CIS Plastic Solar Cells

Elif Arici[1], Harald Hoppe[1], Arndt Reuning[2], N. Serdar Sariciftci[1], Dieter Meissner[1]

[1] Linzer Institut für organische Solarzellen, Physical Chemistry, Johannes Kepler University, Linz, Austria

Tel:+43/732/2468-8787, Fax:+43/732/2468-8770, E-mail: elif.arici@jk.uni-linz.ac.at

[2] Institute of Physical Chemistry, Philipps University, Marburg, Germany

Abstract

First attempts were made to combine classical inorganic photovoltaic materials based on the chalcogenides $CuInSe_2$ and $CuInS_2$ with the plasic solar cell polymers MDMO-PPV and P3HT to form bulk heterojunction solar cells. Whereas the synthesis of $CuInSe_2$ did not give the desired nanometer size of particles, $CuInS_2$ was obtained with an average diameter of 5 nm. This size was preserved even in the very high concentrations necessary for efficient charge transport in composite with the two conductive polymers. An effective photoluminescence quenching proved the intimate contact of the two materials. Also devices with only a few ten nanometer thickness were easy to prepare. However, as yet no photovoltaic response was measurable probably due to as yet not sufficient matching of band positions and non ideal contact formation.

Key Words: Organic Solar Cell-1: $CuInS_2$-2: Heterojunction-3

1. Introduction

Plastic Solar Cells [1] provide the possibility of easy and cheap production of large area photovoltaic devices on low cost polymer substrates. Based on interconnected networks of p-type polymers with percolating electron conducting C_{60} derivatives, our group recently achieved more than 2.5 % solar efficiency in devices of less than 100 nm thickness of the absorber layer, in which only a small portion of the solar light is absorbed [2].

The key for improving organic solar cell efficiencies was the fabrication of an interconnected network structure of p- and n-type materials to form a so-called bulk heterojunction. In such devices the flat interface of classical organic solar cells [3a] is replaced by an extremely rough network such as also used in modern sensitization solar cells [3b]. Photoinduced electron transfer has been demonstrated in composites of conjugated polymer/CdS and CdSe nanocrystals [4-5] and conjugated polymer/TiO_2 [6] composites. However, all as yet used materials in such composite structures exhibit relatively low absorption coefficients in the order of only some $10^4 \, cm^{-1}$. Also, their band gap does not match the solar spectrum very well. In order to overcome this problem we decided to replace the electron transporting fullerene derivative by classical semiconductor nanoparticles. A first example of these new devices will be discussed in this paper.

We investigated blends of our classical plastic solar cell polymer poly (2-methoxy-5-(3´,7´- dimethyloctyloxy)-1,4-phenylene vinylene) (MDMO-PPV) and of regioregular poly (3-hexylthiophene) (P3HT) with copper indium diselenide (CISe) and copper indium disulfide (CIS) nanocrystals, one of the best solar absorbers for photovoltaic applications.

2. Experimental

$CuInSe_2$ (CISe) was synthesized by a solvothermal route described by Y. Qian et al [7]. The particles formed are usually crystalline and don't need post-treatment at high temperatures. Also, no organometallic precursor, which can complicate the system, and no organic stabilizers are used in this route. In solvothermal process, the solvent plays an important role in the formation of the chalcopyrite CISe controlling the form of the particles. We used anhydrous ethylendiamine to form elongated particles, because it is an excellent template for the formation of one-dimensional materials [8]. Because of the bidentante N-chelation capability of ethylendiamine, it can effectively form a stable complex of $[Cu(en)_2]^+$ and thereby prevent the formation of binary copper chalcogenides.

A mixture of Se (2.59 mmol), $CuCl_2 \cdot 2\, H_2O$ (1,26 mmol) and $InCl_3 \cdot 4\, H_20$ (1.29 mmol) was loaded into a 50 ml autoclave, which was than filled with anhydrous

ethylendiamine up to 80% of the total volume. The experiment was performed at 180 °C for 15 h. The product was washed with water and ethanol several times in order to remove the by-products, a crystalline, undefined mixture of Cu, In and Se in beige colour. The product was black in colour.

Synthesis of $CuInS_2$ (CIS) particles was performed by a colloidal route [9]. In order to prevent the aggregation of the particles for long time storage the particles were capped with triphenyl phosphite (TPP). (TPP)-capped particles were synthesized using a two step reaction: $InCl_3$ (0.02 mol) and CuI (0.02 mol) were suspended in a mixture of acetonitrile (200 ml) and TPP (10 ml). The solutions were refluxed in an argon atmosphere for 2 hours to form TPP complexed $InCl_3$ and CuI solutions. After both solutions cooled down, bis (tri methyl sillyl) sulfide was added dropwise to the mixture at room temperature. A remarkable colour chance of the solution occurs from colourless through yellow to orange and red depending on the amount of added bis(tri –methylsilyl) sulfide and on the size of the formed CIS particles. The color of the reaction product changed from deep red to dark green by staying for one day under magnetic stirring, indicating an additional growth of the crystal-size during that time. In order to remove the by-products, the precipitate was washed with ethanol several times and stored in ethanol under cooling. To remove TPP before preparing a composite, CIS was suspended in pyridine, washed in an ultrasonic bath for 30 minutes and precipitated by chlorobenzene.

Composite films were prepared by spin coating a chlorobenzene solution of commercially available P3HT, or MDMO-PPV, kindly provided by Coveon, Frankfurt, with semiconductor particles suspended therein without any high temperature treatment. In the case of CISe, the films has a good naked eyes homogenity for a mixture up to CISe : P3HT = 4:1 by weight. Composites with higher CISe concentrations are not transparent. In the case of CIS/P3HT blends we obtained good qualities for films up to weight ratios of CIS:P3HT = 8:1. The highest concentrated films CISe in MDMO-PPV was in a weight ratio of 7:1 (CIS:MDMO-PPV = 10:1).

3. X-Ray studies

The crystallographic structure of the particles were determined by powder X-ray diffraction using Cu K_α radiation of 1.5418 Å. Figure 1 shows the X-ray diffraction pattern of the CISe and CIS. An intense peak at 2θ =26.6° oriented along the (112) direction and other prominent peaks observed at 44.3° ((220) / (204)) and 52.3° ((312)/ (116)) indicate the chalcopyrite structure of CISe. These pattern are in a good agreement with JCPDS data [10a, 10b].

In contrast, the upper plot shows the results of X-ray diffraction investigations performed on the sulfide CIS. The three now broad reflections at 2θ values of 27.9 (112) ,46,5 (220)/(204) and 55.0 (312)/(116) are those of the chalcopyrite structure of CIS. However, in the range between 15 and 35° a broad halo appears, probably due to an amorphous contribution. This may indicate that still TPP is present, which may not have been removed completely.

Apart from this, a comparison of the diffraction pattern clearly shows a pronounced broadening of the CIS diffraction patterns, which can be evaluated to determine
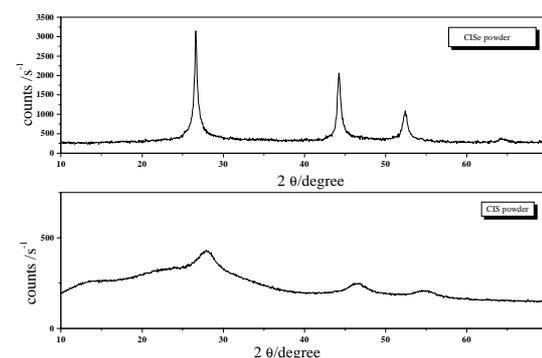

Fig. 1: X-ray diffractogramms of CISe and CIS

the approximate dimensions of the particles using the Scherrer Formula:

$$L = \frac{\lambda}{\Delta'(2\Theta) \cdot \cos\Theta_0}$$

As shown in Table 1 an average size of the CIS particles of ca. 3 nm can be estimated from this analysis.

Table 1: FWHM values of CIS diffraction patterns and the approximate sizes of particles as determined by using the Scherrer formula.

hkl	FWHM of fitting Lorentz curve [deg]	L [nm]	Original FWHM [deg]	L [nm]
112	2,941	2,7	2,407	3,7
220, 204	2,884	2,8	2,738	3,2
312,116	3,590	2,2	2,859	3,1

4. Transmission electron microscopy (TEM) investigations

The morphology and size of the prepared CIS/CISe crystals in polymer blends were studied by transmission electron microscopy on a Jeol 2012 FasTEM at 200 kV. CISe-samples in MDMO-PPV appear to display whisker shaped particles with dimensions of at least 20 nm (Fig.2a). CIS particles in P3HT matrix have also alongated forms with dimensions in the order of 5x20 nm (Fig. 2b). In all cases we found a broad distribution of particle sizes, which can be seen with
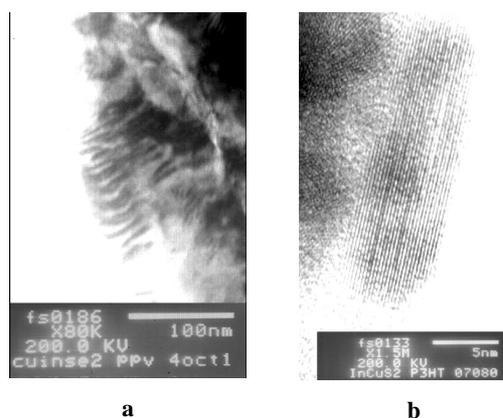

a　　　　　　　**b**

Fig.2: TEM images of CISe (a) and CIS (b) in polymer matrix

crystalline areas up to more than 30 nm. These results may be not in full agreement with the calculated dimensions of CIS by using the Scherrer formula. However, due to the limited resolution of our TEM, very small particles can not be seen here. Therefore the TEM investigation always leads to an overestimation of the average size.

5. Optical Properties

Optical transmission measurements on composite films were carried out using a Varian Cary 3G spectrometer. The shape of the spectra ais given simply by the sum of the absorption spectrum of the polymer and the broad absorbance of the nanoparticles (Fig 4). P3HT shows an absorption maximum centered around 500 nm. There is no indication of a ground state interaction between the polymer and the nanoparticles. We observed no onset of the CIS or CISe absorption in the spectral range between 350 and 900 nm as it would be expected for quantized particles, neither in solution nor in the films.

Figure 4 show the photoluminescence spectra of CISe/P3HT blends of several CISe concentrations including that of the pristine P3HT. Excited at 500 nm, the intensity of the polymer photoluminescence decreases with increasing concentrations of CISe. Note that a maximum photoluminescence quenching is observed for the mixture of CISe/P3HT =2/1. Similar results are observed for a mixture of CIS/P3HT =10/1.

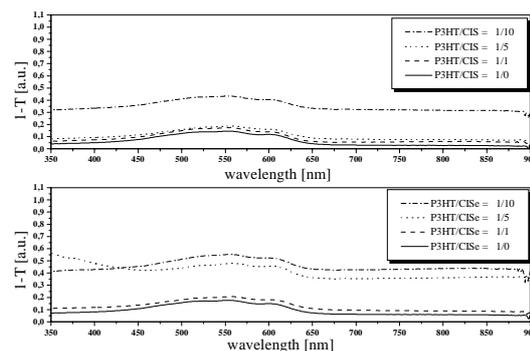The observed quenching is consistent with a rapid charge

Fig. 3: Absorption spectra of CISe and CIS in P3HT

transfer from the photo excited states. Once the singlet exciton has been dissociated, it can no longer decay radiatively to the ground state.

Another possible reason for the photoluminescence quenching may be an energy transfer following the Förster mechanism due to the pronounced overlap of the polymer photoluminescence with the absorption of the particles. Energie transfer can end with nonradiative decay in the nanocrystal. In this case, there is also the possibility of a subsequent hole transfer from the
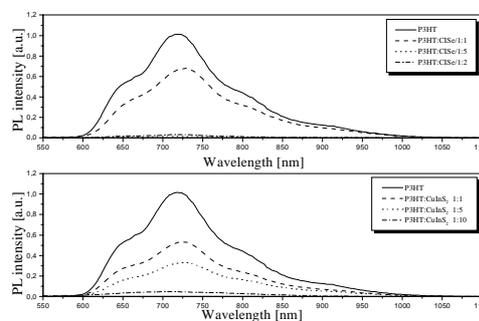

Fig. 4: Photoluminescence of CISe and CIS in P3HT nanoparticles to polymer.

6. Discussion

Based on literature values [11] an energy band diagram of different composite materials is shown in Fig. 5. Exchanging C_{60} derivatives such as PCBM by small band gap materials such as CIS or even CISe requires an extremely careful choice of the corresponding energy band positions. On the one hand side a sufficient driving force is necessary to allow for a charge transfer from the polymer to the nanoparticles as well vice versa. On the other hand a sufficiently large effective band gap must be provided in order to get considerable photo voltages.
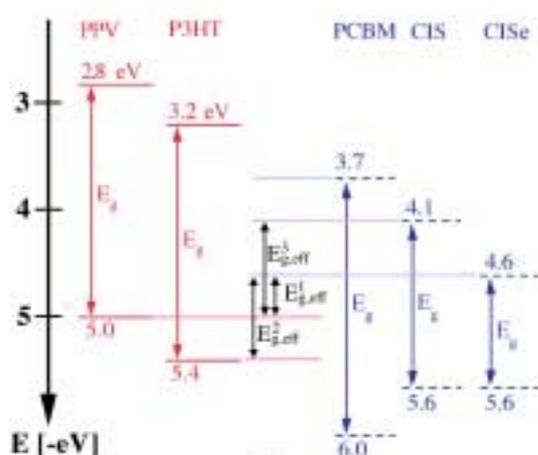

Fig. 5: HOMO and LUMO positions for the materials used as found in the literature [1, 12, 13]

Also, the average distance between formed excitons in one material and the other material should not be larger than the exciton diffusion length (typically 5-15 nm). For an ultrafast charge generation this distance should even be in the range of 1 nm. This requires very small particles, as it is the case for C_{60}-derivatives. For both reasons we expect better results by using the much smaller CIS particles than those we got from CISe.

Unfortunately, photo induced absorption (PIA) measurements for types of particles did not yet show evidence of polaron (a hole in the valence band (HOMO level) of a polymer and corresponding change of surrounding bond lengths) formation in MDMO-PPV or in P3HT. Also, the morphology of the films is not yet favourable for charge transfer due to pronounced clustering of the materials. Although the quenching of the polymer photoluminescence by forming the composite is very encouraging, this may also be due to an energy transfer process caused by the broad overlap of the polymer emission and the nanoparticle absorption. It has not yet been possible to unravel these processes. As a next step we will further investigate flat interface of our materials as has already been started for CISe and polypyrrole [14].

References

[1]   C. J. Brabec, N. S. Sariciftci, J. C. Hummelen, Adv. Funct. Mater. **1** (2001) 15

[2]   S. Shaheen, C. J. Brabec, F. Padinger, T. Fromherz, J. C. Hummelen, N. S. Sariciftci, Appl. Phys. Lett. **78** (2001) 841

[3a]   D. Meissner, D. Wöhrle, Adv. Mater. **30** (1991) 129

[3b]   Christoph J. Brabec, Antonio Cravino, Dieter Meissner, N. Serdar Sariciftci, Adv. Funct. Mater. **11** (2001) 374

[4]   N. C. Greenham, X. Peng and A. P. Alivisatos, Phys. Rew. B vol. 54, **24** (1996) 17628

[5]   N. C. Greenham, X. Peng and A. P. Alivisatos, Synth. Met. **84** (1997) 545

[6]   Q. Fan, B. McQuillin, D.D.C. Bradley, S. Whitelegg, A.B. Seddon, Chem. Phys. Let. (submitted)

[7]   B. Li, Y. Xie, J. Huang, Y. Qian, Adv. Mater. **11** (1999) 1456

[8]   W. Wang, Y. Geng, Y. Qian, M. Ji, X. Liu, Adv. Mater. **10** (1998) 1479

[9]   C. Czekelius, M. Hilgendorff, L. Spanhel, I. Bedja, M. Lench, G. Müller, U. Bloeck, D. Su, and M. Giersig, Adv. Mater. 11 (**1999**) 8, 643

[10a] H. Hwang et al., Thin Solid Films, 67 (**1980**) 83

[10b] D. Suri, K. Nagpal, G. Chadha, J. Appl. Crystallogr. 22 (**1989**) 578

[12]   S. Morita, A. A. Zakhidov, K. Yoshino, Solid State Commun. 4 (**1992**) 249

[13]   H. J. Lewerenz, H. Jungblut: "Photovoltaics", Springer, Heidelberg, Germany, **1995**

[14]   S. Bereznev, J. Kois, E. Mellikov and D. Meissner, these proceedings, paper VA1.19