) under vigorous magnetic stirring at room temperature. Then, 2 mL of 52.9 mM (4 mg) deionized water $NaBH_4$ solution was added drop-wise. After the addition of the reducing agent, the reaction