

# NANOPOROUS CuInS<sub>2</sub> ELECTRODES FOR HYBRID SOLAR CELLS

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## Abstract

In this contribution, we present a new hybrid solar cell design. CuInS<sub>2</sub> nanoparticles were synthesized using a low temperature colloidal route with organic surfactants to form an inorganic nanoporous hole transporting electrode. A soluble fullerene derivate PCBM (1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6) C<sub>61</sub>) was used for electron transport.

We investigated the photovoltaic performance of the cells consisting of these CuInS<sub>2</sub> and PCBM bilayers with and without a surface-adsorbed RuL<sub>2</sub>(NCS)/TBA(2:2) dye complex (where L= 2,2'-bipyridyl-4,4'-dicarboxylic acid; TBA= tetrabutylammonium). The cells containing the dye showed an improved photovoltaic response.

## 1. Introduction

Nanocrystals of inorganic semiconductor materials have been a topic of intensive research over the last decade. Due to the occurrence of quantum confinement in particles with dimensions smaller than the extension of the excitonic wavefunction, the emission and absorption of semiconductor nanocrystals can be tuned by changing the average particle size

[1,2,3,4]. Together with the flexibility offered by the solution processability, this gives the opportunity to utilize these nanocrystals in different optoelectronic devices as selective absorbers/emitters. In conjunction with organic polymeric semiconductors [5,6] or as nanostructured electrodes together with dye sensitization and an electrolyte [7], these semiconductor nanoparticles can be used to produce thin film solar cells. These comprise both inorganic and organic materials in their active layer and are therefore dubbed "hybrid solar cells", combining the unique properties of the two classes of materials.

There are two well known ways of fabricating hybrid solar cells as low cost alternatives to common silicon solar cells. One of them is similar to the bulk heterojunction concept of organic solar cells where p-type semiconducting polymers and n-type C<sub>60</sub> derivatives are processed to monolayers using their dispersions in organic solvents [8,9]. Hybrid solar cells can also be fabricated in a similar way by blending inorganic semiconductor nanocrystals within an organic semiconductor matrix [5,10]. Photoinduced electron transfer as well as photocurrent generation at the interface of donor/acceptor composite materials has already been demonstrated in composites of polymer/CdS and polymer/CdSe nanocrystals [11]. The second way to fabricate hybrid cells is the utilization of inorganic semiconductor nanocrystals like in TiO<sub>2</sub> nanoporous electrodes, leading to the so called "dye sensitized solar cells". In this concept, the cells consist of a sintered nanoporous film of TiO<sub>2</sub> as an electron accepting and transport layer and commonly a Ru-bipyridyl based dye for light absorption and electron injection into the TiO<sub>2</sub> conduction band. An electrolyte solution containing e.g. iodide/triiodide (I<sup>-</sup>/I<sub>3</sub><sup>-</sup>) serves as redox couple to regenerate the photo excited dye molecules by reduction. 10-11 % solar energy conversion efficiency is reported using this concept [7]. Recent efforts are being made by mostly focusing on replacing the liquid electrolyte by p-type

semiconductors like CuI<sup>[12,13]</sup> and CuSCN<sup>[14,15]</sup> or organic hole conductors such as conjugated polymers<sup>[16,17]</sup>.

In this study, solar cells are fabricated using CuInS<sub>2</sub> nanoparticles which were fabricated after the colloidal synthesis. We report on a hybrid solar cell consisting of CuInS<sub>2</sub> as a p-type nanostructured electrode. We realized and investigated bilayers of nanoporous CuInS<sub>2</sub> and PCBM (1-(3-methoxycarbonyl)-propyl-1-1-phenyl-(6,6) with or without using a dye complex of RuL<sub>2</sub>(NCS)/TBA(2:2) (where L= 2,2'-bipyridyl-4,4'-dicarboxylic acid; TBA= tetrabutylammonium).

## 2. Experimental

The solar cells were prepared on indium tin oxide (ITO) substrates. The synthesis of CuInS<sub>2</sub> (CIS) nanoparticles was performed by a colloidal route as presented in<sup>[18]</sup>. CIS particles were shielded by the organic surfactant triphenyl phosphate (TPP) to prevent partly further growth. After the synthesis, CuInS<sub>2</sub> nanoparticles were further treated with methanol. Methanol treatment leads to the precipitation of the nanoparticles since the surfactant TPP is removed by addition of methanol. Then, the nanoparticles were suspended again in pyridine forming a stable dispersion. Nanoporous films of CIS were prepared by doctor blading the CIS suspension onto indium tin oxide (ITO) glass. The films were annealed at 200 °C in air for 15 minutes. The nanomorphology of the films was measured by using Digital Instrument 3100 atomic force microscope (AFM). 15 mg of RuL<sub>2</sub>(NCS)/TBA(2:2) (where L= 2,2'-bipyridyl-4,4'-dicarboxylic acid; TBA= tetrabutylammonium) dye was dissolved in 50 ml ethanol. PCBM solution was prepared by dissolving 30 mg of PCBM in 1 ml chlorobenzene solution. The cells consisting of CuInS<sub>2</sub> and PCBM bilayers were characterized with and without using the dye complex on the surface. Dye coating was done by immersing the CuInS<sub>2</sub> films into

dye solution for 12 hours. PCBM was dropcast on CuInS<sub>2</sub> films. Finally, metal electrodes using LiF (0.6nm) and Al (100 nm) were thermally evaporated.

All current-voltage (I-V) characteristics of the PV devices were measured (using a Keithley SMU 2400 unit) under inert atmosphere conditions (argon) in a dry glove box immediately after sample preparation. A Steuernagel solar simulator, under air mass (AM) 1.5 conditions, was used as the excitation source with an input power of 100 mW cm<sup>-2</sup> of white light illumination. For the electrical characterization cells were illuminated through the ITO side.

For measuring IPCE response between 300 and 900 nm the samples were illuminated under argon atmosphere inside a glovebox with light from a Xenon lamp passing a monochromator (FWHM ~4 nm, illumination intensity ranging between ~ 50 μW cm<sup>-2</sup> and ~200 μW cm<sup>-2</sup>) and chopped with a frequency of 273 Hz. Using an EG&G Instruments 7260 lock-in amplifier the photocurrent of the solar cell was related to the photon flux, determined with a calibrated Si detector. The % IPCE is the percentage of electrons, measured under short circuit current conditions, that are related to the number of incident photons, and is used to obtain information on the number of photons of different energy that contribute to charge generation in the solar cell <sup>[19]</sup>.

### **3. Results and Discussion**

The morphology of the CuInS<sub>2</sub> layers after treatment is shown in figure 1. The surface of CuInS<sub>2</sub> layer is highly porous with a maximum roughness of 500 nm. Formation of CuInS<sub>2</sub> aggregates in layers might be explained by the replacement of the highly viscose surfactant TPP with a boiling point above 360°C by the organic solvent pyridine with a lower boiling point of 115°. Surface modification of CuInS<sub>2</sub> nanoparticles might lead to a preferred

aggregation after drying the layers with a broad absorbance range in the visible range comparable to the absorbance of macroscopic CuInS<sub>2</sub>.

The photovoltaic properties of the solar cells were characterized by measuring current–voltage (I-V) curves in dark and under white light illumination (AM1.5, 100 mW/cm<sup>2</sup>) conditions. Typically, CuInS<sub>2</sub>/PCBM bilayer devices in dark show diode like I-V curves with a rectification ratio (RR= $\pm 2V$ ) 5 (semilogarithmic plot in Fig. 1, linear plot as inset). Under illumination, the CuInS<sub>2</sub> cells produced an open circuit voltage (V<sub>oc</sub>) of only 0.25 V and a short circuit current (I<sub>sc</sub>) of 0.2 mA/cm<sup>2</sup> with a fill factor of 0.3.

Next, we inserted a thin dye interlayer between CuInS<sub>2</sub> and PCBM layers to increase the light absorbance within the cell. For these devices, we achieved typically a V<sub>oc</sub> of 0.5 V and an I<sub>sc</sub> of 0.6 mA/cm<sup>2</sup> with a fill factor of 0.5.

By comparing the spectral response of the solar cells and the optical absorption spectra of the components of the devices, information on the charge-generation mechanism can be obtained. The absorption spectra of the individual components of the fabricated solar cells are shown in figure 4.

Because of the weak interactions between TPP and inorganic surface, we might expect to exchange TPP by pyridine as described in the experimental part. On the other hand, we can also not avoid the aggregation of CuInS<sub>2</sub> nanoparticles to bigger aggregates during this surface modification. After treatment of the particles with methanol and pyridine, the bigger aggregates were precipitated as a powder and removed from the dispersion by filtering. For the CuInS<sub>2</sub> nanoparticles, an absorption edge starting at 580 nm was measured. The Ru- dye used as a sensitizer has a broad absorbance peak with a maximum at 550 nm.

The photo responses of the devices with and without dye complex were shown by the spectral dependence of the incident photon to current efficiency (IPCE) curves in figure 5. We observed a broad photo response for CuInS<sub>2</sub>/PCBM bilayers, which is in agreement with the absorbance behaviour of CuInS<sub>2</sub> nanoparticles. Inserting a thin layer of the Ru-dye, the overall IPCE values increase by a factor of 2.5. Additionally, a maximum at around 500 nm occurs, indicating the superposition of the photo currents from the Ru-dye as well as from the CuInS<sub>2</sub> electrode.

Because of the general increase of the IPCE values of the cells having a dye interlayer, the changes can not be attributed only to the additional dye absorption. By considering the electrically insulating dye as a buffer layer, decreasing the probability of recombination losses at the CuInS<sub>2</sub>/PCBM interface<sup>[20]</sup> may be the reason for the better device performance. The separation of the CuInS<sub>2</sub> and PCBM allows the use of PCBM only as an electron transporting layer and gives an advantage as C<sub>60</sub> derivatives generally offer high charge carrier mobilities.

#### **4. Conclusion**

We fabricated a solid state hybrid solar cell with a thin Ru-dye layer inserted between a p-type semiconducting CuInS<sub>2</sub> as an absorbing nanostructured electrode and a PCBM as an electron accepting and transport layer. This configuration offers new possibilities in the further development of solid state hybrid solar cells. From a technological point of view the low temperature sintering is advantageous since flexible plastic foils can be used instead of glass as a substrate. All active components in this new solar cell configuration are solution processable, therefore allowing a large-area fabrication. A potential advantage of CuInS<sub>2</sub> as photo active electrode might be the construction of thinner devices compared to the TiO<sub>x</sub>-based dye sensitized solar cells. Further improvement is also desirable by replacing the

CuInS<sub>2</sub> to lower band gap semiconductors such as CuInSe<sub>2</sub> or InAs for a better light harvesting.

There are various parameters such as sintering time and sintering environment to optimize the interface between the dye and nanoporous CuInS<sub>2</sub> electrode. Finally a significant goal in the future will be to assort the device processing parameters to develop the performance.

Detailed studies will be undertaken to determine the best parameters for the particle synthesis and deposition, both crucial for the formation of an optimal interpenetrating network of nanoparticles and fullerenes and also investigations with new dyes will be considered.

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### **References:**

- (1) E. Arici, N.S.Sariciftci, D.Meissner, *Encyclopedia of Nanoscience and Nanotechnology* edited by H. S. Nalwa, American Scientific Publishers, California, USA Vol.3 pp 929-944 (2004).
- (2) E. Arici, D. Meissner, F. Schäffler, N. S. Sariciftci, *International Journal of Photoenergy*, 5 (4), 199 (2003).
- (3) S.A. Empodocles, M. G. Bawendi, *Science* 278, 2114 (1997).
- (4) M. Gao, C. Lesser, S. Kirstein, H. Möhwald, A. L. Rogach, H. Weller, *Journal of Applied Physics*, 87, 5, 2297, (2000).
- (5) A.P. Alivisatos, *Science* 271, 933 (1996).
- (6) W. Huynh, J. Dittmer, A. P. Alivisatos, *Science* 295, 2425 (2002).

- (7) M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, R. Liska, N. Vlachopoulos, M. Graetzel, *J. Am. Chem. Soc.* 115, 6382 (1993).
- (8) C.J. Brabec, N.S. Sariciftci, J.C. Hummelen, *Advanced Functional Materials* 1, 15, (2001).
- (9) S. Shaheen, C.J. Brabec, F. Padinger, T. Fromherz, J.C. Hummelen, N. S. Sariciftci, *Applied Physics Letters* 78, 841 (2001).
- (10) E. Arici, N. S. Sariciftci, D. Meissner. *Adv. Funct. Mater.* Vol.13, No. 2, pp 165-171 (2003).
- (11) N. C. Greenham, X. Peng, A. P. Alivisatos, *Synthetic Metals*, 84, 545 (1997).
- (12) K. Tennakone, G.R.R. A. Kumara, A. R. Kumarasinghe, K. G. U. Wijayantha, P. M. Sirimanne, *Sci. Technol.* 10, 1689 (1995).
- (13) K. Tennakone, G.R.R. A. Kumara, I.R.M. Kottegoda, K.G.U. Wijayantha, V.P.S. Perera, *J. Phy. D: Appl. Phy.* 32, 347 (1999).
- (14) B. O'Regan, D. T. Schwartz, *Chem. Mater.* 9, 439 (1997).
- (15) B. O'Regan, D. T. Schwartz, S.M. Zakeeruddin, M. Graetzel, *Adv. Mater.* 12, 1263 (2000).
- (16) D. Gebeyehu, C. J. Brabec, N.S. Sariciftci, D. Vangeneugden, R. Kiebooms, D. Vanderzande, F. Kienberger, H. Schindler, *Synthetic Metals*, 125, 279, (2002).
- (17) J. S. Salafsky, H. Kerp, R. E. I. Schropp, *Synthetic Metals*, 102, 1256, (1999).
- (18) C. Czekelius, M. Hilgendorff, L. Spanhel, I. Bedja, M. Lench, G. Müller, U. Bloeck, D. Su, M. Giersig, *Advanced Materials*, 11 (8), 643, (1999)
- (19) J. Rostalski, D. Meissner, *Sol. Energy Mat. Sol. Cells*, 61, 87, (2000).
- (20) Kay A, Gratzel M, *Chem. Mat.* 14(7), 2930, (2002).

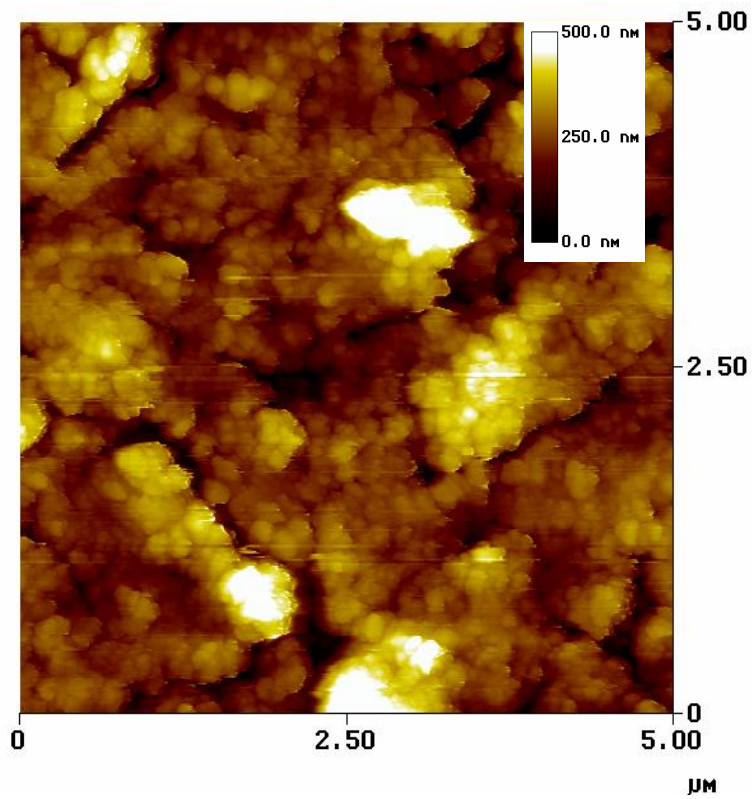


Figure 1. Fig. 1: Atomic force microscopy image of a CuInS<sub>2</sub> layer

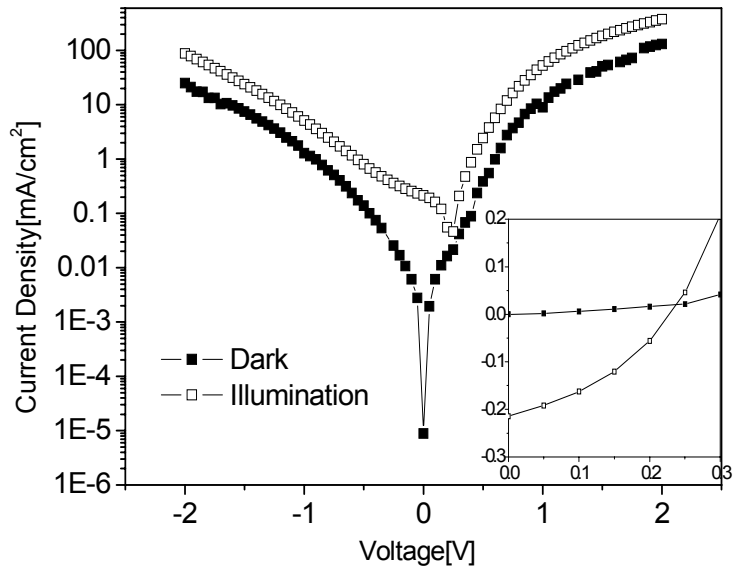


Fig. 2: Current-Voltage (I-V) characteristics of ITO/CuInS<sub>2</sub>/PCBM/LiF/Al solar cells in semilogarithmic scale and in linear scale as inset

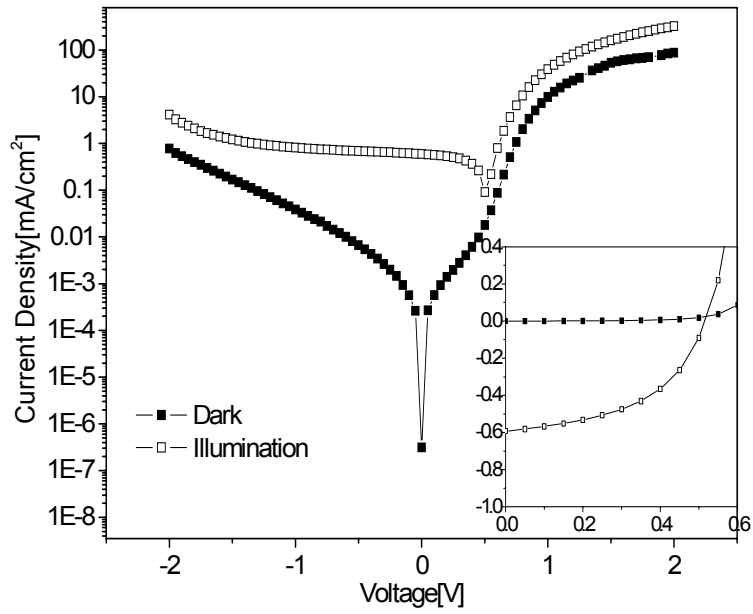


Fig. 3: Current-Voltage (I-V) characteristics of ITO/CuInS<sub>2</sub>/Ru-Dye/PCBM/LiF/Al solar cells in semilogarithmic scale and in linear scale as inset

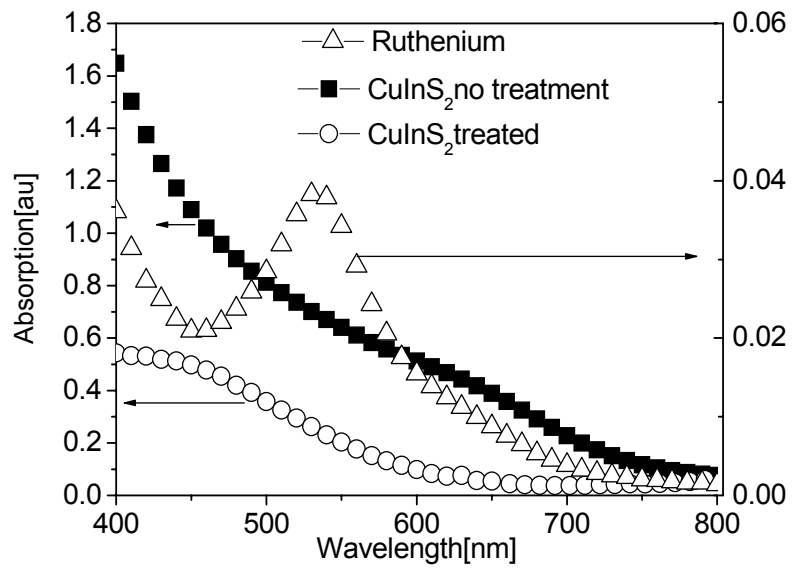


Figure 4: Absorption characteristics of individual components employed in the solar cell configurations

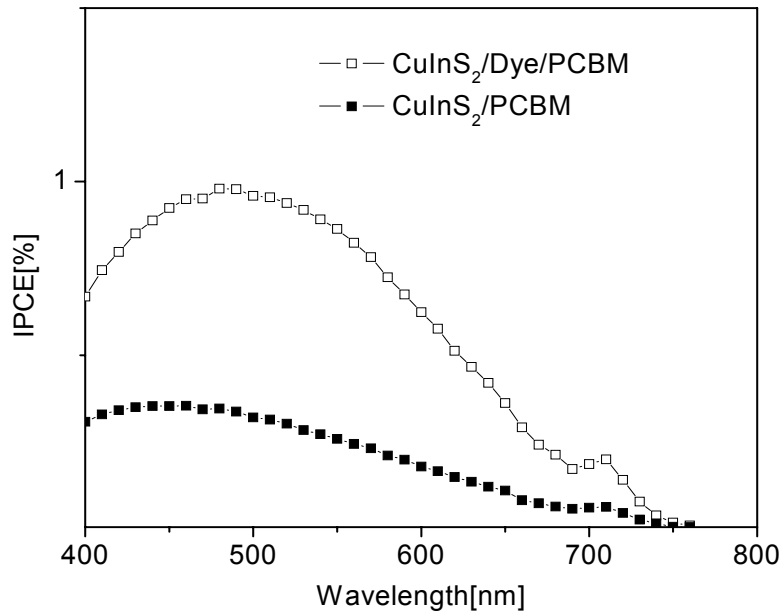


Figure 5: Incident photon to current efficiency (IPCE) of the solar cells ITO/CuInS<sub>2</sub>/PCBM/LiF/Al and ITO/CuInS<sub>2</sub>/Ru-Dye/PCBM/LiF/Al