Metal sulfide–polymer nanocomposite thin films prepared by a direct formation route for photovoltaic applications

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ABSTRACT

Blends of conjugated polymers and inorganic semiconductors are an interesting class of materials with various applications in the field of plastic electronics. This work presents a direct approach to obtain composites consisting of a conjugated polymer, poly(3-(ethyl-4-butanoate)thiophene) (P3EBT), and a sulfur-based semiconductor (i.e. CdS, PbS or ZnS) using an in-situ formation route. The metal sulfide semiconductor is formed by reaction of the corresponding metal salt (cadmium acetate, zinc acetate or lead thiocyanate) dispersed within the conjugated polymer matrix with thiourea at temperatures below 200 °C. Nanoscaled networks are formed in the case of the CdS- and ZnS-P3EBT composites as shown by X-ray diffraction and transmission electron microscopy investigations, whereas the PbS-P3EBT blend exhibits inorganic structures on the μm-scale. The materials were used as active layer in bulk-heterojunction type hybrid solar cells. First photovoltaic devices containing an active layer of CdS- or ZnS-P3EBT show photovoltaic action, though efficiencies are low ($\leq 0.06\%$).

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1. Introduction

The need for energy resources alternative to fossil fuels makes photovoltaics extremely attractive for industry and scientific research. In recent years polymer based solar cells have gained remarkable power conversion efficiencies (PCEs) exceeding 6% [1,2] and their commercialization has already set in [3]. The use of polymer processing technologies and the low consumption of materials are major advantages, which allow the roll-to-roll production of fully flexible photovoltaic modules on a large scale. The best investigated and developed systems are based on blends of conjugated polymers and soluble fullerene derivatives [4,5]. Theoretical considerations predict PCEs up to 10% for these systems [6,7]. In these material combinations, the absorption of light leads to the formation of excitons [8,9]. Assuming an exciton binding energy of a few tenths eVs, only an infinitesimal fraction of the excitons is directly convertible into extractable charge carriers in the absence of a suitable acceptor phase for electrons, and therefore, fullerenes are used as effective electron acceptors. A major criterion for the bulk-heterojunction approach is an optimized phase separation on the nanoscale of the donor (polymer) and the acceptor phase (fullerene). The optimum morphology consists of an interpenetrating network ensuring a high interfacial area needed for charge separation and continuous pathways to the electrodes to optimize charge transport [10,11].

As an alternative, organic–inorganic hybrid materials consisting of an organic donor and a nanostructured inorganic acceptor can be used as active layer in plastic photovoltaics [12–14]. This approach allows an almost infinite number of combinations of inorganic and organic semiconductors. Using inorganic nanostructures, additional tuning parameters are the shape of the semiconductor — i.e. spherical, rod-like, rectangular, and branched crystals — and the size of the structures due to quantum confinement effects [15]. Examples for already realized combinations are blends of a conjugated polymer and nanocrystals of CdSe [16,17], CdS [18], ZnO [19,20], $Zn_{1-x}Mg_xO$ [21], CdTe [22,23], InAs [24], $CuInS_2$ [25], $CuInSe_2$ [26], PbS [27,28], PbSe [29], or TiO_2 [30,31]. Power conversion efficiencies of hybrid plastic solar cells are inferior compared to fullerene based devices reaching efficiencies of about 2.5% [12]. Very recently, PCEs of nanocomposite solar cells based on CdSe-nanostructures have exceeded values of 3% (3.13%) [32]. We attribute the lower PCEs of hybrid solar cells compared to fullerene-polymer solar cells to the following reasons: (1) preparation of semiconductor nanoparticles and nanostructures often involves the application of a

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surfactant (capper) to prevent particle agglomeration, acting as a high barrier for exciton dissociation and charge transport, which cannot be easily removed in many cases; (2) a high surface-to-volume ratio leads to high concentration of surface defects and, (3) compared to fullerene-polymer solar cells, only a fraction of manpower has worked on hybrid photovoltaics, especially when the manifold possibilities of materials combinations are considered.

Most research groups pursue one of the following three synthesis strategies for organic–inorganic hybrid-photovoltaic materials: (1) the synthesis of inorganic nanocrystals, which are then mixed with the organic semiconductor, (2) the creation of inorganic nanostructures on the electrode surface, e.g. aligned nanorods, subsequently infiltrated with the polymer, and (3) the in-situ formation of inorganic nanostructures within the polymer matrix. The major advantages of the latter one are that (1) no separate nanoparticle synthesis step is necessary and (2) no capping agents to prevent agglomeration of nanoparticles are used in this method.

In-situ-formation for hybrid-photovoltaic application has been demonstrated for titania- [33] and zinc oxide-conjugated polymer blends [34,35]. In addition, several papers report on the optical properties of metal–sulfide-conjugated polymer composites using a direct synthesis route, e.g. (poly 3-hexylthiophene)-ZnS using Na_2S as sulfur source [36] or poly(3-octylthiophene)-MeS (Me = Zn, Cd, Cu) composites prepared by Langmuir–Blodgett-techniques and gaseous H_2S as sulfurisation reagent [37]. Alternatively, thioacetamide was used as sulfur source, as e.g. realized in the preparation of CdS-polyvinylpyrrolidone blends in a recent study [38]. Very recently, Liao et al. reported CdS-poly(3-hexylthiophene) nanocomposite solar cells with PCEs up to 3% by preparing CdS nanoparticles directly in the polymer solution from cadmium acetate and elemental sulfur. During the reaction, the polymer acts as capper and prevents extensive particle growth. These solutions were then used for the preparation of solar cells [39].

This contribution introduces a facile preparation method to obtain thin films consisting of metal sulfide-poly(3-(ethyl-4-butanoate)thiophene) (P3EBT)-blends starting from metal salts and thiourea dispersed within the polymer. The sulfur is supplied by the thermal decomposition of thiourea, a well established and very commonly used method to obtain inorganic sulfide semiconductors [40,41]. The reaction takes place at temperatures below 200 °C, which is compatible with many electroactive polymeric materials and flexible substrates. In this study we focus on the preparation and morphological characterization of ZnS, CdS and PbS–polymer nanocomposites. For one specific composite — CdS-P3EBT — we also demonstrate the applicability of such composites in hybrid solar cells.

2. Experimental details

2.1. Materials

Cadmium acetate hydrate ($Cd(Ac)_2 \times nH_2O$, 99.99%), lead thiocyanate ($Pb(SCN)_2$, 99.99%), zinc acetate ($Zn(Ac)_2$), 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. Indium-tin-oxide (ITO)-coated glass slides with a surface resistivity of 20 Ω/sq. were received from Delta Technologies Ltd. Water content in cadmium acetate hydrate was determined to be 7.8%, corresponding to $Cd(Ac)_2 \times 1.08$ H_2O by Karl–Fischer titration. All chemicals were used without further purification.

2.2. Preparation of the nanocomposite layers

For the precursor solutions, the corresponding metal salt was dissolved in pyridine and stirred until a colorless, clear solution was obtained [$c(Cd(Ac)_2 \times 1.08 H_2O = 41.5$ mg/mL (0.17 mmol/mL); $c(Pb(SCN)_2 = 32.6$ mg/mL (0.10 mmol/mL); $c(Zn(Ac)_2 = 45.3$ mg/mL (0.25 mmol/mL)]. P3EBT was added to this solution, $c(P3EBT) = 6$ mg/

mL). The mixture was heated to 50 °C until a clear, orange colored solution was obtained. Finally, fivefold excess of thiourea was added to the metal salt - polymer solution ($c(TU) = 0.84$ mmol/mL; $c(TU) = 0.50$ mmol/mL; $c(TU) = 1.23$ mmol/mL for the CdS, PbS and ZnS precursor solution, respectively). In the case of the samples prepared for X-ray diffraction and transmission electron microscopy measurements, the precursor solution was diluted 1/1 (vol.) with pyridine. The precursor solution was coated onto different substrates (glass-ITO, borosilicate glass, NaCl-single crystal, depending on experiment), and heated in a tube-furnace under vacuum to 180 °C (heating rate: room temperature $\xrightarrow{3\ min}$ 80 °C $\xrightarrow{20\ min}$ 180 °C $\xrightarrow{10\ min}$ 180 °C). Afterwards, the tube was flooded with nitrogen, removed from the furnace and cooled down to ambient temperature within 30 min.

2.3. Characterization methods

Powder-X-ray diffraction (XRD) measurements were performed on a Siemens D-5005 powder-diffractometer (theta-theta geometry, Cu-K_α-radiation). Rietveld analysis was performed using Bruker-TOPAS software. For sample preparation, precursor solutions were drop-coated onto borosilicate glass slides. Samples were heated according to the procedure described above. As prepared layers were scraped off and placed on a silicon sample holder.

The diameters of the crystallites were estimated according to the broadening of the diffraction peaks using the Scherrer relationship (Eq. (1)):

$$D_{XRD} \approx \frac{K * \lambda}{\Delta(2\theta) * cos\theta} \tag{1}$$

with $\Delta(2\theta)$ is the full width at half maximum (FWHM) of the peak in radians, θ is half of the scattering angle 2θ, λ the wavelength of the X-rays, and K is the shape factor (K = 0.9 for spherical particles).

Transmission electron microscopy (TEM) investigations and selected area electron diffraction (SAED) patterns were acquired with a Tecnai 12 microscope (FEI Company, 120 kV, LaB_6 Cathode). High resolution TEM-micrographs were obtained using a Tecnai F 20 microscope (FEI Company, 200 kV, Schottky emitter) equipped with a monochromator (FEI Company), a Gatan energy filter system and an UltraScan CCD camera. For sample preparation, the precursor solutions were spin coated onto NaCl-single crystals which were consecutively heated as described. After cooling to ambient temperature, NaCl substrates were dissolved in distilled water, and the floating nanocomposite films were collected using a Ni-TEM grid.

Atomic force microscopy (AFM) images were recorded using a Veeco NanoMan VS Scanning Probe Microscope. Measurements were taken directly from the surface of the nanocomposite solar cells in the areas between the metal contacts.

UV–Vis spectra were collected using a Shimadzu UV-1800 spectrometer.

2.4. Preparation of nanocomposite solar cells

ITO-glass substrates were coated by spin coating of the precursor solution at ambient conditions and subsequently heated as described above. After cooling down to ambient temperature, aluminum cathodes (thickness: 200 nm; electrode area = 0.1 cm^2) were evaporated at a base pressure of approx. 3×10^{-6} mbar using a Bal-Tec MED-020 evaporation unit. Current–voltage curves were measured under N_2-atmosphere using a Keithley-2400 sourcemeter, samples were illuminated by a halogen lamp ($P_{in} = 100$ mW cm^{-2}, the illumination power was determined using a calibrated KippZonen CMP-11 pyranometer, no spectral mismatch correction).