Organic Electronics 21 (2015) 92–99

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Photovoltaic response of hybrid solar cells with alloyed ZnS–$CuInS_2$ nanorods

Nikolay Radychev *, Björn Kempken, Christopher Krause, Jie Li, Joanna Kolny-Olesiak, Holger Borchert, Jürgen Parisi

University of Oldenburg, Department of Physics, Energy and Semiconductor Research Laboratory, Carl-von-Ossietzky-Str. 9-11, 26129 Oldenburg, Germany

ARTICLE INFO

Article history:
Received 10 January 2015
Received in revised form 26 February 2015
Accepted 27 February 2015
Available online 2 March 2015

Keywords:
ZnS–$CuInS_2$ alloys
Hybrid solar cells
ZCIS nanocrystals
Optical transitions
Cyclic voltammetry
ESR spectroscopy

ABSTRACT

$CuInS_2$ and ZnS are miscible so that quaternary ZnS–$CuInS_2$ alloys can be obtained. This opens the possibility to tune optical properties of the material in a wide range via control of the elemental composition. In the present work, ZnS–$CuInS_2$ nanorods were synthesized by means of colloidal chemistry. Their absorption properties were studied in detail, and different types of optical transitions identified. In view of optoelectronic applications, the nanoparticles were examined for their suitability as absorber material in hybrid polymer/nanoparticle solar cells. Therefore, the nanorods were combined with a common low band gap polymer. Cyclic voltammetry and electron spin resonance were used to study the alignment of the energy levels at the heterojunction as well as the possibility of charge transfer. The material combination forms a type II heterojunction, but with the nanoparticles acting as electron donor material. The blends were implemented in hybrid solar cells. Although the photocurrent density and efficiency achieved were relatively low, the system showed a high open-circuit voltage exceeding the value 1 V.

1. Introduction

Colloidally synthesized semiconductor nanocrystals (NCs) continue to hold considerable attention among the innovative materials for photovoltaic applications [1–6], biomedical labelling [7–10], and light emitting diodes [11–13]. Tuneable optoelectronic features of NCs appear to be the key advantage of their employment in the field of organic/inorganic solar cells. The performance of both hybrid and nanoparticle-based solar cells demonstrated considerable progress in recent years. However, it should be noted that the research generally focused on hybrid blends containing highly toxic cadmium or lead compounds, which are not appropriate for the "green" photovoltaic technology.

A number of important efforts were made to apply more environmentally friendly ZnO [14–16], $CuInS_2$ [17–19] or Cu_2S NCs [20] in hybrid photovoltaic applications, but the energy gap of ZnO nanoparticles does not match the solar spectrum well. In case of Cu-containing NCs, there is no systematic investigation done, and only a few pioneering research documented in literature, including works on $CuInS_2$ NCs synthesized by in situ methods [18]. A promising candidate for inorganic/organic solar cells is quaternary alloys of ZnS and $CuInS_2$ (ZCIS), which belong to the "green" kind of semiconductor materials and exhibit a strong absorption in the visible range. In more detail, the absorption onset as well as the photoluminescence emission wavelength of ZCIS quantum dots can be tuned in a wide wavelength range by adjusting the NCs' size and composition [21–24]. Therefore, ZCIS NCs appear to be a beneficial semiconductor material for hybrid photovoltaic application which in particular has a high potential with respect to band alignment engineering.

In the present article, we report on the colloidal synthesis of the ZCIS NCs with a rod-like shape. The initially stabilized NCs were subjected to a hexanethiol ligand exchange procedure and tested in combination with poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta [2,1-b;3,4-b′]dithiophene)-alt-4,7(2,1,3-benzothiadiazole)] (PCPDTBT) in hybrid solar cells. Comparison of the energy levels determined for the synthesized NCs with the HOMO and LUMO of PCPDTBT shows an uncommon alignment of the energy levels, where ZCIS NCs might play the role of the donor and hole transport material. The photovoltaic performance of the ZCIS/PCPDTBT bulk heterojunction (BHJ) solar cells demonstrates a high open-circuit voltage of 1.15 V, which is state of the art for hybrid photovoltaics. However, we obtained a relatively poor photocurrent in comparison with traditional hybrid solar cells. The limiting factors and possible strategies for improvement of the ZCIS based BHJ solar cells are discussed.

* Corresponding author.
E-mail address: nicolay.radychev@uni-oldenburg.de (N. Radychev).

http://dx.doi.org/10.1016/j.orgel.2015.02.027
1566-1199/

2. Experimental

ZCIS NCs were synthesized by modification of the colloidal method described in detail elsewhere [25]. Briefly, 2.3 mmol zinc acetate, 1.6 mmol copper (I) acetate, 1.1 mmol indium (III) acetate, 16 ml oleic acid, and 10 ml oleylamine were heated together under nitrogen atmosphere to 200 °C. At this temperature, a mixture of 0.25 ml 1-dodecanethiol and 2.5 ml tert-dodecanethiol was quickly injected into the reaction solution, which was subsequently kept at 200 °C for 20 min. After the growth process of the nanorods has been completed, the solution was cooled down to room temperature. ZCIS nanorods were isolated from the side-products of the reaction and unreacted precursors by precipitation with ethanol. The purified precipitate was redissolved in hexane.

The structure of the NCs synthesized was characterized by powder X-ray diffraction (XRD) with a PANalyticalX'Pert PRO MPD diffractometer, while their composition was studied by energy dispersive X-ray spectroscopy (EDX), using a detector integrated into a FEI Quanta 200 3D scanning electron microscope. Rietveld analysis of the XRD pattern was done with the help of the program MAUD [26].

In analogy to ligand exchange procedures reported previously for pure $CuInS_2$ NCs [19], the ZCIS NCs were subjected to a surface modification procedure with hexanethiol. Therefore, the purified ZCIS NCs were precipitated with methanol, and the precipitate isolated by centrifugation was redissolved in hexanethiol (95%, Aldrich) and then heated up under permanent stirring in an oil bath for 24 h at 90 °C. Then, ethanol and acetone were added in excess to precipitate the NCs, and the precipitate was isolated by centrifugation. Afterwards, hexanethiol capped ZCIS NCs were dried under vacuum ($\sim 10^{-2}$ torr) for 30 min, in order to obtain a dry powder. Finally, by applying a sonication procedure under nitrogen atmosphere, the nanocrystals were redissolved in chlorobenzene. The concentration of the colloidal solutions was adjusted to 25 mg/ml.

The optical properties of the ZCIS colloidal solutions have been investigated with a Varian Cary 100 Scan spectrophotometer. The absorption coefficient α was not corrected for reflection. The morphology of the NCs was analyzed with a Zeiss EM 902A transmission electron microscope operating with an acceleration voltage of 80 kV. High resolution TEM (HRTEM) images were taken with a JEOL JEM-2100F microscope at 200 kV.

The electrochemical properties of the ZCIS NCs have been examined by cyclic voltammetry (CV). The measurements were performed in a three-electrode cell based on glassy carbon as working electrode, a platinum wire as counter electrode, and Ag/Ag^+ (Ag wires with 0.01 M $AgNO_3$ in acetonitrile) as reference electrode. The supporting electrolyte consisted of 0.1 M tetrabutyl ammonium hexafluorophosphate ($TBAPF_6$) dissolved in acetonitrile. Colloidal solution of the ZCIS NCs in chlorobenzene was drop-casted on the working electrode and dried under vacuum ($\sim 10^{-2}$ torr) for 30 min. Cyclic voltammograms were recorded on a CH Instruments (CHI660C) electrochemical workstation.

Light-induced electron spin resonance (LESR) measurements have been carried out in a Bruker E500 X-band spectrometer with an attached liquid helium cryostat for sample temperature controlling. All spectra were obtained at 30 K with a maximum temperature variation of 0.2 K during the measurements. The samples were illuminated with 532 nm or 660 nm wavelength from a Coherent Cube semiconductor laser. The laser intensity was set to 20 mW cm^{-2}. Each spectrum obtained consists of 20 scans summed, which evidently improves the signal-to-noise ratio. The ESR samples were prepared via drop casting of the solution on a plastic substrate under nitrogen atmosphere. Finally, the samples were dried and sealed in a quartz tube.

Hybrid blends were obtained by mixing colloidal solutions of the hexanethiol stabilized ZCIS NCs in chlorobenzene with PCPDTBT in a mass ratio of 3:1 (ZCIS:PCPDTBT). With the different densities of ZCIS ($\sim$4.4 g/cm^3) and PCPDTBT ($\sim$1 g/cm^3), this corresponds to a volume ratio of about 40:60 (nanoparticles:polymer), the ligand shell being neglected in this calculation. The ZCIS/PCPDTBT active layer was sandwiched between an ITO-coated glass substrate, covered with a layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Clevios P VPAI 4083) as transparent anode and thermally evaporated Ca/Al layers as cathode. Thereby, the ITO substrates were subjected to structuring and cleaning procedures, as described previously [27]. The interfacial layer of PEDOT:PSS was spin-coated on the cleaned ITO substrate and dried at 180 °C under nitrogen atmosphere for 15 min. The thickness of the PEDOT:PSS layer obtained after annealing was about 30 nm. The active layer has been deposited by spin coating the solutions of ZCIS/PCPDTBT on top of the PEDOT:PSS layer under nitrogen atmosphere in the glove box. The thickness of the active layer was about 80 nm, as measured with a profilometer. Finally, the devices were completed by thermal evaporation of the calcium (15 nm thickness) and aluminum (100 nm thickness) electrodes in vacuum ($\sim 10^{-7}$ torr).

In order to investigate the morphology of the ZCIS/PCPDTBT samples, the active layer was isolated from the solar cells by exposure to water. Water dissolves the underlying PEDOT:PSS layer, so that the active layer floats on the water surface and can be picked up by a TEM grid.

Current–voltage measurements were recorded with a Keithley 4200 source measurement unit. The laboratory solar cells were illuminated with a simulated AM 1.5G spectrum provided by a Photo Emission Tech. solar simulator. The intensity of the incident light of 1000 W/m^2 was calibrated using a monocrystalline Si reference solar cell (Fraunhofer ISE, Freiburg). Spectral mismatch was not taken into account. All current–voltage measurements were carried out at room temperature.

3. Results and discussion

3.1. Structural, optical and electrochemical characterization of the ZCIS nanocrystals

In Fig. 1a, a typical TEM image of the as-synthesized ZCIS NCs (before the ligand exchange procedure) is shown. The NCs, which have nanorod morphology, are uniform in both size and shape. The particles are single crystalline, as can be seen from the HRTEM image in Fig. 1b. In the corresponding fast Fourier transformed (FFT) image (Fig. 1c) we can identify lattice distances of 0.32 nm, 0.24 nm, and 0.18 nm. The determination of the lattice parameters from HRTEM is not possible with enough accuracy to distinguish between ZnS, CIS and an alloy composed of both compounds. Therefore, the crystallographic structure of the nanorods was studied in more detail by X-ray diffraction (Fig. 2). The particles have wurtzite structure and they grow along the *c*-axis. The sizes of the crystallites obtained from Rietveld refinement of the XRD pattern are 26 nm along the *c*-axis and 5.3 nm perpendicular to the *c*-axis, which is in good agreement with dimensions of the nanorods shown in Fig. 1. The lattice parameters of these particles are $a = b = 3.86346$ Å and $c = 6.33097$ Å; these values lie in between those for pure ZnS and CIS, which is an indication for the formation of an alloy between these two materials. Assuming a linear dependence between the lattice parameters and the composition of an alloy (Vegard's law), the fraction of ZnS incorporated into the CIS structure can be calculated [28]. For the case of our particles, this value is 53% ($x = 0.53$ in $(ZnS)_x(CuInS_2)_{1-x}$). In order to confirm this finding, we also measured the composition of the nanorods