

# Investigations on slot die coating and processing of polymer nanoparticle films for hybrid polymer solar cells

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## Introduction

Hybrid solar cells are composed of a photoactive layer which is sandwiched between two electrodes of different work function. Inorganic solar cells employ planar layers of p- and n-type semiconductors. In organic materials however the mobility of charge carriers is much lower so that the average distance an electron hole pair (exciton) travels before recombination (diffusion length) is only in the order of 10 to 30 nm. Therefore active layers of polymer based solar cells are applied from a homogeneous solution of p- and n-type semiconductors which phase separate during drying. The typical domain size of the phase segregated structure (bulk hetero junction, BHJ) should be in the order of the exciton diffusion length [1]. The domain size and degree of crystallinity depend on the drying kinetic [2] and the thermal treatment of the films[3]. Slow drying allows for good phase separation with high degree of crystallinity but also for large domain sizes. In bulk heterojunction hybrid solar cells (HSC) the n-type semiconductor is composed of inorganic semiconducting nanoparticles (here Baydots®, Bayer Technology services GmbH) and the p-type semiconductor is a polymer (here Lisicon®, Poly-(3hexylthiophene) (P3HT), Merck KGaA). In most cases the anode is transparent and composed of a hole transporting polymer layer (here Clevios® Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS), H.C.Starck GmbH) which obstructs a closed pathways for electrons from anode to cathode. Though in principle all of these layers can be processed from liquid phase, here the electrodes are applied by vacuum deposition of metals (Ca, Al, Ag) and transparent conductive oxides (Indium tin oxide (ITO)). This paper focuses on the continuous liquid film deposition by means of a self designed and manufactured mini slot die of the active hybrid layer as well as the hole transport layer of a polymer-nanoparticle hybrid solar cell.

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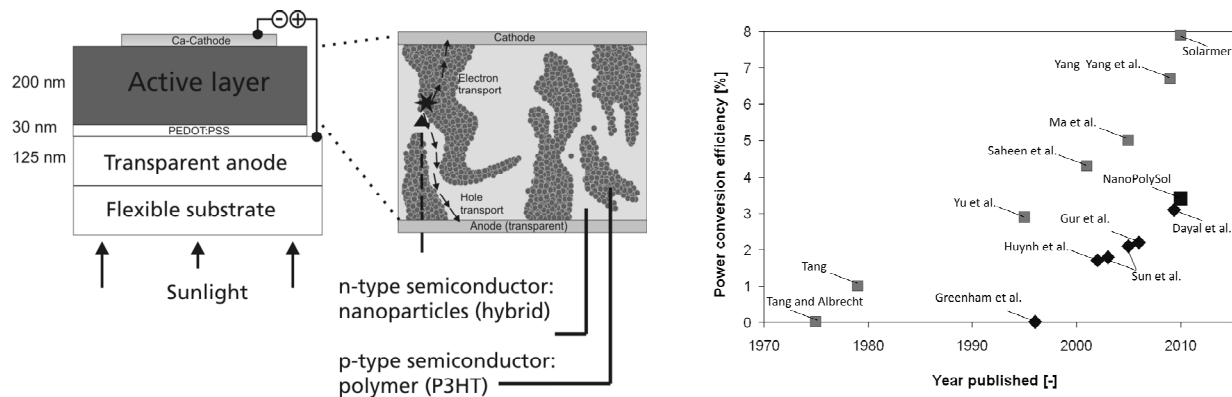


Figure 1: Schematic figure and working principle of hybrid solar cells based on the bulk heterojunction concept (left). Record efficiencies for laboratory cells based on polymer-fullerene (squares) and polymer-nanoparticle (diamonds) films (right).

Hybrid solar cells were discovered in 1996 by Greenham et al. [4]. Since then power conversion efficiencies have increased reaching 3.1 % by the end of 2009 [5] and 2.7 % by January 2010 achieved by our partners within the BMBF funded NanoPolySol project. Purely organic polymer solar cells have been investigated for more than 20 years longer than hybrid systems and have reached a record efficiency of 7.9 % published in March 2010 by Solarmer Energy Inc. [6]. In contrast to conventional photovoltaic technologies organic and hybrid solar cells are produced by liquid phase deposition and thus have the potential for a low cost production on flexible substrate in a continuous roll to roll (R2R) process. Though HSC have currently not reached the efficiencies of pure organic cells, they have the potential of combining high efficiencies of inorganic materials with cost efficient processing of polymer based cells. Due to high light absorption and mobility a power conversion efficiency of 34 % is theoretically possible with the inorganic material systems [7]. By changing the composition, particle size or shape, the optoelectric properties of the n-type semiconductor can be varied to match the properties of the polymeric counterpart [7, 8].

### Designing a slot die coater with minimized holdup for hybrid solar cells

One of the biggest challenges of this emerging technology is the scale up from lab scale spin coating under inert conditions to a roll to roll compatible technical process. Homogeneous, defect free layers of ~30 nm for the hole conducting layer and ~50-200 nm for the active hybrid layer have to be applied by means of a continuous film coating technique. The wet film thicknesses usually range from 5 to 100  $\mu\text{m}$  as most polymers are applied from solutions close to their solubility limit (~4-5 wt.%).

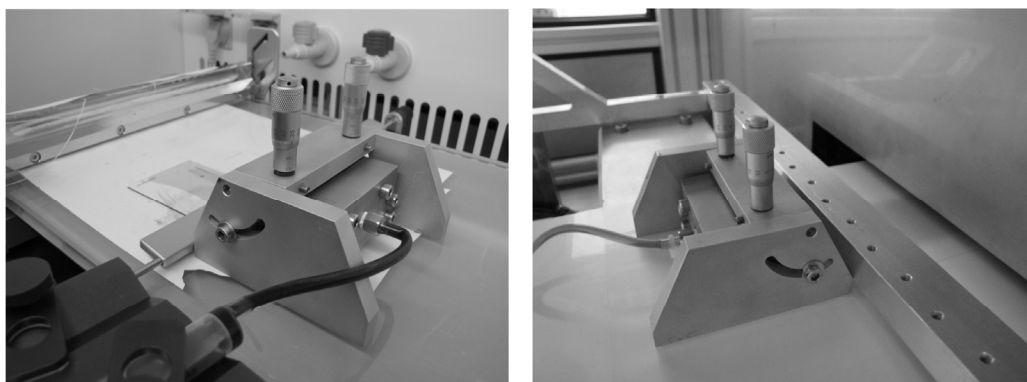


Figure 3: Experimental setup for slot die coating of nanoparticle polymer films from 5 to 100  $\mu\text{m}$  with an overall holdup of less than 2 ml. The coating die can be employed for lab scale coating of glass substrates (left) or pilot scale coating of foils (right).

Applying thicker layers of diluted inks is undesirable as it implies higher energy and capital costs for the drying process. Slot die coating produces especially homogeneous layers and is thus one of the most promising technologies for hybrid cells. In contrast to many other coating technologies the ink is not in contact with air until it is deposited. Commercially available coating dies usually have a holdup volume in the order of 100 ml to 1 liter. Novel materials for hybrid solar cells however are prepared manually and typically only few milliliters of coating ink is available. Addressing this key issue, a slot die for coating of polymer based solar cells was designed and manufactured. By employing a syringe pump and optimizing the die cavity a slot die with less than 2 ml holdup was developed for coating of polymer based solar cells (Figure 3). Hybrid solar cells were prepared on the laboratory scale setup by knife and slot die coating. The ITO coated glass substrates were structured with hydrochloric acid and coated with a homogeneous layer of PEDOT:PSS (54 nm) and QD/P3HT (30 nm). The films were annealed for 5 min at 120 °C before electrode deposition. Both coating methods produced functional solar cells that were characterised under an AM 1.5 radiation.

Table 3: Comparison of hybrid solar cells produced with different coating methods. Devices with 7,85 mm<sup>2</sup> active area were characterized under 1.5 AM radiation. The table shows electrode material, open current voltage (Uoc), short current density (Isc), fill factor (FF) and power conversion efficiency (PCE).

Coating method	Electrode	Uoc [V]	Isc [mA/cm <sup>2</sup> ]	FF [-]	PCE [%]
Spin	Al	0,62	-5,8	0,56	2,0
Knife	Ca/Al	0,61	-4,5	0,43	1,18
Slot die	Al	0,67	-0,28	0,3	0,06

Table 3 shows the characteristic data of the knife and slot die coated samples as well as the highest published value of spherical nanoparticle/P3HT solar cells, published by Zhou et al. [9]. The knife coated devices achieve efficiencies as high as 60 % of the record value for this material combination. The low power conversion efficiency of the slot die coated device is due to problems during post processing. Experiments with slot die coated films and Ca/Al electrodes are currently in preparation. The overall power conversion is limited by the selection of P3HT as electron donor. Higher efficiencies can be expected for optimized material systems with low band-gap polymers.

#### Impact of drying conditions on hybrid polymer solar cells

Schmidt-Hansberg et al. [10] showed that drying is one of the most important steps in the fabrication of polymer solar cells. The drying kinetic determines phase separation and crystallization of polymer and fullerene. Similar effects can be expected for hybrid solar cells as the polymer crystallizes and the particles agglomerate during drying. Active layers were coated and dried on a temperature controlled plate at different drying conditions. A detailed description of the experimental setup for in situ monitoring of the drying process is published in [10].

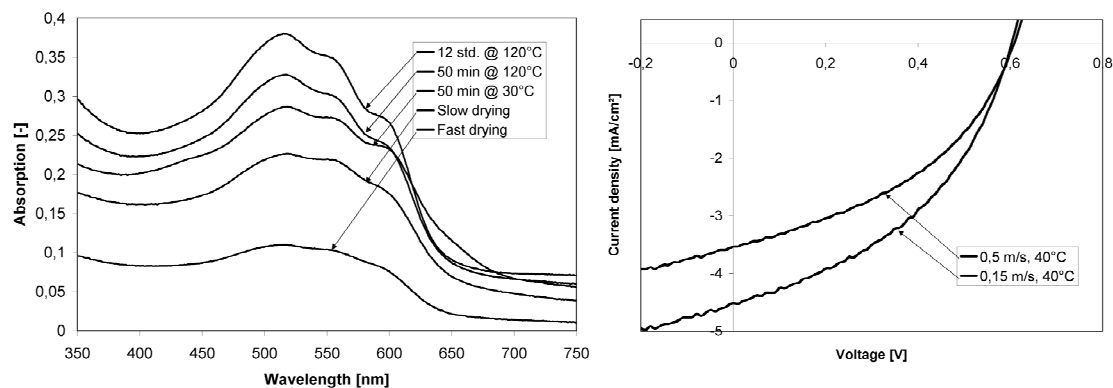


Figure 4: Absorption spectra of 30 nm nanoparticle polymer films that were processed under different drying and annealing conditions (left). Voltage current statistics of hybrid solar cells dried under high (green) and low (blue) drying air flow. Cells were produced at 40°C by knife coating, yielding power conversion efficiencies of 1.18 % and 0.88 % (right).

Figure 3 shows absorption spectra of films that were prepared with different drying and annealing conditions. Absorption increases for lower drying rate, higher annealing temperature and longer annealing times. This effect indicates an increase in crystallization of the polymer. A second requirement for efficient cells is a good electrical particle to particle contact. The particles are stabilized with ligands which have to be removed either during drying or annealing. Figure 4, (right) shows voltage-current characteristics of cells that were produced under different drying conditions. A lower drying air flow results in a higher current density and thus higher PCE. A detailed analysis of the effect of drying conditions is currently in progress.

### Summary

Hybrid solar cells based on polymer nanoparticle films have the potential to produce highly efficient solar cells in a low cost roll to roll process. Record values have increased throughout the last years to a value of 3.4 % power conversion efficiency. The scale up from laboratory to process scale is not trivial because the morphology and efficiency of the films depends strongly on the processing conditions. A better understanding of the influence of individual parameters can be generated from experiments with roll to roll compatible methods. Since new materials are available in small amounts, an experimental setup for slot die coating of hybrid solar cells was developed with an overall holdup of less than 2 ml. The setup allows for coating of glass substrates on lab scale as well as coating of foils in a pilot scale coating line. First hybrid solar cells were produced with roll to roll compatible methods knife and slot die coating. The knife coated cells showed efficiencies comparable to those of spin coated cells thus demonstrating the scalability of the process. The influence of annealing and drying conditions was shown by absorption measurements and first experiments indicate that drying conditions influences cell efficiency.

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