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Zinc oxide nanorod arrays hydrothermally grown on a highly conductive polymer for inverted polymer solar cells

Manuel Reinhard[a,c,*,1], Jonas Conradt[b,c,1], Marco Braun[b,c], Alexander Colsmann[a,c], Uli Lemmer[a,c,*], Heinz Kalt[b,c]

[a] Light Technology Institute, Karlsruhe Institute of Technology (KIT), Engesserstr. 13, 76131 Karlsruhe, Germany
[b] Institute of Applied Physics, Karlsruhe Institute of Technology (KIT), Wolfgang-Gaede-Str. 1, 76131 Karlsruhe, Germany
[c] DFG-Center for Functional Nanostructures (CFN), Karlsruhe Institute of Technology (KIT), Wolfgang-Gaede-Str. 1, 76131 Karlsruhe, Germany

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ABSTRACT

We present fully solution processable hybrid electrodes comprising highly conductive poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) layers and hydrothermally grown zinc oxide nanorods. These electrodes exhibit conductivities of about 1400 S/cm and a transmittance of more than 80%. By incorporating these electrodes into inverted polymer photovoltaic devices, power conversion efficiencies of 1.6% are achieved. Charge carrier lifetime measurements by means of impedance spectroscopy indicate an improved charge carrier extraction from the device upon the incorporation of the nanorod array.

1. Introduction

Organic photovoltaic devices are commonly considered as potential low-cost alternatives as compared to their inorganic counterparts. The concept of bulk heterojunction absorber blends from intermixed polymeric donors and fullerene acceptors allows for power conversion efficiencies exceeding 8% [1]. Due to the large interface within the polymer/fullerene network, photo-generated excitons can be dissociated efficiently. With respect to efficient charge carrier extraction, however, this absorber system suffers from bimolecular recombination, when photogenerated charge carriers travel through the self-organized bi-continuous polymer/fullerene network. In order to promote the formation of suitable charge carrier transport domains, the incorporation of nano-scaled rods has been discussed intensively [2].

Inorganic n-type semiconductors such as zinc oxide (ZnO) have been widely investigated as electron transport materials since their shape can be tailored on the nanoscale. So far, one of the most promising approaches to improve the charge collection efficiency of bulk heterojunction photovoltaic devices is the incorporation of ZnO nanorod arrays into the absorber bulk. These arrays are commonly grown on a dense ZnO seed layer covering a transparent indium tin oxide (ITO) electrode [3,4]. With respect to potentially lower module costs per watt peak and future device fabrication through low-cost printing processes, solution deposited electrode systems are widely preferred over costly sputter deposited ITO electrodes. The solution processable polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) has proven itself to be an appropriate alternative electrode material for both anodes and cathodes with conductivities of up to 1400 S/cm [5–7]. ZnO can be deposited from suitable precursor solutions, too [8,9]. The hydrothermal synthesis also allows for low-temperature deposition of ZnO nanorods from aqueous solution on organic layers. Recently, the growth of ZnO nanorods with a length of several micrometer on a PEDOT:PSS electrode was reported allowing for the preparation of hybrid light emitting devices [10,11]. The deposition of ZnO nanorods requires the deposition of a ZnO seed layer that was formed in Ref. [11] by repeatedly spin-coating ZnO nanoparticles onto the substrate.

In this work, we present dense ZnO nanorod arrays with an average length of less than 100 nm, which are hydrothermally grown on highly conductive PEDOT:PSS electrodes at low temperatures. We use a ZnO precursor allowing for the formation of a nanoparticulate ZnO layer directly on the substrate thereby avoiding the separate synthesis of ZnO nanoparticles and their challenging deposition as

* Corresponding authors at: Light Technology Institute, Karlsruhe Institute of Technology (KIT), Engesserstr. 13, 76131 Karlsruhe, Germany.
E-mail addresses: manuel.reinhard@kit.edu (M. Reinhard), uli.lemmer@kit.edu (U. Lemmer).
[1] These authors contributed equally to this work.

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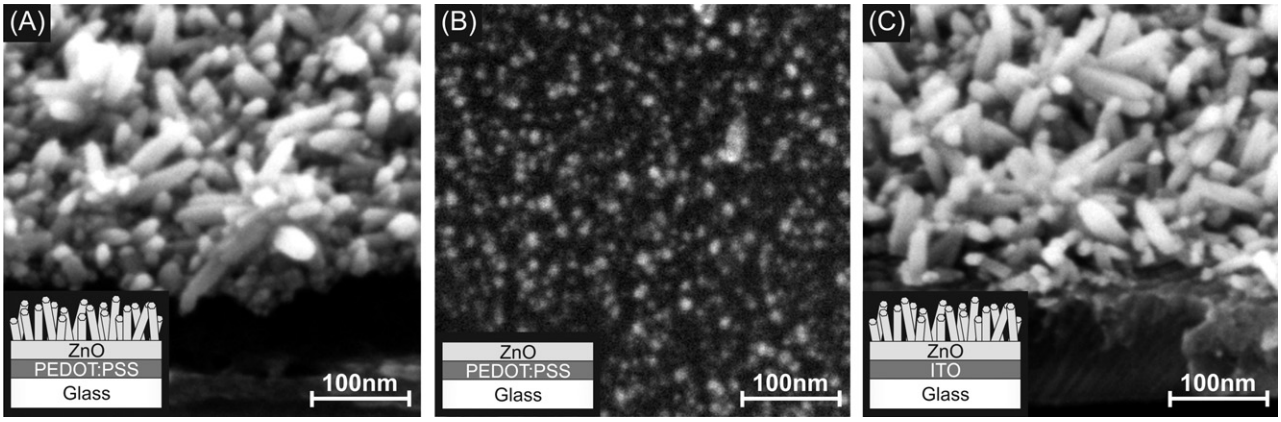

Fig. 1. SEM images and schematic drawings (inset) of the investigated electrodes (A) highly conductive PEDOT:PSS/ZnO layer/ZnO rods (45° side view), (B) highly conductive PEDOT:PSS/ZnO layer (top view), and (C) ITO/ZnO layer/ZnO rods (45° side view).

a thin, dense and covering layer. On these PEDOT:PSS/ZnO nanorod hybrid electrodes we fabricate inverted P3HT:PCBM solar cells with power conversion efficiencies of $\eta \approx 1.6\%$.

2. Experimental

Solution processable hybrid electrodes were prepared by first applying a highly conductive PEDOT:PSS electrode following a previously published route [5]. Briefly, PEDOT:PSS (Heraeus, Clevios PH1000) was mixed with 5 vol% dimethylsulfoxide (DMSO) and 13 vol% isopropanol and spin-coated twice onto pre-cleaned glass substrates. Following the process described by Kim et al. the samples were then immersed into a DMSO bath for 3 min and annealed at 130 °C for 3 min in order to further increase the conductivity [7]. Subsequently, a dense ZnO layer was deposited by spin-coating a filtered zinc acetylacetonate hydrate/ethanol solution (20 g/L), followed by thermal annealing in ambient conditions at 120 °C for 30 s as described in Ref. [9]. This ZnO layer served as both, a seed layer for the following hydrothermal growth of ZnO nanorods and an electron transport layer.

The ZnO nanorods were hydrothermally grown directly onto the substrate, using an equimolar aqueous solution of zinc nitrate (0.25 mM) and hexamethylenetetramine, as presented in Refs. [12,13]. During the deposition the substrates were mounted headlong onto a polytetrafluoroethylene sample holder in order to avoid contamination from precipitates and from the sample holder itself. The solution was kept in a closed crystallizing dish in a precision circulating air oven for 18 min at 95 °C until rods with a length of up to 100 nm were formed. The samples were then removed from the solution and rinsed several times with bi-distilled water prior to blow-drying with nitrogen.

After the synthesis of the nanorods, the substrates were transferred into a glovebox and kept under nitrogen atmosphere (<1 ppm O_2 and H_2O) for the remaining deposition process. Polymer solar cells were fabricated by spin-coating a blend from poly-(3-hexylthiophene-2,5-diyl) (Rieke Metals) and [6,6]-phenyl C_{61}-butyric acid methyl ester (Solenne) (P3HT:PCBM, 40 g/L, 1:0.9 by weight) at 1000 rpm from o-dichlorobenzene solution. The layers were dried slowly under Petri dishes in order to enhance the crystallinity of the blend and the infiltration into the nanorod arrays. Then, the top electrode was deposited by thermal evaporation of 10 nm molybdenum trioxide (MoO_3) and 200 nm aluminum through a shadow mask. The cross-section of both electrodes defined an active area size of 0.24 cm^2. For reference purposes, devices with ITO electrodes were fabricated as well as devices comprising PEDOT:PSS/ZnO electrodes without ZnO nanorods. Three devices of each solar cell configuration were prepared in order to provide a reliable data basis.

Current density–voltage (*JV*) characteristics were recorded under ASTM G-173-03 AM1.5 illumination (100 mW/cm^2) from a spectrally monitored Oriel 300 W solar simulator. Scanning electron microscope (SEM) images were captured with a Zeiss Supra 55 VP. Transmittance spectra were recorded using a Perkin Elmer Lambda 1050 UV/VIS/NIR spectrometer equipped with an integrating sphere in order to collect both direct and scattered light. Sheet resistances were measured with a digital multimeter. For the determination of layer thicknesses a Bruker DektakXT profilometer was used. Bias- and frequency-dependent impedance measurements under dark conditions were performed in the frequency range from 1 MHz to 10 Hz on a Novocontrol Alpha-H dielectric analyzer with an AC-oscillating amplitude of 20 mV (rms).

3. Results and discussion

For a better understanding of the optoelectronic device properties, we investigate and compare three different kinds of electrodes: (A) electrodes comprising PEDOT:PSS/ZnO/ZnO nanorods as described above, (B) electrodes from PEDOT:PSS and a plane ZnO layer and (C) electrodes incorporating ITO/ZnO/ZnO nanorods. Fig. 1 depicts SEM images and schematic drawings of the respective layers.

The hybrid electrodes comprising highly conductive PEDOT:PSS charge transport layers and ZnO layers deposited from the precursor solution are shown in Fig. 1B. The ZnO precursor solution forms a layer comprising small particles and crystalline agglomerates on top of the spin-coated PEDOT:PSS layer. Due to the formation of small ZnO nanocrystallites with a diameter of a few nanometers, the growth of very thin and dense ZnO nanorod arrays is enabled, as visible in Fig. 1A. The average rod length was less than 100 nm allowing for the subsequent deposition of a P3HT:PCBM bulk heterojunction with a reasonable thickness of less than 200 nm that fully covers the tips of the rods and hence prevents shortcuts between the two electrodes. The nanorods are randomly oriented due to the roughness of the underlying seed layer. This is not considered as drawback as the nanorods still effectively serve as electron transport pathways. Since the average shape and the dimensions of the nanorods are identical for both PEDOT:PSS (Fig. 1A) and ITO (Fig. 1C) coated substrates we can conclude that the ZnO seed layer enables the growth of the nanorods and strongly determines their shape.

The PEDOT:PSS bottom layers exhibit sheet resistances of about 45 Ω/□. Their layer thickness can be determined from the cross-section in Fig. 1A and from profilometer measurements