

Organic-Inorganic Semiconductor Blends for Photovoltaic Applications

Sonja Larissegger^(1,2), Michael Edler^(1,2), Achim Fischereeder^(1,2), Andreas Pein^(1,2), Thomas Rath^(1,2), Eugen Maier⁽²⁾, Wernfried Haas^(1,3), Gernot Mauthner^(1,4), Ferdinand Hofer⁽³⁾, Emil List⁽⁴⁾, Gregor Trimmel^(1,2)

(1) Christian Doppler Pilotlaboratory for Nanocomposite Solar Cells

(2) Institute for Chemistry and Technology of Materials (ICTM), Graz University of Technology

(3) Institute for Electron Microscopy and Fine Structure Research (FELMI), Graz University of Technology

(4) NanoTecCenter Weiz Forschungsgesellschaft mbH (NTC)

Introduction

The field of organic photovoltaic's has attracted considerable interest during the last two decades. Advantages like low consumption of materials, cheap (roll to roll) production as well as construction of flexible devices are contrasted by a power conversion efficiency (PCE) yet to low for practical applications and problems with long term stability. Within the numerous materials combinations possible for organic solar cells, our group's focus lies on hybrid architectures, where a conjugated organic polymer and an inorganic semiconductor make up the active layer. Obtaining the blend can be achieved in various ways.^[1] Network formation, penetration of phases and especially the organic – inorganic interface are key issues to achieve high PCE.

In this contribution we present a novel method to prepare nano-scaled inorganic semiconductors directly within a matrix of a conjugated polymer, resulting in a network of organic donor- and inorganic acceptor phase.

The key feature of the new method is that the inorganic phase is created directly within the conjugated polymer; laborious preparation of the inorganic nanoparticles is circumvented and a good interface between organic and inorganic phase is achieved.

In-Situ Formation of Sulfur Based Semiconductors within a Polymer Matrix

Using this novel method the nanoparticles (PbS, CuInS₂, ZnS and CdS) were obtained in-situ by reaction of metal salts together with a sulfur source within a matrix of a conjugated polymer. We used a solution of either Pb(SCN)₂, CuI and InCl₃, ZnAc₂ or CdAc₂ with Thiourea (TU) in Pyridine. After the metal salts were completely dissolved the conjugated polymer Poly[3-(ethyl-4-butanoate)thiophene-2,5-diy] (P3EBT) was added. Afterwards the solution was coated onto suitable substrates (depending on type of experiment). Applying a moderate annealing step (temperatures in the range of 160-200 °C) under inert gas conditions the sulfur, released by decomposing TU, is reacting with the metal ions to produce the metal sulfide within the matrix of the conjugated polymer (Fig. 1).

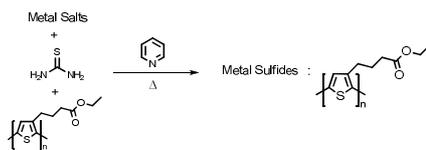


Fig. 1: Reaction scheme of metal sulfide – P3EBT composites

The resulting layers consist of a nano-structured photoactive donor - acceptor blend. As the acceptor phase is obtained directly within the polymer matrix, no precautions in terms of particle agglomeration need to be taken, which makes the use of cappers redundant.

Structural Characterization

The metal sulfide–P3EBT composites were studied using x-ray diffraction (XRD), transmission electron microscopy (TEM) and selected area electron diffraction (SAED). Samples were prepared by air brushing the precursor solution onto a glass substrate (XRD) or spin coating onto a NaCl single crystal (TEM, SAED) followed by thermal annealing at 180 °C for 15 minutes. The diffraction patterns of the nanocomposite layers show that the corresponding metal sulfides are formed (Fig. 2).

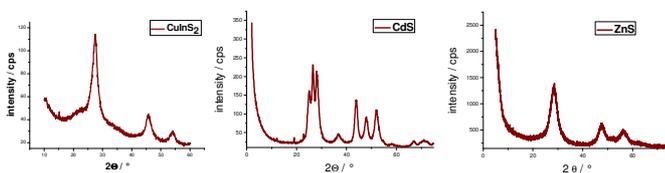


Fig. 2: XRD patterns of CuInS₂, CdS and ZnS in nanocomposite layers

PbS forms very large (diameters up to 2 μm), crystalline particles. Because of this results we focused our resources on the metal sulfides CuInS₂, ZnS and CdS which build up a nanostructured interpenetrating metal sulfide/polymer–network. This is supported by TEM- and SAED-measurements shown in Fig. 3. XRD- and electron diffraction results are both in accordance with literature values. [2-4]

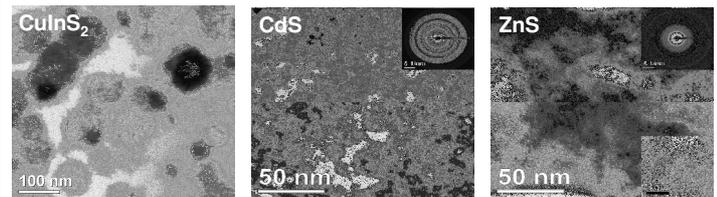


Fig. 3: TEM-image of CuInS₂ and TEM-images and electron diffraction of CdS and ZnS in nanocomposite layers

The TEM images show average particle sizes between 3-5 nm and 2-3 nm for CuInS₂, CdS and ZnS respectively. Similar to the XRD data, analysis of the electron diffraction patterns shows sharper peaks for CdS compared to ZnS caused by a higher crystallinity in the CdS particles. Summing up it can be said that various metal sulfides can be formed within a polymer matrix using the described methods.

Application in Nanocomposite Solar Cells

These devices prepared by a novel method, based on metal sulfides and P3EBT, were investigated in nanocomposite solar cells. For device preparation, a pyridine solution of the metal salt, Thiourea and P3EBT was spin coated on ITO-covered glass substrates, followed by an annealing step at 180 °C for 15 minutes and afterwards evaporation of the cathode (aluminium); device scheme see Fig. 4. The IV-curves, shown in Fig. 5, were collected under inert gas conditions using a tungsten-lamp (P = 100 mW/cm²).

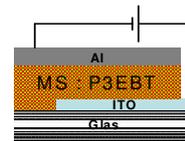


Fig. 4: Device scheme

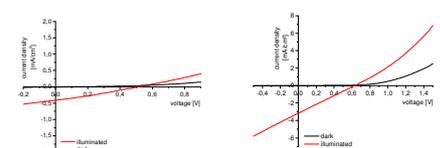


Fig. 5: Typical I/V curve of CdS/P3EBT (left) and CIS/P3EBT (right) solar cells

| metal sulfide | V _{oc} [mV] | I _{sc} [mA/cm ²] | FF |
|--------------------|---------------------------------|---------------------------------------|------|
| PbS | no solar cells were be obtained | | |
| ZnS | 710 | 0,01 | 0,22 |
| CdS | 510 | 0,46 | 0,28 |
| CuInS ₂ | 630 | 3,20 | 0,25 |

Fig. 6: Summarized solar cell parameters

Devices based on ZnS give open circuit voltages up to 710 mV but poor efficiencies. CdS devices reach not so good open circuit voltage as ZnS but they show efficiencies up to approx. 0.1%. CuInS₂-P3EBT devices give a short circuit current up to 3,2 mA/cm² and reaches a efficiency up to approx. 0,6%. As these systems are dominantly influenced by the properties of the metal sulfide particles (size, crystallinity, ...), which can be varied by the preparation conditions, further optimization has to be done to obtain an ideal donor/acceptor network for applications in hybrid photovoltaic's, leading to higher efficiencies.

References / Acknowledgements

- [1] Saunders, B. R.; Turner, M. L. *Adv. Coll.Int. Sci.* **2008**, *138*, 1.
 [2] Leute, V.; Volkmer, N. *Zeitschrift fuer Physikalische Chemie* **1985**, *144*, 145. [3] Ballentyne, D.W.G.; Roy, B. *Physica* **1961**, *27*, 337.
 [4] Xu, Y. N.; Ching, W. Y. *Physical Review B: Condensed Matter and Materials Physics* **1993**, *48*, 4335.

Financial support by the Christian Doppler Research Association, FFG, ISOVOLTA AG and the Austrian Federal Ministry of Economy, Family and Youth