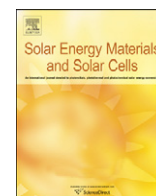




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CuInS₂-Poly(3-(ethyl-4-butanoate)thiophene) nanocomposite solar cells: Preparation by an in situ formation route, performance and stability issues

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ABSTRACT

In this contribution we present an in situ method for the preparation of CuInS₂-poly(3-(ethyl-4-butanoate)thiophene) (P3EBT) nanocomposite layers and their application in nanocomposite solar cells. A precursor solution containing copper and indium salts, thiourea and the conjugated polymer was prepared in pyridine, which was coated onto glass/ITO substrates followed by a heating step at 180 °C. The heating step induced the formation of the CuInS₂ nanoparticles homogeneously dispersed in the conjugated polymer matrix. The formation of the nanocomposite was investigated in situ by X-ray scattering techniques and TEM methods showing that nano-scaled CuInS₂ was formed. By addition of small amounts of zinc salt to the precursor solution, zinc containing CuInS₂ (ZCIS) was formed. ZCIS-P3EBT active layers exhibited higher V_{OC} than CuInS₂-P3EBT layers and showed efficiencies of about 0.4%. Additionally the stability of the solar cells was tested over a time scale of 172 h.

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1. Introduction

Polymer based solar cells have been investigated extensively in recent years and gained remarkable power conversion efficiencies (PCEs) exceeding 7% [1] and their commercialization has already set in. The use of polymer processing technologies and the low consumption of materials, due to the high absorption coefficients of conjugated polymers, are major advantages, which allow a fast and inexpensive production of fully flexible roll-to-roll photovoltaic modules on a large scale [2]. The best investigated and developed

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systems are based on blends of conjugated polymers and soluble fullerene derivatives [3,4]. Alternatively, nanoparticles of inorganic semiconducting materials are used instead of fullerene derivatives. This has the advantage that semiconductors with an appropriate band gap to absorb light in the range of the solar spectrum can significantly contribute to charge generation [5–7]. The approach allows an almost infinite number of combinations of inorganic and organic semiconductors. Additional tuning parameters arise from the structural and morphological variety of inorganic nanostructures as the shape of the semiconductor – i.e. spherical, rod-like, rectangular, and branched crystals – and the size of the structures can be tuned and influence the optical and electrical properties of the active layer. Examples for inorganic semiconductors absorbing in the VIS or NIR range of the spectrum used for nanocomposite solar cells are CdSe [8–10], CdS [11–14], CdTe [15,16], CuInS₂ [17], CuInSe₂ [17], PbS [18,19], and PbSe [20]. Recently, PCEs of nanocomposite solar cells based on CdSe-nanostructures have exceeded values of 3% [21].

Mainly three synthetic strategies are used to prepare organic-inorganic hybrid photovoltaic materials: in the first route the inorganic nanocrystals are prepared separately and are then mixed with the organic semiconductor. The synthesis of nanoparticles often involves the application of a capping ligand to prevent particle

agglomeration, acting as a high barrier for exciton dissociation and charge transport, and cannot be easily removed in many cases. A further method involves the creation of inorganic nanostructures on the electrode surface, e.g. aligned nanorods followed by infiltration with the polymer. The third strategy is the in situ formation of inorganic nanostructures directly within the polymer matrix. Major advantages of the latter one are that no separate nanoparticle synthesis step is necessary and no capping agents are used in this method. Thus, an intimate contact of both semiconductors is realized.

In situ formation of the inorganic structure directly in the polymer layer for hybrid-photovoltaic application has already been demonstrated for titania- and zinc oxide-conjugated polymer blends [22,23]. The nanoparticles of CdS-poly(3-hexylthiophene) solar cells with PCEs of 3.1%, reported by Liao et al., [24] have been directly prepared in a solution containing the polymer. During the reaction, the polymer acts as capper and prevents extensive particle growth. The solution is then used for coating the active layer of the solar cells. A similar method was also used for the preparation of PbS/poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) solar cells [25].

In this contribution an in situ formation route is used to prepare copper indium disulfide-poly(3-(ethyl-4-butanoate)thiophene) (P3EBT) nanocomposite layers directly on transparent indium tin oxide (ITO) electrodes. For this purpose, a precursor solution containing metal salts and thiourea in pyridine is applied onto ITO coated glass substrates. A subsequent heating step decomposes thiourea, which leads to the formation of the metal sulfide-polymer nanocomposite layer. This route is well known for the preparation of metal sulfides [26,27]. In this contribution we show that the method can also be used for the direct preparation of CuInS_2 nanostructures in the presence of a conjugated polymer at temperatures below 200 °C, which is compatible with the thermal stability of many conjugated polymers and polymer substrates. However, limitation for this approach is that all components must be dissolved in one solution before coating. Therefore, we selected poly(3-(ethyl-4-butanoate)thiophene) (P3EBT), a polythiophene with a polar side group, which is necessary to ensure a homogeneous precursor solution of the polymer and the inorganic salts. In the first part we focus on the investigation of the CuInS_2 formation in the layer, in the second part we discuss the application of the materials in nanocomposite solar cells and their stability.

2. Experimental

2.1. Materials and preparation protocols

Copper-I-acetate ($\text{Cu}(\text{Ac})$ 97%), indium-III-chloride (InCl_3 , 99.999% trace metal basis), zinc acetate ($\text{Zn}(\text{Ac})_2$, 99.99% trace metal basis) thiourea (TU, 99.0%), and pyridine (99.9%) were purchased from Sigma-Aldrich. Poly(3-(ethyl-4-butanoate)thiophene) (P3EBT) was acquired from Rieke Metals Inc. All chemicals were used without further purification unless otherwise stated. Indium-tin-oxide (ITO)-coated glass slides with a surface resistivity of 15–25 Ω/sq . were received from Delta Technologies Ltd.

For the preparation of the precursor solutions, the metal salts as well as thiourea were dissolved in various ratios in pyridine and stirred until a yellowish, clear solution was obtained. P3EBT was added to this solution ($c(\text{P3EBT})=6 \text{ mg/mL}$). The anticipated polymer/ CuInS_2 ratio was 1/3 (w/w) in all samples, the Cu/In ratios were varied from 1/1 to 1/2.5 (mol/mol) and 5 equivalents (compared to Cu) of TU were used. For the preparation of CuInS_2 containing small amounts of Zn (ZCIS) 0.05–0.5 equivalents Zn compared to Cu were added additionally. The mixture was heated to 50 °C until a clear, orange solution was obtained. In the case of the XRD- and TEM-samples, the precursor solution was coated onto different substrates (glass-ITO, soda-lime

glass, NaCl-single crystal, depending on experiment), and heated in a tube-furnace (Heraeus Ro 4/25, Heraeus Re 1.1 controller) under vacuum to 180 °C (standard heating rate: RT to 80 °C within 3 min, 80 to 180 °C within 20 min, 10 min hold time at 180 °C). Afterwards, the tube was removed from the furnace, flooded with nitrogen, and cooled down to ambient temperature within 30 min.

For the preparation of the nanocomposite layers, glass/ITO substrates were cleaned in deionized water followed by isopropanol using an ultrasonic bath. The nanocomposite layer was prepared by spin coating of the precursor solution using a Karl Süss CT 62 spincoating unit followed by a heating step in a tube-furnace (Heraeus Ro 4/25, Heraeus Re 1.1 controller) under vacuum at 180 °C (standard heating rate).

Al-cathodes were deposited onto the nanocomposite layer by thermal evaporation of the metal using a BalTec MED-010 or a BalTec MED-020 evaporation unit. Film thickness (typically 100 nm) was determined by means of a quartz micro-balance, the cathode area was 10 mm^2 .

2.2. Characterization techniques

Temperature dependent in situ powder-diffraction measurements were performed with a Bruker D8 Discover diffraction unit with Bragg-Brentano configuration using a monochromatized copper source (wavelength 0.154 nm). The samples were prepared by air brushing the precursor solution onto a monocrystalline silicon wafer and measured in the temperature attachment DHS900 (Anton PAAR GmbH, Austria) [28]. Data were analyzed using Bruker Diffrac-PLUS 2006 software.

2D grazing incident small angle X-ray scattering (GISAXS) measurements were performed at the Austrian SAXS Beamline 5.2L of the electron storage ring ELETTRA (Italy) [29]. The beamline has been adjusted to a q -resolution ($q=4\pi/\lambda \cdot \sin(2\theta/2)$) between 0.1 and 3.1 nm^{-1} using an X-ray energy of 8 keV. The glass/ITO/precursor-substrates were placed in a custom made sample cell with a grazing angle of about 0.18° and were heated from 40 up to 180 °C at a heating rate of approx. 8 °C/min in vacuum. During the temperature scan, data were recorded with 5 s resolution.

SEM micrographs and SEM-EDX measurements were performed on a high-resolution scanning electron microscope (HR-SEM Zeiss ULTRA 55) equipped with a Röntec EDX XFlash 3001 detector. Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were acquired on a Tecnai F 20 microscope (FEI Company) with a Schottky emitter, a Gatan GIF Quantum energy filter system and an UltraScanCCD camera.

UV-vis spectra were acquired using a Shimadzu UV-1800 spectrophotometer.

Electron impact (EI, 70 eV) high resolution mass spectra (HRMS) were recorded on Waters GCT Premier equipped with direct insertion (DI). Data were analyzed using Waters MassLynx software.

I - V curves were obtained under N_2 -atmosphere in a glovebox using a Keithley-2400 source measurement unit operated by a custom made LabView software. The solar cells were illuminated using a Philips 150 W GX5.3 Focusline halogen bulb (no spectral mismatch correction). Homogeneity was ensured using several scattering disks, intensity of the incoming light was set to 60 mW/cm^2 (determined using a KippZonen-CMP-11 pyranometer).

3. Results and discussion

3.1. Investigation of the in situ formation of the nanocomposite films

The CuInS_2 -acceptor phase was obtained by thermal decomposition of the sulfur source during a moderate annealing step ($T \leq 200 \text{ °C}$, $p = 10 \text{ mbar}$, compare Scheme 1). Thermally generated

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